Faculty of Science
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Diffraction-Based Modelling
of Microstructural Size and Strain Effects in Sintered Ceramics

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Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

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Date: 21/7/2003
ABSTRACT

Crystallite (or grain) size and strain within a polycrystalline material may have a profound influence on its physical properties, eg. the fracture toughness, wear and thermal shock resistance. A diffraction pattern for a material conveys information about the strain through the strain-induced changes in the shapes of the Bragg peaks and also through peak shifts. Crystallite size effects also influence the peak shape. Therefore, it is possible, in principle, to extract descriptions of crystallite size and strain from the peak broadening of a diffraction pattern. Various methods for size and strain evaluations have been proposed for extraction of the size and strain information in metals and ceramic powders. However, there appear to be no detailed amounts in the literature to be on the development of models appropriate for sintered ceramic materials.

The objectives for this study were to critically examine the existing models for crystallite size and strain assessments and then to develop a new physically-based model which might be appropriate for sintered ceramics. The principal steps for the research, designed to fulfill the study objectives, were (1) acquiring high-quality diffraction data with synchrotron radiation, laboratory x-ray and neutron diffraction techniques for model evaluation; (2) performing preliminary evaluation using the existing models; (3) developing a new model and the non-linear least-squares calculation software; and (4) performing peak profile analyses using the existing and new models to evaluate the effectiveness of the new model.

A convolution model for crystallite size and strain determination from diffraction line broadening has been developed with particular reference to the characterisation of sintered ceramics. The size profile component function for the convolution model involves the modal size and the size distribution appropriate for ‘normal’ crystallite growth according to the mean-field theory, as proposed recently in a seminal publication by Dr. Brian York of IBM. A Gaussian strain profile component function was considered in the study on the basis that it has been widely used for specimens which exhibit small microstrain (ca. $10^{-3}$ or less). The overall profile describing the diffraction pattern involves convolution of the instrument, size and strain effects. A non-linear least-squares refinement program entitled MOZALX has been developed for profile fitting with the model. Data simulations were performed with the model, and non-linear least-squares optimisations for fitting the simulated data showed that the calculations were reasonable for low-strain sintered ceramics.

The convolution model for size and strain assessments from diffraction line broadening has been evaluated with synchrotron and laboratory x-ray radiation diffraction data (SRD and XRD, respectively). The study made use of MgO ceramics with three different purity levels which had been sintered at a range of temperatures in order to provide
diffraction data with a range of microstructural strain and size effects. The cubic symmetry of MgO provided isotropic size and strain effects as had been anticipated.

The Voigt function, a convolution of the Gaussian and Lorentzian functions, is widely used to extract crystallite size and strain information from powder diffraction data using (1) Fourier transforms, (2) the Rietveld method and (3) integral breadth methods. Size and strain model evaluation carried out using the Voigt-based Rietveld and integral breadth methods assumes that the size effect contributes only to the Lorentzian component and the strain contributes only to the Gaussian component. Size and strain assessment using the Voigt integral breadth single-line and Rietveld methods has been examined in this study with diffraction data for MgO ceramics. Two major outcomes from the evaluation confirmed impressions gained from the literature that:

1. the integral-breadth single-line method can be used as a reliable technique for size and strain analysis;
2. analysis using the Voigt function has no physical basis, is inappropriate for profiles with 'super-Lorentzian' character and is inadequate for size-strain analysis since the function does not take into account the size distribution parameter.

There has been a strong trend recently towards whole-pattern size and strain evaluations which are progressively replacing single-line methods. However, due to time constraints, this study was confined to single-line analysis with the focus being on the development of the model, and with an expectation that the single-line model would readily be extended in the future to use with whole-powder pattern data.

The size-strain analysis results using the convolution model showed that sintering (1) promotes crystallite growth and (2) relieves residual strains in low density sintered ceramics and introduces strains in dense ceramics, presumably due to grain-grain shear interactions. The effect of sintering on the size distribution clearly depends on the crystallite growth behaviour. Comparing the SRD convolution size results with those from scanning electron microscopy (SEM) showed that (1) the "grains" imaged using SEM contain clusters of crystallites and (2) the SEM-derived and convolution size distributions are in a satisfactory agreement. In general, despite the larger uncertainties due to instrument resolution, the XRD results are in agreement with those from SRD.

The size and strain values obtained with the convolution model were compared with those calculated using the Voigt single-line integral-breadth method. The comparison showed that size and strain results for both methods were dependent upon the character of the diffraction peak shapes. The convolution model improves the Voigt model in terms of (1) reliability of models from a physical point of view, (2) the additional size distribution parameter and (3) its applicability to 'super-Lorentzian' profiles. Subsequent research is suggested to further improve the model in dealing with large microstrains and developing a whole powder fitting procedure.
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Table 6.2. Relative integrated intensity of the SRD peaks for the 99% specimens.

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LIST OF KEY ABBREVIATIONS AND SYMBOLS

List of Key Abbreviations

FWHM  full-width at half-maximum
ND    neutron diffraction
rms   root-mean-square
PSF   peak shape function
SEM   scanning electron microscopy
SRD   synchrotron radiation diffraction
TEM   transmission electron microscopy
WPPF  whole-powder pattern-fitting
XRD   x-ray diffraction

List of Key Symbols

$2\theta_0$  Bragg peak position
$\beta$    represents peak breadth (= area/maximum intensity - Chapter 2) and size
distribution parameter (Chapters 5 and 6)
$\beta_f^*$ specimen peak breadth in reciprocal units \( \beta_f^* = \frac{\beta_f \cos \theta}{\lambda} \)
$\beta_L$  Lorentzian peak breadth of a Voigt function
$\beta_G$  Gaussian peak breadth of a Voigt function
$d$       interplanar spacing
$d_b$    Bragg d-spacing
$d^*$    interplanar spacing in reciprocal units \( d^* = \frac{2 \sin \theta}{\lambda} \)
$\varepsilon$ maximum (upper limit) strain
$\langle e^2 \rangle^{1/2}$ mms strain according to York
$f$     specimen profile function
$g$     instrument profile function
$h$     measured data profile function
\( \lambda \)  
- radiation wavelength

\( \theta \)  
- incident beam angle with respect to the specimen surface

\( \theta^* \)  
- sweep rate constant

\( \otimes \)  
- convolution operator

\( I(0) \)  
- peak intensity

\( m \)  
- Pearson VII index

\( \varphi \)  
- pseudo-Voigt mixing parameter

\( \phi \)  
- Voigt shape parameter

\( W \)  
- variance of a peak profile (Chapter 2)

\( W_D \)  
- full-width at half-maximum of the size component in the convolution model (Chapters 5 and 6)

\( W_s \)  
- full-width at half-maximum of the strain component in the convolution model (Chapters 5 and 6)

\( x \)  
- 2\( \theta \) position (in radians)
LIST OF PUBLICATIONS ARISING FROM THE STUDY

Fully-referenced publications:


Conferences Proceedings:


Reports:


CHAPTER 1. INTRODUCTION

1.1. Diffraction Line Broadening due to Crystallite Size and Strain in Polycrystalline Materials

Crystallite (or grain) size and strain within a polycrystalline material may have a profound influence on its performance, e.g. on the fracture toughness, wear resistance and thermal shock behaviour. A diffraction pattern of the material conveys information about the strain through the strain-induced changes in the shapes of the Bragg peaks and also through peak shifts. Crystallite size effects may also distort the line shapes. Therefore, it is possible, in principle, to extract descriptions of the size and strain effects from the peak broadening of a diffraction pattern.

Strategies used to model size and strain effects from Bragg peak shape distortions mainly involve fitting mathematical functions to the measured line shapes, and then extracting strain and size descriptions according to theoretical models for which the mathematical functions are assumed to be physically correct for the material under study. This approach, however, may be inappropriate as (1) the analytical functions used may not be physically acceptable and (2) the models mainly do not take into account the size distribution.

The broad concept underpinning this study is that the changes in Bragg peak shapes should be modelled with physically-appropriate functions which correctly reflect the microstructural environment under which size and strain develop. For example, when a ceramic is sintered, the grains tend to grow as the temperature increases which may lead to reductions in the crystallite size-related broadening of the diffraction profile. This temperature-dependent grain growth may also cause grain size distribution changes. Furthermore, the differences in thermal expansion along different crystallographic directions in a given phase within a material, and differences in thermal expansion between different materials in multiphase ceramics, may induce changes in peak profile shape. Thus, physical modelling of these changes with diffraction data may lead to improved information on the size and strain in ceramic materials, and also the phase crystallite size distribution.
A theory of size broadening was initially given by Scherrer (see, for example, acknowledgement by Warren (1969)) shortly after the discovery of x-ray diffraction. Stokes and Wilson (1944) devised a method to study x-ray line broadening due to size and strain using Fourier transform theory. In subsequent developments (e.g. Langford 1978), line profile analysis was conducted by fitting mathematical functions to the diffraction data followed by the extraction of size and strain descriptions from the fitted functions.

Most research on line broadening analysis theory has focussed on metallic materials (Warren 1969; Klug & Alexander 1974; de Keijser et al. 1982; Langford et al. 1986). Some work has been done more recently on ceramic powders (Langford et al. 1986; Auffredic et al. 1995; Balzar 1999; Louër 1999; Audebrand et al. 2000a; 2000b; Louër et al. 2002), complex fibre-reinforced ceramic composites (Balasingh, Abuhasan & Predecki 1991), and polymeric materials (Somashkar & Somashekarappa 1997). However, to date there have been no detailed reports of studies on the diffraction line-broadening of sintered ceramics produced under controlled conditions which might provide a comprehensive description of the size and strain character of these materials.

1.2. Assessment of Crystallite Size and Strain

Assessments of size and/or strain information from the analysis of single Bragg peaks is problematic in that the shape of the peaks may provide reasonable results for either strain or size modelling, but proves to be more challenging where both effects are present. In the past, a single function was mainly used to separately represent the size and strain components, e.g. Gaussian, Lorentzian (or Cauchy), pseudo-Voigt and Voigt functions. However, both theory and experiment showed that in many cases such approaches may not be appropriate. This is presumably due to the lack of physical basis for the use of particular functions for the material under study.

Klug and Alexander (1974) reviewed three classical methods which can be used for simultaneously extracting crystallite size and strain contributions from x-ray diffraction line broadening data:

1. Fourier transform method
2. Integral breadth method

3. Line profile variance method

In applying these methods for separating crystallite size and strain contributions, deconvolution of 'pure' specimen broadening must be carried out since an observed profile is a convolution of instrumental and pure specimen profiles (Figure 1.1). The (normalised) mathematical expression of the convolution is as follows:

\[ h(x) = \int_{-\infty}^{\infty} g(z) \ast f(y) dy \]  

(1.1a)

or,

\[ h = g \otimes f \]  

(1.1b)

where \( z = x - y \), \( h(x) \) is the observed profile, \( g(z) \) is the instrumental profile, \( f(y) \) is the specimen/physical profile for a certain range of diffraction angles of increment \( x \) from the peak centre, and the symbols \( (\ast) \) and \( \otimes \) denote the convolution. Here, \( f \) represents the combined strain and size contributions to the profile. A standard specimen, showing minimal strain- and size-related broadening, is required for measurement of the peak profiles, \( g \), which describe aberrations associated with instrument optics and wavelength spread.

In these classical methods, microstructural information was deduced directly from experimental data for distorted metals (e.g. Guinier 1963). Consequently, the theory was developed based on the dislocation theory in metals (Warren & Averbach 1950). This approach may not be appropriate for ceramics in which microstrains arise primarily due to thermal expansion mismatch between grains and where dislocations may not be predominant (Balasingh, Abuhasan & Predecki 1991).
Figure 1.1. An observed diffraction peak $h(x)$ is a convolution between ‘pure’ specimen $f(y)$ and instrumental $g(z)$ contributions (after Warren 1969).

The recent intensification of interest in strain-size analysis is attributed to the dramatic improvement in computing power which has allowed profile fitting to be performed more effectively. However, these advances have been limited by the use of profile fitting functions which may not be physically appropriate for particular classes of materials, such as the sintered ceramics considered in this study. Single-line and multi-line methods can be used for the extraction of strain-size information by diffraction profile fitting. Recently, a pattern decomposition method has been accomplished, for the same purpose, by fitting analytical functions to whole diffraction patterns (see for example, Langford 1992). This achievement was followed by the introduction of the whole-powder pattern-fitting (WPPF) approach (Toraya 1986; Scardi 1999; Scardi & Leoni 2001).

There are, in general, two approaches which are commonly used for obtaining crystallite strain and size values from diffraction line-broadening: (1) the application of the integral breadth method and (2) the Warren-Averbach Fourier transform method. Reviews of these methods have been given, for example, by Delhez, de Keijser and Mittemeijer (1982). The first approach involves diffraction data fitting with the symmetric Voigt (a convolution of Gaussian and Lorentzian profile functions) (Langford 1978; de Keijser et al. 1982), pseudo-Voigt (Wertheim et al. 1974) or Pearson VII (Hall et al. 1977) functions which do not necessarily have a physical basis
in terms of microstructural character. Also, these functions do not model the crystallite size distribution parameter (Klug & Alexander 1974; Langford, Louër & Scardi 2000; Popa & Balzar 2002). The second approach is more physically acceptable; however, it has two substantial limitations in that (1) the broadening should be sufficiently large (Delhez, de Keijser & Mittemeijer 1980) and (2) improper determination of the background introduces a severe 'hook' effect in the Fourier reciprocal space (Warren 1969). Moreover, this Fourier technique cannot readily deal with overlapping peaks. As a result, this method tends to be restricted to materials with high crystallographic symmetry. Therefore, the line profile method performed in angular/crystal space is preferred, provided that the model for each effect is known and the overall function can be developed.

Multi-line profile fitting methods should be inherently superior to single-line procedures for strain-size analysis as the angular dependence of the separate strain and size contributions to the specimen function $f$ are markedly different. Two well-known multi-line methods which have been widely used in line broadening analysis are Warren-Averbach (1950, 1952) and Williamson-Hall (1953). In the Warren-Averbach method, Fourier transforms are performed using diffraction data to give information about crystallite size and strain. However, again, the use of Fourier transform may cause some problems in the analysis.

In the Williamson-Hall method (Williamson & Hall 1953), the peak broadening $\beta$ is extracted from

$$\beta \cos \theta = \frac{\lambda}{D} + 4\varepsilon \sin \theta$$  \hspace{1cm} (1.2)

where $D$ is the apparent crystallite size, $\varepsilon$ is the maximum (upper limit) microstrain and $\lambda$ is the radiation wavelength. By plotting $\beta \cos \theta$ against $4\varepsilon \sin \theta$, the crystallite size can be obtained from the intercept of the curve on the $\beta \cos \theta$ axis, i.e. by $D = \lambda/(\text{intercept})$, whereas the slope of the curve directly gives the strain value, $\varepsilon$. This method assumes that the Lorentzian function contributes to both size and strain effects. This assumption may not be a good approximation for strain broadening since a strain profile tends to be Gaussian, particularly for low-strain materials.

Further development of line profile fitting of diffraction data with the Voigt function (Langford 1978) led to the use of this function in the so called ‘average size-
strain’ method (Langford 1992). The Williamson-Hall plot was used only for qualitative inspection in describing if the specimen integral breadth is \(d^*\)-dependent, where \(d^*\) is the interplanar spacing in reciprocal units. A plot of \(\left(\frac{\beta_f}{d^*}\right)^2\) vs. \(\frac{\beta_f^*}{(d^*)^2}\) was then examined to give the mean strain value from the intercept of the plot on the \(\left(\frac{\beta_f^*}{d^*}\right)^2\) axis and the mean apparent size from its slope. It was assumed that strain contributes only to the Gaussian profile and size to the Lorentzian profile. Since the pseudo-Voigt and Pearson VII functions can approximate the Voigt function (de Keijser, Mittemeijer & Rozendaal 1983), the use of these functions for size and strain analysis is possible, however with some additional errors introduced from the approximation. It should be noted again that application of these functions in the analysis has no direct physical basis. Moreover, the crystallite size distribution is not taken into account in using the functions.

The extraction of microstructural information from powder diffraction data has been greatly enhanced by the discovery of the Rietveld method (Rietveld 1967; 1969) which is an approach to fit a structural-based model to a whole powder pattern. Subsequently, it was shown that the method can also be used to extract information about crystallite size and strain (e.g. de Keijser, Mittemeijer & Rozendaal 1983; Delhez et al. 1993; Pratapa, O’Connor & Hunter 2002). The procedure can be accomplished using the Voigt function. It should be emphasised that application of this method with x-ray diffraction data may not be satisfactory since the assumed functions for the instrument and specimen effects may not be appropriate.

Further development in powder diffraction data analysis based on the whole-powder pattern approach was achieved by developing models which do not need complete structural data (WPPF - Toraya 1986; Scardi 1999; Scardi & Leoni 2001). Whole-pattern fitting based on Fourier coefficient calculations has also been introduced recently (Ungár et al. 2001). WPPF may be used at the initial stage of an ab initio structure determination as well as for extraction of microstructural features such as crystallite size and microstrain (Scardi 1999). It is of importance to note that the pattern fitting was performed by applying the analytical functions such as Pearson VII (Toraya 1986) and pseudo-Voigt (Scardi 1999; Scardi & Leoni 2001). The recent
literature indicates a strong trend towards the use of whole-powder diffraction data for acquiring structural and microstructural information from materials. This study, however, used the single-line approach since time did not permit the extension of the model developed in the study for whole-powder diffraction data. It is hoped that the model developed here will be developed to others to its use with whole pattern data.

Even though the results obtained by the approaches described above may be valid for some material types (notably metals), the mathematical assumptions may lead to incorrect results if the assumed size and dislocation models are inappropriate. In such cases, the information gained from the analysis may be unreliable or even meaningless, e.g. the negative values of size parameter calculated using the Williamson-Hall multi-line method for alumina whiskers data reported by Balasingh, Abuhasan and Predecki (1991). Several advances have been made recently in developing more reliable techniques in size-strain analysis. One of the new approaches, which was derived from the mean-field theory of normal grain growth and is of interest to this study, is summarised below.

York (1999, 2003) described a novel approach to strain-size assessment involving the derivation of a line profile function for which the key parameters relate directly to the growth of the microstructure as the material develops. He used a mean-field theory and statistical mechanics to develop crystallite size and strain distribution functions involving a grain-growth parameter and the 'dislocation' or strain density. These profile functions depend on four measurable microstructural parameters: the Bragg $d$-spacing, $d_b$; the average number of lattice planes, $<N>$, and hence average grain size; the rms strain, $(e^2)^{1/2}$, which is proportional to the average dislocation density; and parameter $\beta$, which characterises the width of the size distribution and is functionally related to the kinetic growth parameter of a grain boundary sweep rate constant $\theta'$. The Laue $\frac{\sin^2 N x}{\sin^2 x}$ function is then integrated over both the size and strain distributions to obtain a general profile function. This approach can be challenged by the consideration that a specimen profile is a convolution of separate functions from different effects (Langford 1999).

The overall profile function for the York model has been considered with measured data for thin film materials using non-linear least squares fitting (York 1999;
2003). However, there has been no further report on the development and evaluation of the York method.

1.3. Research Objectives

The principal objectives of this study were to (1) critically examine existing Voigt-based methods for strain-size evaluation; (2) consider whether Voigt-based models might be refined for use in the modelling of size-strain character; and (3) attempt to develop new physically-based modelling methods with particular reference to sintered ceramic materials.

The two main questions to be investigated in this study were:

- Which diffraction-based physical models might be appropriate for modelling crystallite size and strain with particular reference to sintered ceramic materials?

- How effective are these models for representing size and strain in these materials?

A new model was to be developed based on the theory given by York (1999; 2003). Examination of the existing models was to be used to determine the form of the new model.

The codes for the new model were to be written in Fortran 95. The codes were then to be compiled to produce executable software which can perform peak profile fitting in graphical user interface mode to allow users to inspect progress of refinement directly from the display. It was intended that the software should give output of refinements for size and strain analysis. The development of the software was to be limited to single-peak refinement which was a basic for further development in the whole-powder pattern-fitting approach.

Model evaluation was to be performed using high-quality diffraction data collected from x-ray, neutron and synchrotron radiation. Synchrotron radiation diffraction (SRD) was to be employed to enhance the x-ray diffraction (XRD) near-surface results, primarily because the greater radiation intensity can provide better line-broadening information and the greater resolution reduces instrumental broadening. Neutron diffraction (ND) data was to be used to complement XRD and SRD data as ND provides information about the bulk of the material, whereas XRD and SRD gives near-surface characterisation (ca. tens of microns in oxide ceramics).
1.4. Thesis Structure

Chapter 1 summarises the basic theory regarding diffraction line broadening due to crystallite size and non-uniform microstrain in polycrystalline materials. Methods for assessing crystallite size and strain are introduced. Particular attention is then given to the integral-breadth peak-shape function (PSF) profile fitting method with the focus being on the application of the appropriate physical models. The chapter concludes with a statement of the objectives of the study and the associated research plan.

Chapter 2 reviews in detail the relevant literature. Firstly, the sources of diffraction line broadening are surveyed. Then, diffraction broadening for imperfect crystals, attributed to crystallite size and strain effects, is explored. The next section describes size and strain assessment methods with particular reference to the integral-breadth method. The final section considers the influence of materials processing on the size and strain character in sintered ceramic materials.

Chapter 3 overviews the experimental design, followed by a rationale for development of the convolution model, details of materials selection and processing and diffraction data collection. The chapter also describes the use of the convolution model, mathematical PSF profiling and Rietveld modelling for size and strain assessments.

Chapter 4 describes the procedures used to produce standard materials for size and strain analysis and evaluation of the Voigt function in the size and strain assessments. A comparison of results for the single-line integral-breadth and the Rietveld methods is also presented in this chapter.

Chapter 5 summarises the development of the convolution method. The executable Fortran 95 program entitled MOZAIX is introduced in this chapter. The accuracy of the calculations is examined using simulated data. MOZAIX refinement results for sintered MgO ceramics SRD data are reported to show the performance of the program. The chapter concludes with a statement of the key achievements from the chapter.

Chapter 6 considers the application of the convolution model for extracting size and strain from SRD and XRD data for the sintered MgO ceramics. The effect of
sintering temperature on the microstructural development is considered. The chapter also presents a comparison of the effectiveness of the convolution model and the Voigt single-line integral-breadth method.

Finally, Chapter 7 gives an overview of the thesis outcomes with reference to the study objectives. Further research to follow this study is also proposed.
CHAPTER 2. CRYSTALLITE SIZE AND STRAIN
EVALUATIONS FROM DIFFRACTION LINE BROADENING

This chapter reviews the literature on crystallite size and strain evaluations from diffraction line broadening (the term ‘line broadening’ is used subsequently for simplification). Firstly, the definitions of crystallite size and strain are considered with particular attention being given to the line broadening. A review of instrument contributions to the broadening is then presented to provide a description of correcting for instrument effects in size and strain analysis. The sources of the specimen-related line broadening are explored followed by details of the methods for assessing size and strain, viz. the Fourier, variance, whole-powder pattern-fitting and integral breadth methods. The Fourier method is not discussed in detail as the method is not of interest in the study. Also, only a brief explanation is given of the variance method. The Rietveld method is reviewed to describe how this structural-based whole-pattern analysis applies to the size and strain evaluations. Microstructural-based whole-powder pattern-fitting procedures are also briefly addressed. This chapter also presents a sub-section on York model which considers the mean-field theory from a statistical mechanics perspective as a basic approach for developing the new size and strain line profile functions considered in this study. Each section ends with a summary. The chapter closes with a review on processing of ceramic materials which may induce size and strain effects. Note that sintered ceramic materials were used in this study to deal with the size and strain changes as grains developed in the materials.

Size broadening is due to the small size of a particular region which causes the radiation to be incoherently diffracted (Guinier 1963). In polycrystalline materials, a large number of grains with various relative positions and orientations causes variations in the phase differences between the wave scattered by one grain and waves scattered by others, which can take any values between 0 and 2π with equal probability. The total intensity scattered by all grains is the sum of individual intensities scattered by each grain; or, in other words, the grains diffract incoherently or independently. In terms of size and strain, therefore, diffraction peak broadening consists of (1) a size broadening contribution which reflects the size of the grain
(therefore called *grain size*) and (2) a strain broadening component which represents the relative atomic displacements within the grain.

Van Berkum *et al.* (1999) argued that lattice defects which are parts of grains, called *domains*, can also be considered to diffract incoherently with each other. From this point of view, line broadening may consist of a size broadening of domains and a strain broadening from the same domains. The domain concept, however, does not have a clear technical basis since it cannot be confirmed using other characterisation techniques, while ‘grain size’ can be measured by microscopy.

The term ‘crystallite size’ is used by others (Louer 1999; Langford, Louër & Scardi 2000) who have argued that it also represents grain size. The term ‘crystallite size’ is used throughout this thesis to define ‘a finite size of region in a specimen where radiation is diffracted incoherently with respect to other regions’.

Size distribution describes the dispersion of crystallite sizes for a material. It is now well known that size distribution influences diffraction peak shapes (*e.g.* Klug & Alexander 1974; Langford, Louër & Scardi 2000). Therefore, it is possible to extract a size distribution description from line broadening, provided that the appropriate model is used. Recently, there have been some efforts to acquire size distribution character from line broadening by introducing an additional parameter into an analytical profile function such as the pseudo-Voigt function (*e.g.* Popa & Balzar 2002).

From the classical theory of strain in deformed materials, it is assumed that elastic deformation will cause constant changes of lattice plane spacings from one grain to another (Cullity 1978). Such strained materials exhibit macroscopic uniform dimension changes from the original size. These changes, relative to the original dimensions, are called *uniform macrostrains*. If this kind of strain is observed on a microscopic scale (*ca.* as large as a grain several microns in size), the material may be said to exhibit *uniform microstrain*. By contrast, it is known that plastic deformation will cause various changes of lattice plane spacings from one grain to another or one part to another. These lattice spacing changes, relative to the original, are called *non-uniform microstrains*.

Macrostrain describes the line shift related information determined by the $\sin^2 \Psi$ diffractometric residual stress method which is used routinely to characterise
long-range, near-surface tensile and compressive strains (Noyan & Cohen 1987). This category of strain can occur, for example, when a material prone to anisotropic thermal expansion cools during processing. The cooling rate of the inner part is less than that of the outer part so that a compressive residual strain develops in the near-surface of the material.

Microstrain refers to Bragg line shifts and shape distortions associated with grain-grain interactions such as those caused by differences in thermal expansion between grains in a multi-phase material. Uniform microstrain relates to changes in cell parameters caused by these grain-grain tensile or compressive effects, whereas non-uniform microstrain effects are associated with grain-grain shear effects which contribute to line broadening.

Therefore, the microstructural strain-size related items of information which can be extracted from the peak shapes of diffraction data are the non-uniform strain, crystallite size and crystallite size distribution.

2.1. Sources of Diffraction Line Broadening

The ideal peak shape for a diffraction line is a delta function. In reality, however, there are physical effects which may broaden the diffraction line. These effects can be classified into instrument and specimen broadening. This section describes the sources of line broadening in detail. Definitions of peak width and peak-shape functions (Table 2.1) are presented to guide the review.

There are two important measures in line profile analysis of powder diffraction, i.e. the peak position and the peak width (or broadening). The peak position is determined by (Klug & Alexander 1974)

$$
\langle 2\theta \rangle = \frac{\int 2\theta \cdot I(2\theta) \, d(2\theta)}{\int I(2\theta) \, d(2\theta)}
$$

(2.1)
Figure 2.1. A diffraction line profile illustrating the definition of peak, centroid and full-width at half-maximum intensity (FWHM) (Klug and Alexander 1974).

The peak width can be described by the following measures (Klug & Alexander 1974):

1. full-width at half-maximum (FWHM) – the overall width of the line profile at half-maximum intensity measured above the background [see Figure (2.1)].

\[
FWHM = 2\theta_2 - 2\theta_1
\]  

(2.2)

2. integral breadth (\(\beta\)) – the integrated intensity of the line profile above background divided by the peak height, \(I_p\).

\[
\beta = \frac{1}{I_p} \int I(2\theta) d(2\theta)
\]  

(2.3)

3. variance – squared standard deviation of the elements comprising the profile.

\[
W = \left\langle (2\theta - \langle 2\theta \rangle)^2 \right\rangle
\]

\[
= \frac{\int (2\theta - \langle 2\theta \rangle)^2 \cdot I(2\theta) d(2\theta)}{\int I(2\theta) d(2\theta)}
\]  

(2.4)

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Table 2.1. List of basic analytical profile-shape functions (PSFs) cited in this study.

<table>
<thead>
<tr>
<th>No.</th>
<th>Profile-shape function (PSF)</th>
<th>Mathematical form</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gaussian&lt;sup&gt;1&lt;/sup&gt;</td>
<td>$I_G(x) = I(0)e^{-\frac{4\ln2}{w_G^2}x^2}$</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Lorentzian (Cauchy)&lt;sup&gt;2&lt;/sup&gt;</td>
<td>$I_L(x) = \frac{I(0)}{1 + \frac{x^2}{w_L^2}}$</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Pearson VII&lt;sup&gt;3&lt;/sup&gt;</td>
<td>$I_{P7}(x) = \frac{I(0)}{\left[1 + 4(2^{\nu^m} - 1)\left(\frac{x}{w_{p7}}\right)^2\right]^{\nu}}$</td>
<td>Hall et al. 1977</td>
</tr>
<tr>
<td>4</td>
<td>Pseudo-Voigt</td>
<td>$I_{PV}(x) = \phi I_G(x) + (1 - \phi)I_L(x)$</td>
<td>Wertheim et al. 1974</td>
</tr>
<tr>
<td>5</td>
<td>Voigt&lt;sup&gt;4&lt;/sup&gt;</td>
<td>$I_V(x) = I(0)\frac{\beta}{\beta_L}Re\left[erfi\left(\frac{\pi^{1/2}x}{\beta_G} + ik\right)\right]$</td>
<td>Langford 1978</td>
</tr>
</tbody>
</table>

Subscripts $G$, $L$, $P7$, $PV$ and $V$ denote the Gaussian, Lorentzian, Pearson VII, pseudo-Voigt and Voigt functions, respectively.

- $x$ position (in radian)
- $I(0)$ peak intensity
- $w$ full-width at half-maximum intensity (FWHM)
- $\beta$ integral breadth (= area/maximum intensity)
- $m$ Pearson VII index
- $\varphi$ pseudo-Voigt mixing parameter
- $erfi$ complex error function
- $Re$ real part of a complex function

$$k = \frac{\beta_L}{\sqrt{\pi}\beta_G}$$

The Voigt shape factor $\phi$ is defined as

$$\phi = \frac{w}{\beta}$$

(Table 2.1. cont'd)
Table 2.1 (cont’d)

\[ \phi_L = \frac{2}{\pi} = 0.6366 \text{ and } \phi_C = 2\sqrt{\frac{\ln 2}{\pi}} = 0.9394 \]

Therefore,

\[ 0.6366 \leq \phi_v \leq 0.9394 , \text{ where } \phi_v \text{ is the Voigt shape factor.} \]

The Voigt peak shape factor can be approximated using (Ahtee et al. 1984)

\[ \phi \approx \frac{E(1 + Ak + Bk^2)}{(1 + Ck + Dk^2)} \]

where \( A = 0.9039645, B = 0.7699548, C = 1.364219, D = 1.136195, E = 2(\ln 2/\pi)^{1/2} \)

\[ = 0.9394372. \text{ This approximation has a maximum difference from the exact value of} \]

\[ 0.16\% (\text{at } k = 0.15) \text{ (Langford 1999).} \]

\[ ^1 \beta_C = \frac{\pi \nu_G}{2} \]

\[ ^2 \beta_L = \sqrt{\frac{\pi}{\ln 2}} \frac{w_L}{2} \]

\[ ^3 \beta_{pl} = \frac{\pi 2^{2(1-\nu)} \Gamma(2m-1) w_{pl}}{\left(2^{1/m} - 1\right)[\Gamma(m)]^2} \text{ where } \Gamma \text{ is the gamma function} \]

\[ ^4 \beta_C = \beta \exp(k^2)\left[1 - \text{erf}(k)\right] \text{ where } \text{erf} \text{ is the error function} \]

\[ \beta^2 \approx \beta_L \beta + \beta_C^2 \text{ (Halder & Wagner 1966)} \]
2.1.1. Instrument Broadening

The instrument broadening contribution $g$ [Equation (1.1)] in powder diffraction data originates from the non-ideal optical effects of the diffractometer and from the wavelength distribution of the radiation.

A diffraction profile measured from a structurally imperfect material ($h$ profile) is considered as a convolution of the profile $f$ due to crystallite imperfections (non-uniform microstrain and small crystallite size) and the $g$ profile (Figure 1.1). This relationship can be expressed as Equation (1.1). The $g$ profile can be determined either mathematically (Wilson 1963; Timmers et al. 1992) or by measurement with a suitable standard material (e.g. Van Berkum et al. 1995) which is assumed to be free from specimen broadening effects.

The influence of instrument effects on line broadening was reviewed in considerable detail by Klug and Alexander (1974) who considered the effects of x-ray source, flat specimen surface, axial divergence, specimen transparency, receiving slits and instrument misalignment for a Bragg-Brentano diffractometer. The individual effects, which are analytically approximated, may be convoluted with each other. These effects have also been numerically modelled (Cheary & Coelho 1992; Finger, Cox & Jephcoat 1994; Ida & Toraya 2002). An ab initio Monte Carlo approach has also been applied to determine the instrument function by taking into account all possible optical paths (Timmers et al. 1992). Some of the instrument characteristics, however, cannot be determined directly with sufficient accuracy (Van Berkum et al. 1995). Therefore, measuring $g$ for correction of the instrument profile is more precise and reliable, provided that a suitable standard specimen is available.

A standard specimen for instrument correction should meet the following criteria (Van Berkum et al. 1995; Leoni, Scardi & Langford 1998; Reefman 1999):

a. does not exhibit measurable specimen broadening;

b. (ideally) is developed from the same material as the specimen to be investigated;

c. should not exhibit pronounced transparency effect;

d. exhibits minimal errors from crystal statistics caused by surface roughness or large particles.
In cases where a standard material is developed from the same material under investigation, strain-size analysis gives the sample differences not the absolute values (Balzar 1999; Reefman 1999). A specimen showing the least line width can be used as a reference and the relative microstructural information can be determined.

A standard reference material made from a material other than that under analysis can also be used. The primary advantage of using this strategy is that the profile is collected for a range of test materials provided there is no change in the instrument arrangement. Examples of such standards are BaF$_2$ as described by Louër and Langford (1988) and the NIST Standard Reference Material (SRM) 660a LaB$_6$ (Freiman & Trahey 2000). An MgO ceramic material has been developed during this study for x-ray and neutron broadening assessments (Pratapa & O'Connor 2002).

Procedures for convoluting $g$ with a known or assumed $f$ require an approximation of the measured profiles with an analytical function. The measured profiles are fitted with a selected profile function and the fit parameters are extracted. A variation of the parameters with $2\theta$ can be obtained and then the profile for an arbitrary $2\theta$ can be computed with the fit parameters. A split Pearson VII function has been used to model $g$ for x-ray diffractometry (e.g. Howard & Snyder 1989; Balzar 1992). Use of the pseudo-Voigt function has also been reported in x-ray and synchrotron radiation diffractometry (Thompson, Cox & Hastings 1987; Enzo et al. 1988; Will et al. 1988).

2.1.2. Specimen Broadening

The specimen profile $f$, after removal of the instrument effect $g$ from the observed profile $h$, conveys microstructural information representing size effects and lattice distortion (non-uniform microstrain). The overall profile function $f$ is the convolution of the profile functions of these effects (Langford et al. 1988; Langford 1999). The following section summarises the theories of line broadening by lattice imperfections, which consist of small crystallites and non-uniform microstrains.
2.2. Line broadening by Lattice Imperfections

Diffraction theories explaining line broadening phenomena are considered in the following four sub-sections.

2.2.1. Line Broadening by Small Crystallite Size – Analogy to Optical Gratings

A basic theory of size broadening is presented by making an analogy of the effect of crystallite size on a diffraction pattern to the phenomenon associated with optical gratings (Guinier 1963). The optical phenomenon shows that the diffraction maximum depends only on the spacing between gratings and that the width of the diffraction line depends on the number of gratings in a spatial unit. Increasing the density of the grating will decrease the line width.

In the case of radiation diffraction, the number of reflecting lattice planes is analogous to the number of gratings. Reducing the number of lattice planes corresponds to the smaller crystallite size.

Consider a thin plate crystal, large in surface area, which consists of $N$ lattice planes of spacing $d$ (Figure 2.2). A radiation beam of wavelength $\lambda$ incident on the surface of the plate at the Bragg incident angle of $\theta$, such that Bragg’s law applies

$$\lambda = 2d \sin \theta$$

(2.5)

The beam scattered by $N$ planes is in phase producing a scattered ray with amplitude $NA$, where $A$ is the amplitude for a single lattice plane. If the angle of incidence is changed from $\theta$ to $\theta + \delta$, the path difference between two adjacent planes becomes

$$2d \sin(\theta + \delta) = 2d \delta \cos \theta$$

(2.6)

The scattered wave is now the sum of the $N$ waves but with a phase difference of

$$2\phi = \frac{4\pi d}{\lambda} \delta \cos \theta$$

(2.7)
Figure 2.2. Diffraction at the Bragg angle of incident $\theta$ by $N$ lattice planes with lattice spacing of $d$.

It can be shown that the intensity of the diffracted beam in a direction $\theta + \delta$ is (Guinier 1963)

$$I(\delta) = A \frac{\sin^2 N\phi}{\sin^2 \phi}$$  \hspace{1cm} (2.8)

$I(\delta)$ approaches zero as

$$N\phi > \pi \quad \text{or} \quad \delta > \frac{\lambda}{2Nd \cos \theta}$$  \hspace{1cm} (2.9)

which means that the width of the angular domain of the reflection is inversely proportional to $Nd$. The thickness of the crystal ($L = Nd$, where $L$ is perpendicular to the diffracting planes) is associated with the full width at half-maximum (FWHM) according to the following (Guinier 1963)

$$FWHM = \frac{0.9\lambda}{L \cos \theta}$$  \hspace{1cm} (2.10)
2.2.2. Line Broadening by Small Crystallite Size – the Laue Interference Function

Discussion on this topic involves use of the reciprocal lattice. Consider a set of three scalar numbers \((\xi, \eta, \zeta)\) defining a point in reciprocal space at a vector distance \(\xi a^* + \eta b^* + \zeta c^*\) from the origin, where \(a^*, b^*\) and \(c^*\) are the primitive translation vectors of the reciprocal lattice. By defining the unit vector for the incident x-ray radiation as \(s_0\) and the scattered radiation vector as \(s\), the scattering function \(I(\xi, \eta, \zeta)\) gives the maximum intensity when the following conditions of diffraction are met

\[
\frac{(s - s_0)}{\lambda} = \frac{s}{\lambda} = \xi a^* + \eta b^* + \zeta c^* \quad (2.11)
\]

\(I(\xi, \eta, \zeta)\) can then be considered as a distribution in reciprocal space with its value at any point giving the intensity according to the diffraction conditions with the point being the extremity of the vector \(\frac{S}{\lambda}\) (James 1965). The total intensity of the scattered waves \(I(\xi, \eta, \zeta)\) for any point in the reciprocal space is basically a product of two factors: (1) the modulus of the structure factor \(|F(\xi, \eta, \zeta)|^2\), where \(F(\xi, \eta, \zeta)\) is the geometrical structure factor or structure factor, and (2) the Laue interference factor \(I_0(\xi, \eta, \zeta)\), or

\[
I(\xi, \eta, \zeta) = |F(\xi, \eta, \zeta)|^2 I_0(\xi, \eta, \zeta) \quad (2.12)
\]

The geometrical structure factor can be written as

\[
F = \sum f^s \cdot \exp(ik\mathbf{S} \cdot \rho) \quad (2.13)
\]

where the summation is made over all atoms in a unit cell, \(f^s\) is atomic scattering factor, \(k = \frac{2\pi}{\lambda}\) is the wave-number and \(\rho\) is the vector distance of any point in the unit cell from the origin of that cell. Defining

\[
\rho = ua + vb + wc \quad (2.14)
\]

the structure factor can now be expressed as

\[
F(\xi, \eta, \zeta) = \sum f^s \cdot \exp(2\pi i(\xi u + \eta v + \zeta w)) \quad (2.15)
\]
where \((u,v,w)\) and \((a,b,c)\) are a set of numbers and a set of primitive translations in crystal-lattice space, respectively. This structure factor term is of importance in the theory of strain broadening by dislocations. Further details of the theory being given in §2.2.3.

The interference function \(I_0(\xi, \eta, \zeta)\) for a parallelepiped crystal fragment with \(N_1\), \(N_2\), \(N_3\) points parallel to the edges \(a\), \(b\), \(c\) respectively has a general form of (James 1965)

\[
I_0(\xi, \eta, \zeta) = \frac{\sin^2 N_1 \pi \xi}{\sin^2 \pi \xi} \cdot \frac{\sin^2 N_2 \pi \eta}{\sin^2 \pi \eta} \cdot \frac{\sin^2 N_3 \pi \zeta}{\sin^2 \pi \zeta}
\]  
(2.16)

The interference function can be regarded as a representation of a periodic distribution dependent on the vector \(S/\lambda\) in the reciprocal-lattice space. In circumstances where a crystallite consists of a row of \(N\) equally-spaced points along the \(a\) axis, sheets of crystallites form in the \(b^*c^*\) planes of the reciprocal lattice and are perpendicular to the \(a\) axis. Since now \(N_2 = N_3 = 1\), the Laue interference function becomes

\[
I_0(\xi) = \frac{\sin^2 N \pi \xi}{\sin^2 \pi \xi}
\]  
(2.17)

Considering the diffraction condition \(\sin 2\theta = \frac{\lambda}{\alpha}\) and the appropriate crystal-lattice space distance \(x = \frac{\xi}{a}\), the Laue interference function can be written as

\[
I_0 = \frac{\sin^2 N \pi x a}{\sin^2 \pi x a}
\]  
(2.18)

Consider now a system with a large number of identical crystallites. The average intensity of the scattered radiation corresponding to the distribution of the interference function can be calculated by including all possible crystallographic orientations. The calculation gives the average interference function \(\overline{I}_0\) according to diffraction by crystallites with random orientation. Determining the appropriate distribution functions associated with the interference function is, therefore, essential in the intensity calculation.
If \( \overline{OR} \) and \( \overline{OR'} \) are the position vectors for neighbouring reciprocal points \((h, k, l)\) and \((h+\xi, k+\eta, l+\zeta)\), the interference function at \( R' \) can be written as \( I_0(\xi, \eta, \zeta) \) (James 1965). Consider \( ds \) is a small element of the surface area for a sphere of radius of \( OR' \). The diffracted intensity of radiation through an angle \( 2\theta \) over an area \( ds \) at a distance from a point of origin \( \rho = 2\sin\theta = \frac{|S|}{\lambda} \), is determined by

\[
\overline{I_0}(\rho) = \frac{1}{4\pi\rho^2} \int I_0(\xi, \eta, \zeta) ds
\]

(2.19)

The integrated intensity can then be calculated by integrating \( \overline{I_0} \) with respect to \( \rho \). The integral breadth of the line is given by

\[
\beta(\rho) = \frac{\int \overline{I_0}(\rho) d\rho}{\overline{I_0}(m)}
\]

(2.20)

where \( \overline{I_0}(m) \) is the maximum value of \( \overline{I_0} \). James (1965) used a Gaussian function to approximate the interference function for a cubic crystal system and found that the integral breadth of a diffraction line corresponds to the crystallite size following the Scherrer equation

\[
\beta_{sne}(2\theta) = \frac{K\lambda}{L\cos\theta}
\]

(2.21)

where \( K \) is the Scherrer constant where value depends in general on the external form of the crystallites as well as on the order of the diffraction. Values for \( K \) have been tabulated for some cubic crystal solids (Stokes & Wilson 1944). It was argued by Stokes and Wilson (1944) that, usually, \( K = 1 \) is adequate to approximate the cubic crystallites.
2.2.3. Line Broadening by Distorted Crystals – Classical Theory by Stokes and Wilson

This theory was first introduced by Stokes and Wilson (1944) after making use of the structure factor to calculate the non-linear strain (or, lattice distortion) from the integral line-breadth.

Consider a displacement of a unit cell positioned at \( r \) by a vector \( \mathbf{u}(r) \). Another cell is also displaced with a distance \( t \) from the first cell and direction with a unit cell \( \mathbf{n} \). In general, this displacement involves both rotation and translation. However, the rotation will not affect the phase of the scattered radiation unless it is very large compared to the translation. The rotational structure factor contribution can then be neglected (James 1965). Using Equation (2.13), the structure factor for the displaced cells is

\[
F' = F \exp(i\mathbf{k} \cdot \mathbf{S} \cdot \mathbf{u}(r))
\]

\[
F'' = F \exp(i\mathbf{k} \cdot \mathbf{S} \cdot \mathbf{u}(r + nt))
\]

For large values of \( t \), \( F' F'' \) vanishes. For small \( t \), \( \mathbf{u}(r+nt) \) can be expanded in powers of \( t \). Taking the first two terms gives

\[
\mathbf{u}(r + nt) = \mathbf{u}(r) + t \mathbf{n} \cdot \nabla \mathbf{u}
\]

\( \nabla \mathbf{u} \) is a tensor for which the symmetrical part gives the strains in the crystal at the point under consideration. Using the approximation, it follows that the intensity is

\[
J_i = \overline{F' F''} = |F|^2 \exp(i\mathbf{k} \cdot \mathbf{u}) \cdot \nabla \mathbf{u}
\]

If \( \mathbf{n} \) is perpendicular to the \((hkl)\) planes, it can be found that \( \mathbf{S} = n|\mathbf{S}| = 2n \sin \theta \).

Defining \( \mu = \kappa|\mathbf{S}| = \frac{4\pi \sin \theta}{\lambda} \) then

\[
J_i = \overline{F' F''} = |F|^2 \exp(i\mu n \cdot \nabla \mathbf{u} \cdot \mathbf{n})
\]

or,

\[
J_i = |F|^2 \exp(i\mu e_{hh} t)
\]

since \( \mathbf{n} \cdot \nabla \mathbf{u} \cdot \mathbf{n} \) is the tensile strain \( e_{hh} \) in the direction of \( \mathbf{n} \) and perpendicular to the reflecting planes.
The integral breadth of a diffraction line can then be calculated using

\[ \beta (2\theta) = \frac{\lvert F \rvert^2 \lambda}{\cos \theta} \int J_t \, dt \]  

(2.28)

If \( \omega(e) \, de \) is a fraction of a crystal having \( e_{\text{th}} \) between \( e \) and \( e + de \) along the scattering vector, the 'apparent particle size' can be determined using

\[ D_{\text{app}} = \frac{\int J_t \, dt}{\int \frac{\omega(e) \, e \exp(i\mu t) \, de}{|F|^2}} = \frac{\int \omega(e) \, e \exp(i\mu t) \, de}{-\infty} \int \omega(0) \, e \, d\theta \]  

(2.29)

It can be shown that

\[ D_{\text{app}} = \frac{\lambda}{2 \sin \theta} \omega(0) \]  

(2.30)

\[ \beta = \frac{2 \tan \theta}{\omega(0)} \]  

(2.31)

where \( \omega(0) \) is \( \omega(e) \) when \( e = 0 \).

The 'apparent strain' is defined as

\[ \varepsilon_{\text{app}} = \beta \cot \theta = \frac{2}{\omega(0)} \]  

(2.32)

2.2.4. Line Broadening Associated with Dislocations

Dislocations are one-dimensional defects in a crystal. The theory of line broadening by dislocations has been overviewed by Ungár (1999). The theory requires the definitions of vector positions of two cells when they are distorted and undistorted. These are, respectively, \( r_i^0 \) and \( r_i^0 \) for the undistorted cells and \( r_i \) and \( r_i^\prime \) for the distorted cells. According to the theory of kinematical scattering, the intensity of a Bragg reflection for a crystal with one atom in a unit cell is given by

\[ I(\kappa) = f^2 \sum \exp(i\kappa \cdot (r_i - r_i^\prime)) \]  

(2.33)
where $\kappa$ is the diffraction vector $(k-k_0)$, $k$ and $k_0$ being the wave vectors of the scattered and the incident waves, respectively. The diffraction vector can be expressed as

$$\kappa = g + s$$  \hspace{1cm} (2.34)

where $g$ is the reciprocal lattice vector related to the associated Bragg reflection and $s$ is a vector which scans the reciprocal space in the vicinity of $g$.

If $\delta r_s$ is the displacement of a cell from the undistorted position, it follows that

$$r_s = r_s^0 + \delta r_s$$  \hspace{1cm} (2.35)

The intensity of the Bragg reflection can then be written as (Ungar 1999)

$$I(s) = f^2 \sum \exp[s \cdot (r_s^0 - r_s^0)] \exp[i g \cdot (\delta r_s - \delta r_s')]$$  \hspace{1cm} (2.36)

where the term $s \delta r$ is neglected. Equation (2.36) is of significance in the study of line broadening by dislocations from the following perspective:

1. for a large and perfect crystal, the Bragg reflection is a sharp delta function;
2. strain information is contained in the $\delta r$;
3. a Fourier transform of the phase shifts caused by the displacement component is represented in

$$A = \exp[i g \cdot (\delta r_s - \delta r_s')]$$;

4. the equation contains information about the crystal size.

The displacement component $A$ becomes the focus of the theory. Several approaches have been developed by employing the displacement component $A$ from different ways to obtain the strain-related information (Warren & Averbach 1950; 1952; Groma, Ungár & Wilkens 1988; Krivoglaz 1996). It should be emphasised, however, that these approaches are based on dislocation theories for metals and might not be appropriate for ceramic materials where dislocations may not be predominant and the strains are in principle due to shear interactions between grains caused by thermal expansion mismatches.
2.2.5. Interpretation of the Apparent Crystallite Size and Strain

Wilson (1970) expressed the specimen broadening $f$ as the inverse transform of the Fourier transforms of size $[V(t)]$ and strain $[Y(t)]$ effects

$$f(x) = \frac{\int V(t)Y(t)\exp(-2\pi ixt)dt}{U} \tag{2.37}$$

where $U$ is the volume of the unit cell. $V(t)$ can be interpreted as the volume common to a crystallite and its ‘ghost’ displaced a distance $t$ in the direction of the diffraction vector $d^*_{hkl}$ (see Figure 2.3), where

$$|d^*_{hkl}| = \frac{1}{d} = \frac{2 \sin \theta}{\lambda} \tag{2.38}$$

Langford (1999) applied the pattern decomposition approach to interpret the apparent size by employing reciprocal space integral breadth $\beta^*_S$ in the absence of the strain effects. The size integral breadth is

$$\beta^*_S = \frac{V(0)}{\int V(t)dt} \tag{2.39}$$

where $V(0)$ is the mean volume of crystallites and $L$ is the value of $t$ for which $V(t) = 0$ or the maximum thickness (Guinier 1963). The integral breadth apparent size $D_{app,\beta}$ is defined as

$$D_{app,\beta} = \frac{1}{\beta^*_S} \tag{2.40}$$

which can be interpreted as the volume-weighted thickness of crystallites measured in the direction of [hkl] (Langford 1999). The reciprocal of the slope of the Fourier transform of the normalised profile $\frac{V(0)}{V'(0)}$ is also a measure of crystallite thickness known as the Fourier apparent size $D_{app,F}$ (Wilson 1963), or
Figure 2.3. Crystal $A$ of volume $V$ and its 'ghost' $B$ which is displaced by a distance $t$ in the direction of the diffraction vector $d_{hkl}^*$ (Langford 1999).

\[ D_{app,F} = -\frac{V(0)}{V'(0)} \]  

(2.41)

The integral breadth and Fourier sizes, $D_{\beta}$ and $D_F$, are weighted average thickness in a particular direction which does not represent the actual mean dimensions and indication of shapes. It can be shown that the mean crystallite diameter $\langle D \rangle$ for spherical crystallites is given by (Wilson 1962)

\[ \langle D \rangle = \frac{4D_{\beta}}{3} \]  

(2.42)

or

\[ \langle D \rangle = \frac{3D_F}{2} \]  

(2.43)

Relationships between $D$ and crystallite dimensions for various shapes have been reported as well (Langford & Louër 1982; Langford 1992; 1999).
Stokes and Wilson (1944) introduced the concept of apparent strain $\varepsilon_{\beta,\text{app}}$ in association with the strain integral breadth $\beta_D^*$ according to

$$\varepsilon_{\beta,\text{app}} = \frac{2\beta_D^*}{d^*}$$  \hspace{1cm} (2.44)

The apparent strain can be associated with the 'actual strain' $\varepsilon$ according to

$$\varepsilon_{\beta,\text{app}} \approx 5\langle e^2 \rangle^{1/2}$$  \hspace{1cm} (2.45)

where $\langle e^2 \rangle^{1/2}$ is the root mean square strain or $\varepsilon_{\text{rms}}$.

In conclusion, section 2.2 has explored the theories of line broadening due to crystallite size and strain. The discussion does not include line broadening due to mistakes or stacking faults. Two principal ways to introduce size and strain effects to the broadening formulation have been shown, i.e. using the line width (integral breadth method) and the Fourier methods. These principles then become the bases of the crystallite size and strain assessments which are discussed in the following section.

2.3. Methods for Crystallite Size and Strain Assessments

The theory of x-ray line broadening was developed initially using the Fourier transform approach. The application of this theory was performed, for example, by Warren and Averbach (1950, 1952). It was also found that the classical Gaussian and Lorentzian PSF can be used to fit the diffraction pattern (Klug & Alexander 1974). In subsequent developments (e.g. Langford 1978), line profile analysis was conducted by fitting appropriate mathematical functions such as the Voigt function to the diffraction data and then extracting size and strain parameters from the line width.

Various studies have been reported on the development of line broadening analytical methods. Three classical methods which can be used to extract crystallite size and strain contributions from x-ray line broadening data are (Klug & Alexander
1974) (1) Fourier transform method, (2) integral breadth method involving Gaussian and Cauchy functions, (3) line profile variance methods.

As described briefly in §1.2, deconvolution of 'pure' specimen broadening must be carried out since an observed profile \( h \) is a convolution of the instrumental \( g \) and pure specimen \( f \) profiles (Figure 1.1) following Equation (1.1). If \( f \) represents the combined crystallite size and strain contributions to the profile, then \( f \) is a convolution of size and strain functions, \( f_s \) and \( f_\delta \), respectively, (Langford et al. 1988; Langford 1999)

\[
f(x) = f_s(x) \otimes f_\delta(x)
\]  

(2.46)

where \( \otimes \) denotes the convolution.

Classical size and strain analysis methods deduced microstructural information directly from experimental data of distorted metals (Warren & Averbach 1950; 1952; Guinier 1963; Klug & Alexander 1974). Accordingly, the related theory was developed based on the dislocation theory for metals which may not be appropriate for sintered ceramics in which microstrains arise primarily due to thermal expansion mismatch between grains and where dislocations may not be predominant.

Recent improvements in computing power have allowed diffraction pattern fitting to be performed more effectively. However, progress has been limited by the use of profile fitting functions for modelling which may not be physically correct for particular classes of materials, e.g. sintered ceramics. There are three ways to analyse crystallite size and strain by profile fitting, i.e. (1) the use of a function containing microstructural parameters to fit the real-space diffraction data, (2) the use of a function to fit the Fourier transforms of the diffraction data, and (3) the use of an analytical function to fit diffraction data followed by a Fourier-based analysis.

Multi-line profile fitting methods are size and strain assessment techniques which employ more than one diffraction line. These methods might be expected to be superior to single-line procedures as the angular dependence of the separate strain and size contributions to the specimen function \( f \) are markedly different. Two well-known multi-line methods have been widely used in the line broadening analysis, i.e. the Warren-Averbach (1950, 1952) and Williamson-Hall (1953) methods. Single-line methods, however, are recognised as rapid size and strain analysis procedures (de
Keijser et al. 1982; Delhez, de Keijser & Mittemeijer 1982) which are adequate for revealing the microstructural character of the specimen (York 1999).

The following sub-sections explain the approaches which have been widely used for the extraction of strain-size information by x-ray diffraction line profile analysis.

2.3.1. Warren-Averbach Fourier Method

The Warren-Averbach method (1950, 1953) is a multi-line size and strain procedure. If the instrumental profile function \( g \) is assumed, the specimen function \( f \) can be deconvoluted from the observed function \( h \). Consider \( H, G \) and \( F \) are the Fourier transforms of \( h, g \) and \( f \), respectively. The Fourier transform of \( f \), for example, is

\[
f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(n) \exp(-2\pi i n x) dn \tag{2.47}
\]

The deconvolution can be performed in terms of complex Fourier transforms as follows

\[
F(n) = \frac{H(n)}{G(n)} \tag{2.48}
\]

According to the Stokes' method (Stokes 1948), the inverse Fourier transform gives the specimen broadened line profile

\[
f(x) = \frac{1}{\sqrt{2\pi}} \sum_{x} \frac{H(n)}{G(n)} \exp(-\frac{2\pi i n x}{x_m}) \tag{2.49}
\]

where \( x_m \) is the minimum value of \( x \) when the intensity can be considered to have dropped to its background value. The specimen profile can be expanded into sine and cosine terms, according to

\[
f(x) = \frac{1}{\sqrt{2\pi}} \left[ \sum_{r} F_r(n) \cos\left(-\frac{2\pi i n x}{x_m}\right) + \sum_{s} F_s(n) \sin\left(-\frac{2\pi i n x}{x_m}\right) \right] \tag{2.50}
\]

It follows that computations of the Fourier transforms are greatly simplified if the \( h, g \) and \( f \) functions are symmetrical because the sine terms can then be
eliminated. However, symmetric profiles are rarely observed. For instance, if Bragg-Brentano x-ray diffractometer is used, g can be asymmetric due to the introduction of Kα₂ peaks. Corrections for the Kα doublet can be performed by mathematical elimination of the α₂ contribution from the combined Kα₁α₂ functions h and g (Rachinger 1948; Huang & Parrish 1975), by use of the iterative folding (convolution) method (Ergun 1968) or by use of a monochromator (Langford, Cernik & Louër 1991).

According to Equation (2.49), the specimen broadening f can be calculated directly from the observed profile h without knowledge on the peak shape function of the h and g profiles. However, it requires an accurate determination of the background limit xₘ to give accurate f. In addition, the specimen broadening should be sufficiently large relative to the instrument broadening in order to avoid unstable and inaccurate deconvolution (Delhez, de Keijser & Mittemeijer 1980). Furthermore, the truncation of the Fourier series will always produce profile-tail ripples regardless of the extent of the specimen broadening. The major disadvantage is overlapping peaks which cannot be resolved without restoring the profiles with peak-shape functions. This step introduces further biases into the results. As a result, the Stokes deconvolution method can be performed appropriately only for materials with high crystallographic symmetry (Balzar 1999).

In order to deal with overlapping peak difficulties, Balzar (1992) introduced the use of the Voigt function, a convolution of a Lorentzian and a Gaussian functions, as the peak shape of the h and g profiles. Since the convolution of two Voigt functions is also a Voigt function, the integral breadths of h, g and f profiles then have the relationships

\[
\beta_{fL} = \beta_{hL} - \beta_{gL} \quad (2.51)
\]

\[
\beta_{fG}^2 = \beta_{hG}^2 - \beta_{gG}^2 \quad (2.52)
\]

The specimen breadths \(\beta_{fL}\) and \(\beta_{fG}\) can then be used to reconstruct the specimen profile f.
In the Warren-Averbach method, the cosine Fourier coefficients \( A_n \) of \( f \) are used to give information about crystallite size and strain, since the \( A_n \) coefficients are the product of two terms (Warren & Averbach 1950). The first term depends only on the column length (size coefficient \( S \) – see Figure 2.4) and the second term depends only on distortion of the domains (distortion coefficient \( D \)):

\[
A_n = A_n^S A_n^D
\]  

(2.53)

Taking \( l \) as the undistorted distance between two unidirectional crystallographic positions, a linear curve can be developed by plotting \( \ln(A(l)) \) vs. \( l^2 \) since each coefficient can be written as (Delhez, de Keijser & Mittemeijer 1980)

\[
A_n^S = \frac{N(n)}{N_3}
\]  

(2.54)

\[
A_n^D = e^{-2\pi^2 l^2 (s^2(l))}
\]  

(2.55)
where $N(n)$ is the average number per column of pairs of unit cells a distance of $n$ cells apart, $N_j$ is the average domain size in unit cells perpendicular to the reflecting planes, and $\langle e^2(l) \rangle$ is the rms strain. The slope gives the rms strain value whereas the intercept produces the size coefficient function $A_n^S$ from which the average surface-weighted domain size can be obtained by

$$\frac{dA_n^S}{dn} \bigg|_{n \to 0} = -\frac{1}{N_j}$$  (2.56)

Use of the Stokes' deconvolution procedure prior to the Warren-Averbach method, however, may introduce some errors in the microstructural information obtained from the method. Also, the application of this method is limited to high-symmetry materials.

Balzar (1992) proposed an x-ray size-strain analysis procedure which is a combination of the profile fitting and multi-line Warren-Averbach methods. In this approach, the instrumental profile is modelled with a split Pearson-VII function and the specimen profile with a Voigt function. The convolution between the functions is fitted to the measured profile. The Gaussian and Lorentzian components are then used to calculate the cosine Fourier coefficients, $A_n$. Both size and strain contributions were modelled using Voigt functions. The Warren-Averbach method is applied to the Fourier coefficients to determine the volume- and surface-weighted average domain sizes and rms strain. The profile fitting procedure proposed by Balzar is applicable to overlapping peaks. However, the technique requires two orders of reflection of the same plane, which limits its applications.

**2.3.2. Williamson-Hall Method**

In the Williamson-Hall method (1953), it is assumed that particle size broadening of a line at Bragg position $\theta$ follows the Scherrer equation (with $K = 1$)

$$\beta_D = \frac{\lambda}{D \cos \theta}$$  (2.57)

while strain broadening is described by
\[ \beta \epsilon = 4 \epsilon \tan \theta, \]  
(2.58)

where \( D \) is the crystallite size, \( \epsilon \) is the upper limit strain and \( \beta \) is the integral breadth of the peak. It is assumed that both the size and strain broadening contributions of the specimen to the profiles are Lorentzian. Langford (1992) emphasised that this method should not be used quantitatively but can provide qualitative information on the nature of microstructural effects causing peak broadening. The total broadening is described by the sum of equations (2.57) and (2.58) according to

\[ \beta \cos \theta_i = \frac{\lambda}{D} + 4 \epsilon \sin \theta_i \]  
(2.59)

By plotting \( \beta \cos \theta \) against \( 4 \sin \theta \), the crystallite size can be obtained from the intercept of the regression line (in radians), \textit{i.e.} by \( D = \lambda / \text{(intercept)} \), whereas the slope of the line directly gives the maximum strain value, \( \epsilon \).

The use of the Voigt function in an ‘improved’ Williamson-Hall method was introduced by Langford (1992) using a pattern decomposition approach. The integral breadth \( \beta \) of a Voigt function is approximated by (Hadler and Wagner p1966)

\[ \beta^2 \approx \beta_L^2 + \beta_G^2 \]  
(2.60)

where \( \beta_L \) and \( \beta_G \) are the integral breadths of the Lorentzian and Gaussian profiles, respectively, and

\[ \beta_L = \frac{1}{D} \]  
(2.61)

\[ \beta_G = \frac{\epsilon \cdot d^*}{2} \]  
(2.62)

where \( d^* = \frac{2 \sin \theta}{\lambda} \), with the integral breadths being in reciprocal units.

The size-strain analysis is performed by combining the Voigt function properties (see notes below Table 2.1 as well as Equations (2.60, 2.61 and 2.62)) which gives
\[
\left( \frac{\beta}{d^*} \right)^2 = \frac{\beta}{D \cdot (d^*)^2} + \left( \frac{\varepsilon}{2} \right)^2
\]  

(2.63)

By plotting \( \left( \frac{\beta}{d^*} \right)^2 \) versus \( \frac{\beta}{(d^*)^2} \), the linear regression line intercept on the \( \left( \frac{\beta}{d^*} \right)^2 \) axis gives the average strain value \( \langle \varepsilon \rangle \) and the slope gives the average apparent size \( \langle D \rangle \). This procedure is called the ‘average size and strain plot’ (Langford 1992).

Recently, an additional modified Williamson-Hall method has been developed by Ungár and Borbely (1996) using the dislocation theory of metals. Equation (2.59) was modified to give

\[
\cos \theta_b \Delta \theta = \frac{0.9 \lambda}{2d} + \frac{\pi b^2}{2A} \sqrt{\rho C} \sin \theta_b
\]  

(2.64)

where \( \cos \theta_b \Delta \theta \) is the line breadth, \( b \) is the magnitude of the Burgers vector, \( \rho \) is the dislocation density, \( \bar{C} \) is the average value of the ‘contrast factor’ \( C \), and \( A \) is a constant which determines the type of the dislocation. The analysis is conducted by using the line breadths to plot \( \cos \theta_b \Delta \theta \) versus \( \sin \theta_b \).

2.3.3. Variance Method

The profile variance was introduced as a measure of line broadening by Wilson (1962). The use of the variance method for size and strain analysis was summarised by Klug and Alexander (1974). The variance expression used in this approach is

\[
W_{2\theta} = \frac{K \lambda \Delta \theta}{2 \pi^2 p \cos \theta} - \frac{T_a \lambda^2}{4 \pi^2 p^2 \cos^2 \theta} + 4 \tan^2 \theta \langle \varepsilon^2 \rangle
\]  

(2.65)

where \( K \) is the Scherrer constant, \( p \) is the edge length of a cubic crystal and \( T_a \) is the taper parameter which is a measure for describing the changes of the crystallite’s cross section with respect to the displacement of a crystal to its ‘ghost’ (see Figure 2.3). The taper parameter is usually neglected in practical calculations. By plotting
\[
\frac{W_{2\theta} \cos \theta}{\lambda \Delta 2\theta} \quad \text{against} \quad \frac{4 \sin \theta \tan \theta}{\lambda \Delta 2\theta}, \quad p \text{ can be obtained from the ordinate intercept and}
\langle e^2 \rangle \quad \text{from the gradient.}
\]

2.3.4. Single-line Integral Breadth Method

The single-line methods can be performed either in Fourier or real space (Delhez, de Keijser & Mittemeijer 1980; de Keijser et al. 1982). Most of the Fourier methods are vulnerable to deconvolution procedures particularly if the background is determined inappropriately or if the peaks under investigation overlap. Some improvements have been made by employing profile shape functions (de Keijser, Mittemeijer & Rozendaal 1983) so that the required Voigt integral breadths, for example, can be obtained readily by

\[
\frac{dA'_n}{dn} \bigg|_{n \to 0} = -\frac{2\beta'_L}{a} \tag{2.66}
\]

\[
\frac{d^2 A'_n}{dn^2} \bigg|_{n \to 0} = \frac{4(\beta'_L)^2}{a^2} - \frac{2\pi(\beta'_0)^2}{a^2} \tag{2.67}
\]

where \( \beta'_L \) is the Lorentzian breadth of the specimen profile \( f \) and \( a \) is period in a 2\( \theta \) scale. These expressions were derived using Equation (2.56) and approximating the size-broadened profile by a Laue interference function (Delhez, de Keijser & Mittemeijer 1982) to give

\[
\frac{d^2 A'_n}{dn^2} \bigg|_{n \to 0} = \frac{4(\beta'_L)^2}{a^2} \tag{2.68}
\]

The area-weighted average crystallite size \( \langle D \rangle_c \) and the rms strain \( \langle e^2 \rangle^{\frac{1}{2}} \) were calculated using (de Keijser, Mittemeijer & Rozendaal 1983)

\[
\langle D \rangle_c = \frac{\lambda}{2\beta'_L \cos \theta} \tag{2.69}
\]

\[
\langle e^2 \rangle^{\frac{1}{2}} = \frac{\beta'_0 \tan \theta}{2\sqrt{2\pi}} \tag{2.70}
\]
The correlations between the parameters for the pseudo-Voigt and Voigt functions have been parameterised (David 1986) which leads to the possibility of performing size and strain analysis using the pseudo-Voigt function, but with the introduction of additional uncertainties due to the parameterisation.

The integral breadth single-line methods use peak-shape functions to fit a diffraction peak and relate the adjusted peak width parameters with the microstructural information. This method of extraction of strain and/or size information from the analysis of single Bragg peaks is problematic in that the shape of a single Bragg peak may provide reasonable results for either strain or size modelling, but not where both effects are present. In situations where the broadening is likely to be strain-only or size-only, profile fitting is performed by associating the specimen-only function \( f \) with the assumed line width expression for either strain or size broadening, e.g. the Scherrer line width. Furthermore, the method requires use of physically sensible functions for the determination of functions \( g \) and \( h \) which is particularly difficult to achieve for XRD data due to the complex form of the instrument function \( g \).

In the past, a single function such as Gaussian or Lorentzian was mainly used to fit both the size and strain components. However, theory and experiment showed that this approach to be inappropriate (e.g. de Keijser et al. 1982; Balzar 1992) presumably due to the absence of any physical basis for use of the profile functions. The pseudo-Voigt function has also been used to fit x-ray diffraction profiles (Enzo & Schiffini 1999). However, the use of the pseudo-Voigt function also has no physical foundation and may provide unreasonable results.

Langford (1978) made substantial progress in dealing with the complex form of the profile function by employing the Voigt function (a convolution of Gaussian and Lorentzian functions) for x-ray diffraction profile fitting which was found to give a better approximation than its ‘derivatives’, i.e. Gaussian and Lorentzian functions.

The single-line integral-breadth method for extracting size and strain using the Voigt function can be applied according to the procedure proposed by de Keijser et al. (1982) who used Gaussian and Lorentzian breadths (\( \beta_{GC} \) and \( \beta_{LC} \), respectively) to
estimate the specimen-only contributions ($\beta_R$ and $\beta_L$) according to Langford (1978) with the expressions given by Equations (2.51) and (2.52).

The angular dependence of the peak breadth $\beta$ can be analysed to give crystallite size and strain values, by assuming that the Gaussian component ($\beta_R$) is ascribed to strain and the Lorentzian component ($\beta_L$) to size broadening

$$\beta_R = 4\varepsilon \tan \theta_i$$

and

$$\beta_L = \frac{\lambda}{\langle D \rangle_v \cos \theta_i}$$

where $\varepsilon$ is the weighted average strain, $\lambda$ is the radiation wavelength and $\langle D \rangle_v$ is the volume-weighted average size.

### 2.3.5. Whole-Powder Pattern-Fitting Methods for Strain-Size Analysis

The Rietveld method for analysis of powder diffraction data (Rietveld 1967; 1969) involves the fitting of the entire observed profile with a simulated pattern derived using models for the crystal structure and diffraction peak profiles. The method was originally developed for crystal structure analysis. The method may also provide microstructural information from peak profile character. If information about these properties is to be extracted from the pattern, the effects of the instrument must be modelled correctly. This procedure can be accomplished using the Voigt function with the Gaussian component of the peak width $H_G$ being modelled according to Caglioti, Paolelli and Ricci (1958)

$$H_G^2 = U \tan^2 \theta + V \tan \theta + W$$

where $U$, $V$, and $W$ are refinable parameters. Extraction of the size can be achieved by refining the Lorentzian component ($H_L$) which derives from the Scherrer expression

$$H_L = \frac{\lambda}{D \sec \theta}$$
where $\lambda$ is the wavelength.

The refinements involve the adjustment of the $U$ Voigt peak profile and the 'size parameter' $D$. The $V$ and $W$ parameters are constrained to values obtained with a suitable standard by assuming that strain contributes only to the $U$ parameter.

The rms-strain, $e_{rms} = \langle e^2 \rangle^{1/2}$, can be calculated if the $U$ parameter is refined with the $V$ and $W$ values being fixed at values obtained for the unstrained material, using

$$e_{rms} = \left( \frac{U - U_s}{32 \ln 2} \right)^{1/2} \quad (2.75)$$

where $U$ and $U_s$ are the parameters obtained from the strained specimen and a strain-free standard, respectively. Equation (2.75) can be derived from expressions provided by Wilson (1963).

The Rietveld refinements for this study were performed with the program Rietica (Hunter 1998) which derives from the Hill-Howard-Hunter LHPM program (Hill, Howard & Hunter 1995). Rietica calculates the crystallite size $D$, if the Voigt function is applied, using the following expression

$$D = \frac{\lambda}{H_L} \quad (2.76)$$

where $H_L$ is the Lorentzian full-width at half-maximum and $\lambda$ is the wavelength. It should be noted that a physical interpretation of the size parameter is likely to have meaning in the case only of ND data for which the instrumental component of the peak shapes is near-Gaussian in form, while for XRD, both Gaussian and Lorentzian components contribute to the instrumental broadening (Suortti, Ahtee & Unonius 1979).

Following the development of the Rietveld method, the value of the analysis of powder diffraction data became more important in particular with the advancement in computing capabilities. A whole-powder pattern-fitting (WPPF) approach has now been used to extract structural and microstructural information from materials (Toraya 1986; Scardi 1999; Scardi & Leoni 2001). For structural work, WPPF may
be used to give starting values for *ab initio* structure determination (Scardi 1999). To extract microstructural information, an analytical function was used and microstructural effects were assumed to contribute to the broadening of the function. Toraya (1986) employed the Pearson VII function and Scardi (1999) and Scardi and Leoni (2001) used the pseudo-Voigt function in their models. It is evident that microstructural models should use the entire diffraction pattern. This study, however, is confined to single-peak analysis due to time limitations. It is recommended (Chapter 7) that the model developed in this study be extended to accommodate WPPF calculations.

### 2.3.6. Crystallite Size Distribution

The crystallite size distribution may be an important descriptor for materials with regard to the chemical and physical properties. For example, the activity and selectivity of catalysts are influenced by the size distribution. It is therefore desirable to determine this additional size information. This may be achieved through line broadening analysis.

If the Fourier method is used, the size (or, column length) distribution can be determined from the second derivative of the size Fourier coefficient $A^s_n$ (Warren 1969)

$$
\frac{d^2 A^s_n}{dn^2} = \frac{p(n)}{N_3} \tag{2.77}
$$

where $p$ is the column-length distribution function.

The effect of a crystallite size distribution on diffraction line profiles has been investigated by Langford, Louër and Scardi (2000) by summing the intensity in reciprocal space (Equation (2.37), with the absence of the strain component, after applying an assumed Gaussian and lognormal distribution function as a weight factor for a particular morphology. The effect of a unimodal distribution of crystallite size on a diffraction line profile are to reduce its width and to disperse its tail. A line profile analysis was applied to the XRD pattern of CeO$_2$ nanopowder and resulted in a lognormal distribution mean value of 2.3 nm, which differed from the TEM result of 3.5 nm. They argued that this difference can be due to limited number of particles.
considered in the TEM analysis and also due to insufficient sampling. Note that the presence of any microstrain in the specimen was ignored in the study which may contribute to the XRD and TEM sizes difference.

Popa and Balzar (2002) developed an analytical size profile function which includes the empirical lognormal and Poisson distributions. The size function can readily be convolved with the strain and instrument functions. A test using CeO₂ powders showed that a ‘super-Lorentzian’ profile can be modelled with a broad lognormal size distribution. It was also shown that the common Voigt function cannot model very narrow and broad size distributions. It was argued that the crystallite size distribution cannot be fully determined by diffraction analysis. For example, a ‘super-Lorentzian’ character can be caused either by broad lognormal or multimodal size distributions. Transmission electron microscopy may be required to explain the true distribution.

A size profile function which was derived by mean-field theory from statistical mechanics associated with normal grain growth (York 1999) includes a size distribution parameter. The parameter determines a more general dispersion of the size distribution which accommodates the symmetric Gaussian and the lognormal distributions. Details of the subject are presented in §2.4.

2.3.7. Application and Comparison of the Methods

Most research on line broadening analysis has focussed on metallic materials (Warren 1969; Klug & Alexander 1974; Delhez, de Keijser & Mittemeijer 1982). Some work has also been done on line broadening for ceramic powders (Langford et al. 1986; Balzar 1992; Balzar & Ledbetter 1993; Sanchez-Bajo & Cumberera 1999), complex fibre-reinforced ceramic composites (Balasingh, Abuhasan & Predecki 1991), and polymeric materials (Somasekhar & Somashekarappa 1997). However, to date there have been no detailed reports of studies on the diffraction line-broadening of sintered ceramics produced under controlled conditions which provide systematic changes in strain field and size characteristics. Size and strain assessments of some materials are described in the following passages.
The Warren-Averbach method is commonly used in size and strain analysis despite its disadvantages. Some applications of the method, particularly for deformed metals and alloys, were compiled by Klug and Alexander (1974). It appears that the Warren-Averbach method cannot be considered as a general size and strain analysis method due to inherent problems associated with truncation of line profiles and initial slope determination. This is a result of the 'hook' effect which results from inaccurate determination of background level. As a consequence, the Fourier and variance sizes, for instance, are very different by a factor which can be as high as two (Langford et al. 1988).

The Warren-Averbach and 'double-Voigt' methods were applied to the 'classical' materials W and MgO by Balzar (1999). Standard specimens made from the same materials were used to deconvolute the instrument profile. Size and strain analysis was performed to obtain the relative values rather than the absolute values. It was concluded that size and strain profiles may be modelled accurately with the Voigt function. It was also found that there was a consistent relationship between the results for Warren-Averbach and integral breadth methods. In general, however, the methods showed small but systematic disagreement in the results.

The development of microstructure in nanocrystalline cerium oxide prepared by thermal decomposition of cerium (IV) oxide nitrate has been studied with x-ray diffraction data using the pattern decomposition method (Guillou, Auffrédic & Louër 1995). The Williamson-Hall plots were used to test for anisotropy effects and showed no size or strain anisotropy effects. The apparent volume weighted average size and the apparent strain were calculated following the 'average size and strain plot' procedure given by Langford for Equation (2.63) (Langford 1992). It was found that the crystallites could be described as spheroidal, and that their dimensions increased with annealing temperature. The diffraction diameter was markedly smaller than the SEM 'particles' diameter indicating that the SEM 'particles' consist of clusters of coherently diffracting domains. It was also found that the rms strain decreases progressively with annealing temperature.

Another study of microstructure development of nanocrystallite cerium oxide was described (Audebrand et al. 2000b) with particular reference to the growth of the crystallite size. The Williamson-Hall method was used to identify size anisotropy. The size analysis was performed using the Stokes’ deconvolution Warren-Averbach
(Warren & Averbach 1952) and the Langford average size and strain plot (Langford 1992) methods. The values of Fourier and Langford sizes were significantly different which was argued to be due to the presence of a crystallite size distribution. It was found that the distribution becomes narrower when the temperature increases. Again, larger SEM ‘particles’ than the crystallite size were found which was indicative of ‘particles’ composed of clusters of domains. Microstructural investigation using TEM showed that TEM ‘particles’ are crystallites in the sense of coherently diffracting domains (Auffredic et al. 1995).

The Voigt integral breadth single-line method has been applied to various types of materials, for instance metals (de Keijser et al. 1982), β-SiC-whisker+Al₂O₃ composites (Balasingh, Abuhan & Predecki 1991) and MgO sintered ceramics (Pratapa, O’Connor & Hunter 2002). The method relies on the assumption that strain contributes only to the Gaussian component of the Voigt function and that the size broadening contributes only to the Lorentzian component (de Keijser et al. 1982). In general, analysis for different reflections gave results with reasonable agreement. Consistent results for reflections from the same crystallographic family were also obtained when the method was applied to nickel layers (de Keijser et al. 1982). These results support the proposition that size and strain analysis using a single reflection should be adequate in general cases (York 1999). Note, however, that Gaussian-strain and Lorentzian-size assumptions have been challenged recently (e.g. Wu, Gray & Kisi 1998; Stephens 1999) in terms of the anisotropic size and strain effects.

The Rietveld size-strain method has been used widely for strain and size analysis (Thompson, Reilly & Hastings 1987; Wu, Kisi & Gray 1998; Nakamura et al. 2000; Pratapa, O’Connor & Hunter 2002). The peak-shape function incorporated in the fitting procedure is of importance for assessments of the size and strain. The effect of crystallite anisotropy on diffraction peak broadening has been modelled (Greaves 1985; Wu, Gray & Kisi 1998; Stephens 1999), and some Rietveld programs have incorporated anisotropic broadening into the refinement procedures. Larson and von Dreele (1987), for example, included an additional parameter to model the anisotropic size and two additional parameters to model the isotropic and anisotropic strains which were then incorporated into the Lorentzian profile. The model was applied, for instance, by Nakamura et al. (2000) to investigate dislocation
characteristics in LaNi₅ which was subjected to an activation process and hydriding-dehydriding cycles. Reasonable agreement was achieved when the dislocation results were contrasted to TEM data.

In the present study, strain-size evaluations from line broadening for MgO ceramic materials have been compared for single-line integral-breadth and Rietveld procedures using the Voigt function (Pratapa, O'Connor & Hunter 2002). Diffraction data were measured by Bragg-Brentano x-ray diffractometry (XRD) without incident beam monochromatisation, and by neutron diffractometry (ND) to characterise near-surface and bulk effects, respectively. The single-line and Rietveld methods gave similar strain values for both the XRD and ND data within the limits of experimental error, but there were substantial differences between the single-line and Rietveld size estimates determined with the XRD and ND data. Despite the possibility of acquiring strain-size information using the Voigt function, it should be emphasised that the Gaussian-strain and Lorentzian-size assumptions can apply only to conditions where microstrain is small (ca. < 1.0×10⁻³) and the crystallites are monodispersed. Moreover, the crystallite size distribution is not taken into account in the Voigt model. It is therefore of value to develop a model which accommodates these effects and has direct microstructural interpretation. York (1999, 2003) has derived analytical profile functions with parameters which are directly associated with the crystallite size distribution, with the mean crystallite size and with the strain distribution. A review of the physically-based approach, with particular attention to York’s model, is presented in §2.4 followed with an overview on how it might be improved.

Four important observations can be summarised from the literature on strain and size assessment methods:

1. The methods which are commonly used to determine crystallite size and strain from line broadening are (i) Fourier, (ii) variance and (iii) integral breadth methods. The Fourier methods have inherent problems mostly related to the deconvolution process and overlapping peaks.

2. The sources of disagreement among numerical results from size and strain analysis can be due to definitional differences for the parameters being used. The Fourier and integral breadth methods define the crystallite size as the
volume-average dimension perpendicular to the reflecting planes, while the variance method interprets the size as the cube root of the volume of the crystallites. In terms of strain, the Fourier method gives the rms strain \( \langle e^2 \rangle^{1/2} \) in a direction perpendicular to the reflecting planes and averaged over a distance \( L \). The integral breadth method provides an approximation to the strain value as the upper limit \( \varepsilon \) such that \( \varepsilon \approx 1.25 \langle e^2 \rangle^{1/2} \), while the variance method gives \( \langle e^2 \rangle^{1/2} \). The apparent size and strain values can be associated with the rms values after appropriate correction. Mean diameter \( \langle D \rangle \) is \( \frac{4D_{app}}{3} \) (calculated by integral breadth method) or \( \frac{3D_{app}}{2} \) (by Fourier method), while the apparent strain can be associated with either rms strain or upper limit strain, by \( e_{app} \approx 5e_{rms} \) or \( e_{app} = 4\varepsilon \).

3. There is no integral-breadth profile fitting procedure which is based on a physical model related to the microstructure of specimen.

4. Most studies on x-ray diffraction-line broadening have involved metals. However, the study of line broadening of sintered ceramics in a systematic way is not reported in literature and, therefore, deserves more attention since the materials are now widely used. In order to obtain comprehensive results, sintered ceramics with sufficiently wide range microstructural characteristics should be studied.

2.4. Physically-based Approaches for Size and Strain Assessments

Even though the results obtained by the procedures described above may be valid for some material types (notably metals), the mathematical assumptions may lead to incorrect results if the assumed dislocation model is inappropriate. In such cases, the information gained from the analysis may be unreliable or even meaningless, e.g. the negative values of size parameter for alumina whiskers systems reported by Balasingh, Abuhasan and Predecki (1991). Advances have been made
recently in developing more reliable techniques in size-strain analysis. Three strategies are summarised here.

Van Berkum and colleagues (1996) used the so-called strain-field theory in their size-strain model which was found to be applicable only for cubic tungsten. This model calculates the intensity of the broadened diffraction profiles due to lattice distortions causing strain fields in a column parallel to the diffraction vector. The model uses a superposition of component strain fields with statistically determined amplitudes and distances between the projections of the defects onto the column. These parameters are then used to determine the Fourier coefficients of the profiles. The parameters involved in the analysis are the average distance between defects, the extent of the distortion field, and the mean-squared strain.

Other research has been conducted by Ungár and colleagues (1999, 2001) to incorporate physical parameters which were derived from dislocation theories in the line-broadening analysis. They used the modified Warren-Averbach method to assess the strain (size assessment being excluded) by employing

\[ A_n^D = e^{-2\pi i q \cdot \vec{r}} \]  \hspace{1cm} (2.78)

where

\[ \langle e_\vec{r}^2 \rangle \equiv \left( \rho C_b^2 \right) \frac{\ln \left( \frac{R_e}{l} \right)}{4\pi} \]  \hspace{1cm} (2.79)

where \( \rho \) is the dislocation density, \( R_e \) is an effective outer cut-off radius of dislocations (see, for example, Ungar 1999), \( b \) is the modulus of Burgers vector \( \vec{b} \), and \( C_b \) is a contrast factor for the dislocations. The pseudo-Voigt function was employed to fit the diffraction profiles and its Fourier transform was expressed in terms of the mixing parameter \( \eta \) and the half-width at half maximum (HWHM). The contrast factor \( C_b \) was calculated for each reflection based on the correlation between the reflection and Burgers vectors of dislocations and the diffraction vector, respectively. The microstructural parameters, together with Bragg peak \( \theta_b \) and integral breadth \( \beta \) parameters, were used to develop the simulated physical broadening function \( f \) which was then convoluted with the assumed \( g \) function. The simulation parameters (\( \rho, \mu, \) and crystallite size) were optimised until an acceptable
match was obtained between observed and calculated profile widths. Although some results of the analysis were reported, there was no further discussion on the comparison of these results with those from other methods.

York (1999, 2003) described a novel approach to strain-size assessment involving the derivation of a line profile function for which the key parameters relate directly to the growth of the microstructure as the material forms. He used a mean-field theory and statistical mechanics to develop crystallite size and strain distribution functions involving a grain-growth parameter and the ‘dislocation’ or strain density. These profile functions depend on four measurable microstructural parameters: the Bragg d-spacing, \( d_b \); the average number of lattice planes, \( <N> \), hence average grain size; the rms strain, \( <e^2>^{1/2} \), which is proportional to the average dislocation density; and parameter \( \beta \) which characterises the width of the size distribution and is functionally related to the kinetic growth parameter of a grain boundary sweep rate constant \( \theta' \). The product of the distribution function and the Laue \( \frac{\sin^2 Nx}{\sin^2 x} \) function is integrated to obtain the associated profile function. This approach implies that the York model must be appropriate for line profile fitting procedure in size and strain analysis in which the refinable parameters have direct physical interpretation. The following section describes York’s model for size and strain analysis.

2.4.1. Size Distribution and Size Profile Functions

York used the classical mean-field theory to describe the normal grain growth process. According to this theory, grain growth is a process of embedding a single grain into a system, representing the average of all other grains, and involves diffusion of grains from one class of size to another. Although the physics behind a diffusion process between grains with different size classes is not fully understood, it is known that the process follows the minimisation of a grain boundary curvature term defined by grain boundary surface area per unit volume, which has been described, for example, by Hillert (1965) and York [1999 - Equation (2)] in terms of the grain boundary velocity. The expression is claimed by Hillert (1965) to be widely used to model grain growth. The grain boundary velocity is associated with a grain
boundary sweep rate constant which is defined as the number of grains consumed or lost when grain boundaries move to a volume equal to the mean grain volume. The sweep rate constant is independent of the type of material if a steady state grain growth is achieved (see York 1999). Applying the grain growth diffusion equation, the Hillert expression and the sweep rate constant, the normal grain growth equation can be determined as (York 1999, Equation (3))

\[
\frac{\partial \rho(u)}{\partial u} + \nu (1 - \frac{1}{u}) \rho(u) = 0
\]  

(2.80)

where \( \rho \) is the size distribution function, \( u = \frac{R}{R_o} \) (\( R \) is the grain size and \( R_o \) is the mean of the distribution function) and \( \nu \) is the size distribution parameter.

The trivial solution of Equation (2.80) is

\[
\rho(u) = u^\nu e^{-\nu u}
\]  

(2.81)

The size distribution parameter \( \nu \) is dependent on the growth mechanism and has the following significance:

1. relates the physical parameters of sweep rate constant \( \theta^* \) and the Hillert geometric constant \( \alpha \) following

\[
\nu = \left(1 + \frac{3}{2\theta^*}\right) \alpha
\]  

(2.82)

2. controls the dispersion of the size distribution function. For small \( \nu \) values, the distribution function is broad and asymmetric while for larger \( \nu \) values the distribution function approaches a narrow, symmetrical Gaussian distribution. The distribution function approaches a delta function for \( \nu \to \infty \) to give the 'ideal' uniform size distribution.

3. may be valid as a grain consumption parameter where \( \nu = 0 \) means grain consumption does not occur and large \( \nu \) means a rapid grain consumption.
This final size profile function is determined by integrating the Laue function over the size distribution function given by Equation (2.81). The grain size \( R \) can be interpreted as \( N \bar{d} \), where \( N \) is number of diffracting planes and \( d \) is the interplanar spacing. Assuming that a columnar-like grain structure is perpendicular to the diffracting planes with a uniform strain, the integration gives the size profile function \( f_{\text{size}}(\theta) \) as follows

\[
f_{\text{size}}(\theta) = \int_{-\infty}^{\infty} u^N e^{-nu} \frac{N\psi}{\sin^2 \psi} du
\]

(2.83)

where \( \psi = \frac{d \sin \theta}{\lambda} \), \( d \) is the lattice spacing and \( \lambda \) is the radiation wavelength, resulting in an analytical size profile function. After the expansion of \( \theta \) about the peak position \( \theta_0 \), Equation (2.83) has the form [York 1999; after a modification of Equation (5)],

\[
f_{\text{size}}(\theta) = \frac{I_0}{\left[ 1 + \frac{2\pi \left( \frac{2\theta - 2\theta_0}{W_D} \right)^2}{\nu + 1} \right]^{\nu + 1}}
\]

(2.84)

where \( I_0 \) is the maximum intensity and \( W_D \) is the full-width at half maximum (FWHM). The modal size \( D_0 \) is defined by

\[
D_0 = \frac{\lambda}{W_D \cos \theta}
\]

(2.85)

2.4.2. Strain Distribution and Strain Profile Functions

The basis of the theory is to accommodate the mean strain energy based on dislocation interaction between grains in the mean-field calculation to determine the strain probability distribution function \( P(\varepsilon) \). By calculating the hamiltonian energy for the interactions, York [2003; Equation (23)] showed that the strain distribution function can be expressed as

\[
P(\varepsilon) = \exp \left( -\frac{G(\varepsilon - \varepsilon_0)^2}{\kappa \rho} R \right)
\]

(2.86)
where $G$ is the elastic modulus, $R$ is the grain size, $\rho$ is the dislocation density and $\kappa$ is a proportionality constant which take into account elastic, grain shape and dislocation distribution constants. Integrating the Laue function over the strain distribution function gives the strain profile function $f_{\text{strain}}(\theta)$ according to

$$f_{\text{strain}}(\theta) = \int_{-\infty}^{\infty} \exp \left( -\frac{G(\varepsilon - \varepsilon_0)^2}{R\kappa} \right) \frac{\sin^2 N \psi}{\sin^2 \psi} du$$  \hspace{1cm} (2.87)

where $\psi = \frac{2\pi d_b \sin \theta \cdot (1 + \varepsilon - \varepsilon_b)}{\lambda}$ after rescaling the strain $\varepsilon$ so that $d = d_b(1 + \varepsilon - \varepsilon_b)$ where $d_b$ is the Bragg d-spacing of the line.

Assuming large grain sizes with uniform distribution (large $\beta$), the analytical strain function is given by

$$f_{\text{strain}} = N + 2 \sum_{k=1}^{N-1} (N - k) \exp \left( -\frac{\pi^2 d_b \kappa \kappa_0^2 l^2}{D_0} \right) \cos(2\pi kl)$$ \hspace{1cm} (2.88)

where $l$ is the order of the reflection and $D_0$ is the center of the strain distribution function. The exponential term containing the dislocation density $\rho$ acts as a damping factor, reducing the finite size oscillations produced by the cosine term. It was claimed that the damping factor affects the width of the reflection. It has been shown (see Appendix 1) that the strain broadening depends strongly on crystallite size. A large crystallite size is associated with small $N$ and vice versa. As a result, large strain is associated only with small crystallites and vice versa. Due to this behaviour, the strain profile function derived by York (1999; 2003) was not used in this study.

In deriving the total size and strain function $F(2\theta)$, York (2003) used

$$F(2\theta; D; \varepsilon) = \int F_L(2\theta, D, \varepsilon) \cdot \rho(D) \cdot P(\varepsilon) dD d\varepsilon \hspace{1cm} (2.89)$$

where $F_L(2\theta, D, \varepsilon)$ is the Laue function.

This calculation was challenged by Langford (1999) by proposing that

$$F(2\theta; \varepsilon; D) = g \otimes f_{\text{strain}}(\varepsilon) \otimes f_{\text{size}}(D) \hspace{1cm} (2.90)$$
where, instead of having the double integrals as in Equation (2.89), all effects are convoluted to give the overall function. Evaluation of the equation appears to be easier performed numerically. Further explanation of the calculation together with the development of the numerical program is given in Chapter 3 and Chapter 5.

The principle questions underlying the usefulness of these theories are, therefore:

1. which physical models can be used in size and strain analysis?
2. how can the models be improved?
3. how effective are these models in assessing size and strain values?

2.5. Crystallite Size and Strain in Sintered Ceramics

While there is some literature on size and strain analysis of ceramic powders (e.g. Auffredic et al. 1995; Audebrand et al. 2000a; 2000b), there are no detailed studies on line broadening for sintered ceramics. This study deals with the development of size and strain line broadening models with particular reference to sintered ceramics which were produced by controlled conditions to provide a systematic description of the size and strain characteristics in the materials. This section briefly reviews some theories on the processing of ceramic materials and the development of size and strain in such materials.

2.5.1. Ceramic Processing

Sintered ceramics can be produced by compacting raw powders to produce porous green bodies followed by heat treatments to allow densification of the bodies. Ceramic powders, in general, contain agglomerates which can be classified as hard and soft groups. The hard group comprises partially sintered and cemented particles, while the soft group consists of particles which are bound by Van der Waals forces (Lange 1984) and tend to consolidate more easily than the hard agglomerates. Therefore, the degree of agglomeration can strongly influence the evolution of microstructure and grain sizes for densification. In terms of sintering, the degree of agglomeration strongly affects sinterability and sintering kinetics. Dry powders with
particle sizes less than 10 μm can usually be expected to contain soft agglomerates which promote sintering.

Sintering removes pores between particles (accompanied by shrinkage of the materials), produces densification, allows grain growth and strong bonding between adjacent particles (Richerson 1992). In order to favour the process, material transport and energy to initiate and retain the transport should be present. The material transports in sintering are diffusion and viscous flow and the energy used in sintering is in the form of heat.

There are three basic stages in the sintering process (Richerson 1992) as illustrated in Figure 2.5. During the initial stage, the raw particles rearrange and start to form inter-particle ‘necks’. Slight movement and rotation of particles to increase number of contact points occur during rearrangement which is followed by bonding at the contact points where material transport can occur and where surface energy is highest. The second stage, called the intermediate stage, involves the growth of the necks between particles, decrease in porosity, increase in shrinkage and grain growth. At this stage, the grain boundaries start to move so that one particle (or grain) begins to grow while the adjacent grain is consumed. This grain grow causes changes in geometry which are necessary to allow further neck growth and porosity removal. The intermediate sintering causes most of the shrinkage and will not finish until pores become isolated. During the final sintering stage, the remaining porosity is removed by vacancy diffusion along the grain boundary. In order to completely remove the porosity, the pores must have contact with grain boundaries. If this does not occur, for example when the grain growth is fast, the pores can be left isolated inside a grain.
Figure 2.5. Stages in sintering process (after Richerson 1992). (a) initial stage, (b) intermediate stage and (c) final stage. Black areas represent porosities.
If the densification of the green body is controlled by lattice or grain boundary diffusions at the initial stage of sintering, the relationship between linear shrinkage rate \( \frac{\Delta L}{L_0} \) of the green body and time \( (t) \) can be expressed as (Reed 1988)

\[
\frac{\Delta L}{L_0} = \left( \frac{K \gamma a D}{kT r_p} \right)^n t^m
\]

where \( D \) is self-diffusion coefficient, \( \gamma \) is surface energy, \( r \) is particle radius, \( a^2 \) is vacancy volume, \( k \) is the Boltzmann's constant, \( T \) is the absolute temperature, \( t \) is time and \( K, p \) and \( m \) are constants which depend on the diffusion mechanisms and conditions. The value of \( m \) ranges from 0.25 to 0.46, while the exponent \( p \) is typically close to 3 (Richerson 1992).

It is evident from the model that particle diameter has a major effect on the rate of the sintering. Smaller particles enhance the sintering rate. Another major effect is also due to sintering temperature as implicitly indicated by the exponential relationship of temperature to the diffusion coefficient (see, for example, Kingery 1991).

The results for this model agree satisfactorily with those for sintering during the initial stage. A more complex model is required for process where grain growth at final stage is present.

2.5.2. Grain Growth in Ceramics

Grain growth in ceramic materials is associated with grain-boundary motion. The curving boundaries make the chemical potential greater in one side than the other. This chemical potential difference causes atoms or ions to rearrange and develop the structure of the growing grain. This process, called boundary motion, can be rapid because the diffusion distances are in the order of a unit cell dimension.

Grain growth in ceramic materials can occur during densification via sintering. The boundary motion can occur after the necks have fully formed between the sintering particles, i.e. when the initial sintering stage completes. It was observed that grain size increased very slowly during most of the densification process, but increased rapidly after the density reached 90% (Gupta 1972). Within the slow grain
growth regime, the grain is linearly proportional to the density and independent of the sintering temperature and time (Bruch 1962).

If the population of grains is described by the distribution function $p(D) dD$, i.e. the relative number of grains with dimension (for example, volume) between $D$ and $D + dD$, the mean grain dimension $E(D)$ can be calculated by

$$E(D) = \int D \cdot p(D) dD$$

(2.92)

The normalised grain distribution function is expressed by

$$\frac{p(D) dD}{E(D)}$$

Grain growth is a process where the $p(D)$ changes with sintering time $t$ so that

$$p(D, t = 0) \xrightarrow{\text{grain growth}} p(D, t)$$

(2.93)

This process involves the disappearance of some of the grains, usually the smaller ones. Therefore, grain growth is a phenomenon where the change of the grain size and shape depends on the size and shape of both the grain itself and the neighbours which are in contact with the grain under consideration. The condition of the grain growth is (Lazecki et al. 1993)

$$\frac{dE(D, t)}{dt} = \frac{d}{dt} \left[ \int_0^\infty D \cdot p(D, t) dD \right] > 0$$

(2.94)

Normal grain growth occurs if there is no change in the distribution function with time, or if

$$\frac{d}{dt} \left[ p \left( \frac{D}{E(D), t} \right) \right] = 0$$

(2.95)

In the mean-field theory for grain growth, it is assumed that each grain is surrounded by grains of average size (Hunderi and Ryum 1980). Grain growth occurs at a constant total volume; the larger grains grow while the smaller grains are consumed. The constant volume imposes restrictions on the form of the mean-field growth law, which can be expressed mathematically as

$$\frac{dD}{dt} = F(D) - \langle F(D) \rangle$$

(2.96)
where $F(D)$ is an arbitrary function of size $D$, with mean value $\langle F(D) \rangle = E(D)$ over the distribution of sizes. In the case of $F(D) = kD^n$, for example, the growth law becomes

$$\frac{dD}{dt} = k\left(D^n - \langle D^n \rangle \right)$$

(2.97)

with $n, k$ are constants larger than zero to ensure that the small grains shrink.

This mean-field theory for grain growth was used by York (1999, 2003) to derive the size-broadened diffraction profile function as described in §2.4.

2.5.3. Residual Strain in Ceramics

Inhomogeneities such as agglomerates, particle size distribution and spatial density variations in green ceramic bodies can lead to different sintering rates which in turn produce residual stresses, and hence residual macrostrains (Evans 1982). These stresses then cause creep. Therefore, a green body contains inhomogeneities can experience simultaneous densification and creep.

Residual stresses in ceramic materials can also be produced by the processing of the raw material. Milling, for example, is a process of continuous pressing or colliding powders with hard materials to obtain homogeneity. Another example is polishing to remove uneven surface fraction which may result in smooth surface but sheared underneath. The deformed parts cannot rearrange back into the unstrained shape even after the stressing force is removed. These processes will result in the retention of elastic stresses or strains in the material which then referred as residual stresses or strains.

It should be noted that there are two types of strain, *i.e.* macrostrain and microstrain. Macrostrain is of interest to engineers as a bulk quantity and has been extensively studied using various methods, including the $\sin^2 \Psi$ diffraction method. The microstrain which varies at grain level can be classified as (1) linear crystallite strain which is observable from diffraction line shift and (2) non-linear strain observable from line broadening.
In summary, this chapter has reviewed the relevant literature on crystallite size and strain evaluations from diffraction line broadening. The models derived for acquiring size and strain information (1) are based on the Fourier transform strategies, or (2) use peak profile fitting approaches. It is evident that the latter is preferable provided that an appropriate peak shape function is used. Models in use were derived from dislocation theory for metals which might not be appropriate for sintered ceramics used in this study. The chapter considered the York size and strain models which were derived from mean-field theory of normal grain growth which presumably are more appropriate for sintered ceramic materials. The following chapters elaborate the development and evaluation of the size and strain model in this study with particular reference to its application to sintered MgO ceramics.
CHAPTER 3. RESEARCH METHODOLOGY

This Chapter consists of sections describing (1) research design, (2) planning for the development of new models, (3) materials selection and processing, (4) powder diffraction data collection and (5) diffraction data analysis methods.

3.1. Research Design

Experiments and modelling in this study were designed to meet the study objectives presented in §1.3. The principal aspects of the experimental design were:

1. development of models for size and strain analysis,
2. selection of materials,
3. strategies for powder diffraction data measurements, and
4. evaluation of models

3.1.1. Development of Models for Size and Strain Analysis

The development of the new models was designed to achieve the following:

a. Introduce a new approach to line profile analysis with particular reference to physically-based modelling.

b. Develop alternative methods for size and strain analysis with particular application to sintered ceramic materials.

c. Develop interactive software for size and strain analysis.

3.1.2. Materials Selection

The principal criteria for materials selection were:

a. Availability of information on the symmetry and crystal structure of the prospective materials in order to obtain reasonably resolved diffraction peaks to facilitate the evaluation of new models.
b. Sinterability of the materials to provide dense ceramics which might be expected to give grain-grain interactions.

c. Substantial sensitivity of peak broadening to sintering temperature.

d. Cubic symmetry of materials, presumed to give isotropic broadening.

e. Suitability of the materials for XRD, SRD and ND experiments.

f. Information on chemical and thermal stabilities, since impurities and reactions can be considered as sources of defects, which might affect the diffraction profile.

Details of materials selection and processing are given in §3.3.

3.1.3. **Diffraction Data Measurements**

The diffraction data experiments were designed with reference to the following points:

a. Measurement of diffraction data for near-surface size and strain characterisation by XRD and SRD, and also bulk size and strain by ND.

b. Measurement of single peaks and whole patterns.

c. Selection of SRD and ND radiation wavelength which is close to that for XRD (CuKα).

d. Collection of diffraction patterns using ceramic specimens sintered at appropriate temperatures, which might reasonably give systematic changes in broadening.

3.1.4. **Diffraction Data Analysis**

The analysis methods were designed to meet the following criteria:

a. The data were to be analysed using single-line and whole-pattern approaches.

b. Selection of data analysis methods should consider the risk of obtaining inaccurate results due to technical problems such as small specimen broadening effects, strong peak asymmetry and improper background determination.

c. Comparison of results for the new models with those for the existing models were to be performed.
3.2. Development of Models for Size and Strain Analysis

As described in §2.3 and §2.4, physically-based models were to be considered. A profile function which is a convolution of the York size function [Equation (2.84)] and a Gaussian strain function (see Table 2.1 for the Gaussian function) was developed and evaluated. The development of models for size and strain analysis is reported in Chapter 5, with further details being given in Appendix 2. A Fortran 95 non-linear least-squares refinement program for profile fitting, entitled MOZAIX, was developed for model optimisation, and then evaluated with diffraction data of MgO ceramics. Peak profile fitting results using MOZAIX were compared with those using the Voigt function (Chapter 6).

3.3. Materials Selection and Processing

Sintered ceramics were selected in this study in the view of their technological significance and also because there appear to be no detailed studies reported on these materials in regard to their strain and size character as the sintering conditions change. MgO sintered ceramics were examined in the expectation that their cubic symmetry might minimise size and strain anisotropy effects.

The main raw materials used in the experiment were three MgO powders differing in purity and with distinct diffraction broadening characteristics, viz. approximately (1) 99%, Aldrich Chemicals, USA; containing approximately 10% Mg(OH)$_2$ prior to calcination, (2) 99.9%, Merck, Germany and (3) 99.99%, Aldrich Chemicals, USA. A Y$_2$O$_3$ powder (Unocal Molycorp, USA) was also used as a second phase in MgO(99%) – Y$_2$O$_3$ mixtures (10 and 20 wt.% Y$_2$O$_3$) with an expectation that the cubic symmetry of MgO and Y$_2$O$_3$ would give only isotropic size and strain effects in the mixtures. The 99% MgO powder was calcined at 1100°C for 60 minutes to convert the hydroxide. The nomenclature assigned to the samples and densification character are presented in Table 3.1. The bulk density $D$ of the samples was determined by an Archimedes method according to Australian Standard AS 1774.5 (Australian Standard 1989), according to the expression

$$D = \frac{m_D}{m_D - m_i} \times D_i$$  \hspace{1cm} (3.1)
Table 3.1. Nomenclature and densification character of the MgO specimens used in the study.

<table>
<thead>
<tr>
<th>Purity of the MgO specimen</th>
<th>Sintering temperature</th>
<th>Apparent density (%)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99%</td>
<td>1100°C – 2 h</td>
<td>59</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1250°C – 2 h</td>
<td>75</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1450°C – 2 h</td>
<td>97</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>1600°C – 6 h</td>
<td>98</td>
<td>17</td>
</tr>
<tr>
<td>99.9%</td>
<td>1100°C – 2 h</td>
<td>46</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1250°C – 2 h</td>
<td>51</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>1450°C – 2 h</td>
<td>54</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>1600°C – 6 h</td>
<td>89</td>
<td>24</td>
</tr>
<tr>
<td>99.99%</td>
<td>1100°C – 2 h</td>
<td>51</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1250°C – 2 h</td>
<td>56</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1450°C – 2 h</td>
<td>70</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>1600°C – 6 h</td>
<td>79</td>
<td>14</td>
</tr>
</tbody>
</table>

*Diameter shrinkage after sintering

where \( m_D \) is the mass of dried specimen, \( m_i \) is the mass of the test specimen, saturated with and suspended in liquid \( i \), and \( D_i \) is the density of the immersion liquid at the temperature prevailing during the test. In the present work, de-ionized water was used, \( D_i = 0.997 \text{ kgm}^{-3} \) (Hansson 1972).

The powders were uniaxially pressed at \( \approx 38 \) MPa in a metal die to form cylindrical green specimens 19 mm in diameter. The pressed MgO powders were then sintered at temperatures which were found to provide systematic variations in strain and size - 1100°C for 2 hours, 1250°C for 2 hours, 1450°C for 2 hours and 1600°C for 6 hours. The pressed MgO-Y_2O_3 mixtures were sintered at 1550°C for 6 hours. The final sintered ceramics had diameters ranging from 11 – 19 mm due to variations in densification, depending on the sintering temperature and time. The height of the SRD and XRD green specimens was approximately 1.5 mm, while that for the ND specimens was approximately 2 cm.

It is emphasised that there was no evidence from this study of the degradation of sintered MgO to the hydroxide on exposure to the atmosphere.
3.4. Powder Diffractometry Measurements

3.4.1. Laboratory X-ray Powder Diffraction (XRD) Pattern Measurements

X-ray diffraction data were measured at Curtin University of Technology using a step-scanned Siemens D500 Bragg-Brentano instrument [Figure (3.1)] with a post-diffraction graphite analyser and parafocusing geometry which uses a line source diverging beam directed to the sample through an incident beam aperture, comprising the divergence slit components I and II in Figure (3.1). The detector aperture (IV) samples the conical diffracted radiation beam for each reciprocal lattice vector. An antiscatter slit (III) is placed in the diffracted beam and a soller slit is placed between the specimen and detector to reduce off-plane divergence.

The instrument settings are given in Table 3.2 and the conditions of the measurements are as follow:

- Incident beam divergence slit = 0.3° to cover the specimen dimension from 13.5 mm to 1.1 mm over the 2θ data collection range, so that the sample fully collected the incident beam over the range.

- Receiving slit = 0.15° was used to approximately match the effective focal spot width of the tube.

- NaI detector with pulse discrimination and a secondary monochromator were used

- The powder specimens were mounted in an aluminium holder of diameter 23 mm, and the sintered ceramic specimens were placed in the centre of the same aluminium holder.

- Specimen rotation was applied to reduce preferred orientation effect.

- For single-line analysis, the 420 and 422 reflections (2θ = 109.78° and 127.29° respectively) were measured with step-size = 0.02° and counting time = 10 – 12 s.step⁻¹. These peaks were selected since the influences of flat specimen and axial divergence are negligible at high 2θ (> 90°), when compared with the same effect at low 2θ (Klug & Alexander 1974). A detector step size of 0.02° was used to provide appropriate sampling of the peaks (FWHM ≈ 0.1 – 0.3°).
Figure 3.1. Schematic diagram of Bragg-Brentano tube x-ray powder diffractometer (Siemens 1986)

Table 3.2. Curtin XRD Bragg-Brentano Instrument Setting

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Siemens D500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Cu-anode tube, type FF Cu 4KE 60 kV 1.5 kW, operated at 40kV and 30 mA</td>
</tr>
<tr>
<td></td>
<td>Effective focal spot size, 0.04×8 mm²</td>
</tr>
<tr>
<td></td>
<td>Unfiltered</td>
</tr>
<tr>
<td></td>
<td>Wavelength: CuKα ≈1.5418 Å</td>
</tr>
<tr>
<td>Optics</td>
<td>Bragg-Brentano, measuring circle diameter = 401 mm</td>
</tr>
<tr>
<td></td>
<td>Incident beam divergence = 0.3°, receiving slit = 0.15°</td>
</tr>
<tr>
<td></td>
<td>Scatter slits divergence = 1°</td>
</tr>
<tr>
<td></td>
<td>Soller slit divergence = 1°</td>
</tr>
<tr>
<td>Specimen</td>
<td>Holder – circular format, diameter 23 mm</td>
</tr>
<tr>
<td></td>
<td>Rotation ‘on’ for all measurements</td>
</tr>
<tr>
<td>Detection</td>
<td>Graphite diffracted beam monochromator set for CuKα</td>
</tr>
<tr>
<td></td>
<td>NaI scintillator with pulse height analysis</td>
</tr>
<tr>
<td>Acquisition</td>
<td>Step-size, 0.02°</td>
</tr>
<tr>
<td></td>
<td>Angular range in 2θ, 10 – 130°</td>
</tr>
<tr>
<td></td>
<td>Counting time, between 2 – 16 s/step</td>
</tr>
</tbody>
</table>
Whole-pattern data for Rietveld analysis were collected over the 2θ range = 10 – 130° with a step-size of 0.02° and a counting time of 2 s.step⁻¹. The data were not recorded below 10° in 2θ because Bragg angles do not occur below this angle for the materials considered (the position of the first Bragg peak for MgO is approximately 36.9° and for Y₂O₃ is approximately 16.7°).

3.4.2. Synchrotron X-ray Powder Diffraction (SRD) Pattern Measurements

SRD data were collected using the BIGDIFF instrument [Figure (3.2)] at the Australian National Beamline Facility (ANBF) on Beamline 20B at the Photon Factory, Tsukuba, Japan (Barnea et al. 1989). Descriptions of the instrument have been reported elsewhere (Garrett et al. 1995; Sabine et al. 1995; O’Connor et al. 1997). The monochromator was set to deliver a wavelength of 1.54 Å – being close to that of CuKα (1.5418Å). The dimensions of the incident beam were set at a height of 0.2 mm and a width of 2 mm. The ceramic specimens were mounted on an aluminum holder approximately 20 mm in radius and 3 mm depth, and rotated during data collection. The sintered ceramics had diameters ranging from 11 – 19 mm and approximately heights from 1 – 2 mm. Powder specimens were mounted in flat-plate format, with the material being held in borosilicate glass (6 mm × 10 mm × 0.5 mm), and rotated during the measurements. The angle between the incident beam and the specimen surface was fixed at 30° to accommodate all observable peaks since the first Bragg peak for MgO occurs at approximately 2θ ≈ 37.6°. Three erasable-type imaging plates with 400 mm × 200 mm dimensions (Fuji Photo Film Co., Tokyo, Japan) were used to record diffraction patterns spanning from 30 – 150° in 2θ. The exposure time was 15 mins. Details of the measurement conditions are provided in Table 3.3.

3.4.3. Neutron Powder Diffraction (ND) Pattern Measurements

Neutron diffraction data were acquired with the fixed-wavelength, multi-detector, high-resolution powder diffractometer (HRPD) at the Australian Nuclear Science and Technology Organisation (ANSTO) research reactor HIFAR at Lucas Heights, Australia [see Figure (3.3)].
Figure 3.2. Schematic diagram of the SRD powder diffractometer (modified from O'Connor et al. 1997)

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Synchrotron Radiation Powder Diffractometer (SRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Synchrotron radiation</td>
</tr>
<tr>
<td></td>
<td>Wavelength = 1.54 Å</td>
</tr>
<tr>
<td>Optics</td>
<td>Debye-Scherrer</td>
</tr>
<tr>
<td>Specimens</td>
<td>Incident beam angle 30° (fixed)</td>
</tr>
<tr>
<td></td>
<td>Powder specimens were mounted in flat-plate format, with the</td>
</tr>
<tr>
<td></td>
<td>material being held in borosilicate glass (6 mm × 10 mm × 0.5 mm).</td>
</tr>
<tr>
<td></td>
<td>Uniaxially-pressed cylinders (11 – 19 mm diameter, 2 cm height) for</td>
</tr>
<tr>
<td></td>
<td>the sintered ceramic specimens</td>
</tr>
<tr>
<td></td>
<td>Rotation 'on' for all measurements</td>
</tr>
<tr>
<td>Detection</td>
<td>Image plate</td>
</tr>
<tr>
<td>Acquisition</td>
<td>Step-size, 0.010014°</td>
</tr>
<tr>
<td></td>
<td>Angular range in 2θ, 30 – 150°</td>
</tr>
<tr>
<td></td>
<td>Counting time, 15 mins</td>
</tr>
</tbody>
</table>
Figure 3.3. Schematic diagram of the HRPD neutron powder diffractometer (Howard et al. 1983)

Table 3.4. ND Pattern Measurement Conditions at HIFAR

<table>
<thead>
<tr>
<th>Instrument</th>
<th>High-resolution Powder Diffractometer (HRPD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Ge single crystal monochromator, take-off angle 120°</td>
</tr>
<tr>
<td></td>
<td>Wavelength = 1.493 Å</td>
</tr>
<tr>
<td>Optics</td>
<td>Debye-Scherrer</td>
</tr>
<tr>
<td>Specimen</td>
<td>Vanadium can (16 mm diameter, 5 cm height) for non-pressed materials</td>
</tr>
<tr>
<td></td>
<td>Uniaxially-pressed cylinders (11–19 mm diameter, 2 cm height)</td>
</tr>
<tr>
<td></td>
<td>Rotation 'on' for all measurements</td>
</tr>
<tr>
<td>Detection</td>
<td>24 $^3$He detectors, separated by 5° in 2$\theta$</td>
</tr>
<tr>
<td>Acquisition</td>
<td>Step-size, 0.05°</td>
</tr>
<tr>
<td></td>
<td>Angular range in 2$\theta$, 0 – 150°</td>
</tr>
<tr>
<td></td>
<td>Counting time, approximately 13 s/step</td>
</tr>
</tbody>
</table>
The HRPD instrument has been described by others (e.g. Howard et al. 1983). The instrument is configured with 24 He\textsuperscript{3} detectors and has an effective angular range of 0° to 150°. The patterns recorded by each detector were merged during data reduction to allow for counter offsets and relative detection efficiency. The measurement conditions were step-size = 0.05°, counting time per step ≈ 13 s and wavelength 1.493 Å. A step-size of 0.05° was chosen to obtain sufficient steps through each peak. A counting time of approximately 13 s was used to ensure counting statistics with standard deviation of less than 2%. A wavelength of 1.493 Å was chosen because of its comparability with the XRD CuK\textsubscript{α} wavelength, 1.5418 Å. Sintered MgO specimens approximately 11 – 19 mm in diameter and 20 – 25 mm high were positioned on a rotating table. Corrections for incident beam fluctuations were made using an incident-beam monitor.

Details of the ND instrument conditions are given in Table 3.4.

3.5. Diffraction Data Analysis

3.5.1. Format of Data for Analysis

The software packages or programs used in this study require various data formats. Accordingly, data had to be converted to the appropriate format prior to analysis. In most cases, the conversion to a nominated software can be performed using a simple \textit{BASIC} program (for ASCII-type data), a worksheet software such as Microsoft \textit{EXCEL}, or a conversion program available from the internet, such as \textit{ConvX}. In other cases there are requirements to use several conversion steps using different programs to obtain the appropriate format.

Table 3.5 shows the software packages or programs with the associated data format used for analysis in this study.
Table 3.5. Software packages or programs for diffraction data analysis with the associated data format

<table>
<thead>
<tr>
<th>Purpose</th>
<th>Software/program</th>
<th>Data format</th>
<th>Data file extension</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. XRD data</td>
<td>VisualXRD ver 2.6</td>
<td>CPI (one column)</td>
<td>*.cpi</td>
<td>Already in ASCII form</td>
</tr>
<tr>
<td>2. SRD data</td>
<td>N/A</td>
<td>Image data</td>
<td>N/A</td>
<td>Needs analog-to-digital conversion using PHYTON(^2)</td>
</tr>
<tr>
<td>3. ND data</td>
<td>HRPD</td>
<td>Non-ASCII</td>
<td>*.lst</td>
<td>Basic data processing using local programs</td>
</tr>
<tr>
<td>4. Phase analysis</td>
<td>JADE(^3)</td>
<td>RAW format</td>
<td>*.raw</td>
<td></td>
</tr>
<tr>
<td>5. Rietveld analysis</td>
<td>RIETICA(^4)</td>
<td>CPI or 10 columns</td>
<td>*.cpi or *.dat</td>
<td></td>
</tr>
<tr>
<td>6. Peak profile fitting I</td>
<td>SHADOW(^5)</td>
<td>RAW format</td>
<td>*.raw</td>
<td></td>
</tr>
<tr>
<td>7. Peak profile fitting II</td>
<td>MOZAIX(^6)</td>
<td>One column</td>
<td>*.dat</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Program to operate the XRD Siemens D500 (Diffraction Tech. 1999)
\(^2\) Hester 2003
\(^3\) Materials Data Inc. 1999
\(^4\) Hunter 1998
\(^5\) Materials Data Inc. 1999
\(^6\) This study

3.5.2. Profile Fitting

Peak profile fitting is a procedure to fit an analytical or numerical function denoted as profile-shape-function (PSF – see Table 2.1 for traditional PSFs), to a measured diffraction pattern. There are three principal parameters adjusted in refinements during fitting, i.e. the line position, the line intensity (or integrated...
intensity) and the line width, to achieve minimum differences between the measured and the calculated lines.

Profile Fitting with **MOZAIX**

**MOZAIX** is a line profile fitting program developed during this study in which a physically-derived size and a Gaussian strain profile are convoluted to model the specimen profile. The approach for applying these profiles is denoted as a convolution model. The overall **MOZAIX** PSF is obtained by convoluting the specimen and the instrument profiles. This PSF allows direct assessment of crystallite size and strain using the single-line integral breadth method. The development of **MOZAIX** is explained in Chapter 5 and Appendix 2. An example of the **MOZAIX** profile fitting presentation is shown by Figure 3.4. The application of **MOZAIX** with SRD and XRD data for MgO ceramics is reported in Chapter 6.

Profile Fitting with **SHADOW**

**SHADOW** (Howard & Snyder 1983) is a commercial line profile fitting program (Materials Data Inc. 1999). Features of the program include the following:

- Monitoring refinement progress by dynamic plotting
- Gaussian, Lorentzian, intermediate Lorentzian, pseudo-Voigt, Pearson VII and Voigt PSFs are available (the associated mathematical formulas for these PSFs are given in §2.1, Table 2.1).
- Possible use of split profiles, i.e. two 'half-profiles' to generate a single asymmetric line profile
- Accommodating satellite lines (such as Kα₂ lines) and overlapping peaks
- Application of 'Direct Convolution Products' which allows the convolution of the self-generated instrument profile and Lorentzian or Gaussian or Lorentzian and Gaussian (Voigt) PSFs. This option allows the size-strain analysis based on the Williamson-Hall method (see §2.3.2).
Figure 3.4. An example of profile fitting using *MOZAIX*. The observed data are indicated by plus sign and the calculated profile the solid line. The upper plot is the difference between the calculated and measured patterns on the same scale as the calculated and measured patterns.

The following conditions were used for the line profile fitting using *SHADOW* with XRD, SRD and ND data:

- The pseudo-Voigt function was used to develop plots of FWHM versus 2θ.
- The Voigt function was used as the representation of the traditional function to assess size and strain
- Each refinement was performed for a single peak
- Background across the peak was assumed to be constant
- Split profiles were not applied in the refinement
- XRD peaks from Kα₁ and Kα₂ radiation was considered as a compound peak
- Each refinement was terminated when the refinement converged or the iteration cycle limit was achieved
3.5.3. Rietveld Method for Size and Strain Analysis

Rietveld analysis is a least-square-based refinement method which aims to obtain the best fit between the calculated and the observed powder diffraction pattern patterns. As briefly discussed in §2.3.5, Rietveld (1967; 1969) initially proposed the use of this “whole-pattern” method to refine structural parameters for polycrystal samples. This method has been developed more recently to provide composition information (e.g. Hill & Howard 1987; Bish & Howard 1988; O'Connor & Raven 1988). The method is applicable to patterns produced with x-ray, neutron and synchrotron radiation.

In the least-square procedure, a model is presumed to be optimal when the sum \(S\) of the squares of the differences between the measured and the calculated patterns is lowest, that is when

\[
S = \sum w_i (y_i - y_{ci})^2
\]  
(3.2)

reaches a minimum. Here, \(y_i\) is the observed step intensity, \(y_{ci}\) is the corresponding calculated value, and \(w_i\) is the weighting factor for point \(i\) in the pattern which is normally set as the reciprocal of the variance of the measured intensity at point \(i\), i.e. \(w_i = \frac{1}{\sigma^2}\). The calculated intensity is given by summing the contributions from (i) neighbouring Bragg reflections and (ii) background (assuming the crystallites are randomly oriented). The general expression for the calculated intensity \(y_{ci}\) follows (Young 1993)

\[
y_{ci} = s \sum K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{bi}
\]  
(3.3)

where \(i\) is index for the point being calculated, \(s\) is the scale factor, \(K\) represents the Miller indices, \(h, k, l\) for a Bragg peak, \(L_K\) contains the Lorentz, polarisation and multiplicity factors, \(|F_K|\) is the structure factor for \(K\)th Bragg reflection, \(\phi\) is the peak shape function, \(2\theta_i\) and \(2\theta_K\) are the detector angles corresponding to point \(i\) and Bragg peak \(K\), \(P_K\) is the preferred orientation function, \(A\) is an absorption factor and \(y_{bi}\) is the background contribution.
Various mathematical peak profile functions $\phi_{yk}$ are available in Rietveld software. The Voigt function, a convolution of Gaussian and Lorentzian functions, was used for all refinements in the study as it gives peak breadths which can be associated with crystallite size and strain. The function is given by:

$$\phi(2\theta_i - 2\theta_j) = \sqrt{\frac{C_1}{\pi}} \frac{1}{H_{Gj}} \text{Re} \left[ \omega \left( \sqrt{C_1} X_{yj} + i C_2 \frac{H_{Lj}}{H_{Gj}} \right) \right]$$  \hspace{1cm} (3.4)

where $C_1 = 2 \ln 2$, $C_2 = \sqrt{\ln 2}$, $H_{Gj}$ is the FWHM of the contributing Gaussian, $H_{Lj}$ is the FWHM of the contributing Lorentzian, $\omega$ is the complex error function, $\omega(z) = \exp(-z^2) \text{erfc}(-iz)$ and Re denotes its real part. The assumption used in the size and strain analysis is that size contributes only to the Lorentzian component and strain to the Gaussian component (e.g. de Keijser et al. 1982; Langford 1999).

The Gaussian FWHM varies with diffraction angle $\theta$ according to the expression given by Caglioti, Paoletti and Ricci [1958; see Equation (2.73)], while the Lorentzian FWHM according to

$$H_{Lj} = \frac{180}{\pi} \frac{\lambda}{D \sec \theta} + \frac{180}{\pi} S \tan \theta$$  \hspace{1cm} (3.5)

where the $\sec \theta$ term is the Scherrer term associated with the size $D$, and the $\tan \theta$ term is the strain-dependent term.

Peak asymmetry was modelled by (Rietveld 1969)

$$A_y = 1 - AS \left[ \text{sign}(2\theta_i - 2\theta_j) \right] (2\theta_i - 2\theta_j)^2 \cot \theta_j$$  \hspace{1cm} (3.6)

where $AS$ is a refineable parameter.

Crystal data for MgO were taken from the Inorganic Crystal Structure Database (FachInformationsZentrum and Gmelin Institute, Germany) – ICSD Collection Code 9863 (Sasaki, Fujino & Takeuchi 1979). Details of the structure data for MgO are given in Appendix 3.
Refinement quality is assessed using difference plot and figures-of-merit (FoM). The difference plots were used to compare the agreement between calculated and measured patterns. For example, Figure 3.5 shows the agreement between calculated and measured XRD patterns for the 99% MgO ceramic sintered at 1100°C for 2 hours.

The FoM comprises

(i) profile R-factor

\[
R_p = \frac{\sum_i |y_i - y_{ic}|^2}{\sum_i y_i} \tag{3.7}
\]

(ii) weighted profile R-factor

\[
R_{wp} = \left[ \frac{\sum_i w_i |y_i - y_{ic}|^2}{\sum_i w_i y_i^2} \right]^{1/2} \tag{3.8}
\]

(iii) goodness-of-fit (GoF) index

\[
GoF = \left[ \frac{R_{wp}}{R_{exp}} \right] \tag{3.9}
\]

where

\[
R_{exp} = \left[ \frac{N - P}{\sum_i w_i y_i^2} \right] \tag{3.10}
\]

\(N\) is number points and \(P\) is number of parameters involved in a refinement.

(iv) Bragg R-factor

\[
R_B = \frac{\sum_i |I_i - I_{ic}|}{\sum_i I_i} \tag{3.11}
\]

where \(I_i\) and \(I_{ic}\) are the observed and calculated intensities for a Bragg reflection. The observed Bragg intensities here are determined assuming they are in the same proportion as their calculated counterparts determined using structural model.
Figure 3.5. Agreement between calculated and measured XRD patterns for the 99% MgO ceramic sintered at 1100°C for 2 hours. The observed data are indicated by plus sign and the calculated profile the continuous line in the same field. Vertical lines represent the positions of all possible Bragg reflections. The lower plot is the difference between the calculated and measured patterns on the same scale as the calculated and measured patterns. The pattern fitting was performed using RIETICA (Hunter 1998).
CHAPTER 4. EVALUATION OF THE VOIGT-BASED
CONVENTIONAL APPROACHES FOR STRAIN-SIZE
ASSESSMENTS USING MgO CERAMICS

4.1. Introduction

Diffraction line broadening analysis with XRD, SRD and ND data was
carried out with sintered MgO ceramics having three different purities, with a view to
using these data to obtain conventional peak-shape profile size and strain results in
order to compare these with convolution model assessments. XRD and SRD
measurements were carried out to provide near-surface information, while ND
measurement was performed to give bulk, or global, information. The XRD and ND
data were used for evaluation of the Voigt-based approaches for size and strain
assessments (§4.4). The SRD and XRD data were used for size-strain assessment
with the convolution model developed for this study (see Chapters 5 and 6).

Chapter 4 comprises three major sections. The first part presents the
development of the MgO ceramic line broadening reference material for XRD and
ND instrument broadening corrections. A paper on this aspect has been published in
'Advances in X-ray Analysis' (Pratapa & O'Connor 2002). The second part reports
the diffraction broadening characteristics of the MgO ceramics. The final part
evaluates the results for the MgO ceramics, by making use of the standard MgO
ceramic discussed in the preceding section, using the Voigt-based single-line integral
breadth and Rietveld size-strain assessment methods. The key results from this part
of the study have been published in the Journal of Applied Crystallography (Pratapa,
O'Connor & Hunter 2002).
4.2. Development of Standard Materials for Line Broadening Assessments

Studies of size and strain in materials should include an appropriate correction for the contributions of the instrument effects to the observed data, since inadequate correction for instrument effects will result in systematic errors in the results. Instrument line profiles are customarily obtained with data from a standard reference material (SRM) or, alternatively, from an annealed material made from the materials under investigation. This section describes the development of an MgO sintered ceramic standard appropriate for instrument profile corrections, for both XRD and ND data. The rationale for this approach was driven by the unsuitability of the popular NIST SRM 660 LaB$_6$ as a standard for neutron diffraction work.

Figure 4.1 shows the XRD, SRD and ND profiles for line 422 of the 99% MgO ceramics sintered at 1100°C for 2 hours (1100°C – 2 h), 1250°C for 2 hours (1250°C – 2 h), 1450°C for 2 hours (1450°C – 2 h) and 1600°C for 6 hours (1600°C – 6 h), respectively. Profiles for NIST SRM 660 LaB$_6$ (Rasberry 1989), NIST SRM 660a LaB$_6$ (Freiman & Trahey 2000) and NIST 676 $\alpha$-Al$_2$O$_3$ (Reed 1992) are also presented.

Figure 4.2 shows the XRD, SRD and ND pseudo-Voigt FWHMs versus 2$\theta$ for the 99% MgO ceramics according to the sintering conditions. The FWHM relative errors are less than 1% for SRD and ND and 3% for XRD. It is clear that the sintering causes progressive reduction in the XRD and ND FWHMs until 1450°C – 2 h, after which there is an increase in the FWHM when more prolonged sintering is applied. FWHM reduction with temperature for the SRD data is also observed, with the FWHMs for the 99% 1250°C – 2 h and 1450°C – 2 h specimens being similar. The XRD FWHM for the 99% 1600°C – 6 h ceramic is substantially higher than that for the 1450°C – 2 h ceramic over the 2$\theta$ range, whereas the corresponding FWHMs are very similar for the ND data. The SRD FWHM for the 99% 1600°C – 6 h is slightly higher than that for both the 99% 1250°C – 2 h and 1450°C – 2 h ceramics. The XRD and ND FWHM plot behaviours indicate that there is minimal broadening for both the near-surface and the bulk measurements for the 1450°C – 2 h specimen. Therefore, it was possible to develop an MgO standard sintered ceramic
material for XRD and ND instrument broadening corrections. The following
discussion demonstrates the assessment of the 99% 1450°C – 2 h for development of
such a material.

Figure 4.3 shows that the XRD FWHM for the 99% MgO ceramic sintered at
1450°C – 2 h is marginally lower than that for NIST SRM 660 LaB₆. Also shown is a
comparison of the ND FWHM data with values for NIST α-Al₂O₃ powder (NIST
SRM 676) – LaB₆ could not be used for the ND aspect of this work due to severe
absorption. The 99% MgO ND widths are slightly less than the α-Al₂O₃ widths.

Further analysis on the 99% MgO 1450°C – 2 h ceramic was performed from
its Williamson-Hall plots with XRD data. Note that for this instrument broadening
evaluation, peak profiling of the observed data using the Voigt function was
performed and the plot was made with the Lorentzian components. Figure 4.4 shows
that the slope of the line for the ceramic is negative, as is also found for the NIST
SRM 660 LaB₆. This negative slope indicates that strain effect must not be the
dominant source of the broadening (Langford, Cernik & Louër 1991). In contrast
with this result, the positive slope for the MgO 1100°C – 2 h ceramic (Figure 4.4)
indicates the presence of some strain effects causing peak broadening.

Figure 4.5 displays SEM micrographs for the 99% MgO 1450°C – 2 h ceramic
and NIST SRM 660 LaB₆. For both materials, the grain size ranges between
approximately 5 and 10 µm. The MgO grains tend to form regular shapes which tend
to be spherical. With these microstructural characteristics, the ceramic can be
expected to give low errors in intensity due to crystal statistics. Crystallites within
this range of sizes might be expected to give no size broadening (Van Berkum et al.
1995).

Table 4.1 depicts the XRD FWHMs for the 99% MgO standard ceramic (200,
311 and 422 reflections) and the NIST SRM 660 LaB₆ (111, 311, 332, 422
reflections). The reflections were selected to represent the low, medium and high
angle regions, respectively. The Rietveld, Gaussian and Lorentzian FWHMs for the
standards are also presented in the table. It is clear that the broadening for the 99%
MgO standard ceramic is comparable with that for NIST SRM 660 LaB₆. These
results support the observation that the broadening characteristics of the 99% 1450°C
– 2 h ceramic are very similar to the NIST SRM 660 LaB₆.
(a) XRD patterns for line 422 of 99% ceramics

Figure 4.1. (a) XRD (CuKα, $\lambda \approx 1.5418$ Å), (b) SRD (λ ≈ 1.54 Å) and (c) ND (λ ≈ 1.493 Å) patterns for line 422 of 99% MgO ceramics sintered at various temperatures. Patterns for (a) NIST SRM 660 LaB$_6$ (Rasberry 1989), (b) NIST SRM 660a LaB$_6$ (Freiman & Trahey 2000) and (c) NIST 676 $\alpha$-$\text{Al}_2\text{O}_3$ (Reed 1992) are also presented. Peak intensities and peak positions are set identically to give comparable width definition.

(cont'd)
(b) SRD patterns for line 422 of 99% ceramics

(c) ND patterns for line 422 of 99% ceramics

Figure 4.1. (cont’d)
Figure 4.2. FWHM versus $2\theta$ for the 99% MgO ceramics for the XRD, SRD and ND data. Relative errors are less than 1% for SRD and ND and 3% for XRD. Error bars are not shown to clarify curve definition for broadening comparison. Line fits for the data were made with Equation (2.73).

Figure 4.3. FWHM versus $2\theta$ for the 99% MgO ceramic sintered at 1450$^\circ$C for 2 hours and the associated SRMs, i.e. NIST SRM 660 LaB$_6$ (Rasberry 1989) for XRD, NBS SRM 676 $\alpha$-Al$_2$O$_3$ (Reed 1992) for ND and NIST SRMs 660a LaB$_6$ (Freiman & Trahey 2000) for SRD. Line fits for the data were made with Equation (2.73).
Figure 4.4. Williamson-Hall plots for the 99% MgO 1450°C – 2 h ceramic and the SRM 660 LaB₆ made with XRD data. The plot for the strained 99% MgO 1100°C – 2 h ceramic is also presented for comparison. Error bars indicate 1× standard deviation.
Figure 4.5. Scanning electron micrographs (secondary electron mode) for the 99% MgO 1450°C – 2 h standard sintered ceramic (top) and NIST SRM 660 LaB₆ powder (bottom).
Table 4.1. XRD single-line and Rietveld FWHMs for the MgO standard and NIST SRM 660 LaB$_6$. Estimated standard deviations for the least significant digit are given in parentheses.

<table>
<thead>
<tr>
<th>hkl</th>
<th>2θ (°)</th>
<th>FWHM (°)</th>
<th>Rietveld</th>
<th>Gaussian (°)</th>
<th>Lorentzian (°)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gaussian (°)</td>
<td>Lorentzian (°)</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>36.68</td>
<td>0.128(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>74.47</td>
<td>0.131(3)</td>
<td>0.0001(1)</td>
<td>0.0309(3)</td>
<td></td>
</tr>
<tr>
<td>422</td>
<td>127.15</td>
<td>0.171(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaB$_6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>37.28</td>
<td>0.126(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>75.67</td>
<td>0.131(5)</td>
<td>0.0007(3)</td>
<td>0.0320(6)</td>
<td></td>
</tr>
<tr>
<td>332</td>
<td>120.64</td>
<td>0.168(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>422</td>
<td>130.39</td>
<td>0.188(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From these results it can be inferred that strain/size broadening for the 99% MgO 1450°C – 2 h is negligible and that this ceramic is suitable for both XRD and ND instrument profile corrections. As a result of this observation, the 99% MgO ceramic sintered at 1450°C for 2 hours was selected as the standard material for analysis with XRD and ND data in the evaluation of the conventional Voigt methods as described in §4.4.

It was found during the study that the NIST SRM 660a LaB$_6$, which has been commercially produced to replace the NIST SRM 660 LaB$_6$, showed significantly narrower SRD broadening than the 99% MgO 1450°C – 2 h ceramic (Figure 4.3, lower plots). The NIST SRM 660a LaB$_6$ was then selected as the standard reference material for XRD and SRD corrections for the evaluation of the convolution model as reported in Chapter 5 and 6.
4.3. Preliminary Analysis of Line Widths for MgO Ceramics

In order to assess the microstructures according to diffraction broadening, the observed peak widths (notably the FWHMs) were compared with those for the instrument. Figure 4.1 compares the XRD, SRD and ND patterns for line 422 of the 99% MgO ceramics sintered at various temperatures with the patterns for the NIST SRMs of the associated instruments. Comparisons are also given for the 99.9% (Figure 4.6) and 99.99% (Figure 4.8) MgO ceramics. The FWHM variation with 2θ for these specimens produced with XRD, SRD and ND data are presented in Figures 4.2, 4.7 and 4.9, respectively.

In general, the specimen patterns show broader peaks as compared to the MgO standards and the SRMs, suggesting the presence of specimen broadening effects in the materials. Also, changes in peak widths with sintering temperature are evident, indicating that the specimen broadening effects in the materials change with sintering temperature.

An interesting result is found for the XRD and SRD data for the 1100°C - 2 h 99.99% ceramic (Figures 4.8a and 4.8b) which show relatively broad peaks with long tails, but apparently with less width compared to those for the 1100°C - 2 h 99.9% (Figures 4.6a and 4.6b). The presence of long tails and small width in the 99.99% MgO ceramics indicates that the Lorentzian broadening component dominates the peak broadening and the Gaussian component might be negligible. The broadening behaviour in the 99.9% specimens, however, indicates that there are significant contributions from the Gaussian as well as the Lorentzian components. The 99% 1100°C - 2 h specimen (Figure 4.1) exhibits relatively broader peaks than the SRMs but without long tails suggesting the predominant Gaussian contribution. This observation implies that the materials exhibit different size and strain effects.
Figure 4.6. (a) XRD (CuKα, \( \lambda \approx 1.5418 \) Å), (b) SRD (\( \lambda \approx 1.54 \) Å) and (c) ND (\( \lambda \approx 1.493 \) Å) patterns for line 422 of 99.9% MgO ceramics sintered at various temperatures. Patterns for (a) NIST SRM 660 LaB\(_6\) (Rasberry 1989), (b) NIST SRM 660a LaB\(_6\) (Freiman & Trahey 2000) and (c) NIST 676 \( \alpha \)-Al\(_2\)O\(_3\) (Reed 1992) are also presented. Peak intensities and peak positions are set identically to give comparable width definition. The surface of the MgO 1600°C for 6 hours sample was non-flat and hence it was excluded from the analysis.

(continuation)
(b) SRD patterns for line 422 of 99.9% MgO ceramics

(c) ND patterns for line 422 of 99.9% MgO ceramics

Figure 4.6. (cont’d)
Figure 4.7. FWHM versus $2\theta$ for the 99.9% MgO ceramics for the XRD, SRD and ND data. FWHM plots for the MgO standard are also presented for each associated instrument. Relative errors are less than 1% for SRD and ND and 3% for XRD. Error bars are not shown to clarify curve definition for broadening comparison. Line fits for the data were made with Equation (2.73).
(a) XRD patterns for line 422 of 99.99% MgO ceramics

Figure 4.8. (a) XRD (CuKα, λ ≈ 1.5418 Å), (b) SRD (λ ≈ 1.54 Å) and (c) ND (λ ≈ 1.493 Å) patterns for line 422 of 99.99% MgO ceramics sintered at various temperatures. Patterns for (a) NIST SRM 660 LaB₆ (Rasberry 1989), (b) NIST SRM 660a LaB₆ (Freiman & Trahey 2000) and (c) NIST 676 α-Al₂O₃ (Reed 1992) are also presented. Peak intensities and peak positions are set identically to give comparable width definition.

(cont’d)
(b) SRD patterns for line 422 of 99.99% MgO ceramics

(c) ND patterns for line 422 of 99.99% MgO ceramics

Figure 4.8. (cont'd)
Figure 4.9. FWHM versus $2\theta$ for the 99.99% MgO for the XRD, SRD and ND data. FWHM plots for the MgO standard are also presented for each associated instrument. Relative errors are less than 1% for SRD and ND and 3% for XRD. Error bars are not shown to clarify curve definition for broadening comparison. Line fits for the data were made with Equation (2.73).
FWHM vs. $2\theta$ plots made with XRD, SRD and ND data for the 99%, 99.9% and 99.99% ceramics sintered at various temperatures are presented in Figures 4.2, 4.7 and 4.9, respectively. These plots compare the FWHMs of all reflections for the specimens. It is clear that the XRD, SRD and ND FWHMs for the 99.9% and 99.99% specimens are broader than those of the MgO standard. Broadening of the 99% specimens has been discussed in §4.1. It was found that the 99% 1450°C – 2 h specimen exhibited minimal XRD and ND broadening. This material was, therefore, selected as the standard for these instruments. It was found subsequently (see Figure 4.3) that the 99% 1450°C – 2 h exhibited discernibly larger broadening than the NIST SRM 660a LaB$_6$ became available during the study as a replacement for the NIST SRM 660 LaB$_6$. The MgO standard was used for Voigt-based size and strain evaluations with XRD and ND data (see next section) and the NIST SRM 660a LaB$_6$ was used for the appraisal of the convolution model using SRD and XRD data (see Chapters 5 and 6).

Table 4.2 presents the average ratio of the specimen to standard FWHMs. As can be seen from the table, the 99% specimens exhibit the smallest broadening and the 99.9% the largest, while the 99.99% specimens show intermediate broadening. These results indicate that there is no direct correspondence between purity and broadening. This different broadening behaviour is probably attributable to different processes being employed to produce the raw powders.
Table 4.2. Average ratio of specimen to standard FWHMs for 99%, 99.9% and 99.99% MgO ceramics with XRD, SRD and ND data. The MgO standard material is used for all data. The NIST SRM 660a LaB₆ is also used for the SRD data, after corrections for the associated MgO positions and FWHMs are made by interpolation.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>XRD</th>
<th>SRD</th>
<th>ND</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgO</td>
<td>MgO</td>
<td>MgO</td>
</tr>
<tr>
<td>99% 1100°C - 2 h</td>
<td>1.25</td>
<td>1.69</td>
<td>1.93</td>
</tr>
<tr>
<td>99% 1250°C - 2 h</td>
<td>1.10</td>
<td>1.12</td>
<td>1.27</td>
</tr>
<tr>
<td>99% 1450°C - 2 h</td>
<td>1.00</td>
<td>1.00</td>
<td>1.14</td>
</tr>
<tr>
<td>99% 1600°C - 6 h</td>
<td>1.05</td>
<td>1.13</td>
<td>1.28</td>
</tr>
<tr>
<td>99.9% 1100°C - 2 h</td>
<td>1.72</td>
<td>3.56</td>
<td>4.05</td>
</tr>
<tr>
<td>99.9% 1250°C - 2 h</td>
<td>1.72</td>
<td>3.86</td>
<td>4.39</td>
</tr>
<tr>
<td>99.9% 1450°C - 2 h</td>
<td>1.46</td>
<td>1.95</td>
<td>2.22</td>
</tr>
<tr>
<td>99.99% 1100°C - 2 h</td>
<td>1.45</td>
<td>1.86</td>
<td>2.13</td>
</tr>
<tr>
<td>99.99% 1250°C - 2 h</td>
<td>1.37</td>
<td>1.68</td>
<td>1.92</td>
</tr>
<tr>
<td>99.99% 1450°C - 2 h</td>
<td>1.32</td>
<td>1.48</td>
<td>1.70</td>
</tr>
<tr>
<td>99.99% 1600°C - 6 h</td>
<td>1.28</td>
<td>1.32</td>
<td>1.53</td>
</tr>
</tbody>
</table>

The FWHM vs. 2θ and the Williamson-Hall plots may be used as a qualitative appraisal of whether the data require further analysis in terms of structural imperfections such as contributions from structural 'mistakes' (Langford 1992). The plots in Figures 4.4, 4.7 and 4.9 show that there is no significant scatter for the FWHMs of the specimen (cf the data for the MgO standard). This behaviour is indicative of there being no discernible size and strain anisotropy effects. Further analysis was performed using the Williamson-Hall plots, such as those in Figure 4.10, for 99% and 99.9% MgO specimens. The nature of the broadening due to imperfections in these specimens can be examined by inspecting whether or not there is hkl dependence. The assessments were conducted following procedures given by Langford (1992; 1999), by plotting $\beta_f' \left( = \frac{\beta_f \cos \theta}{\lambda} \right)$ vs. $d' \left( = \frac{2 \sin \theta}{\lambda} \right)$, where $\beta_f$ is
the pure specimen broadening. Interpretations for the plots are given by Langford (1999). The figures show that:

(a) although some scatter is found along [111] for the 99% 1100°C – 2 h material, in general, there is negligible scatter in the values of \( \beta'_f \) from straight lines for all specimens, indicating that the sizes in the materials are isotropic and the crystallites are, on average, spherical. The expected isotropic characteristic which determined the selection of cubic MgO (see research rationale in §3.1) is confirmed by these results.

(b) the values of \( \beta'_f \) for the materials are almost independent of \( a' \), except for the 99% 1600°C – 6 h and 99.9% 1450°C – 2 h specimens, indicating that strain broadening is very small. The plots for 99% 1600°C – 6 h and 99.9% 1450°C – 2 h specimens have a small slope with negligible scatter, indicating the presence of small isotropic strain, and intercept the \( \beta'_f \), implying that the specimens exhibit size broadening. The estimated strains in these materials, calculated from the slope, are 0.8 and 0.2 \( \times 10^{-3} \), respectively. It is argued that the strain values in the MgO ceramics used in this study can be considered as relatively small (ca. in the vicinity of \( 10^{-3} \) or less).

(c) the specimens do not exhibit ‘mistakes’ which normally can be identified from the systematic variation of \( \beta'_f \) with lattice direction.
Figure 4.10. The Williamson-Hall plots for the 99% (top) and 99.9% (bottom) MgO ceramics. SRD data, with instrument correction made with NIST SRM 660a LaB$_6$ were used. Plots for the 99.99% specimens cannot be made since these materials exhibit 'super-Lorentzian' character (see discussion in §5.4.3 and §6.2).
The values of the pseudo-Voigt FWHMs and Voigt breadths for line 422 of the MgO ceramics, for XRD, SRD and ND data, are presented in Tables 4.3 and 4.4, respectively. In the succeeding discussion on the character of the line widths for the specimens, particular attention is given to the SRD data which show largest peak broadening as compared with that produced by the associated instrument profile (see Table 4.2).

The following commentary on the character of the line widths for the MgO materials refers to the SRD data. The profile for the 99% specimen (Figure 4.1b) has a tail which drops quickly with 2θ, indicating it has small broadening from both size and strain effects (with the pseudo-Voigt FWHM for the 1100°C – 2 h specimen = 0.1367(9) (°2θ) and the corresponding φ = 0.61(1)). By contrast, specimen 99.9% (Figure 4.6b) has a broad peak and relatively long tail with FWHM for the 1100°C - 2 h specimen = 0.2640(8) and φ = 0.63(1) indicating larger strain and size effects.

An interesting feature was found for the 99.99% 1100°C – 2 h specimen which showed a relatively broad peak and long tail (Figure 4.8b). Traditional refinement gave a pseudo-Voigt FWHM = 0.2142(20) and φ = 1.00(1), which indicates a pure Lorentzian profile. Further inspection shows that the 99.99% peak has FWHM = 0.2360(12) and φ = 1.1801(9), which is indicative of a 'super-Lorentzian' profile (see, for example, Young & Sakhtivel 1988; Louër 1999). This behaviour is often observed in materials with small crystallite size (Louër 1999). In this case, it is therefore inappropriate to use the Voigt function for the size-strain evaluation (Langford 1999). As can be seen from Table 4.4, the Voigt Gaussian breadth for the 99.99% specimen is 0.011(4) (°2θ) which is much less than that for the NIST SRM 660a (0.058(1)). It was further found that the Pearson VII index (or the exponential m) for this material is 0.985(6) which also indicates that the line profile is 'super-Lorentzian' (Langford 1999).

It is clear that the Voigt function cannot deal with 'super-Lorentzian' peaks such as those found for the 99.99% MgO ceramics SRD data, which limits its use for size and strain analysis. It will be shown in Chapter 5 that the convolution model developed in this study can deal with this peak shape.
Table 4.3. The values for the pseudo-Voigt FWHMs and mixing parameter ($\phi$) for the line 422 of the MgO ceramics produced using XRD, SRD and ND data. Profile fitting was conducted using SHADOW (Materials Data Inc. 1999).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>XRD</th>
<th>SRD</th>
<th>ND</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FWHM</td>
<td>$\phi$</td>
<td>FWHM</td>
</tr>
<tr>
<td>99% 1100°C - 2 h</td>
<td>0.232(2)</td>
<td>0.59(2)</td>
<td>0.1367(9)</td>
</tr>
<tr>
<td>99% 1250°C - 2 h</td>
<td>0.189(2)</td>
<td>0.49(2)</td>
<td>0.0807(4)</td>
</tr>
<tr>
<td>99% 1450°C - 2 h</td>
<td>0.171(2)</td>
<td>0.44(1)</td>
<td>0.0755(2)</td>
</tr>
<tr>
<td>99% 1600°C - 6 h</td>
<td>0.185(2)</td>
<td>0.47(2)</td>
<td>0.0917(6)</td>
</tr>
<tr>
<td>99.9% 1100°C - 2 h</td>
<td>0.372(4)</td>
<td>0.67(2)</td>
<td>0.3026(11)</td>
</tr>
<tr>
<td>99.9% 1250°C - 2 h</td>
<td>0.349(3)</td>
<td>0.70(2)</td>
<td>0.2640(8)</td>
</tr>
<tr>
<td>99.9% 1450°C - 2 h</td>
<td>0.287(4)</td>
<td>0.75(2)</td>
<td>0.1858(17)</td>
</tr>
<tr>
<td>99.99% 1100°C - 2 h</td>
<td>0.350(4)</td>
<td>0.96(2)</td>
<td>0.2142(20)</td>
</tr>
<tr>
<td>99.99% 1250°C - 2 h</td>
<td>0.298(4)</td>
<td>0.86(2)</td>
<td>0.1847(14)</td>
</tr>
<tr>
<td>99.99% 1450°C - 2 h</td>
<td>0.285(8)</td>
<td>0.85(6)</td>
<td>0.1679(15)</td>
</tr>
<tr>
<td>99.99% 1600°C - 6 h</td>
<td>0.214(2)</td>
<td>0.61(2)</td>
<td>0.1012(7)</td>
</tr>
</tbody>
</table>
Table 4.4. The values for the Lorentzian and Gaussian breadths ($\beta_L$ and $\beta_G$) and the peak shape factor ($\phi$) of the Voigt function for the line 422 of the MgO ceramics produced using XRD, SRD and ND data. Profile fitting was conducted using SHADOW (Materials Data Inc. 1999). The peak shape factor ($\phi$) values were calculated using the expression given by Ahsee et al. (1984 – see the notes for Table 2.1). Values for the NIST SRM 660a LaB$_6$ were calculated using an interpolation. ND data for the NIST SRM 660a LaB$_6$ was not collected, due to severe absorption.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>XRD</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\beta_L$</td>
<td>$\beta_G$</td>
<td>$\phi$</td>
<td>$\beta_L$</td>
<td>$\beta_G$</td>
<td>$\phi$</td>
<td>$\beta_L$</td>
<td>$\beta_G$</td>
<td>$\phi$</td>
</tr>
<tr>
<td>NIST SRM 660a LaB$_6$</td>
<td>0.164(1)</td>
<td>0.131(4)</td>
<td>0.751</td>
<td>0.0483(14)</td>
<td>0.0578(10)</td>
<td>0.792</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>99% 1100°C - 2 h</td>
<td>0.222(4)</td>
<td>0.211(6)</td>
<td>0.768</td>
<td>0.1441(9)</td>
<td>0.0849(17)</td>
<td>0.722</td>
<td>0.243(4)</td>
<td>0.310(3)</td>
<td>0.798</td>
</tr>
<tr>
<td>99% 1250°C - 2 h</td>
<td>0.173(3)</td>
<td>0.171(4)</td>
<td>0.772</td>
<td>0.0735(3)</td>
<td>0.0677(5)</td>
<td>0.695</td>
<td>0.175(5)</td>
<td>0.311(2)</td>
<td>0.828</td>
</tr>
<tr>
<td>99% 1450°C - 2 h</td>
<td>0.167(1)</td>
<td>0.139(3)</td>
<td>0.755</td>
<td>0.0573(3)</td>
<td>0.0701(3)</td>
<td>0.692</td>
<td>0.000(-)</td>
<td>0.285(2)</td>
<td>0.939</td>
</tr>
<tr>
<td>99% 1600°C - 2 h</td>
<td>0.187(1)</td>
<td>0.168(4)</td>
<td>0.763</td>
<td>0.0838(5)</td>
<td>0.0768(8)</td>
<td>0.707</td>
<td>0.000(-)</td>
<td>0.289(1)</td>
<td>0.939</td>
</tr>
<tr>
<td>99.9% 1100°C - 2 h</td>
<td>0.395(4)</td>
<td>0.22(1)</td>
<td>0.716</td>
<td>0.3199(9)</td>
<td>0.1941(18)</td>
<td>0.724</td>
<td>0.221(5)</td>
<td>0.302(3)</td>
<td>0.804</td>
</tr>
<tr>
<td>99.9% 1250°C - 2 h</td>
<td>0.367(5)</td>
<td>0.19(1)</td>
<td>0.710</td>
<td>0.2794(8)</td>
<td>0.1641(15)</td>
<td>0.721</td>
<td>0.225(6)</td>
<td>0.300(4)</td>
<td>0.802</td>
</tr>
<tr>
<td>99.9% 1450°C - 2 h</td>
<td>0.296(6)</td>
<td>0.14(1)</td>
<td>0.703</td>
<td>0.1965(20)</td>
<td>0.1030(29)</td>
<td>0.713</td>
<td>0.205(4)</td>
<td>0.299(3)</td>
<td>0.811</td>
</tr>
<tr>
<td>99.99% 1100°C - 2 h</td>
<td>0.245(16)</td>
<td>0.083(12)</td>
<td>0.679</td>
<td>0.0870(170)</td>
<td>0.0110(44)</td>
<td>0.646</td>
<td>0.414(2)</td>
<td>0.272(4)</td>
<td>0.732</td>
</tr>
<tr>
<td>99.99% 1250°C - 2 h</td>
<td>0.252(30)</td>
<td>0.068(17)</td>
<td>0.666</td>
<td>0.0797(161)</td>
<td>0.0121(50)</td>
<td>0.647</td>
<td>0.474(3)</td>
<td>0.287(5)</td>
<td>0.724</td>
</tr>
<tr>
<td>99.99% 1450°C - 2 h</td>
<td>0.281(20)</td>
<td>0.117(21)</td>
<td>0.693</td>
<td>0.0703(160)</td>
<td>0.0104(48)</td>
<td>0.647</td>
<td>0.420(2)</td>
<td>0.296(4)</td>
<td>0.739</td>
</tr>
<tr>
<td>99.99% 1600°C - 6 h</td>
<td>0.226(2)</td>
<td>0.138(4)</td>
<td>0.725</td>
<td>0.1076(49)</td>
<td>0.0358(35)</td>
<td>0.665</td>
<td>0.261(2)</td>
<td>0.284(2)</td>
<td>0.782</td>
</tr>
</tbody>
</table>
4.4. Size-Strain Determination using Conventional Voigt-based Methods

Since the introduction of the Voigt function for analysing diffraction line broadening (Langford 1978), size-strain evaluations based on this function developed rapidly. Two developments used line profile fitting in the real space, i.e. (1) single-line integral breadth (de Keijser et al. 1982) and (2) Rietveld (e.g. Madsen & Hill 1990). These methods were applied in this study to determine the size and strain only for the 99% MgO ceramics as the peak broadening character for these materials decreases with temperature and then increases slightly after prolonged sintering and also does not show 'super-Lorentzian' behaviour. Detailed appraisals of the methods are given in accordance with the development of the convolution method described in Chapter 6. A comparison of the Voigt single-line integral breadth and Rietveld results with XRD and ND data for 99% MgO ceramics has been published recently (Pratapa, O'Connor & Hunter 2002) which also includes data for the associated MgO powder and MgO – Y₂O₃ ceramic composites (10 and 20 wt.% Y₂O₃) prepared by sintering at 1550°C for 2 hours.

The 99% MgO ceramic sintered at 1450°C – 2 h has been employed as the standard for instrument broadening corrections to evaluate strain and size in the 99% specimens with XRD and ND data. The NIST SRM 660 LaB₆ could not be used for ND instrument correction due to severe neutron absorption. In the Voigt single line analysis, the 420 and 422 reflections (2θ = 109.78° and 127.29° respectively) were selected since the influences of flat specimen and axial divergence in the XRD experiments are likely to be negligible at high 2θ (> 90°) when compared with the same effect at low 2θ (Klug & Alexander 1974).
4.4.1. Line Broadening

The FWHM versus 2θ plots for the 99% MgO powder and sintered ceramics, for the XRD and ND data, are shown in Figure 11a. It was found for both that the FWHM decreases with sintering temperature, reaching a minimum at 1450°C for 2 hours (1450°C – 2 h). The XRD FWHM for the 1600°C – 6 h ceramic is substantially higher than that for the 1450°C – 2 h ceramic over the 2θ range, whereas the corresponding FWHMs are similar for the ND data. Figure 10b compares the FWHM vs. 2θ plots for MgO ceramic sintered at 1450°C – 2 h (0% Y$_2$O$_3$) and the composites. As can be seen from this figure, the FWHM for the 0% Y$_2$O$_3$ ceramic is substantially less than those for the composites indicating that the broadening increases with the level of Y$_2$O$_3$ addition. This result shows that addition of a second phase will broaden the diffraction peak widths.

Figure 4.11 clearly indicates that the powder and the composites show substantial broadening. The broadening amounts to 1.5 – 2 times that for the 1450°C – 2 h ceramic for which there is minimal broadening. The broadening is considerably less than the values typically observed for deformed metals and ultrafine nanocrystallites (e.g. Klug & Alexander, 1974; Guillou et al., 1995). Comparing the broadening of these materials, it appears that the 99% MgO materials have relatively large size and small strain.

The effect of the sintering on both XRD and ND Gaussian and Lorentzian peak breadths is shown in Figure 4.12a. It is evident that the breadths decrease with sintering temperature up to 1450°C for 2 hours, and that further sintering causes broadening of the XRD Gaussian and Lorentzian profile components. A slight increase in the ND Gaussian breadth at 1600°C for 6 hours is also observed, whereas the ND Lorentzian breadth vanishes for the 1450°C – 2 h and 1600°C – 6 h data sets. These results are indicative of variation of size and strain character in the 99% MgO ceramics.
(a) FWHM versus 2\(\theta\) for the 99% MgO powder and ceramics produced using XRD and ND

(b) FWHM versus 2\(\theta\) for 99%MgO-Y\(_2\)O\(_3\) composites produced using XRD and ND

Figure 4.11. FWHM versus 2\(\theta\) for XRD and ND data. (a) 99% MgO powder and ceramics (b) 99% MgO ceramic sintered at 1450°C – 2 h (0% Y\(_2\)O\(_3\)) and 99% MgO – Y\(_2\)O\(_3\) composites.
Figure 4.12. Effects of sintering on the FWHM Gaussian and Lorentzian components of the FWHM values for the 422 reflection of the 99% MgO specimens using XRD and ND data: (a) from integral breadth analysis; (b) from Rietveld analysis. The legend for the horizontal axis denotes the sintering temperature and time (e.g. 1100°C for 2 hours). Error bars indicate 1 × the standard uncertainty.
The effect of sintering on the XRD and ND Rietveld peak shape parameters $U$ [Equation (2.73)] and $H_L$ [Equation (2.74)] is shown in Figure 4.12b. Again, it was found that both XRD parameters decrease with sintering temperature up to 1450°C – 2 h and then increase at 1600°C – 6 h. Similar trends were observed for the ND parameters, however, with less effect at 1600°C – 6 h. This observation supports the interpretation that size and strain broadening changes with differing sintering temperatures and the broadening is minimal for the 99% 1450°C – 2 h ceramic.

These results confirm the decision made to select the 1450°C – 2 h MgO ceramic as the standard for instrument broadening corrections.

4.4.2. Strain Assessments

Figure 4.13 shows the XRD and ND strain values for the MgO ceramics as a function of sintering temperature. It is obvious from the XRD single-line and Rietveld results (Figure 4.13a) that sintering up to 1450°C for 2 hours causes strain-relief and further sintering generates additional strain. It appears that intragranular shear interactions during prolonged sintering increase the additional strain in the 1600°C – 6 h sample. With specimen apparent density being very close to unity (see Table 3.1), further grain growth to occupy porous regions is not possible. As a result, grains tend to interact and thus non-uniform microstrain develops. The corresponding ND data (Figure 4.13b), representing strain at depth, are similar to the XRD data with the exceptions that (i) the ND strain for the powder is slightly less than the XRD estimates, and (ii) the enhanced uncertainties for the ND data (attributed to the increased instrumental widths for ND) would mask any increase in ND-derived strain for the 1600°C – 6 h sample.

The effect of $Y_2O_3$ as a second phase on the XRD and ND strain estimates can also be seen in Figure 4.13 (right side of the figures). It is clear from both single-line and Rietveld results that the presence of $Y_2O_3$ introduces additional strain, which increases with $Y_2O_3$ content. The increase of the strain is possibly due to shear interactions between the MgO and $Y_2O_3$ grains as a result of the lattice mismatch between the phases. This observation is found for other composites, such as zirconia-dispersed $\alpha$-alumina sintered ceramics (van Riessen 1997).
Figure 4.13. Microstrain values versus sintering temperature and Y$_2$O$_3$ content for the 99% MgO ceramics obtained from (a) XRD data and (b) ND data. The composites were sintered at 1550°C for 6 hours. The data labelled 0% Y$_2$O$_3$ are the same as the 1600°C – 6 h MgO data. Error bars indicate $1 \times$ the standard uncertainty.
4.4.3. Size Assessments

The single-line size estimates show that sintering favours crystallite growth in the pure MgO specimens (Figure 4.14). The Rietveld results give the same trend, but with significantly smaller size values for the XRD analysis and larger values for the ND data. The single-line XRD estimate for the $1250^\circ\text{C} - 2\ \text{h}$ specimen, for example, is approximately 1000 nm, whereas the Rietveld estimate is 250 nm. Further, the single-line size estimates seem to be more reasonable in that constraints on grain growth for the bulk (ND results) should be more substantial than might apply to the near-surface (XRD). The generally higher Rietveld size estimates found from the ND data, relative to XRD, appear to be unreasonable.

Single-line size estimates could not be made for the ND $1600^\circ\text{C} - 6\ \text{h}$ data (Figure 4.14) as the Lorentzian breadths for this specimen and for the $1450^\circ\text{C} - 2\ \text{h}$ sample were the same within experimental limits (see Figure 4.12).

Figures 4.15a to 4.15c show the secondary electron (SE) mode SEM micrographs for the 99% MgO powder, $1250^\circ\text{C} - 2\ \text{h}$ and $1450^\circ\text{C} - 2\ \text{h}$ specimens. It is evident from the SEM micrographs that sintering favours grain growth. Figure 4.15a shows the SEM micrograph of the MgO powder which has a range of grain sizes between 300 and 1000 nm, with an average size of approximately 500 nm (see also Table 4.5). SEM measurement for the $1250^\circ\text{C} - 2\ \text{h}$ ceramic gave grain sizes in the range 800 – 1700 nm with an average value of 1400 nm (Figure 4.15b and Table 4.5). Finally, the grain size for the $1450^\circ\text{C} - 2\ \text{h}$ specimen ranges between approximately 5 and 10 µm. It appears that the sizes measured using SEM are larger than those obtained using the single-line and Rietveld method. These results are consistent with the SEM 'particles' containing an ensemble of coherently diffracting domains which represent the crystallites. Similar observations have been reported by others (Guillou, Auffrédiuc & Louër 1995; Audebrand et al. 2000b). Further discussion regarding comparison of the diffraction broadening sizes and the SEM-derived sizes for the 99.9% and the 99.99% MgO specimens is given in Chapter 6.
Figure 4.14. Size values versus sintering temperature and Y₂O₃ content for the 99% MgO ceramics obtained from (a) XRD data and (b) ND data. The single-line ND crystallite size for 1600°C – 6 h cannot be determined as the associated Lorentzian components are zero (see Figure 4.12). Error bars indicate 1 × the standard uncertainty.
Figure 4.15. Secondary electron mode SEM micrographs for the 99% MgO (a) powder, (b) 1250°C – 2 h and (c) 1450°C – 2 h specimens. The surface of the 1250°C – 2 h and 1450°C – 2 h specimens were polished with 1 μm diamond grit. Note the different scale bars.
(b) SEM micrograph for the 99% MgO ceramic sintered at 1250°C for 2 hours

(c) SEM micrograph for the 99% MgO ceramic sintered at 1450°C for 2 hours

Figure 4.15. (cont’d)
Figure 4.14 also indicates that for both methods (XRD and ND) the presence of Y₂O₃ as a second phase inhibits crystallite growth. The single-line method shows that the estimated crystallite size for MgO in the composites is similar to that in the powder. The Rietveld size decreases with the level of Y₂O₃ addition, and the Rietveld sizes are consistently larger than the single-line sizes. The role of a second phase in constraining grain growth in ceramic materials is widely known (Kingery, Bowen & Uhlmann 1976). For example, ZrO₂ inhibits grain growth in Al₂O₃ ceramics (Lange & Hirlinger 1984).

Table 4.5. Selected Voigt single-line and SEM-derived sizes for the 99% MgO materials.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>XRD Voigt size</th>
<th>ND Voigt size</th>
<th>SEM-derived size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(nm)</td>
<td>(nm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average¹</td>
<td>Average¹</td>
<td>Range</td>
</tr>
<tr>
<td>Powder</td>
<td>155</td>
<td>80</td>
<td>300-1000</td>
</tr>
<tr>
<td>1250°C - 2 h</td>
<td>1000</td>
<td>330</td>
<td>800-1700</td>
</tr>
<tr>
<td>1450°C - 2 h²</td>
<td>-</td>
<td>-</td>
<td>3000-10,000</td>
</tr>
</tbody>
</table>

¹ Calculated as the average value from lines 420 and 422.
² Used as the standard material for instrument broadening correction

4.4.4. Discussion

Strain and size results

The systematic change in strain values with sintering temperature can be explained as follows. At the initial stage of sintering, presumably below 1100°C, the grains start growing and residual internal strains, present due to powder processing, reduce. When the sintering process is completed, the grain size has become much larger than the initial powder size, the porosity is minimal and the residual strains are also minimal. If additional heat treatment is given, the grains will grow further. However, with the absence of porosity, the grains will tend to undergo further interactions causing shear strains. This process will develop non-uniform strains as shown by the increase in Gaussian broadening.
Figure 4.16 shows the ratios of the 420/422 and Rietveld/422 strain values for the XRD and ND data. The consistency of the single-line results is apparent from the ratios being very close to unity. The Rietveld/422 strain ratios deviate more from unity, which could be due to different scattering angle sampling. The diffraction lines considered in the Rietveld refinement are mainly in the lower and medium scattering angles while the derived sample broadening and accuracy are relatively low, whereas the single line method have used the diffraction lines only at high angle which results in much larger broadening and accuracy. However, both ratios do not deviate from unity by more than 2 standard deviations. The overall conclusion from these comparisons is that there is sound agreement between the strain estimates from the XRD and ND data. Therefore, the Voigt model shows that the near-surface strain is similar to the bulk strain.

The nominal crystallite size normally observable from diffraction broadening is less than 100 nm (Klug & Alexander 1974). This study shows that crystallite size up to 300 nm is quantifiable with relatively low uncertainty (Figure 4.14 for the 99% 1100°C – 2 h specimen). Larger sizes can also be quantified, however, with large uncertainty (Figure 4.14 for the 99% 1450°C – 2 h specimen). This is evident from Equation (2.78) and Figure 4.15 where the size uncertainty is inversely proportional to the specimen Lorentzian broadening and proportional to the size value.

Figure 4.17 shows the ratios of the 420/422 and Rietveld/422 size values for the XRD and ND data. It appears that the model for crystallite size determination by the Rietveld method gives inconsistent results. Presumably, this is due to the model for the instrument profile which, for both XRD and ND, is assumed to be Voigtian. The ND peak shape for the standard specimen is very close to Gaussian as observed by others (e.g. Suortti, Ahtee & Unonius 1979; Albinati & Wilis 1982), while the instrument profile model for XRD is more complicated (Klug & Alexander 1974; Suortti, Ahtee & Unonius 1979). It should also be noted that the Voigt function adopted for this line profile analysis does not take into account the influence of there being a particle size distribution, rather than a monosize microstructure, which may lead to dubious size values.
Figure 4.16. Ratios of microstrain values for the 420 and 422 single-line estimates and the Rietveld and 422 single-line microstrain values for (a) XRD data and (b) ND data obtained for 99% MgO ceramics. Error bars for the 1250°C – 2 h and 1600°C – 6 h ND microstrain values are off the scale. Error bars indicate 1 × the standard uncertainty.
Figure 4.16. Ratios of size values for the 420 and 422 single-line estimates and the Rietveld and 422 single-line microstrain values for (a) XRD data and (b) ND data obtained for 99% MgO ceramics. Error bars indicate 1 $\times$ the standard uncertainty.
Quality of the Rietveld assessments

The strain-size assessments from the Rietveld method are less consistent than those using the single-line method. The results obtained from XRD and ND data for the MgO ceramics show that the Rietveld strain differs appreciably from the single-line determinations with, in general, inferior precision. It is also found that the Rietveld size values disagree with the single-line sizes.

Despite the possibility of acquiring strain-size information using the Voigt function, it should be emphasised that the Gaussian-strain and Lorentzian-size assumptions have no physical basis. Moreover, the Gaussian-strain assumption is appropriate only for small strains and Lorentzian-size assumption for monodispersed crystallites. It is therefore of value to model each effect following considerations which have direct microstructural interpretation. York (1999) has derived analytical profile functions with parameters which are directly correlated to crystallite size distribution, average crystallite size and strain distribution. The next chapter discusses the development of a convolution model which might give more appropriate results.

Near-surface and bulk strain evaluations

The similarity of strain values obtained with the XRD and ND data indicates that both the near-surface and the bulk exhibit similar shear-strain (or non-uniform microstrain) behaviour. It is well-known that when a ceramic material is cooled during sintering, differences in contraction behaviour between the surface and the bulk might cause tensile and compressive stresses, respectively (Kingery, Bowen & Uhlmann 1976). This behaviour, however, appears not to be correlated with the non-uniform microstrain. It is expected that this behaviour is associated with the uniform microstrain, which can be determined by assessing the diffraction line-shifts.

Different XRD and ND size values for the ceramics might be caused by either the difference in the average near-surface and bulk grain size or in the near-surface and bulk crystallite size distribution. The latter could not be obtained from this study as it is not taken into account in the Voigt function.
4.5. Conclusion

1. The 99%, 99.9% and 99.99% MgO ceramics used in this study differ in broadening character which is indicative of different size and strain effects. The 99% ceramics exhibited the least specimen broadening whereas the 99.9% and 99.99% specimens had relatively broad peaks, the latter showing ‘super-Lorentzian’ character.

2. The Williamson-Hall plots for the MgO ceramics indicated the presence of (1) isotropic size and strain and (2) small strain (ca. in the vicinity of $10^{-3}$ or less). The plots also showed no indications of structural ‘mistakes’.

3. The 99% MgO ceramic sintered at 1450°C for 2 hours with slow annealing during cooling is suitable for instrument profile corrections applied to both XRD and ND data. The XRD strain broadening and the microstructural characteristics of the ceramic are very similar to those for the NIST SRM 660 LaB$_6$. The use of the MgO ceramic standard can be extended to ND for which LaB$_6$ cannot be used due to severe neutron absorption.

4. The 99% MgO 1450°C – 2 h standard has been used successfully to evaluate strain-size in the 99% MgO ceramics. The results obtained by both the single-line and Rietveld methods using the Voigt function applied to XRD and ND data showed that sintering relieves residual strain and induces crystallite growth in MgO ceramics. Both methods also show that further sintering in pure MgO develops strain, which is presumably due to the shear interactions between neighbouring grains.

5. In general, consistent strain values were obtained for the Voigt single-line and Rietveld methods using both XRD and ND data whereas there are marked differences between the size estimates from the two methods. The inconsistency of the results indicates that there is a requirement to improve the profile functions based upon a more appropriate physical basis and involving parameters representing crystallite size distribution.

6. Strain and size results obtained with the single-line Voigt and Rietveld methods (Pratapa, O'Connor & Hunter 2002) using the XRD and ND data gives relatively large uncertainties, which can be attributable to large instrument effects.
Therefore, it became imperative to use high-resolution synchrotron radiation diffractometer to improve the quality of the results. Development of the new convolution model for strain and size analysis is described in Chapter 5, and evaluation of the model is made with the SRD data. Application of the model with SRD and XRD data for MgO ceramics with three different purity levels sintered at various temperatures is presented in Chapter 6.

7. This chapter also confirms that the Voigt function cannot be applied to diffraction lines with 'super-Lorentzian' peak shape. As will be shown in Chapter 5 and 6, the convolution model can be used to extract size and strain information from such peak profiles.
CHAPTER 5. DEVELOPMENT OF THE CONVOLUTION MODEL FOR SIZE AND STRAIN LINE BROADENING

5.1. Introduction

The Voigt-based size-strain assessment method has been evaluated in Chapter 4 using XRD and ND data for 99% MgO ceramics. It was found that the method can be used to give reasonable strain values but dubious size values. The latter observation could be attributed to the Voigt function not accommodating the size distribution. Moreover, the Voigt function is used for size and strain analysis by assuming that size contributes only to the Lorentzian component and strain to the Gaussian component. Further investigation showed that the Voigt function cannot be used if the diffraction line shape lies outside the Gaussian and Lorentzian regions, notably within the ‘super-Lorentzian’ region. Despite these limitations, the Voigt function provides the insight that a specimen profile function should be a convolution of functions from individual microstructural effects, viz. a convolution of Gaussian-strain and Lorentzian-size profiles.

This chapter describes the development of a new convolution model for crystallite size and strain determination from diffraction line broadening. The size profile component function for the model, as proposed by York (1999, 2003) for normal crystallite growth according to the mean-field theory, involves a size parameter and a size distribution parameter which describes the dispersion of crystallite sizes. The involvement of the size distribution parameter is expected to advance the existing models for size and strain evaluations. The strain profile component function is Gaussian which can be used for strain modelling of small strain (ca. in the order of $10^{-3}$ or less) (Warren 1969; Delhez et al. 1993; Balzar 1999). It has been shown in §4.3, using the Williamson-Hall plots, that the estimated strain in the materials under study is smaller than $10^{-3}$.

The overall profile describing the diffraction pattern involves the convolution of instrument, size and strain effects. A non-linear least-squares refinement program entitled MOZAIK, written in Fortran 95, has been developed for model optimisation with diffraction data.
This chapter presents the *MOZAIK* results for SRD data acquired with MgO ceramics which show distinctly different broadening characteristics. More detailed descriptions of the broadening character of these ceramics have been given in Chapter 4. The cubic symmetry of MgO was expected to give size and strain effects which are independent of crystallographic direction. The isotropic size and strain effects have been confirmed – see discussion on the Williamson-Hall plots in §4.2. Comparison of the size-strain evaluations with results for the Voigt single-line method is also reported.

5.2. Mathematical Background

The use of the Voigt function in line profile analysis can be considered as an example of a convolution method, where it is assumed that the strain contributes only to the Gaussian component and the size contributes only to the Lorentzian component (e.g. Delhez, de Keijser & Mittemeijer 1982). Application of this method to sintered MgO ceramic materials has been discussed in Chapter 4. Inconsistency in size results was observed, particularly when the crystallite size values from the single-line method were compared with those from the Rietveld method. It was argued that the inconsistency was due to the Voigt function being adopted for the line profile analysis which does not consider the influence of there being a particle size distribution. Rather it assumes a monodisperse microstructure, which may lead to the extraction of dubious values. Langford et al. (2000) showed that the size profile function for a unimodal size distribution is not generally Lorentzian. It is, therefore, important to correct this assumption. The following section explains briefly the derivation of a size profile based on the mean field theory of normal grain growth which is expected to be more appropriate for study of sintered ceramics.

Radiation scattering from a polycrystalline material, in effect, comprises the average of the individual intensities from numerous crystallites. An observed profile \(F\) is a convolution of instrumental \(g\) and specimen \(f\) profiles, consisting of strain and size components. The whole profile function can be expressed as

\[
F(\varepsilon; D) = g \otimes f(\varepsilon) \otimes f(D)
\]

(5.1)
where $\otimes$ denotes the convolution, $\varepsilon$ represents non-uniform strain and $D$ is crystallite size. In this model, each profile contributes independently to the total specimen profile (Langford 1999). This approach is similar, in the sense of the independent contribution of size and strain effects, to the use of the Voigt function (de Keijser et al. 1982) in which $f(\varepsilon)$ is a Gaussian function and $f(D)$ is Lorentzian. When the $g$ profile is known, the least-squares calculation can be performed by convolving the individual functions.

The mean field approach for time-independent normal grain growth (York 1999) results in the partial differential equation for the size distribution $\rho(u)$

$$\frac{\partial \rho(u)}{\partial u} + \beta(1 - \frac{1}{u})\rho(u) = 0$$

(5.2)

which has a trivial solution

$$\rho(u) = u^\beta e^{-\beta u}$$

(5.3)

where $u$ is the dimensionless size parameter $D/D_0$, for the modal size $D_0$, and $\beta$ determines the shape of the size distribution. Parameter $\beta$ may be physically interpreted as a parameter describing the kinetics of the grain growth process (York 1999; see also §2.4.1). Figure 5.1 shows the size distribution function $\rho(u)$ as a function of size distribution parameter $\beta$. The modal size is found at $D = D_0$. Parameter $\beta$ controls the width of the size distribution. As $\beta$ decreases, the width of the distribution increases, indicating inhomogenous size. A monodisperse microstructure corresponds to $\beta \to \infty$. 

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Figure 5.1. Size distribution function plot for size distribution parameter $\beta$ values = 0.5, 1.0, 2.0 and 5.0 computed with Equation (5.3). The function peaks at the modal size $D = D_0$. A relatively large $\beta$ corresponds to a more symmetric distribution.
Assuming that a columnar-like grain structure is normal to the diffracting planes with a uniform strain, the Laue function centered about the first order can be integrated over the normalised size distribution to give

$$f_{size}(\theta) = \int_{-\infty}^{\infty} u e^{-\beta u \sin^2 N\psi} \frac{du}{\sin^2 \psi}$$  \hspace{1cm} (5.4)

where $\psi = \frac{d \sin \theta}{\lambda}$, $d$ is the lattice spacing and $\lambda$ is the radiation wavelength. The corresponding analytical size profile function, after the expansion of $\theta$ about the peak position $\theta_0$, has the form [York 1999 – after a modification of Equation (5)],

$$f_{size}(\theta) = \frac{I_0}{\beta^2 \left[ 1 + \frac{2\pi}{\beta} \left( \frac{2\theta - 2\theta_0}{W_D} \right)^2 \right]^{\frac{\beta+1}{2}}}$$  \hspace{1cm} (5.5)

where $I_0$ is the maximum intensity and $W_D$ is the full-width at half maximum (FWHM). The modal crystallite size $D_0$, which is associated with the size distribution peak determined using Equation (5.3), is defined by

$$W_D = \frac{\lambda}{D_0 \cos \theta}$$  \hspace{1cm} (5.6)

which represents the ‘volume-weighted’ size – similar to that in Equation (2.72) for the single-line integral breadth method using the Voigt function.

The shape of the size profile function is determined by $W_D$ and $\beta$ - see Figure 5.2. It is clear that the size distribution parameter strongly influences the tail as well as the width of the profile. Similar effects have been observed by others (Langford, Louër & Scardi 2000; Popa & Balzar 2002). As $\beta$ increases, and therefore a more homogenous crystallite size distribution develops, the profile shape approaches pure Gaussian. A sample plot of the size profile function given by equation (5.5) is presented in Figure 5.3, along with the pseudo-Voigt and Pearson VII functions. It is evident that the size function, equation (5.5), is very similar to the Pearson VII function.
A Gaussian strain profile function was assumed which should be adequate, according to others (e.g. de Keijser et al. 1982; Delhez et al. 1993; Wu, Gray & Kisi 1998), for samples with microstrain values in the vicinity of $10^{-3}$ or less. Examples for the adequacy of the use of the Gaussian strain profile were found in CeO$_2$ powders (ca. $0.33 \times 10^{-3}$ – Popa & Balzar 2002), α-Al$_2$O$_3$ whisker composites (ca. $0.7 \times 10^{-3}$ – Balasingh, Abuhasan & Predecki 1991) and cold-work nickel, nitrided steel and liquid-quenched AlSi alloy (ca. $2.0 \times 10^{-3}$, $1.4 \times 10^{-3}$ and $1.3 \times 10^{-3}$, respectively – de Keijser et al. 1982). It is worth noting that the Gaussian strain distribution function describes the configuration of strain probability in the crystal space, while the Gaussian profile function specifies a profile-shape function. The strain profile function takes the form

$$f_{\text{strain}}(\theta) = I_0 e^{-\left(\frac{2\theta - 2\theta_0}{W\varepsilon}\right)^2}$$

(5.7)

where $W\varepsilon$ is the full-width at half maximum intensity and can be associated with the integral breadth for strain $\beta_\varepsilon$ as

$$\beta_\varepsilon = \frac{W\varepsilon}{\sqrt{\pi}}$$

(5.8)

The maximum (upper limit) strain, $\varepsilon$, can be calculated using

$$\beta_\varepsilon = 4\varepsilon \tan \theta_0$$

(5.9a)

where $\theta_0$ is the Bragg peak position. For Gaussian strain distribution, the root mean square strain, $\varepsilon_{ms}$, can be determined as (Stokes & Wilson 1944)

$$\varepsilon_{ms} = \frac{2}{\sqrt{\pi}}\varepsilon$$

(5.9b)

The strain terminology used in this study is the maximum strain, $\varepsilon$. 

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Figure 5.2. Plot for equation (5.5) for various $W_D$ and $\beta$ combinations. Both parameters control the shape of the profile. A relatively large $\beta$ causes the shape profile function to trend to Gaussian form.

Figure 5.3. Comparison of the size profile function (equation (5.5) - with $W_D = 0.10^\circ$ and $\beta = 2.0$) and traditional pseudo-Voigt and Pearson VII functions. The size profile function is similar in form to the Pearson VII function (see also York 1999; 2003).
The overall convolution profile function for both size and strain effects can then be expressed as

\[
F(\varepsilon, D, \beta) = S \cdot g \otimes e^{-\left(\frac{2\theta-2\theta_0}{W_\varepsilon}\right)^2} \otimes \frac{1}{1 + \left(\frac{2\pi}{\beta} \left(\frac{2\theta-2\theta_0}{W_\beta}\right)^2\right)^{\beta+1}}
\]  \tag{5.10}

where \(S\) is a scale factor which keeps the area under the profile constant.

5.3. The Algorithm for the Convolution Model

5.3.1. The Convolution

In MOZAIX, the instrument profile \(g\) was modelled by the pseudo-Voigt function (Thompson, Cox & Hastings 1987; Will et al. 1988), which is a linear mix of Lorentzian and Gaussian functions, with mixing parameter \(\phi = 1\) representing pure Lorentzian and \(\phi = 0\) representing pure Gaussian character. The convolution product of a point \(i\) for two functions \(f_1\) and \(f_2\) can be performed using the algorithm (Howard & Snyder 1989)

\[
f_1 \otimes f_2(i) = \sum_{j=-l}^{l} f_1(i+j) \cdot f_2(j)
\]  \tag{5.11}

where \(l\) is the number of points from the peak to the limits of the tails.

The overall MOZAIX PSF uses two convolutions of three functions which are associative (Kreyszig 1993), viz.

\[
F(\varepsilon; D) = g \otimes (f(\varepsilon) \otimes f(D)) = (g \otimes f(\varepsilon)) \otimes f(D)
\]  \tag{5.12}

5.3.2. Non-linear Least-squares Optimisation

The non-linear least-squares calculation for fitting the function to the data in MOZAIX was designed to minimise
\[ Residual = \sum_i w_i [I_i - F_i(\sigma, D, \beta)]^2 \]  
\hspace{1cm} (5.13)  

where \( I_i \) is the observed intensity and \( w_i \) is the observation weight which assigns the value \( (I_j)^{-1} \) on the basis of counting variance.

The non-linear least-squares refinement Fortran 95 code has been written for profile fitting, using equation (5.10), based on the standard algorithm given by Marquardt, which is also known as the Marquardt or Levenberg-Marquardt method (Marquardt 1963; Press et al. 1989). The Marquardt optimisation algorithm was also used to develop the \textit{SHADOW} program (Howard & Preston 1989) and shows advantages over the simplex (Nelder & Mead 1965) and traditional Gauss-Newton methods in terms of robustness, precision of values and dependence on initial estimates.

The Marquardt method requires the first derivative of the profile function with respect to each refinable parameter. The derivative of a convolution profile function \( F \) with respect to a parameter \( a_i \) is calculated according to

\[
\frac{\partial F}{\partial a_i} = \frac{\partial}{\partial a_i} \left[ f_1(a_1, a_2, \ldots, a_N) \otimes f_2(a_1, a_2, \ldots, a_N) \right]  
= \frac{\partial}{\partial a_i} \left[ f_1(a_1, a_2, \ldots, a_N) \right] \otimes f_2(a_1, a_2, \ldots, a_N)  
+ f_1(a_1, a_2, \ldots, a_N) \otimes \frac{\partial}{\partial a_i} \left[ f_2(a_1, a_2, \ldots, a_N) \right] \hspace{1cm} (5.14)  
\]

where the \( a \)'s are refinable parameters. The first derivatives of the \textit{MOZALX} function (Equation (5.10)) with respect to \( W_D, W_\sigma, \beta \) and \( 2 \theta_0 \) are presented in Appendix 2a.

The Fortran codes for the key subroutines are given in Appendix 2b. The code writing was mainly based on the non-linear least-squares calculation subroutines given by Press et al. (1989, 1992). The codes were compiled to obtain the executable \textit{MOZALX} file with Lahey-Fujitsu Fortran 95 version 5.5 program and Winteracter Starter Kit for graphical display under Windows (see Appendix 2c for code compilation). The codes and the executable program can be obtained from the author.
5.3.3. Criteria of Fit and Parameter Correlation

The goodness-of-fit (GoF) is used in the refinement:

\[
GoF = \left( \frac{\text{Residual}}{N - P} \right)^{\frac{1}{2}}
\]  \hspace{1cm} (5.15)

where \( N \) is the number of points in an interval and \( P \) is the number of parameters being refined. Difference plots between the observed and the calculated data are constructed for visual evaluation of model refinement quality.

The correlation coefficients between two refined parameters \( i \) and \( j \) (\( C_{ij} \)) is calculated from their covariance (Cov) using

\[
C_{ij} = \frac{\text{Cov}(i,j)}{\sqrt{\text{Cov}(i,i) \cdot \text{Cov}(i,j)}} \hspace{1cm} (5.16)
\]

5.3.4. Standard Deviations Calculation

The estimated standard deviation for a refined parameter is calculated using the covariance matrix component \( \text{Cov}(i,i) \) associated with the parameter \( i \).

The estimated standard deviations for the crystallite size and microstrain parameters (\( \sigma(D) \) and \( \sigma(\varepsilon) \), respectively) were calculated from the relative error of the associated peak width according to equations (5.6) and (5.9) as follows:

\[
\sigma(D) = \frac{\sigma(W_D)}{W_D} D \hspace{1cm} (5.17)
\]

\[
\sigma(\varepsilon) = \frac{\sigma(\beta \varepsilon)}{\beta \varepsilon} \hspace{1cm} (5.18)
\]

The error for the peak position is very small as compared to those for the widths so that it is neglected in the calculation.
5.4. Peak-profile Refinement using Convolution Model with MOZAIX

5.4.1. Refinement Procedure

The standard procedure for refinement using MOZAIX is as follows:

- Open a data file which is saved in *.dat form (an example of the data file is given in Appendix 2d). A typical display for MOZAIX is shown in Figure 5.4.

- Select a peak for analysis and the appropriate number of points in order to accommodate correctly the profile tails and background.

- Select the type of instrument.

- Select a profile-shape function for a refinement.

- Perform the refinement.

- Inspect output from the refinement.

It should be noted that the success of a refinement and the final refinement results depend on the initial values, particularly for small specimen broadening. In order to deal with these problems, MOZAIX allows the alteration of the initial values and observation of the measured and calculated patterns.

A more detailed explanation of the refinement procedure, including the display for each step, is given in Appendix 2d.

5.4.2. Refinements with Simulated Data

MOZAIX was used to generate simulated diffraction data, calculated with equation (5.10), for various crystallite size and strain values. The associated FWHM values, \( W_D \) and \( W_e \) respectively, range from 0.02 to 0.10 °2\( \theta \) for both parameters. The instrument profile used was 0.015 °2\( \theta \), which represented the FWHM of the SRD (\( \lambda \approx 1.54 \text{ Å} \)) at 2\( \theta \approx 40° \).
Figure 5.4. A typical *MOZAIX* display after the opening of a data file. Pull-down menus are used to assist the refinement procedure. Details of the procedure are given in Appendix 2c.
Refinements for the simulated patterns were performed to test the validity of the least-square optimisations. Figure 5.5 plots the refinement output from the simulated data for various $W_D$ and $W_\alpha$ respectively (while the other parameters were kept constant). It was found that the deviations of the calculation results from the expected values were less than 0.5%.

5.4.3. Application to Measured Data

Non-linear least-squares refinements with MOZAIX were carried out for model optimisation with SRD data acquired for three MgO ceramics showing markedly different broadening characteristics. The conditions for the SRD data collection are described in Chapter 3. The results of the refinements with MOZAIX are reported in this sub-section and compared with those for Voigt, pseudo-Voigt and Pearson VII models. Peak profiling with the pseudo-Voigt, Pearson VII and Voigt functions was performed with SHADOW version 4.2 (Materials Data Inc. 1999). The size and strain values obtained by the Voigt model are also examined.

The NIST SRM 660a (Freiman & Trahey 2000) was used as the instrument standard material for evaluation of the convolution model, as it shows less broadening compared to the sintered MgO standard reported previously (see Chapter 4). The NIST SRM 660a LaB$_6$ became commercially available to replace the NIST SRM 660 LaB$_6$ which has similar broadening character to the 99% MgO 1450°C – 2 h standard developed for this study (see §4.3). The test materials used for model evaluation were MgO 99%, 99.9% and 99.99% ceramics sintered at 1100°C for 2 hours. The 99% MgO powder had been calcined at 1000°C for 60 minutes to remove the hydroxide present in the raw powder, which may have resulted in reduction in specimen broadening prior to sintering. The raw powders for the 99.9% and 99.99% specimens did not contain the hydroxide phase and were, therefore, immediately made into ceramic compacts prior to sintering. It was found that there was no evidence of the degradation of sintered MgO ceramics to the hydroxide on exposure to the atmosphere.
Figure 5.5. Data simulation test using equation (5.10) by (a) varying $W_D$ with $W_e$ and $\beta$ being constant and (b) varying $W_e$ with $W_D$ and $\beta$ being constant. Gaussian instrument profile with FWHM = 0.02° was used in the simulation. Lines indicate the designated simulated values which should be confirmed using the test.
Line broadening character

The FWHM versus 2θ plots for the MgO ceramics are shown in Figure 5.6. The specimen broadening is approximately 2 - 5 times that for the LaB₆ SRM patterns. It is found that the FWHM for the 99% specimen is lower than that for the others, presumably due to the calcination at 1100°C. Such heating can cause strain relief and hence reduce peak broadening (see Chapter 4). The FWHM of the 99.9% specimen is larger than that for the 99.99% specimen. This result suggests that the purity level does not correspond directly to the size and strain character in the materials. It is argued that the differences in the broadening behaviour, which does not appear to depend upon purity level in an obvious way, are due to different processes for producing the raw materials.

Figure 5.7 shows the line profile at $2\theta \approx 127.15^\circ$ for the three MgO specimens (line 422) and for NIST SRM 660a LaB₆. The plot for LaB₆ was made with a pseudo-Voigt function with the FWHM and $\phi$ values at the designated peak position determined by an interpolation.

Table 5.1 compares the peak profile results for the specimens using pseudo-Voigt, Voigt, Pearson VII and the convolution functions. The profile for the 99% specimen, as shown in Figure 5.7, has a tail which drops quickly with $2\theta$. The peak profile showed that this peak has pseudo-Voigt FWHM = 0.1367(9) (°2θ) and $\phi = 0.61(1)$. The 99.9% specimen has a broad peak and relatively long tail with FWHM = 0.2640(8) and $\phi = 0.63(1)$. The 99.99% specimen has a relatively broad peak and long tail with pseudo-Voigt FWHM = 0.2142(20) and $\phi = 1.00(2)$, which signifies a pure Lorentzian profile. Further inspection shows that the 99.99% peak has FWHM = 0.2360(12) and $\phi = 1.18(1)$, which is known as a 'super-Lorentzian' profile (see, for example, Young & Sakhtivel 1988; Langford 1999; Popa & Balzar 2002). Louër (1999) argued that 'super-Lorentzian' character is often observed in materials with small crystallite size and, in such a case, it is inappropriate to use the Voigt function for the size-strain evaluation (Langford 1999). As can be seen from Table 5.1, the Voigt Gaussian breadth for the 99.99% specimen is 0.011(4) (°2θ), which is much less than that for the standard material (0.058(1)). It was further found that the Pearson VII index (or the exponential $m$) for this material is 0.985(6) which also
indicates that the line profile is 'super-Lorentzian' (Langford 1999). Further investigation of the 'super-Lorentzian' profiles using the convolution and pseudo-Voigt functions is described in Appendix 2e, which shows that 'super-Lorentzian' character can be observed in materials with small crystallite size and small microstrain. It is therefore argued that the 99.99% specimen has a small crystallite size and small microstrain.

Figure 5.8 shows the line profiles for the 99.9% specimen. It is clear that the convolution function (Fig. 5.8c) gives an improved fit to the data as compared to the Pearson VII and pseudo-Voigt functions (Fig. 5.8a and 5.8b); as also indicated by the GoF values in Table 5.1. It is worth noting that the estimated standard deviations for the results using the convolution method are generally lower than those when the mathematical functions were used indicating the more precise convolution results.

Size and strain assessments

Table 5.1 also presents results from line profile analysis performed with the analytical Voigt, pseudo-Voigt and Pearson VII functions and the convolution function for the ceramic materials. Crystallite size and maximum strain values obtained by applying the Voigt function were calculated using the method given by de Keijser et al. (1982) and those for the convolution function were calculated using Equations (5.6) and (5.9a), respectively.

The estimated microstrain for the 99.9% specimen is larger than that for the other specimens. This is most likely due to the different processes employed to prepare the raw powders. For the 99% specimen, it is possible that the calcination to remove the hydroxide in the raw powder has caused some microstrain relief. Also, it is plausible that the refining process employed to produce the 99.99% powder resulted in a fine powder with small strain. The 99.9% raw powder might have been produced by a process where milling was used, which resulted in a powder with relatively enhanced microstrain.
Figure 5.6. FWHM versus 2θ for the MgO ceramics SRD data compared with data for the LaB₆ powder (NIST SRM 660a).

Figure 5.7. SRD broadening characteristics of the MgO ceramics (line 422), with three purity levels, sintered at 1100°C for 2h. NIST LaB₆ Standard Reference Material 660a was used as the standard. Line profile analysis showed that the 99.99% ceramic exhibits 'super-Lorentzian' behaviour.
Table 5.1. SRD data peak profile refinement results for MgO ceramics sintered at 1100°C for 2h (line 422) using various profile functions. Microstructural values were calculated for the Voigt and the convolution functions only. NIST SRM 660a LaB₆ was used as the standard material representing the instrument broadening. Numbers in parentheses indicate 1× estimated standard deviation for the figures to the left.

<table>
<thead>
<tr>
<th>Profile function¹</th>
<th>MgO ceramics suite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>99%</td>
</tr>
<tr>
<td>1. Convolution²</td>
<td></td>
</tr>
<tr>
<td>Strain width, $W_e$</td>
<td>0.0096(13)</td>
</tr>
<tr>
<td>Size width, $W_S$</td>
<td>0.1194(1)</td>
</tr>
<tr>
<td>Size distribution</td>
<td>1.41(1)</td>
</tr>
<tr>
<td>parameter, $\beta$</td>
<td>Microstrain ($\times1000$)</td>
</tr>
<tr>
<td></td>
<td>Modal Size (nm)</td>
</tr>
<tr>
<td></td>
<td>GoF</td>
</tr>
<tr>
<td>2. Voigt³</td>
<td></td>
</tr>
<tr>
<td>Gaussian breadth, $\beta_G$</td>
<td>0.084(1)</td>
</tr>
<tr>
<td>Lorentzian breadth, $\beta_L$</td>
<td>0.144(1)</td>
</tr>
<tr>
<td>Microstrain ($\times1000$)</td>
<td>0.1330(30)</td>
</tr>
<tr>
<td>Crystallite Size (nm)</td>
<td>207(4)</td>
</tr>
<tr>
<td>GoF</td>
<td>1.93</td>
</tr>
<tr>
<td>3. Pseudo-Voigt</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>0.1367(9)</td>
</tr>
<tr>
<td>Mixing Parameter, $\phi$</td>
<td>0.61(1)</td>
</tr>
<tr>
<td>GoF</td>
<td>2.25</td>
</tr>
<tr>
<td>4. Pearson VII</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>0.1297(4)</td>
</tr>
<tr>
<td>Index, $m$</td>
<td>1.345(5)</td>
</tr>
<tr>
<td>GoF</td>
<td>1.12</td>
</tr>
</tbody>
</table>

¹ The mathematical functions are as described in Young and Wiles (1982). See also Chapter 2.

² Equation (5.10) was used.

³ Microstrain and size were calculated using the procedures given by Keijser et al. (1982). NP = not possible, Voigt function is not applicable to ‘super-Lorentzian’ profiles (Langford 1999). LaB₆ SRM 660a has $\beta_L = 0.048(1)$ and $\beta_G = 0.058(1)$.
(a) Profile fitting using the Pearson VII function

Figure 5.8. Profile fitting of 99.9% MgO ceramic pattern (line 422) using (a) Pearson VII, (b) pseudo-Voigt and (c) the convolution functions. Note that the instrument profile \( g \) has been included in the convolution function (Equation 5.1). Values for the refined parameters and microstructural information obtained by the convolution method are presented in Table 5.1.
(a) Profile fitting using the pseudo-Voigt function

(b) Profile fitting using the convolution function

Figure 5.8. (cont'd)
The crystallite size values calculated with the convolution model decrease with purity level. The larger size for the 99% specimen is due to the crystallite growth which may occur during calcination of the raw powder. However, there is no clear indication of the cause of the trend for the other specimens.

Table 5.2 gives correlation coefficients for selected parameters for a refinement with SRD data for MgO ceramics using the convolution model. It is obvious that the specimen FWHM parameters, \( W_e \) and \( W_D \), show very strong correlation as both contribute to the width of a peak. The size distribution parameter \( \beta \) and the size FWHM, \( W_D \), also are strongly correlated as both influence both the width and tails of a profile. The correlation between \( \beta \) and \( W_e \) can be reasonably strong if the profile is broad and has long tails such as in the 99.9% specimen sintered at 1100°C for 2 hours.

The convolution sizes for the 99% specimens are slightly smaller than those for the Voigt model, whereas the convolution sizes for the 99.9% specimens are slightly larger. The slight differences in the size results indicate that the Lorentzian component in the Voigt model may be used to estimate the crystallite size, within approximately 10% deviation, if the Voigt function fits appropriately to the data. The differences are simultaneously caused by the effect of the size distribution parameter both on the width and the tail of a line profile. The size distribution parameter and the strain simultaneously influence the Gaussian component of the convolution model, leading to a significant refinement correlation between \( W_e \) and \( \beta \), which reaches approximately 74% in the 99.9% specimen. The size distribution parameter also affects the tails of the profiles (see Figure 5.2 and the corresponding discussion).

The strong correlation between the size distribution parameter and Gaussian width results in markedly different strain values from the Voigt and convolution models. Moreover, the Voigt model cannot be used to determine the size and strain values for the ‘super-Lorentzian’ 99.99% specimen. It is argued, therefore, that the convolution model gives generally more reliable results than the Voigt model.
Table 5.2. Correlation matrix for selected parameters from refinement using the convolution model with SRD data for 99% and 99.9% MgO ceramics sintered at 1100°C for 2 hours. Matrix elements are presented as % values.

A. 99% MgO ceramic

<table>
<thead>
<tr>
<th>Parameters</th>
<th>FWHM Strain, $W_e$</th>
<th>FWHM Size, $W_D$</th>
<th>Size Distribution, $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM Strain</td>
<td>100.0</td>
<td>-50.7</td>
<td>37.1</td>
</tr>
<tr>
<td>FWHM Size</td>
<td></td>
<td>100.0</td>
<td>85.5</td>
</tr>
<tr>
<td>Size Distribution</td>
<td></td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

B. 99.9% MgO ceramic

<table>
<thead>
<tr>
<th>Parameters</th>
<th>FWHM Strain, $W_e$</th>
<th>FWHM Size, $W_D$</th>
<th>Size Distribution, $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM Strain</td>
<td>100.0</td>
<td>-93.1</td>
<td>74.1</td>
</tr>
<tr>
<td>FWHM Size</td>
<td></td>
<td>100.0</td>
<td>88.7</td>
</tr>
<tr>
<td>Size Distribution</td>
<td></td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

Size distribution

It has been demonstrated that the convolution model can be applied to peak profiles with typical Voigt shape as shown by the 99% and 99.9% specimens as well as ‘super-Lorentzian’ shape for the 99.99% specimen. The convolution model gives crystallite size and size distribution parameter values of 166(1) nm and 1.41(1), 75(1) nm and 1.27(2), and 67(0) nm and 0.86(1) for the 99%, 99.9% and 99.99% specimens, respectively (see Table 5.1). The plots of the normalised distributions of the crystallite size for these materials are shown in Figure 5.9. The ‘super-Lorentzian’ 99.99% specimen shows a relatively broad size distribution. The form of the dispersion of the 99.99% specimen size is in agreement with the observation by Langford et al. (2000) that a crystallite size distribution lengthens the tail of a line profile, which may result in a ‘super-Lorentzian’ shape. Moreover, this result also agrees with that from Popa and Balzar (2002) who showed that such profiles can be due to a broad lognormal size distribution for which the Voigt function is not applicable.
The 99% and 99.9% specimens have less dispersed size distributions than the 99.99% specimen. This observation suggests that the broadening of the distribution increases with purity level. The source of this trend, however, is not clear.

Comparison of the convolution and SEM-derived sizes

Figure 5.10 shows SEM micrographs for fractured specimens of MgO 99.9% and 99.99% ceramics sintered at 1250°C for 2 hours, while Figure 5.11 and Table 5.3 show the associated SEM-derived grain size distribution and the corresponding convolution crystallite size and size distribution parameter values. As can be seen from the figures, the distribution for the 99.9% specimen exhibits less asymmetry than that for the 99.99% specimen. This observation is supported by the results for the size distribution parameters ($\beta$) for the 99.9% and 99.99% specimens which are 1.2 and 0.9, respectively. Also, it is evident that the shapes of the SEM-derived distributions are similar to the corresponding convolution model distributions. This result demonstrates that the convolution size distribution agrees reasonably well with the SEM-derived size distribution.

The SEM-derived modal grain sizes are larger than those obtained from the convolution model. The respective SEM-derived modal grain sizes are 190 nm for the 99.9% specimen and 220 nm for the 99.99% specimen, which are approximately twice those for the associated convolution sizes, i.e. 95 nm and 109 nm, respectively (line 422). It can be argued that, in general, the SEM-derived grain size does not represent the diffraction crystallite size. Rather, as also reported by others (Guillou, Auffrédic & Louër 1995; Audebrand et al. 2000b), the ‘grains’ observed by SEM may be composed of clusters of crystallites.

Figure 5.12 displays the SEM micrograph of the fractured 99.99% MgO ceramic sintered at 1600°C for 6 hours which, according to the convolution model, has an average size of 250 nm. The SEM-derived grain sizes of the ceramic ranges between 1 µm and 2 µm. The presence of clusters of smaller ‘particles’ in each grain with sizes between 200 nm and 300 nm is evident. The results confirm that SEM-derived grain size is not the same as the diffraction crystallite size since the grains comprise ensembles of crystallites.
Figure 5.9. Normalised distributions of crystallite size for the 99%, 99.9% and 99.99% MgO ceramics sintered at 1100°C for 2 hours. The plots were made using Equation (5.3) with β values for the corresponding specimens given in Table 5.1.
Figure 5.10. Fractured-surface SEM micrographs for the (a) 99.9% and (b) 99.99% MgO ceramics. Both were sintered at 1250°C for 2 hours. Note the different scale bars.
Figure 5.11. SEM grain distribution and the SRD convolution crystallite size distribution for 99.9% (diamonds and dotted line) and 99.99% (circles and solid line) specimens sintered at 1250°C for 2 hours.

Table 5.3. SRD convolution and SEM-derived sizes for the 99.9% and 99.99% MgO ceramics sintered at 1250°C for 2 hours.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Convolution Model</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Modal size (nm)</td>
<td>Modal size (nm)</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td></td>
</tr>
<tr>
<td>99.9% 1250°C − 2 h</td>
<td>95</td>
<td>190</td>
</tr>
<tr>
<td>99.99% 1250°C − 2 h</td>
<td>109</td>
<td>220</td>
</tr>
</tbody>
</table>
The SEM and diffraction results show that there is both grain and crystallite growth during sintering. With grains being composed of clusters of crystallites, the crystallites grow within the grains. It appears, however, that the rates of growth are different as, in general, different SEM-derived grain size to convolution crystallite size ratios are observed for the specimens. For approximate example, the ratio for the 99.99% specimen sintered at 1250°C for 2 hours is about 2 while that for the associated 1600°C - 6 h specimen is approximately 10. Therefore, the growth rate for the grains appears to be more rapid than that for the crystallites.

The convolution size distribution cannot be confirmed using SEM-derived grain size as a grain may contain crystallites with different sizes. However, the SEM-derived grain distribution, on average, agrees satisfactorily with the crystallite distribution (see Figure 5.11). As can be seen from the figure, the 99.9% specimen has narrower size dispersion (with the convolution \( \beta = 1.2 \)) than the 99.99% specimen \( (\beta = 0.9) \).

![Figure 5.12. Fractured-surface SEM micrograph for the 99.99% MgO ceramic sintered at 1600°C for 6 hours, showing clusters of crystallites. The inset shows a magnified view of a grain with clusters of crystallites.](image-url)
5.5. Conclusion

1. The convolution model for size-strain line profile analysis developed in this study has been tested using simulated data which shows excellent agreement with the simulated size and strain values. The key refinable parameters, viz. crystallite size, size distribution and non-linear microstrain are extracted from the non-linear least-squares calculations.

2. The results showed that the purity level does not influence the broadening character of the specimens in a simple manner. The different broadening characteristics may be associated with the preparation of the raw powders. It was found that the crystallite size and size distribution parameter change systematically with purity, but the source of the trends needs further investigation.

3. Tests using SRD data for three suites of MgO ceramics show that the convolution model performs appropriately for line profile analysis. Comparison of size-strain evaluations using the convolution and Voigt models shows that the convolution model gives more appropriate results, as compared to the Voigt function which is in particular not applicable to the 'super-Lorentzian' profile and does not take into account the size distribution parameter. Further study using SEM confirms the size distribution results. The convolution sizes, however, are smaller than the SEM-derived grain sizes; with there being clear evidence that grains consist of clusters of diffracting domains.
CHAPTER 6. APPLICATION OF THE CONVOLUTION MODEL FOR STRAIN-SIZE ASSESSMENTS USING MgO CERAMICS

6.1. Introduction

Sintered ceramics are important materials for structural, electronic, optical and biological applications (Richerson 1992). Their properties are dependent upon their microstructure notably the representative grain size, the size distribution and the residual strain. It is therefore valuable to characterise the materials with respect to these descriptors in order to better understand the microstructure-property relationships. Diffraction analysis of size and strain is of critical importance in that peak broadening conveys size and strain information.

Sintering of ceramics is a heating process which consolidates compacted raw ceramic powders through inter-grain diffusion of participating particles to enhance grain growth which results in the porosity reduction, shrinkage and densification of the ceramic bodies. As described in Chapter 4, sintering can also favour the development of crystallite size and either relieve or introduce strains. Therefore, sintering may cause microstructural changes which then may result in changes in material properties. Accordingly, size-strain assessment will improve comprehension of the material design prior to its application. Strain and size evaluation of systematically sintered ceramics using an appropriate model is, therefore, of importance to obtain correct microstructural information from such materials.

This chapter reports the application of the convolution model (see Chapter 5 for description of the model) for assessing the size and strain parameters in sintered MgO ceramics using SRD and XRD data. Results for ND data are not presented since they show small specimen broadening relative to the instrument broadening, which tends to result in unstable least-squares calculations. The three sets of MgO ceramics with different purity levels, and sintered at various temperatures, were considered. The NIST SRM 660a LaB₆ standard was used for the SRD and XRD instrument broadening corrections since it shows significantly narrower broadening relative to the sintered MgO standard (see Chapter 4). For this final part of the study, NIST SRM 660a LaB₆ was preferred to NIST SRM 660 LaB₆ which shows similar
broadening character to the 99% MgO 1450°C – 2 h standard produced for this study (see §4.3). Comparison of the convolution size and strain values were made with those for the Voigt single-line integral breadth analysis with the rationale being (1) the latter showed results for lines 420 and 422 were in reasonable agreement (see §4.4), and (2) both methods use the convolution of size and strain effects in the analyses. In keeping with the approach adopted in the Voigt single-line integral breadth analyses, only the 420 and 422 lines were considered in the convolution model analyses. The size values are then compared with electron microscopy values. Finally, the strengths and limitations of the convolution model are discussed.

6.2. Strain and Size Assessments with SRD Data

6.2.1. Line Broadening Analysis

The Lorentzian and Gaussian component values from profile refinements using the Voigt function for the 422 line of the 99%, 99.9% and 99.99% ceramics, made with SRD data, are given in Table 4.4, and the trend for each component with sintering temperature is shown in Figure 6.1. In general, these values decrease with temperature indicating that size and strain character in the materials changes systematically with temperature. For the 99% ceramics, the Lorentzian component, which represents the size component in the Voigt model, decreases with sintering temperature, reaching a minimum for the specimen sintered at 1450°C – 2 h and then increases for the 1600°C – 6 h specimen. For the same ceramics, the Gaussian component, which represents the strain component in the Voigt model, decreases with sintering temperature, reaching a minimum at 1250°C - 2 h and then, however, increases for the specimens sintered at higher temperatures. These results indicate that minimum size broadening does not always occur in accordance with minimum strain broadening. Further investigation would be required to obtain the optimum conditions for minimum size and strain broadening.
Figure 6.1. Effects of sintering on the Gaussian and Lorentzian components for the 422 reflection of the 99%, 99.9% and 99.99% MgO specimens using SRD data from integral breadth analysis with the Voigt function. The legend for the horizontal axis denotes the sintering temperature and time (e.g. 1100°C for 2 hours). $\beta_{SG}$ and $\beta_{SL}$ indicate the instrument Gaussian and Lorentzian components, respectively. Error bars represent 1 × the standard uncertainty. Error bars for some points are invisible since the uncertainties are negligible compared to the graph scales.
Both the Lorentzian and Gaussian components for the 99.9% ceramics decrease with temperature, indicating systematic changes of size and strain up to 1450°C for 2 hours. The 1600°C – 6 h specimen was excluded from the analysis as it exhibited a non-flat (curved) surface after sintering. It is clear from Table 4.4 that the Lorentzian and Gaussian components for the 99.9% ceramics are significantly higher than those for the 99% ceramics suggesting that the 99.9% ceramics have smaller size and larger strain than the 99% ceramics. Further discussion on size and strain results is provided in §6.2.2.

Figure 6.1 shows that the Gaussian components for the 99.99% specimens are smaller than those for the instrument (indicated by a straight line labelled as $\beta_{g,L}$). The Lorentzian components for the same specimens are larger than those for the instrument (indicated by a straight line labelled as $\beta_{g,L}$) but with larger uncertainties compared to those for other data points. This broadening character is typical for ‘super-Lorentzian’ peak shapes. In cases where ‘super-Lorentzian’ character is found, the Voigt size and strain analysis procedure cannot be used (Langford 1999). As shown in Chapter 5, the convolution model developed in this study can be applied to profiles with such character and provide reasonable results.

### 6.2.2. Strain and Size Assessment Results

Table 6.1 shows that acceptable refinements using the convolution and Voigt functions were achieved for the SRD data for the 99%, 99.9% and 99.99% specimens as indicated by the ‘goodness-of-fit’ (GoF) values which are less than 4%, with only two exceptions. These are line 420 of the 99% specimen sintered at 1600°C for 6 hours, which can be associated with small specimen broadening; and lines 420 and 422 for the 99.9% specimen sintered at 1450°C for 2 hours, which can be associated with peak asymmetry. Therefore, size and strain analysis can readily be performed for these specimens. Note that in the analysis described in the following sub-sections, the SRD instrument broadening corrections were made using NIST SRM 660a LaB$_6$.

The convolution strain, modal size and size distribution and the Voigt single-line strain and size values for the 99%, 99.9% and 99.99% MgO specimens obtained with the SRD data for the 420 and 422 lines are given in Table 6.1. In general, comparable convolution results were obtained for the strain, modal size and size
distribution values between the two lines. Relatively large differences were found in the 420 and 422 strain values for specimens with small specimen broadening (e.g. 99% 1450°C – 2 h ceramic, the 420/422 ratio being 1.3) or for specimens with dominant size effects (e.g. 99.99% ceramics). Differences in size values for the two lines were obtained for specimens with small specimen broadening (99% 1450°C – 2 h and 1600°C – 6 h ceramics; 420/422 ratios of 0.7 and 0.6). Significant strain differences also were found for the Voigt single-line results, for example, a 420/422 ratio of 1.3 was obtained for the 99.9% 1450°C – 2 h specimen and of 1.2 for the 99% 1100°C – 2 h and 1450°C – 2 h and the 99.9% 1100°C – 2 h and 1250°C – 2 h specimens. The 99% specimens also show different Voigt single-line size for the 420 and 422 lines, demonstrated by the 420/422 size ratio being approximately 0.7. It appears that, generally, small specimen broadening (presumably less than 1.2 x that of the instrument – see Table 4.1) may give inconsistent results. Inconsistent size and strain results become more obvious if the Voigt single-line model is used, presumably due to the omission of size distribution effects.

It is evident from the results in Table 6.1 that the uncertainties for the values obtained with the convolution model are smaller than those obtained with the Voigt model. For the SRD results, the convolution model results are more precise than those for the Voigt single-line model. Also, in general, the relative uncertainty for each value is less than 3%. Larger absolute uncertainties are obtained for (1) materials with a specimen-to-instrument broadening ratio less than 1.2, for example, the 99% 1450°C – 2 h ceramic (see Table 4.1), or (2) materials exhibit significant strain contribution, as the uncertainty is proportional to the strain value, for example, for the 99.9% 1100°C – 2 h and 1250°C – 2 h ceramics.

The convolution sizes for the ‘super-Lorentzian’ 99.99% 1100°C – 2 h, 1250°C – 2 h and 1450°C – 2 h specimens from lines 420 and 422 are in reasonable agreement (Table 6.1). As shown in Appendix 2e, ‘super-Lorentzian’ character is due to the domination of the Lorentzian component compared with the Gaussian component when the size distribution parameter value is less than unity. It appears, however, that the domination of the size effect in the profile causes a large reduction of the uncertainties for the size values. By contrast, the small strain effect cannot be determined with reasonable precision as indicated by the disagreement between the
strain values from the 420 and 422 lines. As can be seen from Table 6.1, in general, the size distribution parameter values from both lines are in a reasonable agreement. Observing the Voigt results, it is obvious that only size values can be calculated, with the values from the 420 and 422 being remarkably different and having large uncertainties. These results indicate that the convolution model can be used to extract size information, with acceptable uncertainties, and strain, with fair precision, from profiles with ‘super-Lorentzian’ character.

The average values for the strain and size parameters from lines 420 and 422 are plotted with reference to sintering conditions in Figures 6.2 – 6.4 for the strain, size and size distribution, respectively. The error bars in the figures, were computed according to the expression for error (σ) for parameter a,

\[
\sigma(a) = \sqrt{\frac{\sum_{i=1}^{n} (a_i - \bar{a})^2}{2}}
\]  

(6.1)

where \(\bar{a}\) is the average value of parameter \(a\) for lines 420 and 422.

The average strain values for the 99%, 99.9% and 99.99% MgO specimens obtained with the SRD data are plotted against sintering temperature in Figures 6.2a–c, respectively. Figures 6.3a–c give the associated average size values. The average size distribution parameter values, estimated using the convolution method, are given in Figures 6.4.

The average strain value for the 99% specimens from both methods decreases with temperature up to 1250°C – 2 h, whereas the associated size value increases (Figure 6.2a). The 99% 1450°C – 2 h specimen exhibits larger size (Figure 6.3a) and larger strain than the 99% 1250°C – 2 h specimen. It appears that intragranular shear interactions associated with growth of large crystallites, notably with convolution size larger than 500 nm, during sintering at temperatures higher than 1450°C for 2 hours, increase the strain. It is interesting to note that the apparent density for the 1450°C – 2 h specimen is 97% (Table 3.1). At this density level, it appears that further sintering does not favour a significant porosity reduction and results in grain-grain interactions which introduce additional strain. This observation shows that sintering favours crystallite growth, relieves strain in relatively low density ceramics and introduces additional strain in dense ceramics.
Table 6.1. Strain, modal size and size distribution parameter values for the 420 and 422 reflections of the 99%, 99.9% and 99.99% MgO specimens, using SRD data from size and strain analysis using the convolution model. Strain and size analysis results obtained using the integral breadth Voigt method are also presented for comparison. Estimated uncertainties for the least significant digits are given in parentheses. NIST SRM 660a LaB₆ was used as the standard material for instrument corrections.

<table>
<thead>
<tr>
<th>Specimen¹</th>
<th>Line</th>
<th>Strain (× 1000)</th>
<th>Size (nm)</th>
<th>Size distribution</th>
<th>GoF² (%)</th>
<th>Strain (× 1000)</th>
<th>Size (nm)</th>
<th>GoF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99% 1100°C – 2 h</td>
<td>420</td>
<td>0.0203(1)</td>
<td>156(1)</td>
<td>1.41(1)</td>
<td>2.7</td>
<td>0.163(7)</td>
<td>184(4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0200(1)</td>
<td>166(1)</td>
<td>1.43(1)</td>
<td>1.5</td>
<td>0.133(5)</td>
<td>207(4)</td>
<td>1.9</td>
</tr>
<tr>
<td>99% 1250°C – 2 h</td>
<td>420</td>
<td>0.0161(4)</td>
<td>472(4)</td>
<td>1.66(2)</td>
<td>3.2</td>
<td>0.073(8)</td>
<td>589(42)</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0154(2)</td>
<td>662(9)</td>
<td>1.39(2)</td>
<td>3.1</td>
<td>0.076(8)</td>
<td>788(44)</td>
<td>2.6</td>
</tr>
<tr>
<td>99% 1450°C – 2 h</td>
<td>420</td>
<td>0.0238(4)</td>
<td>508(10)</td>
<td>3.51(10)</td>
<td>2.9</td>
<td>0.100(5)</td>
<td>1504(273)</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0184(2)</td>
<td>876(26)</td>
<td>2.36(8)</td>
<td>2.7</td>
<td>0.086(3)</td>
<td>2210(346)</td>
<td>2.1</td>
</tr>
<tr>
<td>99% 1600°C – 6 h</td>
<td>420</td>
<td>0.0146(1)</td>
<td>401(5)</td>
<td>1.86(3)</td>
<td>5.6</td>
<td>0.101(9)</td>
<td>520(35)</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0123(7)</td>
<td>402(4)</td>
<td>1.74(3)</td>
<td>3.6</td>
<td>0.110(4)</td>
<td>560(23)</td>
<td>2.9</td>
</tr>
<tr>
<td>99.9% 1100°C – 2 h</td>
<td>420</td>
<td>0.2989(12)</td>
<td>70(1)</td>
<td>1.49(2)</td>
<td>1.5</td>
<td>0.470(6)</td>
<td>71(1)</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.3089(17)</td>
<td>75(1)</td>
<td>1.27(2)</td>
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<td>0.394(4)</td>
<td>73(0)</td>
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<tr>
<td>99.9% 1250°C – 2 h</td>
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<td>0.2944(15)</td>
<td>85(1)</td>
<td>1.29(2)</td>
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<td>0.384(5)</td>
<td>83(1)</td>
<td>1.7</td>
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<tr>
<td></td>
<td>422</td>
<td>0.2960(22)</td>
<td>92(1)</td>
<td>1.15(2)</td>
<td>1.3</td>
<td>0.336(4)</td>
<td>86(1)</td>
<td>1.2</td>
</tr>
<tr>
<td>99.9% 1450°C – 2 h⁵</td>
<td>420</td>
<td>0.1256(5)</td>
<td>120(1)</td>
<td>1.10(1)</td>
<td>5.5</td>
<td>0.224(13)</td>
<td>121(3)</td>
<td>5.4</td>
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<tr>
<td></td>
<td>422</td>
<td>0.1296(4)</td>
<td>116(1)</td>
<td>1.11(1)</td>
<td>11.6</td>
<td>0.175(10)</td>
<td>135(3)</td>
<td>3.6</td>
</tr>
<tr>
<td>99.9% 1600°C – 6 h⁶</td>
<td>420</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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</table>

(Cont'd)
Table 6.1. (cont’d)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Line</th>
<th>Strain (x 1000)</th>
<th>Size (nm)</th>
<th>Size distribution</th>
<th>GoF (%)</th>
<th>Strain (x 1000)</th>
<th>Size (nm)</th>
<th>GoF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.99% 1100°C - 2 h</td>
<td>420</td>
<td>0.0265(2)</td>
<td>62(0)</td>
<td>0.99(1)</td>
<td>2.1</td>
<td>-</td>
<td>295(81)</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0220(0)</td>
<td>67(0)</td>
<td>0.86(1)</td>
<td>1.9</td>
<td>-</td>
<td>357(120)</td>
<td>1.5</td>
</tr>
<tr>
<td>99.99% 1250°C - 2 h</td>
<td>420</td>
<td>0.0289(1)</td>
<td>91(0)</td>
<td>0.87(1)</td>
<td>2.8</td>
<td>-</td>
<td>494(226)</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0128(14)</td>
<td>95(0)</td>
<td>0.93(1)</td>
<td>2.0</td>
<td>-</td>
<td>633(325)</td>
<td>1.9</td>
</tr>
<tr>
<td>99.99% 1450°C - 2 h</td>
<td>420</td>
<td>0.0305(0)</td>
<td>102(0)</td>
<td>0.95(1)</td>
<td>3.5</td>
<td>-</td>
<td>320(89)</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0187(1)</td>
<td>107(0)</td>
<td>0.93(1)</td>
<td>3.2</td>
<td>-</td>
<td>901(656)</td>
<td>3.2</td>
</tr>
<tr>
<td>99.99% 1600°C - 6 h</td>
<td>420</td>
<td>0.0162(4)</td>
<td>225(1)</td>
<td>1.16(1)</td>
<td>2.7</td>
<td>-</td>
<td>264(9)</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0156(1)</td>
<td>268(1)</td>
<td>0.99(1)</td>
<td>2.4</td>
<td>-</td>
<td>335(9)</td>
<td>4.8</td>
</tr>
</tbody>
</table>

1 MgO sintered ceramics. Purity level and sintering conditions are used as identifier of the specimens.
2 Strain is calculated using Equation (5.9a), size using Equation (5.6) and size distribution is β in Equation (5.3).
3 GoF = ‘Goodness-of-Fit’ is determined using Equation (5.14).
4 Strain and size are calculated using Equation (2.71) and (2.72), respectively. Despite the single-line Voigt method results, the 99.99% specimens exhibited ‘super-Lorentzian’ character.
5 Peaks for 99.9% MgO exhibit strong asymmetry. Peak position cannot be refined in conjunction with other parameters.
6 The 99.99% specimen exhibited curved surface and therefore was excluded from the analysis.
(a) SRD convolution and Voigt single-line strains for the 99% MgO specimens.

Figure 6.2. Convolution and Voigt single-line strain values versus sintering temperature obtained from SRD data for (a) 99%, (b) 99.9% and (c) 99.99% MgO ceramics. The strain values were obtained by averaging those from lines 420 and 422 in Table 6.1. Error bars indicate 1x standard deviation as calculated using Equation (6.1).
(b) SRD convolution and Voigt single-line strains for the 99.9% MgO specimens. Data for 99.9% 1600°C – 6 h specimen are excluded from the analysis as the specimen exhibits curved surface.

(c) SRD convolution and Voigt single-line strains for the 99.99% MgO specimens. The Voigt single-line strain values cannot be extracted from the 99.99% set since the specimens exhibit 'super-Lorentzian' peak shape.

Figure 6.2. (cont'd)
(a) SRD convolution and Voigt single-line sizes for the 99% MgO specimens

Figure 6.3. Convolution and Voigt single-line size values versus sintering temperature obtained from SRD data for (a) 99%, (b) 99.9% and (c) 99.99% MgO ceramics. The size values were obtained by averaging those from lines 420 and 422 in Table 6.1. Error bars indicate \(1\times\) standard deviation as calculated using Equation (6.1).
(b) SRD convolution and Voigt single-line sizes for the 99.9% MgO specimens. Data for 99.9% 1600°C – 6 h specimen are excluded from the analysis as the specimen exhibits curved surface.

(c) SRD convolution and Voigt single-line sizes for the 99.99% MgO specimens. The Voigt single-line size values cannot be extracted from the 99.99% set since the specimens exhibit 'super-Lorentzian' peak shape.
Figure 6.4. Crystallite size distribution parameter ($\beta$) values *versus* sintering temperature obtained from SRD data for 99%, 99.9% and 99.99% MgO ceramics. The size distribution values were obtained by averaging those from lines 420 and 422 in Table 6.1. Error bars indicate $1 \times$ standard deviation as calculated using Equation (6.1).
The size results suggest that the development of the crystallite may advance beyond a limit where extinction may occur (Sabine 1985) such as may be in the case of the 99% 1600°C – 6 h specimen. The primary extinction phenomenon, which is common in materials with mosaic blocks (Warren 1969; Klug & Alexander 1974), can be observed from the decrease in the integrated intensity as shown in Table 6.2. A reduction in integrated intensity by a factor of 2 due to primary extinction was observed by Sabine (1985) in MgO specimen which had been produced by hot-pressing and had a mean grain diameter of 14 µm. Figure 6.5 shows an SEM micrograph of the fractured surface of the MgO 99% 1600°C – 6 h specimen from this study. Large grains with SEM-derived size more than 10 µm are evident. However, smaller grains with SEM-derived sizes less than 2 µm can also be observed. Note that grain pull-out might occur when the specimen was fractured. The size results indicate that large crystallites tend to grow by consuming those with smaller size. Some small grains, however, were not consumed by the large grains leading to the observation of diffraction peaks from specimen with larger size broadening. The grain growth mechanism appears to be in agreement with the mean-field theory for normal grain growth (Hunderi 1979; York 1999; 2003), which considers that (1) grain growth occurs at constant total volume and (2) larger grains grow by consuming smaller grains. In the case of the 99% specimens, the constant total volume can probably be associated with a slight increase in shrinkage (1%) of the sintered ceramics from 1450°C – 2 h to 1600°C – 6 h (see Table 3.1). The growth of the large grains can be observed from the SEM figure for the 99% 1600 – 6 h ceramic (Figure 6.5), however, with the growth process being incomplete leaving some small grains contributing to the diffraction peak broadening.
Table 6.2. Relative integrated intensity of the SRD peaks for the 99% specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Relative integrated intensity* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100°C – 2 h</td>
<td>100</td>
</tr>
<tr>
<td>1250°C – 2 h</td>
<td>100</td>
</tr>
<tr>
<td>1450°C – 2 h</td>
<td>79</td>
</tr>
<tr>
<td>1600°C – 2 h</td>
<td>57</td>
</tr>
</tbody>
</table>

* Integrated intensities of all reflections were used and the relative values were calculated with reference to the 1100°C – 2 h specimen.

Figure 6.5. SEM micrograph of the fractured surface of the 99% 1600°C – 6 h ceramic showing large grains (larger than 10 \( \mu \text{m} \) in size) and also small grains (smaller than 2 \( \mu \text{m} \) in size).
The SRD average size distribution values generally increase with temperature for the 99% specimen (Figures 6.4) but decrease with temperature for the 99.9% specimen. The 99.99% specimens show a constant size distribution value up to 1450°C – 2 h, and then a higher distribution value at 1600°C – 6 h. The 99.99% specimens show the least size distribution parameter, indicating that the crystallite size is the most dispersed as compared to the other specimens. As the sintering temperature increases the average size increases (see Figures 6.3c) and the size distribution for the 1600°C – 6 h specimen is more symmetric. Similar behaviour is obtained for the 99% specimens sintered at 1100°C for 2 hours to 1450°C for 2 hours. The 1450°C – 2 h specimen shows a larger and more symmetric size distribution than the 1600°C – 6 h, implying that large crystallites with similar sizes are dominant in the former and the distribution of the smaller ‘observable-to-diffraction’ crystallites in the latter is more dispersed.

The average strain values estimated from the convolution method with SRD data are generally smaller than those from the single-line Voigt method. In the case of the 99.9% 1100°C – 2 h and 1250°C – 2 h specimens (Figure 6.2b), the convolution average strain is smaller than the Voigt strain by approximately 25%. However, the average strain values for the 99% specimen obtained by the convolution method are approximately 5 times smaller than those from the Voigt method (Figure 6.2b). For these specimens, the convolution and Voigt sizes are in reasonable agreement (Table 6.1 and Figure 6.3). As discussed in Chapter 5, the decrease in strain values can be associated with the size distribution effect which alters both the width and tails of a profile. The change in strain parameter during refinement is influenced by the size distribution. It appears that in specimens where contributions from the Lorentzian and Gaussian components are similar, i.e. the Voigt shape factor is approximately 0.7 such as the 99% and 99.9% MgO ceramics (see Table 4.2), size distribution tends to strongly influence the strain broadening but does not significantly affect the size broadening.

The strain in the 99% 1600°C – 6 h specimen is smaller than that in the 1450°C – 2 h which probably is due to the consideration that the broadening is caused by (1) small radiation-material interaction volume for synchrotron radiation and (2) less diffracting domains with less grain-grain interactions.
The strain values for the 'super-Lorentzian' 99.99%, calculated with the convolution model, do not change with temperature up to 1450°C for 2 hours (at a value of approximately $0.02 \times 10^3$), and then decreases at 1600°C for 6 hours (Figure 6.2c). The constant average strain may be due to the negligible effect of the Gaussian component in the profile for the 99.99% 1100°C – 2 h, 1250°C – 2 h and 1450°C – 2 h specimens. Simulation calculations with the convolution model show that 'super-Lorentzian' character is found in materials with dominant size effect and size distribution parameter value less than 1.0 (see Appendix 2e). The negligible Gaussian effect causes larger strain uncertainties when refinement using the convolution model is performed. It has been shown in Chapter 5 (Figure 5.12 and the related discussion) that clusters of crystallites in these specimens composed the SEM-derived grains and that the convolution crystallite sizes are in a reasonable agreement with those derived from SEM (see inset in Figure 5.12). Moreover, the convolution size distribution reasonably agrees with the SEM-derived size distribution. It is argued that the convolution model can be applied to 'super-Lorentzian' profiles to give acceptable size and size distribution information and useful strain information.

Figure 6.3a shows the convolution and Voigt single-line average size values with respect to sintering temperature for the 99% specimens obtained from SRD data. The development of crystallite size during sintering is evident, particularly from the results for the 1100°C – 2 h and 1250°C – 2 h temperatures. The development of the crystallites for the 99.9% and 99.99% specimens is also obvious from Figures 6.3b and 6.3c, respectively. Similar trends in crystallite growth was observed in CeO$_2$ powder as annealing temperature was increased (Audebrand et al. 2000b). These results show that the MgO crystallite grows steadily with sintering temperature. Again, all data for the 99.9% 1600°C – 6 h specimen and the Voigt single-line data for 99.99% specimens are not presented, as explained previously.

The 99.9% average sizes obtained by both the convolution and Voigt single-line methods are similar, showing that the Lorentzian function, as a size component in the Voigt function, might represent an appropriate size profile to give an approximate crystallite size, presumably if the contributions from the Gaussian and Lorentzian components to the Voigt function are similar and if $1.0 \leq \beta \leq 1.5$.  

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It appears that the agreement between size and strain values from the convolution and Voigt methods depends upon crystallite size values. For crystallite size smaller than 100 nm, such as in the case of 99.9% MgO 1100°C – 2 h and 1250°C – 2 h specimens (Figure 6.3b), the difference is insignificant, with approximate strain values of $0.3 \times 10^{-3}$ for the convolution method and $0.4 \times 10^{-3}$ for the Voigt single-line method (Figure 6.2b). Note also that both methods give similar size results (Figure 6.3b), presumably due to the slow sintering process between these temperatures, as indicated by the slight increase in the specimen shrinkage from 8% for the 1100°C – 2 h specimen to 9% for the 1250°C – 2 h specimen (Table 3.1). The strain difference becomes very large when the size increases over 100 nm such as for the 99.9% specimen sintered at 1450°C – 2 h (Figure 6.2b) and the 99% specimens (Figure 6.2a). It is proposed that the Voigt single-line method may represent reasonable strain and size estimates only for specimens with size values less than 100 nm.

The 99.9% specimens show a decrease in average size distribution value with temperature (Figure 6.4). This decrease may be attributed to (1) larger grains grow faster than the smaller grains and (2) strain inhibits grain growth in smaller grains. In the former case, according to mean-field theory, larger grains consume those with smaller sizes. The grains grow at different rates; the larger grows faster than the smaller. As a result, the size increases but the size distribution broadens.
6.3. Strain and Size Assessments with XRD Data

6.3.1. Line Broadening Analysis

Figure 6.6 shows the Lorentzian and Gaussian component values from the profile refinement using the Voigt function for the 422 line of the 99%, 99.9% and 99.99% ceramics made with XRD data. The results which confirm those from SRD are the as follows.

(1) In general, the Lorentzian and Gaussian values decrease with temperature.

(2) The Lorentzian and Gaussian components for the 99.9% ceramics are higher than those for the 99% ceramics, suggesting that the 99.9% ceramics have smaller size and larger strain than the 99% ceramics.

(3) As also observed from Figure 6.1 for SRD data, the XRD Gaussian components for the 99.99% specimens are lower than those for the instrument (Figure 6.5 – top section) and the XRD Lorentzian components, for these materials have relatively larger uncertainties than those of the 99% and 99.9% specimens. This character is typical for 'super-Lorentzian' peak shapes. Therefore, the Voigt function cannot be properly applied with the 99.99% specimens for size and strain analysis.

A minor difference in trend between Lorentzian and Gaussian components for the XRD and SRD was observed for the 99% ceramics. The XRD Lorentzian and Gaussian components decrease with sintering temperature, reaching a minimum for the specimen sintered at 1450°C – 2 h, and then increases for the 1600°C – 6 h specimen. This observation indicates that (1) sintering temperature reduces the size and strain effects, but further sintering introduces additional broadening and (2) the 99% 1450°C – 2 h specimen shows minimal size and strain effects. The difference in the trend for the XRD and SRD components is unexpected as both measurements were used to obtain near-surface microstructural information. If primary extinction is biasing the results, the smaller synchrotron radiation beam may be in interaction with less diffracting domains as compared with the larger XRD beam.
Figure 6.6. Effects of sintering on the Gaussian and Lorentzian components for the 422 reflection of the 99%, 99.9% and 99.99% MgO specimens using XRD data from integral breadth analysis using the Voigt function. The legend for the horizontal axis denotes the sintering temperature and time (e.g. 1100°C for 2 hours). $\beta_{G}$ and $\beta_{L}$ denote the instrument Gaussian and Lorentzian components, respectively. Error bars indicate $1 \times$ the standard uncertainty. Error bars for some points are invisible since the uncertainties are negligible compared to the graph scales.
The 99% 1450°C – 2 h specimen which showed minimal XRD broadening was used as a standard reference material for XRD and ND instrument broadening corrections and has been used for size and strain analysis of the 99% ceramics (§4.3 and §4.4). Note that, however, the NIST SRM 660a LaB₆ was used as a standard material for instrument broadening correction in the following analysis.

6.3.2. Strain and Size Assessment Results

Table 6.3 depicts the convolution strain, modal size and size distribution parameter values and the Voigt strain and size values for the 99%, 99.9% and 99.99% MgO specimens obtained with the XRD data for the 420 and 422 lines. The use of the convolution and Voigt models for the peak profile fitting give GoF values less than 2% which indicate that the refinements were acceptable.

The XRD strain and size results for the 420 and 422 lines are, in general, in fair agreement. The average values of the parameters for both lines can then be calculated. These average values are plotted against sintering conditions in Figures 6.7 – 6.9. Figure 6.7 displays average strain values for the (a) 99%, (b) 99.9% and (c) 99.99%, and the associated values of size and size distribution parameters are given in Figure 6.8 and 6.9, respectively. The error bar for each data point was calculated with Equation (6.1).

Table 6.3 and Figure 6.6b also show that agreement between XRD convolution and Voigt results is achieved only for the 99.9% specimens which exhibit significant strain and size broadening. These results support those for SRD in showing that the Voigt model can be used to provide reasonable size and strain results if (1) size and strain effects contribute broadening with comparable proportions, presumably for pseudo-Voigt mixing parameter values between 0.5 and 0.7 (see Table 4.2) and (2) both size and strain effects are significant, presumably when specimen broadening is 2× or larger than the instrument broadening (see Table 4.1).
Table 6.3. Strain, modal size and size distribution parameter values for the 420 and 422 reflections of the 99%, 99.9% and 99.99% MgO specimens. Using XRD data from size and strain analysis using the convolution model. Strain and size analysis results obtained using the integral breadth. Voigt method are also presented for comparison. Estimated uncertainties for the least significant digits are given in parentheses. The NIST SRM 660a LaB₆ was used as the standard material for instrument corrections.

<table>
<thead>
<tr>
<th>Specimen ¹</th>
<th>Convolution function ²</th>
<th>Strain (x 1000)</th>
<th>Size (nm)</th>
<th>GoF (%)</th>
<th>Voigt function ⁴</th>
<th>Strain (x 1000)</th>
<th>Size (nm)</th>
<th>GoF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99% 1100°C - 2 h</td>
<td>420</td>
<td>0.049(3)</td>
<td>1.80(21)</td>
<td>1.2</td>
<td>0.22(3)</td>
<td>204(6)</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>99% 1250°C - 2 h</td>
<td>422</td>
<td>0.036(2)</td>
<td>1.58(5)</td>
<td>1.7</td>
<td>0.28(2)</td>
<td>246(7)</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>99% 1450°C - 2 h</td>
<td>422</td>
<td>0.045(2)</td>
<td>1.56(29)</td>
<td>1.5</td>
<td>0.14(4)</td>
<td>531(38)</td>
<td>1.5</td>
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</tr>
<tr>
<td>99% 1600°C - 6 h</td>
<td>422</td>
<td>0.016(6)</td>
<td>310(65)</td>
<td>1.3</td>
<td>0.11(3)</td>
<td>677(47)</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>99.9% 1100°C - 2 h</td>
<td>422</td>
<td>0.202(3)</td>
<td>1.77(73)</td>
<td>1.2</td>
<td>0.13(4)</td>
<td>2861(777)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>99.9% 1250°C - 2 h</td>
<td>420</td>
<td>0.140(3)</td>
<td>2.58(69)</td>
<td>1.4</td>
<td>0.12(3)</td>
<td>6186(55)</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>99.9% 1450°C - 2 h</td>
<td>420</td>
<td>0.405(33)</td>
<td>84(8)</td>
<td>1.0</td>
<td>0.47(3)</td>
<td>847(76)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>99.9% 1600°C - 6 h</td>
<td>420</td>
<td>0.419(54)</td>
<td>95(15)</td>
<td>1.1</td>
<td>0.38(3)</td>
<td>86(2)</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>99.99% 1100°C - 2 h</td>
<td>420</td>
<td>0.316(21)</td>
<td>108(3)</td>
<td>1.2</td>
<td>0.30(2)</td>
<td>124(4)</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>99.99% 1250°C - 2 h</td>
<td>422</td>
<td>0.225(20)</td>
<td>112(2)</td>
<td>1.7</td>
<td>0.12(6)</td>
<td>151(9)</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

(Cont'd)
Table 6.3. (cont’d)

<table>
<thead>
<tr>
<th>Specimen⁠¹</th>
<th>Line</th>
<th>Strain (x 1000)</th>
<th>Size (nm)</th>
<th>Size distr.²</th>
<th>GoF³ (%)</th>
<th>Voigt function⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.99% 1100°C – 2 h</td>
<td>420</td>
<td>0.0507(6)</td>
<td>65(1)</td>
<td>0.96(3)</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0531(6)</td>
<td>69(1)</td>
<td>0.87(2)</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>99.99% 1250°C – 2 h</td>
<td>420</td>
<td>0.0661(6)</td>
<td>85(1)</td>
<td>1.00(3)</td>
<td>1.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0487(5)</td>
<td>91(1)</td>
<td>1.13(3)</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>99.99% 1450°C – 2 h</td>
<td>420</td>
<td>0.0645(7)</td>
<td>96(1)</td>
<td>1.08(3)</td>
<td>1.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0441(4)</td>
<td>101(2)</td>
<td>1.18(3)</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>99.99% 1600°C – 6 h</td>
<td>420</td>
<td>0.0419(66)</td>
<td>171(12)</td>
<td>1.45(11)</td>
<td>1.1</td>
<td>0.23(5)</td>
</tr>
<tr>
<td></td>
<td>422</td>
<td>0.0458(13)</td>
<td>214(8)</td>
<td>1.41(7)</td>
<td>1.9</td>
<td>0.10(8)</td>
</tr>
</tbody>
</table>

¹ MgO sintered ceramics. Purity level and sintering conditions are used as identifier of the specimens.
² Strain is calculated using Equation (5.9a), size using Equation (5.6) and size distribution is β in Equation (5.3).
³ GoF = ‘Goodness-of-Fit’ is determined using Equation (5.14).
⁴ Strain and size are calculated using Equation (2.71) and (2.72), respectively. Despite the single-line Voigt method results, the 99.99% specimens exhibited ‘super-Lorentzian’ character.
⁵ Unstable refinement.
⁶ Peaks for 99.9% MgO exhibit strong asymmetry. Peak position cannot be refined in conjunction with other parameters.
⁷ The 99.99% specimen exhibited curved surface and therefore was excluded from the analysis.
(a) XRD convolution and Voigt single-line strains for the 99% MgO specimens.

Figure 6.7. Convolution and Voigt single-line strain values versus sintering temperature obtained from XRD data for (a) 99%, (b) 99.9% and (c) 99.99% MgO ceramics. The strain values were obtained by averaging those from lines 420 and 422 in Table 6.2. Error bars indicate 1× standard deviation as calculated using Equation (6.1).
(b) XRD convolution and Voigt single-line strains for the 99.9% MgO specimens. Data for the 99.9% 1600°C - 6 h specimen are excluded from the analysis as the specimen exhibits curved surface.

(c) XRD convolution and Voigt single-line strains for the 99.99% MgO specimens. The Voigt single-line strain values cannot be extracted from the 99.99% set since the specimens exhibit ‘super-Lorentzian’ peak shape.

Figure 6.7. (cont’d)
(a) XRD convolution and Voigt single-line sizes for the 99% MgO specimens.

Figure 6.8. Convolution and Voigt single-line size values versus sintering temperature obtained from XRD data for (a) 99%, (b) 99.9% and (c) 99.99% MgO ceramics. The size values were obtained by averaging those from lines 420 and 422 in Table 6.2. Error bars indicate 1× standard deviation as calculated using Equation (6.1).
(b) XRD convolution and Voigt single-line sizes for the 99.9% MgO specimens. Data for the 99.9% 1600°C – 6 h specimen are excluded from the analysis as the specimen exhibits curved surface.

(c) XRD convolution and Voigt single-line sizes for the 99.99% MgO specimens. The Voigt single-line strain values cannot be extracted from the 99.99% set since the specimens exhibit 'super-Lorentzian' peak shape.

Figure 6.8. (cont'd)
Figure 6.9. Size distribution parameter ($\beta$) values versus sintering temperature obtained from XRD data for 99%, 99.9% and 99.99% MgO ceramics. The size distribution values were obtained by averaging those from lines 420 and 422 in Table 6.2. Error bars indicate $1\times$ standard deviation as calculated using Equation (6.1).
The relative uncertainties for the convolution values are generally less than 10% except for (1) materials with small specimen broadening, such as the 99% ceramic sintered at 1450°C for 2 hours, or (2) materials with relatively large strain values, such as the 99.9% ceramics since the strain uncertainty is proportional to the strain value. The convolution uncertainties are, on average, similar to the Voigt uncertainties. The XRD results are obviously less precise than those for SRD which is due to the better resolution of the SRD instrument.

Figure 6.7a shows that both XRD convolution and Voigt average strains decrease with sintering temperature up to 1450°C for 2 hours. Further sintering at 1600°C for 6 hours introduces additional strains. The average crystallite size for the 1600°C - 6 h specimen is smaller than that for the 1450°C - 2 h. This suggests that primary extinction biases the data for the 1600°C - 6 h specimen, as has also been observed in the SRD results (see §6.2.2). Further investigation shows that the XRD integrated intensity decreases significantly at 1600°C (Table 6.4), indicating that there is a decrease in number of crystallites contributing to the pattern. Further grain growth occurs at 1600°C with larger grains consuming smaller grains. As a result, grains with SEM-derived sizes larger than 10 μm are observed, but smaller grains are also present (Figure 6.5). The smaller grains are believed to be those which contribute to the diffraction pattern.

Figure 6.7a also shows that the XRD convolution average strain values for the 99% specimens are up to 5 times smaller than the Voigt single-line values. The absence of size distribution parameter in the Voigt model is believed to be responsible for this difference. It is also evident from the figure that the absolute uncertainties for the convolution strains are smaller than those for the Voigt strains. Therefore, as also observed from SRD data, the XRD results for the convolution model are more precise than those for the Voigt single-line model.

Figure 6.7b shows the XRD average strain values for the 99.9% specimens. Both the convolution and the Voigt average strains for the 99.9% specimen reduce with temperature. For these materials, the average strain values are, in general, similar to the Voigt values within uncertainty limits. Again, this result is consistent with that for SRD.
The average strain values for the ‘super-Lorentzian’ 99.99% specimens cannot be obtained using the Voigt single-line method with XRD data. The convolution strain does not change significantly with temperature up to 1450°C for 2 hours and then decreases slightly at 1600°C for 6 hours. As also observed from the SRD results, constant strain is obtained since the strain effect on the ‘super-Lorentzian’ profiles is negligible. When a refinement using the convolution model is performed, the small amount of strain can be obtained but with relatively large uncertainty, as can be seen from results for the 1250°C – 2 h and 1450°C – 2 h specimens (Figure 6.7c).

Figure 6.8a shows the convolution and Voigt single-line average size values with respect to sintering temperature for the 99% specimens obtained from XRD data. The results for the 1100°C – 2 h and 1250°C – 2 h specimens indicate that crystallites grow during sintering. Comparable convolution and Voigt average size values are obtained only for the 1100°C – 2 h specimen. As a result of the small size broadening in the 99% 1450°C – 2 h specimen, the uncertainties for the convolution and the Voigt single-line sizes are large, (e.g. 2500(500) nm for the Voigt single-line method).

Crystallite growth in the 99.9% and 99.99% specimens is evident from the XRD results shown in Figures 6.8b and 6.8c. The XRD results are consistent with those for the SRD in that the convolution and Voigt sizes for the 99.9% specimens are similar, indicating that the Lorentzian function might be used to provide the size profile giving crystallite size estimates for specimens exhibiting comparable size and strain broadening effects. The XRD average size values for the ‘super-Lorentzian’ 99.99% specimens obtained with the Voigt model have large uncertainties indicating that fitting ‘super-Lorentzian’ profiles with the Voigt function is possible but results in indefinable strain values and erroneous size values.
Table 6.4. Relative integrated intensity of the XRD peaks for the 99% specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Relative integrated intensity* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100°C – 2 h</td>
<td>100</td>
</tr>
<tr>
<td>1250°C – 2 h</td>
<td>99</td>
</tr>
<tr>
<td>1450°C – 2 h</td>
<td>85</td>
</tr>
<tr>
<td>1600°C – 2 h</td>
<td>67</td>
</tr>
</tbody>
</table>

* Integrated intensities of all reflections were used and the relative values are calculated with reference to the 1100°C – 2 h specimen.

Figure 6.9 displays the convolution average size distribution values for the 99%, 99.9% and 99.99% specimens. The values for the 99% and 99.99% specimens increase with sintering temperature, while that for the 99.9% specimen does not change with sintering temperature. The dispersion of crystallite sizes for the 99.99% specimen is larger than those for the 99.9% and 99% specimens. The differences in size distribution character are probably caused by different crystallite size development which depends on the initial character of the raw powders.

6.4. Quality of the Convolution Model

It is obvious from the convolution and Voigt single-line methods that, in general, sintering favours crystallite size development, relieves strains in low density ceramics and introduces additional strain in dense ceramics. The following subsections compare the strain and size results obtained with SRD and XRD data to describe the quality of the convolution model.

6.4.1. Comparison of SRD and XRD Strain Results

The trends in the SRD and XRD strain values with sintering temperature for the 99% specimens are similar, except the reduction in the SRD convolution value in the 1600°C – 6 h specimen (Figures 6.2a – left panel). The SRD and XRD convolution strain values for the 1600°C – 6 h specimen, which is approximately
0.018 \times 10^{-3}, are in reasonable agreement within uncertainty limits. The 1100°C – 2 h and 1250°C – 2 h specimens show up to 2× larger XRD convolution strain than the corresponding SRD strain. The maximum value of strain observed is 0.05 \times 10^{-3} and the uncertainties for the SRD results are smaller than those for the XRD indicating the superiority of the SRD instrument over the XRD. The inconsistent agreement may be the result of small specimen broadening which, in these materials, is less than 2× for SRD and 1.3× for XRD that of the associated instrument broadening (Table 4.1).

Figures 6.2b and 6.7b show the SRD and XRD average strain values for the 99.9% specimens, respectively, which reduce with temperature. It can be seen from both figures that the SRD and XRD strains are similar, i.e. the SRD-to-XRD strain ratio is approximately 0.9. For these materials, the convolution strain values are similar to the corresponding Voigt values.

The convolution strain values for the ‘super-Lorentzian’ 99.99% obtained with the SRD data are approximately one half those obtained with XRD data. The maximum strain value is 0.03 \times 10^{-3} for SRD and 0.07 \times 10^{-3} for XRD, which again can be categorised as small strain. This difference could be due to the minimal strain broadening in the materials which cannot be extracted with precision by the refinement using the convolution model. Smaller uncertainties are obtained for the SRD data than for the XRD as a consequence of the superior precision of the SRD instrument.

In conclusion, the convolution model performs adequately in extracting strain values. Consistent SRD and XRD results for relatively large strain values of more than 0.2 \times 10^{-3} were achieved. Reasonable agreement between the two techniques, however, is difficult to achieve for strain smaller than 0.05 \times 10^{-3}. Nevertheless, the convolution model gives more precise results than the Voigt single-line method.

### 6.4.2. Comparison of SRD and XRD Size Results

Figures 6.3a and 6.8a show the convolution average size values with respect to sintering temperature for the 99% specimens obtained from SRD and XRD data, respectively. The trends of the SRD and XRD convolution sizes with sintering
temperature are similar. The SRD and XRD convolution sizes for these specimens are in agreement within the uncertainty limits for the XRD sizes.

The SRD and XRD convolution average size results for the 99.9% and 99.99% specimens obviously show a reliable agreement (Figures 6.3b, 6.3c, 6.8b and 6.8c). The uncertainties for the SRD sizes are smaller than those for the XRD sizes due to the superior SRD resolution.

These results demonstrate that the convolution model performs satisfactorily in providing size values. Moreover, it provides more precise results than the Voigt single-line model.

6.4.3. Comparison of SRD and XRD Size Distribution Parameter Results

Both SRD and XRD results show that the average size distribution parameter values generally increase with temperature for the 99% and 99.99% specimens (Figures 6.4 and 6.9). The size distribution value for the 99.9% specimen obtained with SRD data increases with temperature, however it remains constant with temperature for the XRD data.

The XRD average size distribution parameter results are generally in satisfactory agreement with the SRD results, i.e. the SRD-to-XRD ratio ranges from 0.8 to 1.2. Very different XRD and SRD results were obtained for the 99% ceramics sintered at 1450°C for 2 hours and 1600°C for 6 hours which have ratios of approximately 0.4 and 1.8, respectively. The different SRD and XRD results for the 99% 1450°C – 2 h and 1600°C – 2 h ceramics may be attributed the small size broadening effect observed for these materials.

High resolution SRD gave smaller uncertainties in the size distribution results than the laboratory XRD.

The sound performance of the convolution model in extracting size distribution information is evident. This finding also stresses the advantages of the convolution model over the Voigt model which does not take into account size distribution effect.
6.4.4. Comparison of the Convolution and SEM Size Results

A discussion on the comparison of the convolution crystallite size and SEM grain size results has been provided in §5.4.3. The following aspects are reconsidered:

1. The grain sizes, as measured by SEM, are larger than the convolution crystallite sizes which indicates that the apparent 'particles' may be composed of clusters of crystallites (Guillou, Auffrédic & Louër 1995; Audebrand et al. 2000b) – see Figure 5.12.

2. The shapes of the SEM-derived distributions are similar to the corresponding convolution model distributions.

3. The SEM and diffraction methods show that sintering favours grain and crystallite growths.

To summarise, the convolution model developed in this study describes satisfactorily the size distribution and size information extracted from the diffraction patterns for sintered MgO ceramics. Reasonable strain information can also be extracted from the diffraction pattern with the convolution model which uses the Gaussian-strain model applicable for low-strain materials such as the sintered MgO ceramics used in this study.

6.5. Overall Value of the Convolution Model

Despite the satisfactory size and strain evaluation results using the SRD and XRD data for MgO ceramics, there are some limitations to the use of the convolution model with MOZAIX which can be described as follows:

1. The convolution model is unstable for data with relatively small specimen broadening as compared to the measurement step size and the instrument broadening such as in the ND data for the 99%. (see Table 4.2 and Figure 4.1). Specimen broadening which is much smaller than the step size causes instability of the convolution algorithm to determine the correct parameter values, which
seems to be inherent in convolution calculations (Materials Data Inc. 1999 – user manual).

2. The convolution model cannot deal with very asymmetric peak shapes. Unstable refinement will occur if the peak position is adjusted in conjunction with other parameters. Example plots for symmetric and asymmetric peak shapes are given in Figure 6.10 where profile refinement is performed using the pseudo-Voigt function. The 99.9% MgO ceramic exhibits symmetric peak shapes when sintered at 1250°C for 2 hours but asymmetric peak shapes at 1450°C for 2 hours. The split pseudo-Voigt peak width parameters are (a) left-side FWHM = 0.313(3), right-side FWHM = 0.292(3), left-side mixing parameter = 0.60(1) and right-side mixing parameter = 0.62(1) for the symmetric peak and (b) left-side FWHM = 0.230(2), right-side FWHM = 0.142(3), left-side mixing parameter = 0.60(1) and right-side mixing parameter = 0.91(2) for the asymmetric peak. Note that further sintering to 1600°C for 6 hours causes curvature in the surface of the specimen, leading to exclusion of the specimen from the analysis.

3. Refinement results from the convolution model are, in some cases, dependent upon the initial values. This problem is typical of optimisation procedures where non-singular minima may be found. The initial values for the refinement using the convolution model in MOZAIK can be approximated by parameterising the convolution function with the pseudo-Voigt function (see Appendix 2e). Note that the non-linear least-square optimisation is calculated based on the standard algorithm given by the Marquardt or Levenberg-Marquardt method (Press et al. 1989). It is therefore important to note that (1) only reasonable initial values can be given to the model and (2) there is a possibility of improving the optimisation procedure to give more appropriate results.
Figure 6.10. (a) Symmetric and (b) asymmetric peak shapes fitted with the pseudo-Voigt function. In refining the asymmetric peak, the peak position cannot be refined in conjunction with other parameters, which may result in dubious values.
4. The development of a size and strain model by line profile fitting should be attempted to its application to entire diffraction data. The convolution model in *MOZAIX*, however, currently can only be applied to single-peak diffraction data. Due to time constraints, the development of the model could not be extended to whole-pattern data. Accordingly, further work for extending the current achievement to whole-powder pattern data using the convolution model is recommended.

6.6. Conclusion

1. The convolution model developed in this study performed well in extracting size, size distribution and strain information from the SRD and XRD data for sintered MgO ceramic materials. Consistent size and size distribution results were obtained and fair agreement strain results were achieved using the model.

2. The convolution model appeared to be superior to the Voigt single-line model as demonstrated by (1) the use of the more appropriate physically-based models, (2) relatively better precision, (3) inclusion of size distribution descriptor, (4) generally consistent size, size distribution and strain results and (5) ability to deal with 'super-Lorentzian' peak profiles.

3. The convolution and Voigt single-line models show that, in general, sintering favours crystallite growth and relieves strains in relatively low density ceramics and introduces strains in dense ceramics probably due to grain-grain shear interactions. However, there are points which should be addressed:

   a. crystallite growth may proceed to a limit where primary extinction can occur and result in the observation of sizes smaller than those seen by imaging.

   b. the relationship between size and strain estimates from both models depends on the crystallite size. It appears that the Voigt single-line method provides reasonable size and strain estimates only for specimens with convolution size values less than 100 nm.
c. the Lorentzian size component in the Voigt function might be used give an approximate crystallite size, presumably if the contributions from the Gaussian and Lorentzian components to the Voigt function are similar and if \( 1.0 \leq \beta \leq 1.5 \).

4. The convolution model shows that sintering causes changes in crystallite size distribution which possibly depends on (1) the crystallite growth rate and (2) the presence of strain. The convolution size distribution is in satisfactory agreement with the SEM grain distribution results. The convolution crystallite size, however, is smaller than the SEM-derived grain size because the latter consists of clusters of crystallites.

5. Results from XRD data are, generally, in agreement with those from SRD data which means the application of the convolution model can be performed in the more accessible XRD machines – however with a larger degree of uncertainties in the results.

6. In spite of the success of the application of the convolution model using *MOZAIX* to the SRD and XRD data for MgO ceramics, the model has limitations, being: (1) its use with lower resolution ND data, (2) its application to peaks with strong asymmetry and (3) the dependence of the success of the refinement and the results on the initial parameter values for cases where specimen broadening is only \( 1.1 \times \) that of the instrument. Further research is proposed for improving the model to overcome these limitations as well as to extend the convolution model in *MOZAIX* for the application to whole-powder pattern diffraction data.
CHAPTER 7. CONCLUSION

7.1. Re-Statement of Study Objectives

The overview of results from Chapters 4, 5 and 6, given below, is presented in relation to the objectives (Section 1.3) which are restated here for the convenience of the reader:

(1) to critically examine existing methods for strain-size evaluation;

(2) to consider whether existing models might be refined for use in the modelling of size-strain character;

(3) to attempt to develop new physically-based modelling methods with particular reference to ceramic materials.

The two main questions to be investigated in the study were:

- Which diffraction-based physical models might be appropriate for modelling crystallite size and strain with particular reference to ceramic materials?
- How effective are these models for representing size and strain in these materials?

7.2. Overview of Results

The study addresses the effectiveness of a proposed convolution and the Voigt models for diffraction line fitting to acquire size and strain information. The principal results and conclusions from the study are as follows:

1. The convolution model, which uses a physically-derived size profile from York and a Gaussian-strain profile for the line profile fitting and accommodates the modal size, size distribution and strain parameters, has been successfully developed and then applied with diffraction data for sintered MgO ceramics. The model evaluation showed that the convolution model performs with considerable effectiveness in acquiring modal size, size distribution and strain information from the diffraction data. Consistent size descriptors were obtained and a fair agreement between strain values was also achieved. The convolution size distribution results
agree satisfactorily with those from scanning electron microscopy (SEM). The SEM-derived grain sizes, however, are larger than the convolution crystallite sizes indicating that apparent grains contain clusters of crystallites.

2. The use of the Voigt function for size and strain analysis by fitting with diffraction data is popular because it favours the deconvolution procedures as well as the separation of size and strain effects in the analysis. The approach appears to give adequate information about size and strain values, however, has three deficiencies according to literature, i.e. (1) uses the physically unjustified Lorentzian-size and Gaussian-strain assumptions, (2) does not take into account the size distribution information and (3) cannot deal with ‘super-Lorentzian’ profiles. These deficiencies were confirmed in this study using diffraction data for sintered MgO ceramics which gave some unacceptable results.

3. The convolution of the Lorentzian-size and Gaussian-strain profiles in the Voigt function led to a basic insight that an overall function is a convolution of separate size and strain profile functions. This convolution approach has been adopted in this study to develop the convolution model as described above.

Following are additional results and conclusions from the study:

1. The proposed convolution model for size-strain line profile analysis, which has been programmed with MOZAIX, has been tested using simulated data which appeared to give reasonable results.

2. Strain and size evaluations using SRD data for three suites of MgO ceramics confirmed that the convolution model is advantageous for line profile analysis particularly over the mathematical or analytical Pearson VII, pseudo-Voigt and Voigt models. Size-strain evaluations showed that the convolution model gives more acceptable results as compared to the Voigt function which, in particular, is not applicable to the 'super-Lorentzian' profile and does not take into account size distribution effects.

3. Results obtained with the convolution and Voigt single-line models show that, in general, sintering relieves strains in low density sintered ceramics, introduces strains in dense ceramics probably due to grain-grain shear interactions and also favours crystallite growth as expected. The size and strain values for both models
vary with the peak shape character. The convolution sizes are similar to those of
the Voigt single-line method if both size and strain effects contribute substantially
to the specimen broadening, while the convolution strains are generally smaller
than those of the Voigt single-line method. The convolution model results showed
that the effect of sintering on the size distribution can be unpredictable. In the least
broadened suite, MgO 99%, the size distribution parameter increases with
temperature, indicating that the grains become more homogenous with
temperature. By contrast, the 99.9% specimens showed the decrease of this
parameter with temperature while that for the 99.99% increases slightly with
temperature. It appears that the purity level does not affect the specimen
broadening in a simple fashion.

4. Strain and size evaluation results from XRD data using the convolution model are,
generally, in agreement with those from SRD data, however, with larger
uncertainties. Therefore, moderately reliable size and strain analysis can be
performed using more accessible XRD machines.

5. Application of the convolution model with MOZAIK to the SRD and XRD data for
MgO ceramics has been performed and gave generally satisfactory results.
However, there were some issues arising from the study regarding modelling
deficiencies: (1) dealing with relatively small broadening which is dominated by
instrument broadening found here for ND data; (2) coping with peak shapes with
strong asymmetry; and (3) the dependence of the success of the refinement and the
results on the initial parameter values in some cases. While the convolution model
has been applied with some success to single-peak data, the method needs further
development for application to whole-powder diffraction data.

6. An MgO ceramic sintered at 1450°C for 2 hours with slow annealing during
cooling is suitable for instrument profile corrections using both XRD and ND data.
The XRD strain broadening and the microstructural characteristics of the ceramic
are very similar to those for the LaB₆ NIST SRM 660. During the study, it was
found that a new NIST SRM of LaB₆ had been released and it was found to show a
narrower broadening than that obtained for the MgO standard developed for this
study. Nevertheless, the MgO standard can be used (1) for ND work for which
LaB₆ is not suitable due to severe neutron absorption or (2) for relative size and
strain analysis of MgO materials.
7. The results obtained by both the single-line and Rietveld methods using the Voigt function applied to XRD and ND data showed that introduction of $Y_2O_3$ as a second phase increases strain and constrains crystallite growth.

8. Reasonably consistent strain values were obtained for the Voigt single-line and Rietveld methods using both XRD and ND data whereas there were marked differences between the size estimates from the two methods. The inconsistency of the results indicates profile functions involving parameters representing crystallite size distribution should be applied for providing correct crystallite size descriptions for Rietveld analysis.

### 7.3. Recommendations for Further Research

During the research for this thesis, several issues were raised but could not be addressed due to time constraints, as follows:

1. The Gaussian strain profile is appropriate only for a Gaussian strain distribution and small strain values (ca. $10^{-3}$ or less). A new function for the strain profile should be developed for more general applications.

2. There is now a strong consensus that modelling of microstructural effects in powder diffraction should use the whole diffraction pattern. Whole-pattern refinement using the convolution model is possible particularly with recent progresses in computation with high-speed computers. It is hoped that the convolution model in MOZAIK, which currently handles only single-line diffraction data, will be applicable to whole-pattern diffraction data in the future.

3. The convolution model performed satisfactorily for MgO specimens which exhibit isotropic size and strain character. It is hoped that further research to develop the model for specimens with anisotropic broadening character will follow this study.
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APPENDIX 1. OVERVIEW OF THE YORK-STRAIN MODEL
(York 1999; 2003)

The equation for the average energy $U_\varepsilon$ from the statistical mechanics (York, 1999 - Equation 10):

$$U_\varepsilon = \langle H(q) \rangle = \frac{\int H(q)e^{-\varepsilon_{\text{eff}}(q)/k_B T}dq}{\int e^{-\varepsilon_{\text{eff}}(q)/k_B T}dq}$$ (A1.1)

The mean-field strain energy $E_\varepsilon$ can then be expressed as (York, 1999 - Equation 11; or York, 2003, Equation 21)

$$E_\varepsilon = \frac{N(\varepsilon - \varepsilon_0^* )^2}{G_{hkl}\rho^*}(Nd)A$$ (A1.2)

where $\rho^*$ is the dislocation density; $G_{hkl}$ is a constant dependent on burger vector $b$, shear modulus $G$ and lattice parameters; $(Nd)A$ is the grain volume; and $\varepsilon_0^*$ is related to the internal stress from grain boundary dislocations.

The strain probability is then given by (York, 1999 - Equation 12)

$$P(\varepsilon) = e^{-\frac{N^2(\varepsilon - \varepsilon_0^*)^2}{f(N)}}$$ (A1.3)

where

$$f(N) = \left\{ N^2(\varepsilon - \varepsilon_0^*)^2 \right\} = a_{hkl}\rho^* N$$ (A1.4)

There are several forms of $f(N)$ and one of them is (York, 1999)

$$f(N) = aN + b$$ (A1.5)

This function can be related to the variance of the strain probability function $\langle \varepsilon^2 \rangle$.

The strain profile can then be determined from (York, 1999 - Equation 13)
\[ F(d_b, f(N), N, \theta) = \int_{-\infty}^{\infty} p(N, \epsilon) g(N, \theta, \epsilon) d\epsilon \]
\[ = \int_{-\infty}^{\infty} \frac{N^2(\epsilon - \epsilon_b)^2}{f(N)} \frac{\sin^2(2\pi NL(1 + (\epsilon - \epsilon_b)))}{\sin^2(2\pi L(1 + (\epsilon - \epsilon_b)))} d\epsilon \]

(A1.6)

By the trigonometric identity (York, 1999 - Equation 14),
\[ \frac{\sin^2(2\pi NL(1 + (\epsilon - \epsilon_b)))}{\sin^2(2\pi L(1 + (\epsilon - \epsilon_b)))} = N + 2 \sum_{k=1}^{k=N-1} (N - k) \cos(2\pi kL(1 + (\epsilon - \epsilon_b))) \]

(A1.7)

It can be shown that (York, 1999 - Equation 15)
\[ F(d_b, f(N), N, \theta) = N + 2 \sum_{k=1}^{k=N} (N - k) e^{\frac{f(N)}{N^2 k^2 L^2} \cos(2\pi kL)} \]

(A1.8)

where \( L = \frac{2d_b \sin \theta}{\lambda} \)

(A1.9)

The normalised form of \( F(d_b, f(N), N, \theta) \) can be derived as follows. It can be shown that (see Burrington, 1973)
\[ \int_{-\infty}^{\infty} e^{-x^4} \cos(b(1 + x)) dx = \sqrt{\pi} \alpha e^{-\frac{1}{4} \alpha^2} \cos(b) \quad \text{and} \quad \int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi} \]

(A1.10)

Therefore, for \( a^2 = \frac{f(N)}{N^2} \) and \( b = 2\pi k L \),
\[ \int_{0}^{\infty} e^{-x^4} \frac{N^2(\epsilon - \epsilon_b)^2}{f(N)} \cos(2\pi kL(1 + (\epsilon - \epsilon_b))) d\epsilon \]

(A1.11)

\[ = \frac{1}{N} \sqrt{\pi} \cdot \frac{f(N)}{e^{\frac{1}{N^2} \cdot \cos(2\pi k L)}} \]

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and hence

\[ F(d_b, f(N), N, \theta) = \]
\[ \int_{-\infty}^{\infty} \frac{N^2(\varepsilon-\varepsilon_b)^2}{f(N)} \frac{\sin^2(2\pi NL(1 + (\varepsilon-\varepsilon_b)))}{\sin^2(2\pi L(1 + (\varepsilon-\varepsilon_b)))} d\varepsilon \]
\[ = \int_{-\infty}^{\infty} \frac{N^2(\varepsilon-\varepsilon_b)^2}{f(N)} \left[ N + 2 \sum_{k=1}^{k=N-1} (N - k) \cos(2\pi kL(1 + (\varepsilon-\varepsilon_b))) \right] d\varepsilon \]
\[ = \sqrt{\pi} \cdot f(N) + \frac{2}{N} \sqrt{\pi} \cdot f(N) \sum_{k=1}^{k=N-1} (N - k)e^{-\frac{f(N)\pi^2k^2d_b^2}{2\sin^2\theta}} \cos\left(\frac{4\pi kd_b \sin \theta}{\lambda}\right) \]
\[ = \sqrt{\pi} \cdot f(N) + \frac{2}{N} \sqrt{\pi} \cdot f(N) \sum_{k=1}^{k=N-1} (N - k)e^{-\frac{C}{N^2} \left( \frac{f(N)\pi^2k^2d_b^2}{\sin^2\theta} \right)} \cos\left(2Ck \sin \theta\right) \]

(A1.12)

where \( C = \frac{2\pi d_b}{\lambda} \) is a constant.

Expanding \( \theta \) about the Bragg peak position \( 2\theta_0 \) gives

\[ F(d_b, f(N), N, \theta) \approx \sqrt{\pi} \cdot f(N) + \]
\[ \frac{2}{N} \sqrt{\pi} \cdot f(N) \sum_{k=1}^{k=N-1} (N - k)e^{-\frac{f(N)\pi^2k^2d_b^2}{2\sin^2\theta}} \cos\left(\frac{2\pi kd_b (2\theta - 2\theta_0)}{\lambda}\right) \]

(A1.13)

The other forms of \( f(N) \) have been given by others:

1. \( f(N) = a/N + b \) (Houska & Kuzel 1999);
2. \( f(N) = aN^b \) (Lutterotti & Scardi 1992);
3. \( f(N) = a/N^b \) (Adler & Houska 1979);

The expression \( f(N) = aN + b \) was used here for reviewing the York-strain model. Figure A1.1 shows plots of Equation A1.13 for various cell number \( N \) values (\( N \) is proportional to the crystallite size). Table A1.1 presents the parameter values in Equation A1.13 used to give plots in Figure A1.1.
Figure A1.1. York-strain profile function (Equation A1.13) plots for $N = 50, 100, 200$ and 400.

Table A1.1. Parameter values in Equation A1.13 used to plot Figure A1.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation wavelength, $\lambda$ (Å)</td>
<td>1.50</td>
</tr>
<tr>
<td>Interplanar spacing, $d_b$ (Å)</td>
<td>4.20$^1$</td>
</tr>
<tr>
<td>Strain coefficient 1, $a$</td>
<td>1.00</td>
</tr>
<tr>
<td>Strain coefficient 2, $b$</td>
<td>1.00</td>
</tr>
<tr>
<td>Diffraction angle increment</td>
<td>0.02°</td>
</tr>
</tbody>
</table>

$^1$ The interplanar spacing was selected to accommodate [100] line profiles for MgO

As can be seen from Figure A1.1, size parameter represented by $N$ has a strong influence on the strain peak shape. Large strain broadening occurs for small $N$, hence small crystallite size, and vice versa. This condition limits the application of the York-strain model since it implies that it is impossible to obtain large strains in materials with large grains such as sintered ceramics. Further investigation is required to identify the sources of strains in association with the available strain models. For this reason, the York-strain model is not used in this study.
APPENDIX 2. DEVELOPMENT OF MOZAIK PROGRAM

Appendix 2a. The Convolution Size and Strain Profiles and Their Derivatives with Respect to the Refinable Parameters

Strain profile \( f_{\text{strain}}(\theta) \) and its derivatives with respect to the refinable parameters:

\[
f_{\text{strain}}(\theta) = I_0 \cdot e^{-\left(\frac{2\theta - 2\theta_0}{W_\varepsilon}\right)^2}
\]

\[
\frac{\partial}{\partial 2\theta_0} \left[f_{\text{strain}}(\theta)\right] = \frac{2I_0(2\theta - 2\theta_0)}{W_\varepsilon^2} e^{-\left(\frac{2\theta - 2\theta_0}{W_\varepsilon}\right)^2}
\]

\[
\frac{\partial}{\partial W_\varepsilon} \left[f_{\text{strain}}(\theta)\right] = \frac{2I_0(2\theta - 2\theta_0)^2}{W_\varepsilon^3} e^{-\left(\frac{2\theta - 2\theta_0}{W_\varepsilon}\right)^2}
\]
Size profile $f_{\text{size}}(\theta)$ and its derivatives with respect to the refinable parameters:

$$f_{\text{size}}(\theta) = \frac{I_0}{\left[1 + \frac{2\pi}{\beta} \left(\frac{2\theta - 2\theta_0}{W_D}\right)^2\right]^{\frac{\beta+1}{2}}}$$  \hspace{1cm} (A2a.4)

$$\frac{\partial}{\partial 2\theta_0} [f_{\text{size}}(\theta)] = \frac{2\pi I_0(\beta+1)(2\theta - 2\theta_0)}{\beta W_D^2 \left[1 + \frac{2\pi}{\beta} \left(\frac{2\theta - 2\theta_0}{W_D}\right)^2\right]^{\frac{\beta+3}{2}}}$$  \hspace{1cm} (A2a.5)

$$\frac{\partial}{\partial W_D} [f_{\text{size}}(\theta)] = \frac{2\pi I_0(\beta+1)(2\theta - 2\theta_0)^2}{\beta W_D^3 \left[1 + \frac{2\pi}{\beta} \left(\frac{2\theta - 2\theta_0}{W_D}\right)^2\right]^{\frac{\beta+3}{2}}}$$  \hspace{1cm} (A2a.6)

$$\frac{\partial}{\partial \beta} [f_{\text{size}}(\theta)] = -\frac{I_0}{\frac{1}{2} \ln \left(1 + \frac{2\pi}{\beta} \left(\frac{2\theta - 2\theta_0}{W_D}\right)^2\right)} - \frac{\pi(\beta+1)(2\theta - 2\theta_0)^2}{\beta W_D^2 \left[1 + \frac{2\pi}{\beta} \left(\frac{2\theta - 2\theta_0}{W_D}\right)^2\right]^{\frac{\beta+3}{2}}}$$  \hspace{1cm} (A2a.7)
Appendix 2b. Fortran 95 Codes for Key Subroutines

Appendix 2b.1. York-size and Gaussian-strain profile functions

SUBROUTINE fYS(x,a,instr,y,dyda)
USE nrtype; USE numlib
USE nx
IMPLICIT NONE
REAL(SP), DIMENSION(:,), INTENT(IN) :: x,a,instr
REAL(SP), DIMENSION(:,), INTENT(OUT) :: y, dyda
REAL(SP), DIMENSION(:,,:), ALLOCATABLE :: xG,yG,yY,Ytemp,cmp,dt
REAL(SP), DIMENSION(SIZE(x)) :: argG,exG,facG,factor
REAL(SP), DIMENSION(SIZE(x)-1) :: argY1,facY1,facY2, inst
REAL(SP) :: argY2, minus
REAL(SP), DIMENSION(:,,:), ALLOCATABLE :: dydaG,dydaY, &
   dydaYtemp, dt
REAL(SP) :: d2th, delta, K0, K1, K2, Ka
INTEGER(4B) :: i,j,na,nx,ni, isign, k2pos
INTEGER(4B) :: right, left, max_loc, min_loc
INTEGER(4B), DIMENSION(:,,:), ALLOCATABLE :: ind

nx=assert_eq(size(x),size(y),size(dyda),1,'fGaussYork: nx')
na=assert_eq(size(a),size(dyda),2,'fGaussYork: na')
ni=nx-1
ALLOCATE(xG(nx),yG(nx),yY(ni),YY(ni),dt(ni),dtt(ni,na), &
   Ytemp(ni), ind(ni))
ALLOCATE(dydaG(nx,na),dydaY(ni,na),dydaYtemp(ni,na))

! Initialising the components
xG(:)=x(:)
do i=1,ni
   xy(i)=x(i)
   instr(i)=instr(i)
end do
max_loc=0
left=0
right=0
ind(:,)=0
yG(:)=0.0
yY(:)=0.0
Ytemp(:,)=0.0
dydaG(:,,:)=0.0
dydaY(:,,:)=0.0
dydaYtemp(:,,:)=0.0
dtt(:,,:)=0.0
dt(:,,:)=0.0
y(:,,:)=0.0
factor(:,)=0.0_sp
!

! Gaussian function
argG(:)=(xG(:)-a(i+1))/a(i+2)
exG(:)=exp[-Pi*argG(:,)**2]
facG(:)=2.0_sp*Pi*argG(:)*exG(:)
yG(:)=yG(:)+exG(:)

dydaG(:,i+1)=2.0_sp*Pi*(xG(:)-a(i+1))*exG(:,a(i+2)**2.0_sp
dydaG(:,i+2)=2.0_sp*Pi*(xG(:)-a(i+1))*2.0_sp*exG(:,a(i+2)**3.0_sp
!

! York-size function
\[
\text{argY1}() = 2\pi a/(i+4) \times (xG() - a(i+1))^{2}/a(i+3)\times2
\]
\[
\text{argY2} = (a(i+4)+1.0)/2.0
\]
\[
\text{facY1}() = 1.0 + \text{argY1}()
\]
\[
\text{facY2}() = \text{argY1}() \times \text{argY2} / \text{facY1}()
\]

! calculate and rearrange the function
\[
y\text{temp}() = 1.0 / \text{facY1}() \times \text{argY2}
\]
\[
dt() = y\text{temp}()
\]
\[
\text{max loc} = \text{MAXLOC}(y\text{temp}, 1)
\]
\[
\text{left} = n+1 - \text{max loc}
\]
\[
\text{right} = \text{max loc}
\]
\[
\text{if} (\text{max loc} < n/2) \text{ then}
\]
\[
\text{ind}(1:left) = \text{art}(l, 1, \text{left})
\]
\[
\text{else}
\]
\[
\text{ind}(1:right) = \text{art}(1, 1, \text{right})
\]
\[
\text{end if}
\]
\[
yY(\text{ind}(1:left)) = \text{dt}(\text{max loc} + \text{ind}(1:left) - 1)
\]
\[
yY(\text{left} + \text{ind}(1:right) - 1) = \text{dt}(\text{ind}(1:right))
\]

! calculate and rearrange the first derivative
\[
dy\text{daYtemp}(i-1) = 4 \times y\text{temp}() \times \text{argY2} \times \pi \times (xG() - a(i+1)) / (a(i+4) \times (a(i+3) \times 2) \times \text{facY1}())
\]
\[
ddt() = dy\text{daYtemp}(i)
\]
\[
dy\text{daY}(\text{ind}(1:left), i+1) = dy\text{daYtemp}(\text{max loc} + \text{ind}(1:left) - 1, i+1)
\]
\[
dy\text{daY}(\text{left} + \text{ind}(1:right) - 1, i+1) = dy\text{daYtemp}(\text{ind}(1:right), i+1)
\]

! calculate and rearrange the first derivative
\[
dy\text{daYtemp}(i) = 4 \times y\text{temp}() \times \text{argY2} \times \pi \times (xG() - a(i+1)) \times 2 / (a(i+4) \times (a(i+3) \times 3) \times \text{facY1}())
\]
\[
ddt() = dy\text{daYtemp}(i, i+3)
\]
\[
dy\text{daY}(\text{ind}(1:left), i+3) = dy\text{daYtemp}(\text{max loc} + \text{ind}(1:left) - 1, i+3)
\]
\[
dy\text{daY}(\text{left} + \text{ind}(1:right) - 1, i+3) = dy\text{daYtemp}(\text{ind}(1:right), i+3)
\]

! calculate and rearrange the first derivative
\[
dy\text{daYtemp}(i+4) = -y\text{temp}() \times (0.5 \times \text{LOG} (\text{facY1} / \text{facY2}) / a(i+4) \times 2)
\]
\[
ddt() = dy\text{daYtemp}(i, i+4)
\]
\[
dy\text{daY}(\text{ind}(1:left), i+4) = dy\text{daYtemp}(\text{max loc} + \text{ind}(1:left) - 1, i+4)
\]
\[
dy\text{daY}(\text{left} + \text{ind}(1:right) - 1, i+4) = dy\text{daYtemp}(\text{ind}(1:right), i+4)
\]

! convoluting Gaussian and York-size profiles
\[
y(i) = y(i) + e(i) \times \text{convolv} (yG(), yY(1:ni, isign)) + a(i+5)
\]
\[
dy\text{da}(i, i) = \text{convolv} (yG(), yY(1:ni, isign))
\]
\[
dy\text{da}(i, i+1) = e(i) \times \text{convolv} (dy\text{daG}(i, i+1), yY(1:ni, isign))
\]
\[
dy\text{da}(i, i+2) = e(i) \times \text{convolv} (dy\text{daG}(i, i+2), yY(1:ni, isign))
\]
\[
dy\text{da}(i, i+3) = e(i) \times \text{convolv} (yG(), dy\text{daY}(1:ni, i+3, isign))
\]
\[
dy\text{da}(i, i+4) = e(i) \times \text{convolv} (yG(), dy\text{daY}(1:ni, i+4, isign))
\]
\[
dy\text{da}(i, i+5) = 1.0 \times \text{sp}
\]
\[
dy\text{da}(i, i+6) = 0.0
\]
\[
dy\text{da}(i, i+7) = 0.0
\]
\[
dy\text{da}(i, i+8) = 0.0
\]

end do

! convoluting the profiles with the instrument profile

! instrument profile is set to identity matrix for simulation

do i=1, na-1, 9
\[
y(i) = \text{convolv} (y(i), \text{inst}(1:ni, isign))
\]
\[
dy\text{da}(i, i) = \text{convolv} (dy\text{da}(i, i), \text{inst}(1:ni, isign))
\]
\[
dy\text{da}(i, i+1) = \text{convolv} (dy\text{da}(i, i+1), \text{inst}(1:ni, isign))
\]
\[
dy\text{da}(i, i+2) = \text{convolv} (dy\text{da}(i, i+2), \text{inst}(1:ni, isign))
\]
\[
dy\text{da}(i, i+3) = \text{convolv} (dy\text{da}(i, i+3), \text{inst}(1:ni, isign))
\]
\[
dy\text{da}(i, i+4) = \text{convolv} (dy\text{da}(i, i+4), \text{inst}(1:ni, isign))
\]
\[
dy\text{da}(i, i+5) = dy\text{da}(i, i+5)
\]
\[
dy\text{da}(i, i+6) = 0.0
\]
\[
dy\text{da}(i, i+7) = 0.0
\]
\[
dy\text{da}(i, i+8) = 0.0
\]
end do
DEALLOCATE(xG,yG,xY,yYtemp,ind,dydaG,dydaY,dydaYtemp)

! Introduction to Kalpha-2 peak
Kal=a(7)
Ka2=a(8)
d2th=a(9)
Ka=(2.0_sp*Ka1+1.0_sp*Ka2)/3.0_sp
delta=2.0_sp*TAN(a(2)*Pi/360.0_sp)*(Ka2-Ka1)/Ka*180.0_sp/Pi
k2pos=NINT(delta/d2th)+1
if (k2pos.EQ.0) then
  do i=1,na-1,9
    y(:,i) = y(:,i)
dyda(:,i) = dyda(:,i)
dyda(:,i+1) = dyda(:,i+1)
dyda(:,i+2) = dyda(:,i+2)
dyda(:,i+3) = dyda(:,i+3)
dyda(:,i+4) = dyda(:,i+4)
dyda(:,i+5) = dyda(:,i+5)
dyda(:,i+6) = 0.0_sp
dyda(:,i+7) = 0.0_sp
dyda(:,i+8) = 0.0_sp
  end do
else
  factor(:,1)=0.0_sp
  factor(k2pos)=1.0_sp
  do i=1,na-1,9
    y(:,i) = y(:,i) + 0.5*convolv(y(:,i),factor(1:ni),isign)
dyda(:,i) = dyda(:,i) + &
    0.5*convolv(dyda(:,i),factor(1:ni),isign)
dyda(:,i+1) = dyda(:,i+1) + &
    0.5*convolv(dyda(:,i+1),factor(1:ni),isign)
dyda(:,i+2) = dyda(:,i+2) + &
    0.5*convolv(dyda(:,i+2),factor(1:ni),isign)
dyda(:,i+3) = dyda(:,i+3) + &
    0.5*convolv(dyda(:,i+3),factor(1:ni),isign)
dyda(:,i+4) = dyda(:,i+4) + &
    0.5*convolv(dyda(:,i+4),factor(1:ni),isign)
dyda(:,i+5) = dyda(:,i+5) + &
    0.5*convolv(dyda(:,i+5),factor(1:ni),isign)
dyda(:,i+6) = 0.0_sp
dyda(:,i+7) = 0.0_sp
dyda(:,i+8) = 0.0_sp
  end do
END if
END SUBROUTINE fYS
Appendix 2b.2. Convolution

The following code calculates the convolution of data and respsns data set if isign = 1. The code is taken from Fortran Numerical Recipes (Press et al. 1989).

FUNCTION convlv(data, respsns, isign)
USE nrtype; USE numlib, ONLY : assert, nrerror
USE nr, ONLY : realf
IMPLICIT NONE
REAL(SP), DIMENSION(:,:), INTENT(INOUT) :: data
REAL(SP), DIMENSION(:,:), INTENT(IN) :: respsns
INTEGER(I4B), INTENT(IN) :: isign
REAL(SP), DIMENSION(size(data)) :: convlv
INTEGER(I4B) :: no2,n,m
COMPLEX(SPC), DIMENSION(size(data)/2) :: tmpd,tmpr
n=size(data)
m=size(respsns)
call assert(iaand(n,n-1)==0, 'n must be a power of 2 in convlv')
call assert(mod(m,2)==1, 'm must be odd in convlv')
convlv(l:m)=respsns(:)
convlv(n-(m-3)/2:n)=convlv((m+3)/2:m)
convlv((m+3)/2:n-(m-1)/2)=0.0
no2=n/2
call realft(data,1,tmpd)
call realft(convlv,1,tmpr)
if (isign == 1) then
  tmpd(1)=cmlpx(real(tmpd(1))*real(tmpd(1)))/no2, &
    aimag(tmpd(1))*aimag(tmpd(1))/no2, kind=spc
  tmpd(2)=tmpd(2)*tmpd(2)/no2
else if (isign == -1) then
  if (any(abs(tmpd(2)) == 0.0) .or. real(tmpd(1)) == 0.0 &
    .or. aimag(tmpd(1)) == 0.0) call nrerror &
    ('deconvolving at response zero in convlv')
  tmpd(1)=cmlpx(real(tmpd(1))/real(tmpd(1))/no2, &
    aimag(tmpd(1))/aimag(tmpd(1))/no2, kind=spc)
  tmpd(2)=tmpd(2)/tmpd(2)/no2
else
  call nrerror('no meaning for isign in convlv')
end if
end function convlv
END FUNCTION convlv
Appendix 2b.3. Least-squares calculations

The following three subroutines are used to perform the least-squares calculations. The code is taken from Fortran Numerical Recipes (Press et al. 1989).

```
SUBROUTINE gaussj(a,b)
  USE xrtype, USE numlib, &
  ONLY : assert_eq,nrerror,outerand,outerprod,swap
IMPLICIT NONE
REAL(SP), DIMENSION(:,,:), INTENT(INOUT) :: a,b
INTEGER(4B), DIMENSION(size(a,1)) :: ipiv,indxr,indxc
LOGICAL(LGT), DIMENSION(size(a,1)) :: lpiv
REAL(SP) :: pivinv
REAL(SP), DIMENSION(size(a,1)) :: dumc
INTEGER(4B), TARGET :: irc(2)
INTEGER(4B) :: i,l,n
INTEGER(4B), POINTER :: icol
n=assert_eq(size(a,1),size(a,2),size(b,1),'gaussj')
irc => irow(1)
icol => irow(2)
ipiv=0
do i=1,n
  lpiv = (lpiv == 0)
icr=maxloc(abs(a),outerand(lpiv,lpiv))
ipiv(icol) = piv(ipiv(icol)+1)
if (lpiv(icol) > 1) call nrerror('gaussj: &
  singular matrix (1)')
if (irow /= icol) then
  call swap(a(irow,:),a(icol,:))
call swap(b(irow,:),b(icol,:))
end if
indxr(l) = irow
indxc(l) = icol
if (a(icol,icol) == 0.0) &
  call nrerror('gaussj: singular matrix (2)')
pivinv=1.0_sp/a(icol,icol)
a(icol,icol) = 1.0
a(icol,:) = a(icol,:) * pivinv
b(icol,:) = b(icol,:) * pivinv
dumc(:,icol) = 0.0
a(icol,icol) = pivinv
a(l:icol-1,:) = a(l:icol-1,:) - &
  outerprod(dumc(l:icol-1,:),a(icol,:))
b(l:icol-1,:) = b(l:icol-1,:) - &
  outerprod(dumc(l:icol-1,:),b(icol,:))
a(icol+1,:) = a(icol+1,:) - outerprod(dumc(icol+1,:),a(icol,:))
b(icol+1,:) = b(icol+1,:) - outerprod(dumc(icol+1,:),b(icol,:))
end do
do l=l-1
call swap(a(:,indxr(l)),a(:,indxc(l)))
end do
END SUBROUTINE gaussj

SUBROUTINE covsrt(covar,maska)
  USE xrtype, USE numlib, ONLY : assert_eq,swap
IMPLICIT NONE
REAL(SP), DIMENSION(:,,:), INTENT(INOUT) :: covar
LOGICAL(LGT), DIMENSION(:,), INTENT(IN) :: maska
INTEGER(4B) :: ma,mfit,j,k
ma=assert_eq(size(covar,1),size(covar,2),size(maska),'covsrt')
mfit=count(maska)
covar(mfit+1:ma,1:ma)=0.0
```
covar(l:ma,mfit+l:ma)=0.0
k=mfit
do j=ma,1,-1 if (maska(j)) then call swap(covar(l:ma,k),covar(l:ma,j)) call swap(covar(k,l:ma),covar(j,l:ma)) k=k-1 end if end do

END SUBROUTINE covsrt

SUBROUTINE mrqmin(x,y,sig,instr,a,maska,covar,alpha,chiq,funcs,alamda)
USE nrtype; USE numlib, ONLY : assert_eq, diagmult
USE nr, ONLY : covsrt, gaussj
IMPLICIT NONE
REAL(SP), DIMENSION(:), INTENT(IN) :: x,y,sig,instr
REAL(SP), DIMENSION(:), INTENT(INOUT) :: a
REAL(SP), DIMENSION(:,:), INTENT(INOUT) :: covar,alpha
REAL(SP), INTENT(INOUT) :: chiq
REAL(SP), INTENT(INOUT) :: alamda
LOGICAL(LGT), DIMENSION(:), INTENT(IN) :: maska

INTERFACE
SUBROUTINE funcs(x,a,instr,yfit,dyda)
USE nrtype
REAL(SP), DIMENSION(:), INTENT(IN) :: x,a,instr
REAL(SP), DIMENSION(1,:), INTENT(OUT) :: yfit
REAL(SP), DIMENSION(:,:), INTENT(OUT) :: dyda
END SUBROUTINE funcs

END INTERFACE
INTEGER(I4B) :: ma,ndata
INTEGER(I4B), SAVE :: mfit
call mrqmin_private
CONTAINS

!BL
SUBROUTINE mrqmin_private
REAL(SP), SAVE :: ochiq
REAL(SP), DIMENSION(:,:), ALLOCATABLE, SAVE :: atry,beta
REAL(SP), DIMENSION(:,:), ALLOCATABLE, SAVE :: da
ndata=assert_eq(size(x),size(y),size(sig),'mrqmin: ndata')
ma=assert_eq(size(a),size(maska),size(covar,1),size(covar,2),
size(alpha,1),size(alpha,2)/), 'mrqmin: ma')
mfit=count(maska)
if (alamda < 0.0) then allocate(atriy,ma,beta,ma,da,ma,1)
alamda=0.001_sp
call mrqcoef(instr,a,alpha,beta)
ochiq=chiq
atry=a
end if
covar(l:mfit,1:mfit)=alpha(1:mfit,1:mfit)
call diagmult(covar(l:mfit,1:mfit),1.0_sp+alamda)
da(1:mfit,1)=beta(1:mfit)
call gaussj(covar(l:mfit,1:mfit),da(1:mfit,1:1))
if (alamda == 0.0) then call covsrt(covar,maska)
call covsrt(alpha,maska)
deallocate(atry,beta,da)
RETURN
end if
atry=a+unpack(da(1:mfit,1),maska,0.0_sp)
call mrqcoef(instr,atry,covar,da(1:mfit,1))
if (chiq < ochiq) then alamda=0.1_sp*alamda
ochiq=chiq
alpha(1:mfit,1:mfit)=covar(l:mfit,1:mfit)
beta(1:mfit)=da(1:mfit,1)
a=atry
else
alamda=10.0_sp*alamda
chisq=ochisq
end if
END SUBROUTINE mrgmin_private
!
SUBROUTINE mrgcof(instr,a,alpha,beta)
REAL(SP), DIMENSION(:), INTENT(IN) :: instr,a
REAL(SP), DIMENSION(:,:), INTENT(OUT) :: beta
REAL(SP), DIMENSION(:,:), INTENT(OUT) :: alpha
INTEGER(4B) :: j,k,l,m
REAL(SP), DIMENSION(size(x),size(a)) :: dyda
REAL(SP), DIMENSION(size(x)) :: dy,sig2i,wt,ymod
call funcs(x,a,instr,ymod,dyda)
sig2i=1.0_sp/(sig**2)
dy=y-ymod
j=0
do l=1,ma
   if (masks(l)) then
      j=j+1
      wt=dyda(:,l)*sig2i
      k=0
do m=1,l
         if (masks(m)) then
            k=k+1
            alpha(j,k)=dot_product(wt,dyda(:,m))
            alpha(k,j)=alpha(j,k)
         end if
      end do
   end if
   beta(j)=dot_product(dy,wt)
end do
chisq=dot_product(dy**2,sig2i)
END SUBROUTINE mrgcof

END SUBROUTINE mrgmin
Appendix 2c. Compiling the MOZAIX Code

Compilation of MOZAIX requires the following:

1. Lahey-Fujitsu Fortran 95
2. Winteracter Starter Kit (would presumably be appropriate for the full-version of Winteracter as well)
3. Fortran 95 files:
   a. mozaix_v10.f90
   b. reafit.f90 (from Numerical Recipe)
   c. fourrow.f90 (from Numerical Recipe)
   d. four1.f90 (from Numerical Recipe)
   e. numlib.f90 & num_lib.f90 (modified from a Numerical Recipe nrutil.f90 file for graphical user interface with Winteracter).
   f. constants.f90
4. Winparam.h file
5. Menu.rc file

To compile and make the executed file, the following batch file should be run in the directory where the above fortran files are present:

> LF95 mozaix_v10 reafit four1 fourrow numlib num_lib constants menu.rc -wisk
Appendix 2d. Performing Line Profile Analysis with MOZAIX

MOZAIX requires formatting of data which includes the following:

Line 1: Heading
Line 2: Initial \(2\theta\) (°)
Line 3: Final \(2\theta\) (°)
Line 4: Step-size (°)
Line 5: Radiation used
Line 6: Wavelength 1 (e.g. for Cu K\(\alpha_1\) = 1.54056Å)
Line 7: Wavelength 2 (set the same to Wavelength 1 for monochromatic radiation)
Line 8: Measurement date
Line 9: Counting time (second)
Line 10: Specimen identity
Line 11: Instrument used

Line 12-13: Consists of 5 columns of data representing the instrument full-width at half-maximum (FWHM) following the expression:

\[
FWHM = c_1(2\theta)^2 + c_2(2\theta) + c_3
\]

where \(c_1, c_2\) and \(c_3\) are numbers in column 3, 4 and 5, respectively. Numbers in column 1 and 2 denote the \(2\theta\) range which follows the FWHM expression.

Line 14-15: Consists of 5 columns of data representing the instrument pseudo-Voigt mixing parameters (\(\eta\)) following the expression:

\[
\eta = k_1(2\theta)^2 + k_2(2\theta) + k_3
\]

where \(k_1, k_2\) and \(k_3\) are numbers in column 3, 4 and 5, respectively. Numbers in column 1 and 2 denote the \(2\theta\) range which follows the \(\eta\) expression.

Line 16: A sign for start of intensity data
Line 17 - end: Intensity data
Following is an example of the data file:

<table>
<thead>
<tr>
<th>Time</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
<th>Value 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>90.00</td>
<td>0.000000146909</td>
<td>0.00024139700</td>
<td>0.01238680000</td>
<td></td>
</tr>
<tr>
<td>90.00</td>
<td>180.00</td>
<td>0.000000146909</td>
<td>0.00024139700</td>
<td>0.01238680000</td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td>90.00</td>
<td>0.000046900094</td>
<td>-0.00946780000</td>
<td>0.64990800000</td>
<td></td>
</tr>
<tr>
<td>90.00</td>
<td>180.00</td>
<td>0.000046900094</td>
<td>-0.00946780000</td>
<td>0.64990800000</td>
<td></td>
</tr>
</tbody>
</table>
Following is the procedure to perform refinement using *MOZAIX*:

1. Double-click on the MOZAIX_V10.exe file. The following display will appear on the screen. Click OK.

2. Open a *.dat file from File-Open menu or use Ctrl-O. Select the file and click OK.
3. Select the type of radiation to allow setting the number of points (can be altered by Range-Base menu or Alt-B).

4. Select Range-2theta or Alt-N to choose a peak for analysis.
5. Search the peak position by pressing Search menu or Alt-S.

6. Select the convolution profile function through the Profile–MozaiXYG menu or by pressing Alt-M.
7. Give initial values prior to refinement. Click OK and observe the calculated and the difference pattern (blue and green solid lines, respectively). Adjust values of parameters and intensity scaler if required. *MOZAIX* allows change of number of cycle and handling of asymmetric peak by exclusion of refinement of peak position.
8. Perform refinement through the Refinement – Run menu or by pressing Alt-R. Main information are given in the root window. Details of results are given from the Show-Results menu. First section gives the criteria of fit, the second gives the strain and size results and the third provides the correlation coefficients between parameters.
9. The size distribution plot can be observed from the Show-Size distribution menu.

10. Refinement results and data for plotting (observed, calculated and difference patterns) can be saved through the File-Save-Results and File-Save-Plots menus, respectively. The refinement results are saved as *.mou file and the data for plotting are saved as *.plt file.
11. Other features included in MOZAIK are the following:

a. refinement using the Gaussian, Lorentzian and pseudo-Voigt functions

b. simulation of diffraction patterns using the pseudo-Voigt and convolution functions. Simulation involves the convolution of the selected function and the instrument profile which is developed using the pseudo-Voigt function.

c. estimation of initial values for the convolution function by a refinement using the pseudo-Voigt function.

d. change of the base width through Range-Base menu or Alt-B.
Appendix 2e. Data Simulation and Refinement Using The Convolution and Pseudo-Voigt Functions

Table A2.1 shows the pseudo-Voigt refinement results for selected simulated patterns made with the convolution model. The simulated patterns were made with values for interplanar spacing is 4.2 Å, wavelength 1.5 Å and peak position 127.0°2θ.

<table>
<thead>
<tr>
<th>Specimen Characters</th>
<th>Simulated Pattern$^1$</th>
<th>Refinement$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ (nm)</td>
<td>$\varepsilon$ (x 1000)</td>
<td>$W_D$</td>
</tr>
<tr>
<td>100</td>
<td>0.05</td>
<td>0.1926</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
<td>0.1926</td>
</tr>
<tr>
<td>150</td>
<td>0.05</td>
<td>0.1284</td>
</tr>
<tr>
<td>150</td>
<td>0.1</td>
<td>0.1284</td>
</tr>
<tr>
<td>100</td>
<td>0.4</td>
<td>0.1926</td>
</tr>
<tr>
<td>150</td>
<td>0.4</td>
<td>0.1284</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
<td>0.1926</td>
</tr>
<tr>
<td>100</td>
<td>0.4</td>
<td>0.1926</td>
</tr>
<tr>
<td>100</td>
<td>0.05</td>
<td>0.1926</td>
</tr>
<tr>
<td>100</td>
<td>0.4</td>
<td>0.1926</td>
</tr>
</tbody>
</table>

$^1$ Simulated patterns were made using the convolution function.

$^2$ Refinement of the simulated patterns was performed using the pseudo-Voigt function.

$^3$ The size distribution parameter, $\beta$, should also be considered as a characteristic of a material.

Following are points which can be deduced from the table:

1. If size broadening is dominant, for $\beta = 1.0$, the profile is a pure-Lorentzian.

2. If size broadening is dominant, for $\beta = 0.8$ (presumably for $\beta < 1.0$), the profile is ‘super-Lorentzian’, indicated by the mixing parameter values which are larger than unity.
APPENDIX 3. CRYSTAL STRUCTURE MODELS FOR MgO, LaB₆ AND Y₂O₃

1. Crystal structure for Magnesium Oxide, MgO (Sasaki, Fujino & Takeuchi 1979).

Space group : F m ̅3 m (225) - cubic
Unit cell parameters : a = b = c = 4.217 Å

<table>
<thead>
<tr>
<th>Atom Position</th>
<th>Wyckoff Code</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>4b</td>
<td>½</td>
<td>½</td>
<td>½</td>
</tr>
</tbody>
</table>

2. Crystal structure of lanthanum hexaboride, LaB₆ (Korsukova et al. 1984)

Space group : P m ̅3 m (221) - cubic
Unit cell parameters : a = b = c = 4.157 Å

<table>
<thead>
<tr>
<th>Atom Position</th>
<th>Wyckoff Code</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>6e</td>
<td>0.19956(16)</td>
<td>½</td>
<td>½</td>
</tr>
</tbody>
</table>