Comparison of thermal stability in $\text{MAX} \, 211$ and $312$ phases

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Abstract. The susceptibility of four $\text{MAX}$ phases ($\text{Ti}_2\text{AlC}$, $\text{Cr}_2\text{AlC}$, $\text{Ti}_3\text{AlC}_2$, and $\text{Ti}_3\text{SiC}_2$) to high-temperature thermal dissociation in vacuum has been investigated using in-situ neutron diffraction. In high vacuum, these phases decomposed above $1400^\circ\mathrm{C}$ through the sublimation of $M$ and $A$ elements, forming a surface coating of $MC$. The apparent activation energies for the decomposition of sintered $\text{Ti}_3\text{SiC}_2$, $\text{Ti}_3\text{AlC}_2$, and $\text{Ti}_2\text{AlC}$ were determined to be $179.3$, $-71.9$, and $85.7 \, \text{kJ \, mol}^{-1}$, respectively. The spontaneous release of $\text{Ti}_2\text{AlC}$ and $\text{TiC}$ from de-intercalation during decomposition of $\text{Ti}_3\text{AlC}_2$ 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]. $\text{MAX}$ phases are layered hexagonal (space group $P\bar{6}_3/mmc$) $Z = 2$. In brief, the $M_X$ octahedra are edge sharing and are identical to the $\text{NaCl}$-type structure of the corresponding binary carbides. These $M_X$ octahedra are interleaved by close-packed planes of the $A$ element [7-10]. Ternary carbides such as $\text{Ti}_3\text{AlC}_2$, $\text{Ti}_3\text{SiC}_2$, $\text{Ti}_2\text{AlC}$, and $\text{Cr}_2\text{AlC}$ are common representatives of the $\text{MAX}$ phases. The electrical and mechanical properties, and the oxidation 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 $\text{MAX} \, 211$ ($\text{Ti}_2\text{AlC}$ and $\text{Cr}_2\text{AlC}$) and $312$ phases ($\text{Ti}_3\text{AlC}_2$ and $\text{Ti}_3\text{SiC}_2$) 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 $\lambda = 1.660 \, \text{Å}$ from 15 to $135^\circ \, 2\theta$ with a step size of $0.125^\circ$, 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_{wp}), R-weighted pattern (R_{wp}), R-expected (R_{wp}), and the goodness-of-fit (\chi^2), were evaluated. In Rietica, \chi^2 is defined as the square of the ratio of R_{wp} to R_{wp}.

Fully-dense solid bars of hot-isostatically-pressed Ti_{2}AlC, Cr_{2}AlC, Ti_{3}SiC_{2}, and spark-plasma sintered Ti_{3}AlC_{2} were used in this study [2, 16]. 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°C at a heating rate of 10°C/min and thereafter at 5°C/min to 1550°C. The dwell times at between 1000 and 1550°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 (°C) | Dwell time (min) | Temperature (°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. The 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_{3}SiC_{2}, it decomposed to TiC above 1300°C (Fig. 2a). A weight loss of ~ 4% was observed for decomposed Ti_{3}SiC_{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_{3}AlC_{2}, its decomposition into TiC and Ti_{2}AlC as lower order or intermediate phase was observed at ≥ 1400°C (Fig. 2b). However, at higher temperatures, when compared to TiC, a smaller growth rate for Ti_{2}AlC may indicate that Ti_{3}AlC experienced further decomposition into TiC via the sublimation of Al and Ti, similar to decomposition of Ti_{3}SiC_{2}. In contrast to Ti_{2}AlC, no intermediate or lower order phase was observed for the decomposition of Ti_{3}SiC_{2}. This difference can be attributed to the fact that Ti_{3}SiC_{2} is the only stable ternary phase in Ti-Si-C system. For Ti_{2}AlC (Fig. 2c), the formation of TiC results mainly from the decomposition of Ti_{3}AlC_{2} as the impurity phase. Ti_{2}AlC would only decompose above 1450°C by sublimation of Ti and Al. Figure 2(d) shows the excellent stability of Cr_{2}AlC up to 1450°C where no observable phase dissociation was detected. However, it started to react with the vanadium wire and became unstable above 1450°C. Like Ti_{2}AlC, it would only decompose above 1450°C via the sublimation of Cr and Al.

The existence of a lower order 211(Ti_{2}AlC) phase in Ti_{3}AlC_{2} is believed to be responsible for its unique two-step decomposition behaviour when compared to Ti_{3}AlC, Cr_{2}AlC, Ti_{3}SiC_{2} which do not possess such a lower order phase. As a consequence, the former undergoes an initial spontaneous decomposition to lower order Ti_{2}AlC phase, followed by eventual decomposition of Ti_{2}AlC through the sublimation of Al and Ti at higher temperature. On the contrary, the latter decompose at elevated temperature in vacuum through the direct sublimation of M and A elements with the concomitant release of a binary carbide (MX) as follows:

\[ M_{n+1}AX_n \rightarrow nMX + A + M \]
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 an Arrhenius equation \[ k = A \exp(-E/RT) \], 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$_3$SiC$_2$ | 179.3 kJ mol$^{-1}$ | \( Ti_3SiC_{2(s)} \rightarrow 2TiC_{(s)} + Ti_{(g)} + Si_{(g)} \) (1) |
| Ti$_3$AlC$_2$ | -71.9 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$_2$AlC | 85.7 kJ mol$^{-1}$ | \( Ti_2AlC_{(s)} \rightarrow TiC_{(s)} + Ti_{(g)} + Al_{(g)} \) (3) |
| Cr$_2$AlC | 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$_3$AlC$_2$ 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$_2$AlC at higher temperature (see
Equation 2b) would involve a small but positive activation energy. It follows that the high activation energy obtained for Ti$_3$SiC$_2$ 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$_2$AlC (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$_3$SiC$_2$, Ti$_3$AlC$_2$ and Ti$_2$AlC were determined to be 179.3, -71.9 and 85.7 kJ mol$^{-1}$, respectively. The negative activated energy for Ti$_3$AlC$_2$ can be attributed to the release of lower order Ti$_2$AlC and TiC from the crystal structure via spontaneous de-intercalation.

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