

Editorial Manager(tm) for Journal of Physics: Conference Series
Manuscript Draft

Manuscript Number: ICNS5

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Article Type: Contributed (note: 4 page limit)

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Comparison of thermal stability in MAX 211 and 312 phases

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Abstract. The susceptibility of four MAX phases (Ti_2AlC , Cr_2AlC , Ti_3AlC_2 , and Ti_3SiC_2) to high-temperature thermal dissociation in vacuum has been investigated using *in-situ* neutron diffraction. In high vacuum, these phases decomposed above 1400°C through the sublimation of *M* and *A* elements, forming a surface coating of MC. The apparent activation energies for the decomposition of sintered Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC were determined to be 169.6, -71.9, and 85.7 kJ mol^{-1} , respectively. The spontaneous release of Ti_2AlC and TiC from de-intercalation during decomposition of Ti_3AlC_2 resulted in a negative activation energy.

1. Introduction

A group of layered ternary ceramics with the general formula $M_{n+1}AX_n$ ($n = 1-3$, *M* is an early transition metal, *A* is a group A element, and *X* is either carbon and/or nitrogen) were found to be excellent candidate materials for high temperature applications, due to the unique combination of both metallic and ceramic properties [1-6]. MAX phases are layered hexagonal (space group P_{63}/mmc) $Z = 2$. In brief, the M_6X octahedra are edge sharing and are identical to the NaCl-type structure of the corresponding binary carbides. These M_6X octahedra are interleaved by close-packed planes of the *A* element [7-10]. Ternary carbides such as Ti_3AlC_2 , Ti_3SiC_2 , Ti_2AlC , and Cr_2AlC are common representatives of the MAX phases. The electrical and mechanical properties, and the oxidation characteristics of these four compounds has been well studied [9, 11-21], however, very little is published on their susceptibility to high-temperature phase dissociation in vacuum.

In this paper, the thermal stability and the corresponding phase dissociation of these ternary carbides in vacuum was investigated using high-temperature *in-situ* neutron diffraction. The apparent activation energies of phase decomposition were calculated. The characteristics of thermal stability in MAX 211 (Ti_2AlC and Cr_2AlC) and 312 phases (Ti_3AlC_2 and Ti_3SiC_2) are compared and discussed.

2. Experimental

The collection of high-temperature *in-situ* neutron diffraction data were collected using Wombat (the high-intensity neutron powder diffractometer) at the OPAL source in Australia. Data were collected

using neutrons with incident wavelength of $\lambda = \sim 1.660 \text{ \AA}$ from 15 to $135^\circ 2\theta$ at a step size of 0.125° , with the use of the oscillating tertiary collimator. Rietica 1.7.7 was used for phase identification and Rietveld refinement. The optimized parameters during refinement were background coefficients, zero-shift error, peak shape parameters, cell parameters, and anisotropic thermal factors. The residual values of the refinement, statistical reliability factor of Bragg (R_B), R-weighted pattern (R_{wp}), R-expected (R_{exp}), and the goodness-of-fit (χ^2), were evaluated. In Rietica, χ^2 is defined as the square of the ratio of R_{wp} to R_{exp} .

Solid bars of Ti_2AlC , Cr_2AlC , Ti_3AlC_2 , and Ti_3SiC_2 were used in this study. The temperature of sample environment was controlled by a closed cylindrical niobium vacuum furnace (10^{-6} - 10^{-8} torr). The sample was held by vanadium wire and heated to $1000^\circ C$ at a heating rate of $10^\circ C/min$ and thereafter at $5^\circ C/min$ to $1550^\circ C$. The dwell times at between 1000 and $1550^\circ C$ are shown in Table 1. Diffraction patterns were collected every minute from starting to the end of the experiment.

Table 1. Heating schedule during the in-situ neutron diffraction study.

Temperature ($^\circ C$)	Dwell time (min)	Temperature ($^\circ C$)	Dwell time (min)
1000	30	1400	200
1100	30	1450	200
1200	30	1500	200
1300	30	1550	200

The decomposition rates at different temperatures were calculated and the corresponding apparent activation energies were determined in order to understand further the mechanism of high-temperature phase dissociation in vacuum.

3. Results and Discussion

3.1 Phase Transitions during Thermal Dissociation of MAX 211 and 312 Phases

The phase evolution of MAX phases and the relative phase abundances at various temperatures as revealed by in-situ neutron diffraction is shown in Figure 2. Samples used in this experiment were not single-phase with TiC as the most common impurity. The starting compositions of each sample are shown in Figure 2. For Ti_3SiC_2 , it decomposed to TiC above $1300^\circ C$ (Fig. 2a). A weight loss of $\sim 4\%$ was observed for decomposed Ti_3SiC_2 which may be attributed to the release of gaseous Ti and Si by sublimation during the decomposition process. These results agree with those reported by Low and co-workers [22-23]. For Ti_3AlC_2 , its decomposition into TiC and Ti_2AlC as intermediate phase was observed at $\geq 1400^\circ C$ (Fig. 2b). However, at higher temperatures, when compared to TiC, a smaller growth rate for Ti_2AlC may indicate that Ti_2AlC experienced further decomposition into TiC via the sublimation of Al and Ti, similar to decomposition of Ti_3SiC_2 . In contrast to Ti_3AlC , no intermediate phase was observed for the decomposition of Ti_3SiC_2 . This difference can be attributed to the fact that Ti_3SiC_2 is the only stable ternary phase in Ti-Si-C system. For Ti_2AlC (Fig. 2c), the formation of TiC results mainly from the decomposition of Ti_3AlC_2 as the impurity phase. Ti_2AlC would only decompose above $1450^\circ C$ by sublimation of Ti and Al. Figure 2(d) shows the excellent stability of Cr_2AlC up to $1450^\circ C$ where no observable phase dissociation was detected. However, it started to react with the vanadium wire and became unstable above $1450^\circ C$. Like Ti_2AlC , it would only decompose above $1450^\circ C$ via the sublimation of Cr and Al. In general, the decomposition process of both 211 and 312 phases can be described by the reaction of: $M_{n+1}AX_n \rightarrow nMX + A + M$.

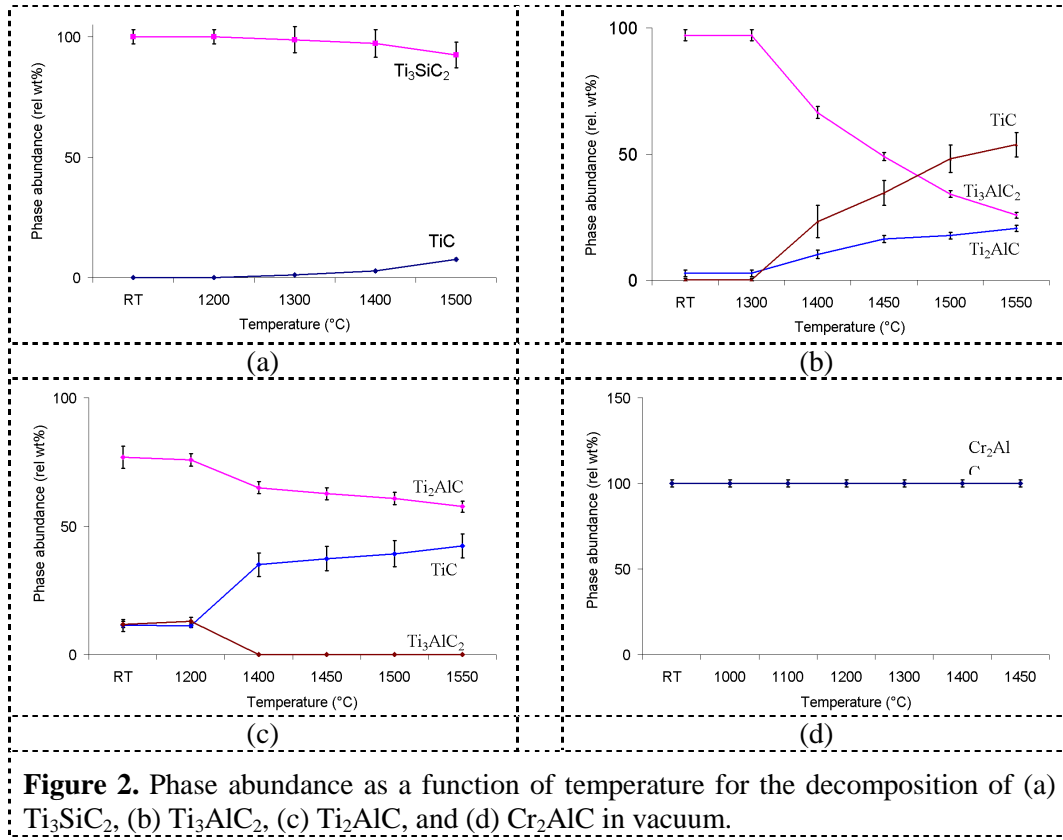


Figure 2. Phase abundance as a function of temperature for the decomposition of (a) Ti_3SiC_2 , (b) Ti_3AlC_2 , (c) Ti_2AlC , and (d) Cr_2AlC in vacuum.

3.2 Apparent Activation Energies during Isothermal Decomposition

During the isothermal decomposition of 211 and 312 phases at different temperatures, the decomposition rates were calculated by analyzing the relationship between the phase abundances and soaking time. These rates were used to determine the corresponding apparent activation energy of decomposition using the Arrhenius equation [24], $k = A \exp(-E/RT)$, where k is the reaction rate, E is activation energy, R is gas constant, T is absolute temperature and A is a constant.

The calculated apparent activation energies for the four MAX phases and the proposed reactions are summarized and listed in Table 1.

Table 1. Comparison of the decomposition of MAX 211 and 312 phases.

MAX phase	Apparent activation energy	Proposed reactions
Ti_3SiC_2	$169.6 \text{ kJ mol}^{-1}$	$Ti_3SiC_{2(s)} \rightarrow 2TiC_{(s)} + Ti_{(g)} + Si_{(g)}$ (1)
Ti_3AlC_2	$-71.9 \text{ kJ mol}^{-1}$	$Ti_3AlC_{2(s)} \rightarrow Ti_2AlC_{(s)} + TiC_{(s)}$ (2a)
		$Ti_2AlC_{(s)} \rightarrow TiC_{(s)} + Ti_{(g)} + Al_{(g)}$ (2b)
Ti_2AlC	85.7 kJ mol^{-1}	$Ti_2AlC_{(s)} \rightarrow TiC_{(s)} + Ti_{(g)} + Al_{(g)}$ (3)
Cr_2AlC	Stable in vacuum up to 1450 °C.	$2Cr_2AlC_{(s)} \rightarrow Cr_3C_{2(s)} + Cr_{(g)} + 2Al_{(g)}$ (4)

A negative activation energy obtained for Ti_3AlC_2 can be attributed to the presence of weak Ti-Al bonds [25] which will favour spontaneous decomposition through the de-intercalation of TiC from the crystal structure (see Eq. 2a). Subsequent decomposition of released Ti_2AlC at higher temperature (see

Equation 2b) would involve a small but positive activation energy. It follows that the high activation energy obtained for Ti_3SiC_2 can be attributed to much stronger bonding between Ti and Si, leading to better resistance against thermal dissociation *via* sublimation of Ti and Si from the crystal structure. The lower but positive activation energy observed for decomposition of Ti_2AlC (see Eq. 3) is related to weaker Ti-Al bonds and thus its susceptibility to sublimation in vacuum at elevated temperature.

4. Conclusions

The high-temperature thermal stability of MAX 211 and 312 phases in vacuum has been studied using in-situ neutron diffraction. Both 211 and 312 phases were susceptible to decomposition above 1400°C through sublimation of M and A elements, resulting in a surface coating of TiC being formed. The apparent activation energies for the decomposition of sintered Ti_3SiC_2 , Ti_3AlC_2 and Ti_2AlC were determined to be 169.6, -71.9 and 85.7 kJ mol^{-1} , respectively. The negative activated energy for Ti_3AlC_2 can be attributed to the release of Ti_2AlC and TiC from the crystal structure via spontaneous de-intercalation.

Acknowledgements

This work was funded by an ARC Discovery-Project grant (DP0664586) and an ARC Linkage-International grant (LX0774743) for one of us (IML). The collection of diffraction data was conducted at the OPAL research reactor in ANSTO with financial support from AINSE (08/329 & 09/606).

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