



Diffraction Study of Thermal Dissociation of Ti_3AlC_2 in Vacuum

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Abstract

Titanium aluminum carbide exhibits a unique combination of characteristics of both metals and ceramics coupled with an unusual combination of mechanical, electrical and thermal properties. In this paper, the effect of high-vacuum annealing on the phase stability and phase transition of Ti_3AlC_2 at up to 1550°C was studied using *in-situ* neutron diffraction. The decomposition of Ti_3AlC_2 into TiC was observed from the change of relative phase abundances as a function of temperature. The apparent activation energies of phase decomposition was determined to be -71.9 kJ/mol. Near-surface composition depth profiling using grazing-incidence synchrotron radiation diffraction has revealed a graded phase composition in vacuum-decomposed surfaces.

Keywords: Ti_2AlC , Ti_3AlC_2 , Thermal stability, Neutron diffraction, GISRD

BADANIA DYFRAKCYJNE PRÓŻNIOWEGO ROZKŁADU TERMICZNEGO Ti_3AlC_2

Węglik tytanowo-glinowy wykazuje unikalną kombinację cech metalicznych i ceramicznych sprzężonych z niezwykłą kombinacją właściwości mechanicznych, elektrycznych i cieplnych. W niniejszym artykule zbadano za pomocą dyfrakcji neutronów, zachodzącej *in-situ*, wpływ wygrzewania do 1550°C w wysokiej próżni na skład fazowy i przejście fazowe Ti_3AlC_2 . Rozkład Ti_3AlC_2 do TiC zaobserwowano na podstawie zmiany liczebności faz w funkcji temperatury. Pozorne energie aktywacji procesu rozkładu fazowego określono na -71.9 kJ/mol. Wyznaczenie głębokościowego profilu składu przypowierzchniowego za pomocą dyfrakcji promieniowania synchrotronowego padającego pod małym kątem (GISRD) ujawniło zmieniający się stopniowo skład fazowy w próbkach rozkładanych próżniowo.

Słowa kluczowe: Ti_2AlC , Ti_3AlC_2 , stabilność termiczna, dyfrakcja neutronów, GISRD

1. Introduction

MAX phases are nano-layered ceramics with the general formula $M_{n+1}AX_n$ ($n = 1-3$), 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 [1-9]. 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. Although the oxidation properties of Ti_2AlC and Ti_3AlC_2 have been well studied [10-12]; there is very little information on their high-temperature thermal stability in vacuum.

In order to comprehend the thermal stability of the Ti-Al-C ternary system, it is important to obtain fundamental understanding on its bonding nature. Zhang *et al.*, Madvedeva *et al.* and Wang *et al.* [13-15] have reported the *ab initio*

calculations for Ti_3AlC_2 . There are essentially three types of chemical bonds in the Ti-Al-C system, namely Ti(1)-C, Ti(2)-C and Ti(2)-Al. The calculations showed that Ti(2)-Al bonds are the weakest and whereas the Ti(2)-C bonds are the strongest. This suggests that the thermal stability of Ti_2AlC and Ti_3AlC_2 will be strongly dictated by the weak Ti(2)-Al bonds. Wang *et al.* [15] studied the phase stability of Ti_2AlC and attributed the great mobility of Al to the formation of a sub-stoichiometry of $Ti_2Al_{0.5}C$. Moreover, the existence of Ti-Al anti-bonding weakens the interplanar coupling and leads to the instability of defective Ti_2Al_xC . In another study, Chen *et al.* [16] investigated the thermal stability of Ti_3AlC_2/Al_2O_3 composites and observed decomposition of Ti_3AlC_2 when soaking at 1150°C for 30 h, forming $TiC_{0.67}$ with the concomitant release of gaseous Al and Ti. This resulted in the irregular morphology of on-stoichiometric TiC_x .

In this paper, the high-temperature thermal stability of Ti_3AlC_2 in vacuum at up to 1550°C was studied using *in-situ* neutron diffraction. The apparent activation energy of phase decomposition was calculated using the Arrhenius' equation. The compositional depth profiles at the near surface of

vacuum-decomposed samples are discussed in the light of grazing-incidence synchrotron radiation diffraction results.

2. Experimental procedure

2.1. Material synthesis

A pulse-discharge sintering method was used to fabricate Ti_3AlC_2 samples from a powder mixture of TiH_2 , Al and TiC [17, 18].

2.2. In-situ high temperature neutron diffraction

The *in-situ* high temperature neutron diffraction data were collected at the Bragg Institute of ANSTO using the high-intensity powder diffractometer (WOMBAT) with neutron beam of wavelength 1.660 Å. The diffractograms were obtained from 15 to 140° 2 θ with a step size of 0.125°. The crystalline phase identification and Rietveld refinement were carried out using Rietica 1.7.7. The optimized parameters used during refinements 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. It is noted that the χ^2 in Rietica is defined as the square of the ratio of R_{wp} to R_{exp} .

A rectangular bar with dimensions of 5×5×40 mm³ was cut from the as-sintered samples. The bar sample was placed into a cylindrical niobium vacuum furnace. The temperature of sample environment was controlled by the closed cylindrical niobium vacuum furnace. The vacuum level was control in the range of 10⁻⁶ to 10⁻⁸ torr. The sample was heated up to 1550°C according to the heating protocol shown in Fig. 1. Diffraction patterns were collected every minute from the starting to the end of the experiment.

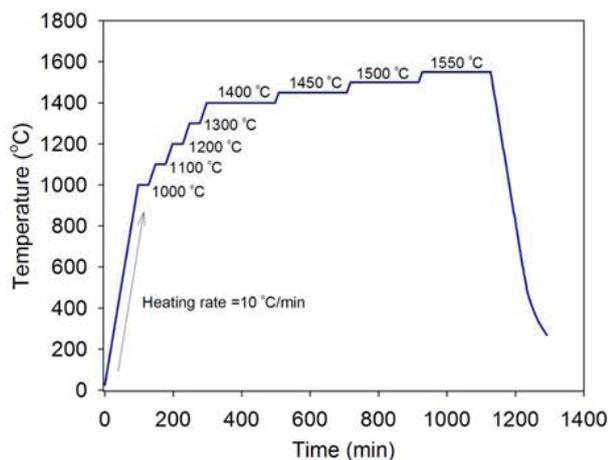


Fig. 1. Heating protocol for *in-situ* high-temperature neutron diffraction experiment.

The decomposition rates (k) at different temperatures were calculated and used to determine the apparent activation energy for the decomposition of Ti_3AlC_2 using the Arrhenius's equation:

$$k = k_0 \cdot \exp\left(-\frac{E}{R \cdot T}\right), \quad (1)$$

where k_0 is constant, R is gas constant, and T is temperature in Kelvin.

2.3. Grazing-incidence synchrotron radiation diffraction (GISRD)

Thin slices were cut from the as-annealed samples following the high-temperature neutron diffraction experiment. The slices were ultra-sonically cleaned prior to GISRD depth-profiling experiments. Diffraction data were collected using beam-line BL-20B at the Photon Factory in Japan. The diffractograms were recorded from 3 to 145° 2 θ with a step size of 0.01°. Image plates were used to record the diffraction patterns at grazing angles of 0.1, 0.4, 0.6, 0.8, 1.0 and 3.0° with a fixed wavelength of 0.7 Å. The computer program "DIFFRA^{plus} EVA" was used to identify the crystalline phases present.

3. Results and discussion

3.1. Phase evolution and activation energy

The Rietveld method was used to analyze the neutron diffraction patterns. The residual values of refinements R_{wp} and R_{exp} ranged from 3.40 to 3.95 and 2.30 to 2.65, respectively. The goodness-of-fit, χ^2 , ranged from 1.90 to 2.63.

Fig. 2 shows the phase transition during thermal decomposition of Ti_3AlC_2 in vacuum at up to 1550°C. Here, Ti_3AlC_2 decomposed directly into Ti_2AlC and TiC at temperatures above 1300°C (see Eq. (2)). Beyond 1400°C, Ti_2AlC decomposed into TiC, in conjunction with the sublimation of Al and Ti (see Eq. (3)). This result is consistent with the work of Chen *et al.* [16].

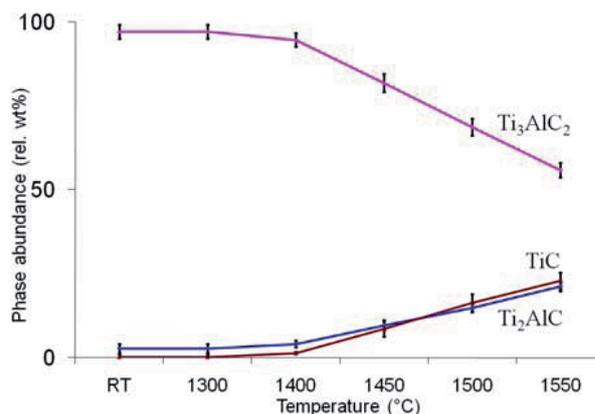
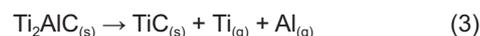
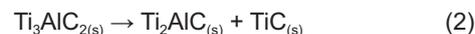


Fig. 2. Phase abundance as a function of temperature for thermal decomposition of Ti_3AlC_2 at up to 1550°C.

Applying the decomposition or reaction rate obtained to Arrhenius equation (Eq. 1), the Arrhenius plot (Fig. 3) shows that the apparent activation energy of the decomposition of Ti_3AlC_2 in vacuum is determined to be -71.9 kJ/mol. A negative activation energy obtained for Ti_3AlC_2 can be attributed to the presence of weak Ti-Al bonds [19], which will favour spontaneous decomposition through the de-intercalation of TiC from the crystal structure (see Eq. (2)). Subsequent

decomposition of released Ti_2AlC at higher temperature (see Eq. (3)) would involve a small but positive activation energy.

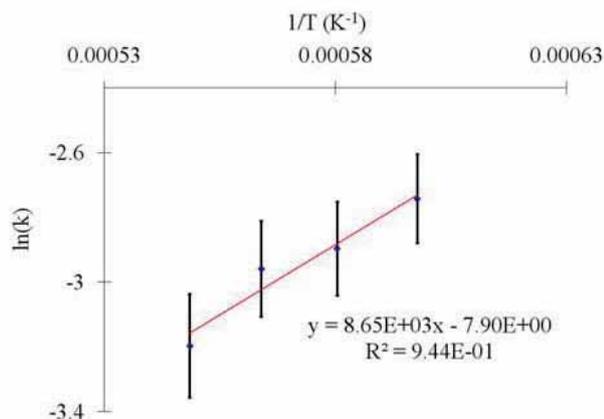


Fig. 3. Regression line with positive slope for decomposition of Ti_3AlC_2 .

3.2. Near surface depth profiling of thermally decomposed Ti_3AlC_2

The compositional depth profiles of vacuum-decomposed Ti_3AlC_2 were studied by GISRD. Fig. 4 shows the near-surface composition of vacuum-annealed Ti_3AlC_2 at different grazing-incidence angles or information depths. It is evident that a graded surface composition exists with an outer layer of TiC and an inner mixture layer of TiC and an unknown phase. The unknown phase could not be identified by the "DIFFRA^{plus} EVA" program, which suggests that it is not in the current ICSD or PDF database. This implies that the process of high-temperature dissociation in the Ti-Al-C system is more complex than has been anticipated. Further work is required to unravel the complex chemistry of thermal dissociation in these MAX phases. Furthermore, the absence of Ti_3AlC_2 phase on the near-surface suggests that the decomposed surface layer is more than 100 microns thick, which is the upper detection limit of synchrotrons with the energy used.

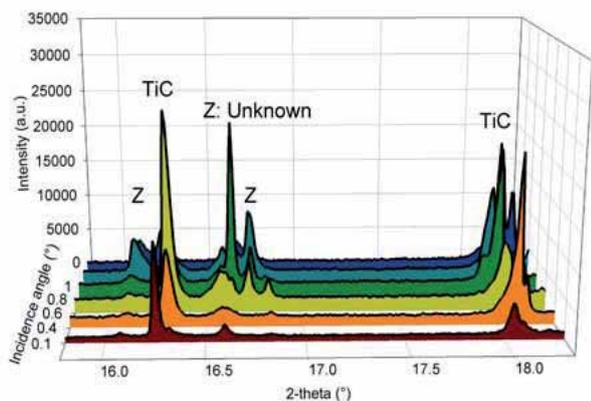


Fig. 4. Near-surface composition depth profiles of vacuum-decomposed Ti_3AlC_2 . [Legend: Z is unknown phase.]

4. Conclusions

The *in-situ* high temperature thermal dissociation of Ti_3AlC_2 in vacuum has been studied by neutron diffraction. Ti_3AlC_2 was stable in vacuum at up to 1300°C but it decomposed spontaneously into Ti_2AlC and TiC, resulting in a nega-

tive activation energy. Ti_2AlC further decomposed directly into TiC at $\geq 1400^\circ C$ via the sublimation of Al and Ti. A graded composition at the near-surface of vacuum-decomposed Ti_3AlC_2 has been revealed by grazing-incidence synchrotron radiation diffraction.

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