

STUDY OF HIGH-TEMPERATURE THERMAL STABILITY OF MAX PHASES IN VACUUM

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ABSTRACT

The susceptibility of two *MAX* phases (Ti_2AlN and Ti_4AlN_3) to high-temperature thermal dissociation in a dynamic environment of high-vacuum has been investigated using *in-situ* neutron diffraction. In high vacuum, these phases decomposed above 1400°C through the sublimation of Ti and Al elements, forming a surface coating of TiN. The kinetics of isothermal phase decomposition was modelled using the Avrami equation and the Avrami exponent (n) of isothermal decomposition of Ti_2AlN and Ti_4AlN_3 was determined to be 0.62 and 0.18 respectively. The characteristics of thermal stability and phase transitions in Ti_2AlN and Ti_4AlN_3 are compared and discussed.

INTRODUCTION

MAX phases are nano-layered ceramics with the general formula $\text{M}_{n+1}\text{AX}_n$ ($n = 1-3$), where M is an early transition metal, A is a group A element, and X is either carbon and/or nitrogen. These materials exhibit a unique combination of characters of both ceramics and metals.¹⁻⁵ Like ceramics, they have low density, low thermal expansion coefficient, high modulus and high strength, and good high-temperature oxidation resistance. Like metals, they are good electrical and thermal conductors, readily machinable, tolerant to damage, and resistant to thermal shock. The unique combination of these interesting properties enables these ceramics to be a promising candidate material for use in diverse fields, especially in high temperature applications.

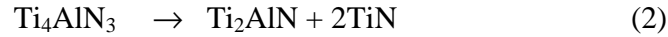
However, these *MAX* phases, Ti_3SiC_2 in particular, have poor wear resistance due to low hardness (~ 4 GPa) and are susceptible to thermal dissociation at $\sim 1400^\circ\text{C}$ in inert environments (e.g., vacuum or argon) to form a protective surface coating of TiC.⁶⁻¹¹ Depth-profiling by x-ray diffraction of Ti_3SiC_2 annealed in vacuum at 1500°C has revealed a graded phase composition with more than 90 wt% TiC on the surface and decreasing rapidly with an increase in depth.^{6,7} A similar phenomenon has also been observed for Ti_3AlC_2 whereby it decomposes in vacuum to form TiC and Ti_2AlC .¹⁰ It follows that this process of thermal dissociation to form protective coatings of binary carbide, nitride or carbo-nitride will also occur in other *MAX* phases such as Cr_2GeC , Ta_4AlC_3 , Ti_2AlN , Ti_4AlN_3 and $\text{Ti}_2\text{AlC}_{0.5}\text{N}_{0.5}$. The formation of a graded surface coating such as TiC, TiN or TiCN has the potential to impart high hardness and wear-resistance to the otherwise soft but damage-resistant substrate.^{1,4}

The fundamental knowledge about the thermal stability of technologically important *MAX* phases is still very limited and the actual process of phase dissociation is poorly understood. This limited understanding has generated much controversy concerning the high-temperature thermochemical stability of *MAX* phases.¹²⁻¹⁷ We have recently investigated the thermal stability of Ti_3SiC_2 , Cr_2AlC , Ti_2AlC and Ti_3AlC_2 in vacuum at up to 1550°C and the results indicated 211 phases to be more resistant to phase dissociation than 312 phases.⁸⁻¹⁰ For instance, both Ti_3SiC_2 and Ti_3AlC_2 decompose readily to TiC forming an intermediate phase of $\text{Ti}_5\text{Si}_3\text{C}$ and Ti_2AlC respectively. The apparent activation energies for the decomposition of sintered Ti_3SiC_2 , Ti_3AlC_2 and Ti_2AlC were determined to be 179.3, -71.9 and 85.7 kJ mol^{-1} , respectively.¹⁰

Hitherto, virtually no work has been reported for ternary nitrides such as Ti_2AlN and Ti_4AlN_3 . It also remains unknown whether these *MAX* phases will decompose like 211 and 312 ternary carbides via the sublimation of group *M* element and the de-intercalation of group *A* element as follows:



In addition, the 413 phase is expected to form a lower order 211 phase during the initial decomposition process as follows, prior to the sublimation of *A* and *M* elements (see equation 1):



In this paper, we describe the use of high-temperature neutron diffraction to study the dynamic processes of phase stability of Ti_2AlN and Ti_4AlN_3 in high-vacuum. The kinetics of isothermal phase decomposition was modelled using the Avrami equation and the Avrami constants were evaluated. The characteristics of thermal stability and phase transitions in Ti_2AlN and Ti_4AlN_3 are compared and discussed.

EXPERIMENTAL PROCEDURE

Dense hot-pressed cylindrical bars of Ti_2AlN , and Ti_4AlN with diameter 10 mm and height 20 mm were used for the study. The samples were not single phase but contained 6.9 and 0.8 wt% TiN. High temperature time-of-flight neutron diffraction in a vacuum furnace ($\sim 10^{-5}$ torr) fitted with tantalum elements was used to monitor the structural evolution of phase decomposition in the *MAX* phases from 20 to 1800°C in real time. A precision electronic scale with reading to five decimal places was used to measure the weight of samples before and after vacuum-decomposition at a particular temperature. Neutron diffraction data were collected using the Polaris medium resolution, high intensity powder diffractometer at the UK pulsed spallation neutron source ISIS, Rutherford Appleton Laboratory.¹⁸ The diffraction patterns were collected at 20°C and then at between 1500 and 1800°C with a heating rate of 20°C/min. The data acquisition times were 15 min for the room temperature diffraction pattern, and between 15 – 120 min for each of the diffraction patterns collected at elevated temperatures. Normalised data collected in the highest resolution, backscattering detector bank over the *d*-spacing range of ~ 0.4 - 3.2\AA were analysed using (a) the LAMP software and (b) the Full-Prof software to compute the changes in the phase content of *MAX* phases and *MN* during vacuum-annealing at elevated temperatures. In the former, the integrated peak intensities of lines (013) and (111) were used for calculating the relative phase content of Ti_4AlN_3 and TiN respectively. In the latter, the Rietveld method was used to compute the changes in the phase content of Ti_2AlN and TiN during vacuum-annealing.

The kinetic behaviour of the isothermal decomposition of Ti_4AlN_3 and Ti_2AlN at 1500 and 1550°C respectively was modeled using the Avrami equation to describe the fraction of decomposed *MAX* phase (*y*) as a function of time (*t*) as follows:¹⁹

$$y(t) = y(0) + \exp(-kt^n) - 1 \quad (3)$$

where *k* and *n* are time-independent constants for the particular reaction.

RESULTS AND DISCUSSION

(a) Thermal Decomposition and Phase Transitions

The phase evolutions of Ti_2AlN and Ti_4AlN_3 at various temperatures as revealed by in-situ neutron diffraction are shown in [Figures 1-3](#). Samples used in this experiment were not single-phase

with TiN as the main impurity. For Ti_4AlN_3 , it began to decompose to TiN quite slowly at 1450°C but became more rapid above 1500°C (Fig. 1). It was almost completely decomposed after annealing at 1600°C for less than 30 min. A total weight loss of $\sim 11.6\%$ and 5.9% was observed for decomposition at 1600 and 1500°C respectively, which may be attributed to the release of gaseous Al and Ti by sublimation during the decomposition process. These results concur with our previous work on ternary carbides.⁹⁻¹² However, in contrast to Ti_3AlC which undergoes an intermediate decomposition to the lower order Ti_2AlC ,⁹⁻¹¹ such a lower order Ti_2AlN was not observed during the decomposition of Ti_4AlN_3 . Nevertheless, such a decomposition process via an intermediate 211 phase cannot be completely ruled out, i.e.

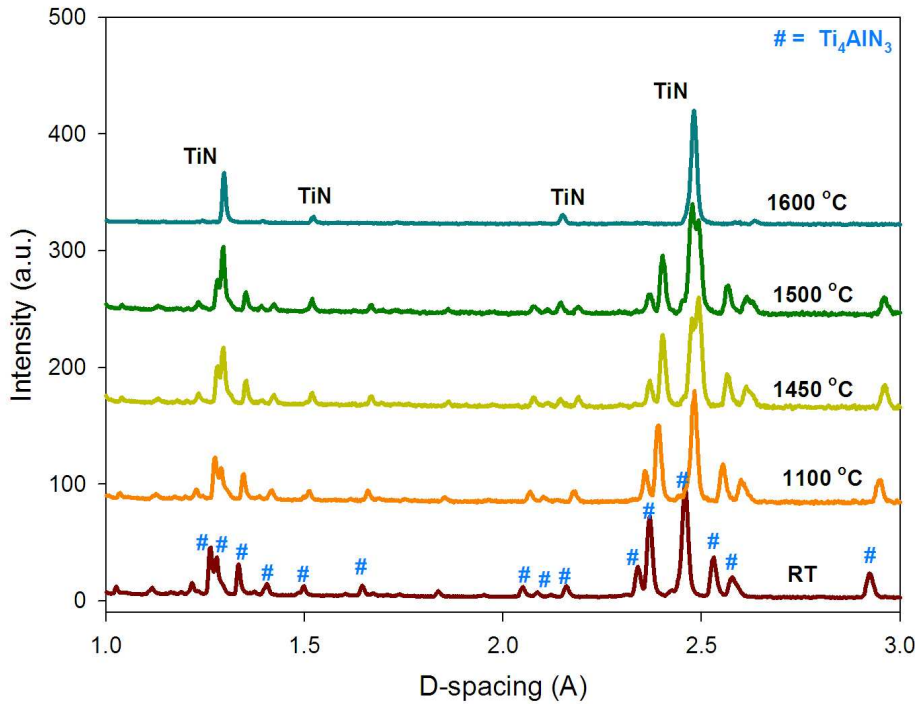


Fig. 1: Phase transitions during the decomposition of Ti_4AlN_3 at up to 1600°C .

In spite of having a higher content of TiN as impurity, Ti_2AlN appeared to be much more stable against decomposition than Ti_4AlN_3 . It began to decompose to TiN slowly after 1550°C but became quite rapid at 1600°C (Fig. 2). It was almost completely decomposed after annealing at 1700°C for just over 2 hours and at 1800°C for about 20 min. A total weight loss of more 20.0% was observed for decomposition at 1600°C and above. Below 1600°C , the weight loss was 5.0% and 0.95% at 1550°C and 1500°C respectively.

A closer look at Figure 2 shows that a new phase Ti_4AlN_3 formed when Ti_2AlN was vacuum-annealed at 1600°C and its abundance increased with time and persisted when cooled down to room

temperature (Fig. 3). However, it disappeared when the temperature was increased to 1700°C and above. Possible reactions for the formation of Ti_4AlN_3 during the decomposition of Ti_2AlN and its subsequent disappearance are as follows:

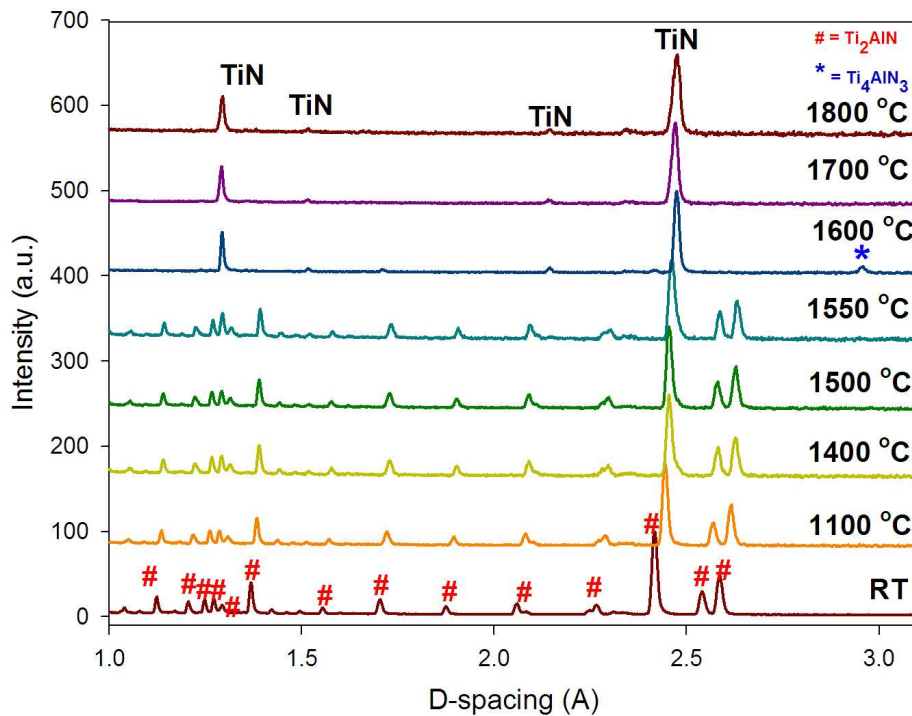
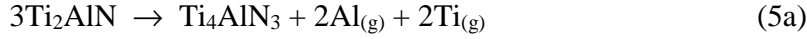


Fig. 2: Phase transitions during the decomposition of Ti_2AlN at up to 1800°C.

As previously mentioned, the weight losses of up to 6% and over 20% in decomposed Ti_2AlN and Ti_4AlN_3 respectively can be attributed to the release of gaseous Al and Ti by sublimation during the decomposition process because the vapor pressures of both Al and Ti exceed the ambient pressure of the furnace (i.e. $\leq 5 \times 10^{-5}$ torr) at $\geq 1500^\circ C$.²⁰ Since the vapor pressure of a substance increases non-linearly with temperature according to the Clausius-Clapeyron relation,²¹ the volatility of Al and Ti will increase with any incremental increase in temperature. Figure 4 shows the vapour pressures of various elements at elevated temperature and at a vapour pressure of 5×10^{-5} torr in the vacuum furnace, Al and Ti become volatile at temperature greater than 950 and 1450°C respectively. Thus, at the temperature of well over 1500°C used in this study, both Al and Ti should become volatile and sublime readily and continuously in a dynamic environment of high vacuum. When the vapor pressure becomes sufficient to overcome ambient pressure in the vacuum furnace, bubbles will form inside the bulk of the substance which eventually appear as voids on the surface of decomposed MAX phase.⁹⁻¹²

The evidence of voids formation can be clearly discerned from the porous surface damage of decomposed Ti_2AlN and Ti_4AlN_3 (Fig. 5). A closer look at Fig. 4 also explains why Ti_3SiC_2 is more resistant to decomposition than Ti_3AlC_2 or Ti_4AlN_3 because Si has a lower vapour pressure than Al. Thus, the use of vapor pressure of elements such as Fig. 4 can be used to predict the susceptibility of MAX phases to thermal decomposition. Alternatively, the sublimation pressure of an element can be estimated from the following equation:²²

$$\ln P_{solid}^S = \ln P_{liquid}^S - \frac{\Delta H_m}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (6)$$

where P_{solid}^S = sublimation pressure of the solid component at the temperature $T < T_m$; P_{liquid}^S = extrapolated vapor pressure of the liquid component at the temperature $T < T_m$; ΔH_m = heat of fusion; R = gas_constant; T = sublimation temperature, and T_m = melting point temperature.

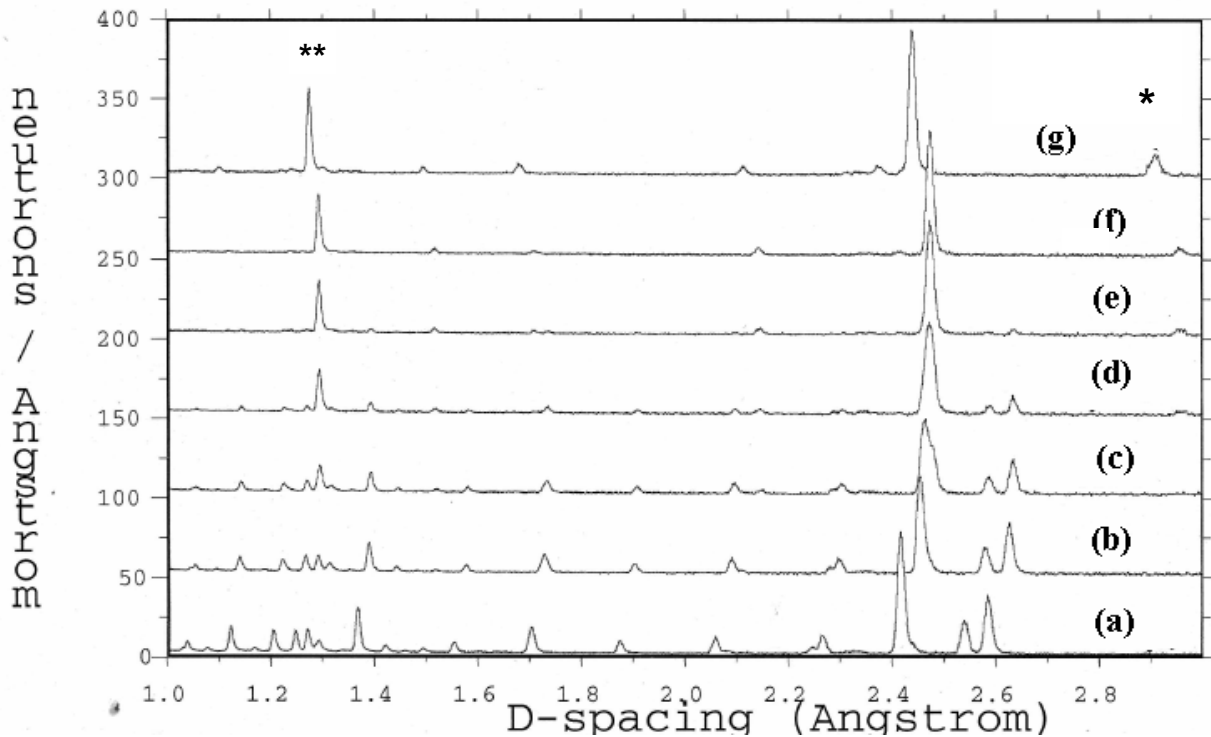


Fig. 3: Diffraction patterns of Ti_2AlN vacuum annealed at: (a) 20°C; (b) 1400°C; (c) 1600°C/10 min; (d) 1600°C/40 min; (e) 1600°C/80 min; (f) 1600°C/130 min, and (g): Cooled to 20°C. Note the formation of Ti_4AlN_3 at 1600°C. [Legend: * = Ti_4AlN_3 ; ** = TiN]

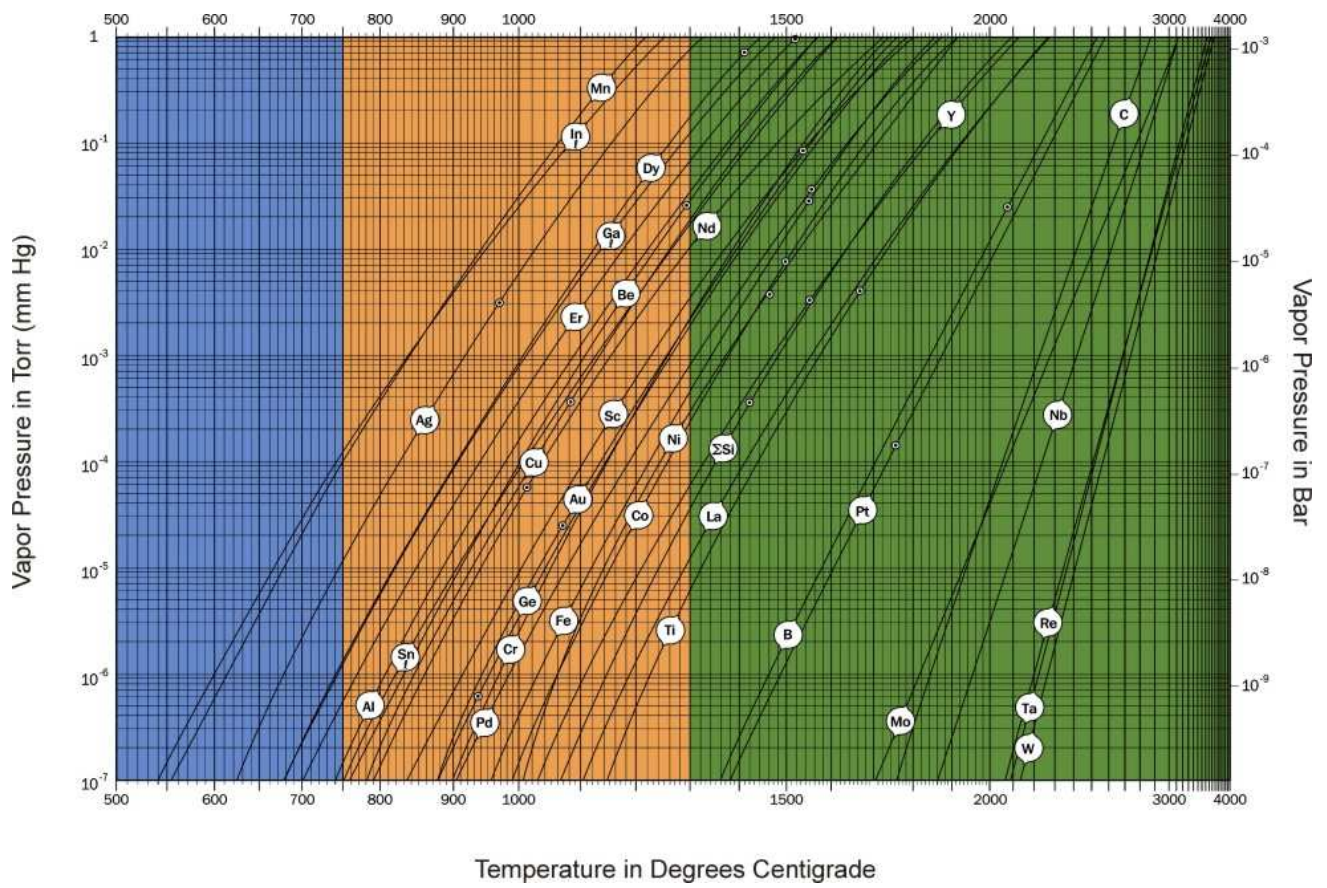
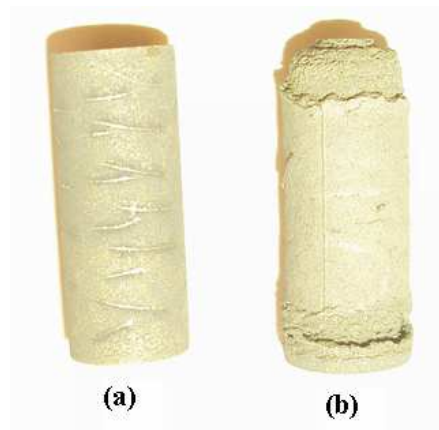
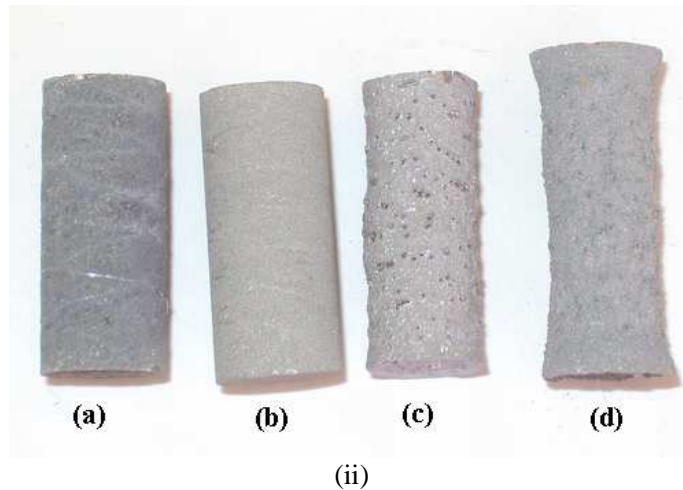


Fig. 4 Vapor pressure of elements at various temperatures.²⁰



(i)

[(a) Before decomposition; (b) after decomposition at 1600°C for 440 min.]



(ii)
 [(a) Before decomposition; (b-d) after decomposition at 1500°C/120 min, 1550°C/460 min & 1600°C/420 min]

Fig. 5: Surface conditions of (i) Ti_4AlN_3 and (ii) Ti_2AlN before and after thermal decomposition in vacuum.

(b) Isothermal Phase Decomposition and Avrami Kinetics

Fig. 6 shows the isothermal decomposition of Ti_4AlN_3 at 1500°C which was quite rapid initially but slowed down significantly after 30 minutes dwell. More than 40% of Ti_4AlN_3 decomposed after vacuum annealing at 1500°C for 400 minutes. In contrast, the extent of decomposition for Ti_2AlN was much less with only 20% decomposed after 300 minutes dwell at 1550°C (Fig. 7). This implies that Ti_2AlN has a significantly higher resistance to thermal decomposition than Ti_4AlN_3 . A possible reason for the high susceptibility of Ti_4AlN_3 to decomposition is either the existence of a lower order 211 phase or the much weaker Al-Ti bonding in this more complex layered compound where Al lies in every fifth layer.³ In contrast, every third layer in the 211 compound lies the Al atoms, resulting in shorter but stronger Al-Ti bonds which provides more resistance to decomposition via out-diffusion of Al from the bulk to the surface.

During the isothermal decomposition of 211 and 413 phases at 1550 and 1500°C respectively, the Avramii kinetics of decomposition was modeled using Equation (3) and the Avrami constants were evaluated. The Avrami fit of the isothermal decomposition of Ti_4AlN_3 and Ti_2AlN is shown in Fig. 6 and Fig. 7 respectively. The calculated Avrami exponent (n) and Avrami constant (k) for the two MAX phases are summarized in Table 1. In general, when the value of n is large (e.g. 3 or 4), a 3-dimensional nucleation and growth processes are involved.²³ High values of n can also occur when nucleation occurs on specific sites such as grain boundaries or impurities which rapidly saturate soon after the transformation begins. Initially, nucleation may be random and growth unhindered leading to high values for n . Once the nucleation sites are consumed the transformation will slow down or cease. Furthermore, if the distribution of nucleation sites is non-random then the growth may be restricted to 1 or 2-dimensions. Site saturation may lead to n values of 1, 2 or 3 for surface, edge and point sites, respectively.¹⁹ Since the values of n obtained in this study for both 211 and 413 phases are less than 1.0, this implies that the decomposition process is driven by highly restricted out-diffusion of aluminium from the bulk to the surface of the sample and into the vacuum.

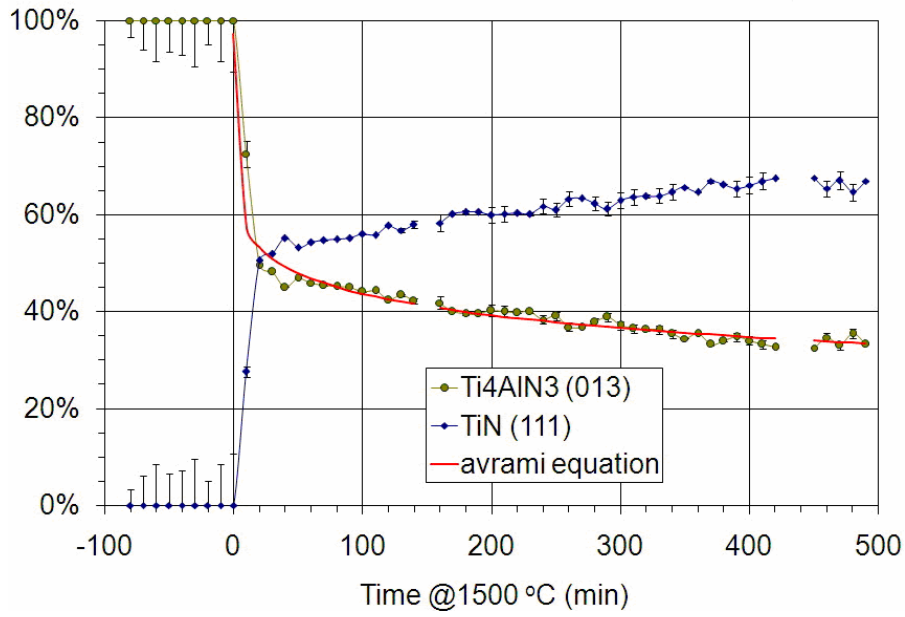


Fig. 6: Time-dependent phase abundance and Avrami fit of isothermal decomposition of Ti_4AlN_3 at 1500°C .

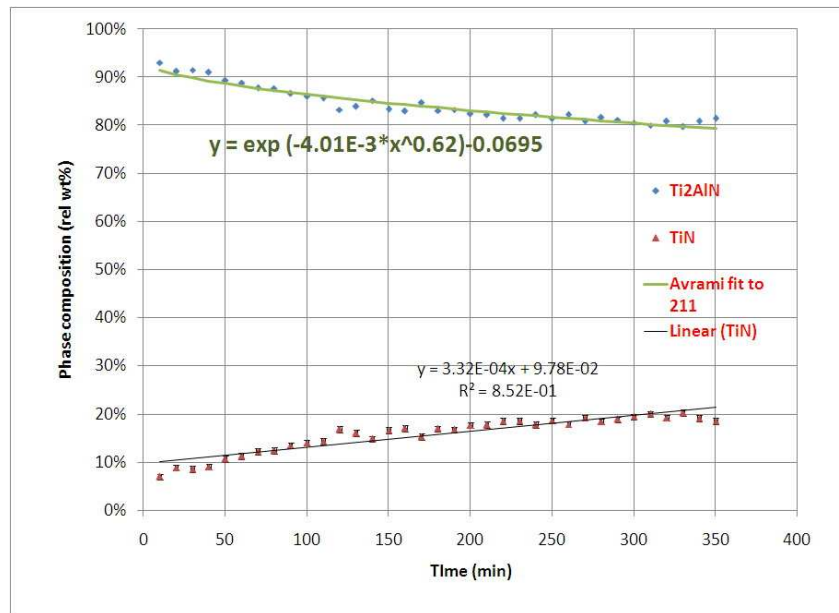


Fig. 7: Time-dependent phase abundance and Avrami fit of isothermal decomposition of Ti_2AlN at 1550°C .

Table 1. Comparison of the decomposition of MAX 211 and 413 phases.

MAX phase	Avrami exponent (n)	Avrami constant (k) $\text{mol\%} \cdot (\text{min})^{-n}$
Ti_4AlC_3	0.18	0.37
Ti_2AlN	0.62	4.01×10^{-3}

CONCLUSIONS

The high-temperature thermal stability of Ti_2AlN and Ti_4AlN_3 in a dynamic environment of high-vacuum has been studied using in-situ neutron diffraction. Both 211 and 413 phases were susceptible to decomposition above $1400^\circ C$ through sublimation of Al and Ti elements, resulting in a surface coating of TiN being formed. The kinetics of isothermal phase decomposition was modelled using the Avrami equation and the Avrami constants (n and K) of isothermal decomposition of Ti_2AlN and Ti_4AlN_3 were determined to be 0.62, 0.18 and 4.01×10^{-3} , $0.37 \text{ mol\%} \cdot (\text{min})^{-n}$ respectively.

ACKNOWLEDGEMENTS

This work formed part of a much broader project on the thermal stability of ternary carbides which is funded by an ARC Discovery-Project grant (DP0664586) and an ARC Linkage-International grant (LX0774743) for one of us (IML). Neutron beamtime at ISIS (RB920121) was provided by the Science and Technology Facilities Council together with financial support from an AMRFP grant and LIEF grant (LE0882725).

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