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Effect of Vacuum Annealing on the Thermal Stability of Ti_3SiC_2/TiC/$TiSi_2$ Composites

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Abstract
Titanium silicon carbide (Ti_3SiC_2) possesses a unique combination of properties of both metals and ceramics, for it is thermally shock resistant, thermally and electrically conductive, damage tolerant, lightweight, highly oxidation resistant, elastically stiff, and mechanically machinable. In this research, the effect of high vacuum annealing on the phase stability and phase transitions of Ti_3SiC_2/TiC/$TiSi_2$ composites up to 1550°C was studied using *in-situ* neutron diffraction. The role of TiC and $TiSi_2$ on the thermal stability of Ti_3SiC_2 during vacuum annealing is discussed. TiC reacts with $TiSi_2$ between 1400-1450°C to form Ti_3SiC_2. Above 1400°C, decomposition of Ti_3SiC_2 into TiC commenced and the rate increased with increased temperature and dwell time. Furthermore, the activation energy for the formation and decomposition of Ti_3SiC_2 was determined.

Keywords: *MAX* phase, thermal stability, vacuum-annealing, decomposition, Ti_3SiC_2, neutron diffraction.

INTRODUCTION

Many attempts have been made to produce new materials with a unique combination of the ductility, conductivity, and machinability of metals, and with the high strength, high modulus, high thermal stability, and superior high-temperature-oxidation resistance of ceramics. Ternary carbides, such as Ti_3SiC_2 and Ti_3AlC_2, are hexagonal layered compounds belonging to a family with the general formula: $M_{n+1}AX_n$, where n is 1, 2 or 3, M is an early transition metal, A is an A-group (mainly group III-A and IV-A) element, and X is either carbon or nitrogen [1-12]. Ti_3SiC_2 has high toughness, high Young's modulus, low hardness, and moderate flexural strength. Furthermore, it exhibits plasticity at high temperature, good electrical conductivity, high thermal shock resistance, and good machinability [3, 5, 7, 9, 11, 13]. The salient combination of properties makes ternary carbides ideal candidate materials for high-temperature applications.

The thermal stability of Ti_3SiC_2 in vacuum has attracted little attention [10, 14-16]. Emmerlich *et al.* [14] investigated the thermal stability of Ti_3SiC_2 thin films and reported that the rapid decomposition of Ti_3SiC_2, associated with Si out-diffusion and de-twinning of as-relaxed Ti_3C_2 slabs into oriented $TiC_{0.67}$ layers, is observed when annealing at 1100-1200 °C. Radhakrishnan *et al.* [16] reported similar results for the decomposition of Ti_3SiC_2 in vacuum and stated that Ti_3SiC_2 did not dissociate up to 1800 °C but was found susceptible to carburization and oxidation. Oo *et al.* [15] studied the thermal stability of Ti_3SiC_2 in argon with low oxygen partial pressure and reported that Ti_3SiC_2 decomposed into TiC and $Ti_5Si_3C_x$. Sun *et al.* [10] reported the occurrence of transformation between α- and β- Ti_3SiC_2, and that α-Ti_3SiC_2 is more stable than β-Ti_3SiC_2.

It is difficult to synthesize a Ti_3SiC_2 sample with 100 % purity due to its high propensity to dissociate into TiC. As indicated in the Ti-Si-C phase diagram (Fig. 1), the equilibrium state of a single phase of Ti_3SiC_2 only occupies a small area which is intersected by the boundaries of TiC, SiC, and $TiSi_2$. In this study, two Maxthal Ti_3SiC_2 samples with different amounts of TiC and $TiSi_2$ were used. The role of TiC and $TiSi_2$ on the thermal stability and phase transition of Ti_3SiC_2 was investigated using *in-situ* high-temperature neutron diffraction. Furthermore, a comparison of surface composition in as-received and annealed samples was investigated by flat-plate synchrotron radiation diffraction (SRD).

EXPERIMENTAL

Sample Preparation

Maxthal Ti_3SiC_2 samples (15 mm in diameter and 50 mm in length) were fabricated using a proprietary method developed by Kanthal AB, Sweden. The density of these samples was ~4.47 g/cm^3 with ~1 % porosity. Two Maxthal Ti_3SiC_2 samples (A and B) with different amounts of TiC and $TiSi_2$ were used. The contents of TiC and $TiSi_2$ present in Samples A and B were 34.8 and 7.0 mol %, and 50.8 and 9.9 mol %, respectively.

In-situ neutron diffraction

The collection of high-temperature *in-situ* neutron diffraction data was conducted using Wombat (the high-intensity neutron powder diffractometer) at the OPAL source in Australia. Data were collected using neutrons with incident wavelength of λ = ~1.660 Å from 15 to 135° 2θ at a separation 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 cylindrical bars with dimensions 15 mm (diameter) x 20 mm (height) cut from as-received samples were used in this study. The temperature of the 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 1550 °C according to the heating protocol shown in Fig. 2. Diffraction patterns were collected every minute.

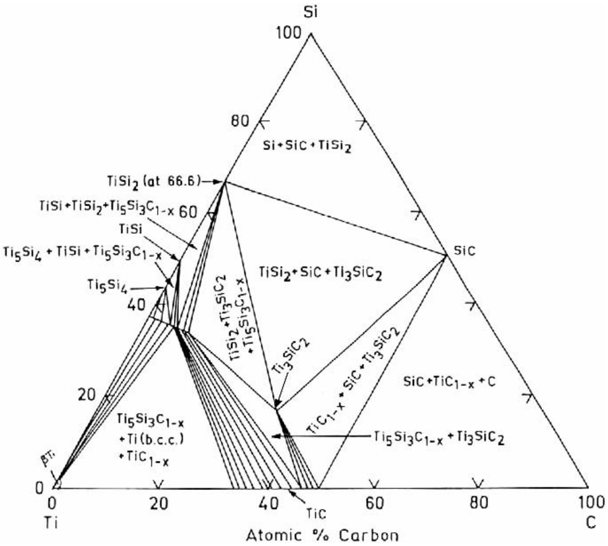


Fig. 1: Ti-Si-C ternary phase diagram at isothermal section at 1250 °C [17].

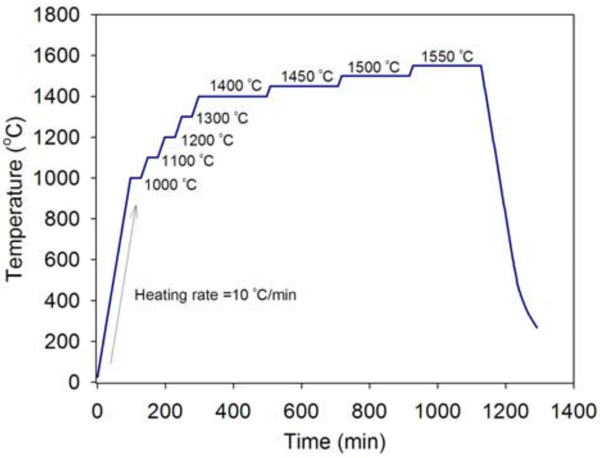


Fig. 2: Heating protocol for *in-situ* high-temperature neutron diffraction experiment.

Synchrotron radiation diffraction (GISRD)

The diffraction patterns were collected using BIGDIFF (the synchrotron powder diffractometer) at the Australian Synchrotron Research Program Facility (ANBF), beam-line BL-20B, at the Photon Factory, KEK, Tsukuba, Japan. The diffractograms were recorded from 3° to 145° 2θ with a step size of 0.01°. The computer program "*DIFFRAplus* EVA" was used to identify the crystalline phases present. A diamond blade was used to cut thin slices (~1 mm thick) from the as-received and as-annealed samples. The slices were cleaned ultra-sonically prior to SRD experiment. The compositional information was measured using flat-plate SRD and image plates were used to record the diffraction patterns at 3.0° with a wavelength of 0.7Å.

RESULTS AND DISCUSSION

Phase Transition during Vacuum Annealing

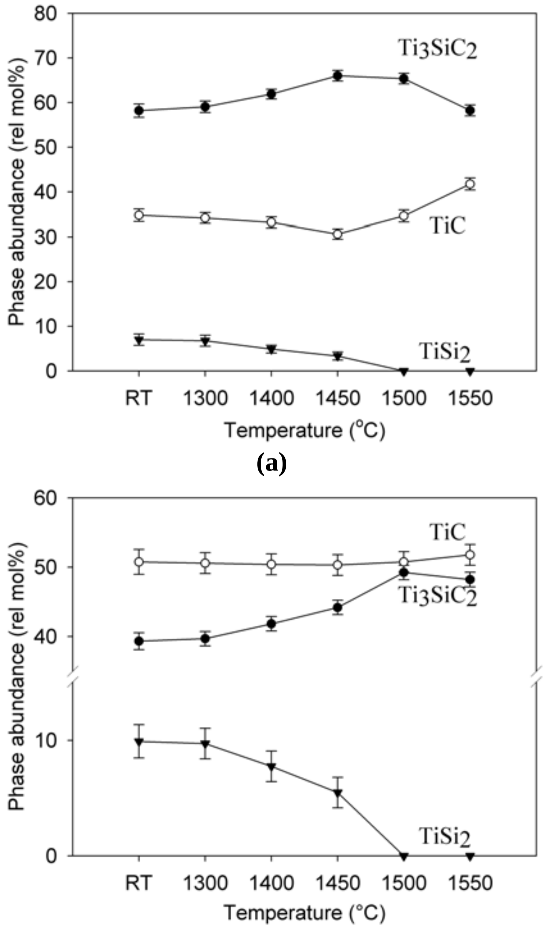
Results in Fig. 3a and 3b show the phase transition of Sample A and Sample B annealed in vacuum at temperature up to 1550 °C. For Sample A, $TiSi_2$ reacted with TiC during vacuum annealing to form Ti_3SiC_2 at temperatures above 1300 °C as follows:

$$TiSi_{2\,(s)} + 2TiC_{(s)} \rightarrow Ti_3SiC_{2\,(s)} + Si_{(g)} \tag{1}$$

This reaction resulted in the increased amounts of Ti_3SiC_2. By 1500 °C, $TiSi_2$ was fully consumed to form Ti_3SiC_2, and at the same time, a pronounced decrease in Ti_3SiC_2 content from 65.4 ±1.22 to 58.3 ±1.22 mol % was observed. The reduction of Ti_3SiC_2 with a complementary increase in TiC suggests that the decomposition of Ti_3SiC_2 into TiC occurs (*via* the sublimation of Ti and Si gaseous) as follows:

$$Ti_3SiC_{2\,(s)} \rightarrow 2TiC_{(s)} + Ti_{(g)} + Si_{(g)} \tag{2}$$

On the other hand, Sample B, consisting of more TiC than Sample A, showed better stability in vacuum. Here, Ti_3SiC_2 also formed from the reaction of $TiSi_2$ and TiC at 1400-1500 °C. Once $TiSi_2$ was depleted, there was only a small decrease in Ti_3SiC_2 content from 1500 to 1500 °C. However, within experimental and/or calculation errors, the Ti_3SiC_2 decomposition was not clearly observed, which implies better thermal stability for Sample B in vacuum at up to 1550 °C.



(a)

(b)

Fig. 3: Phase abundance as a function of temperature during vacuum annealing for (a) Sample A and (b) Sample B.

Table 1: Phase abundances before and after vacuum treatment for sample A and B.

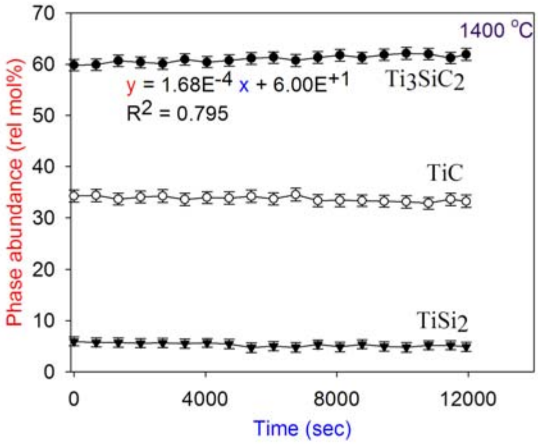
Phases	**Phase abundance (rel. mol%)**			
	Sample A		**Sample B**	
	Before	**After**	**Before**	**After**
Ti_3SiC_2	58.2±1.48	58.3±1.19	39.3±1.46	48.2±1.22
TiC	34.8±1.40	41.8±1.41	50.8±1.34	51.8±1.36
$TiSi_2$	7.0±1.28	0	9.9±1.30	0

A comparison of phase abundances between Samples A and B before and after vacuum annealing is summarized in Table 1. It shows that the consumption of $TiSi_2$ did not contribute to the increase of Ti_3SiC_2 in Sample A, but did increase the amount of Ti_3SiC_2 in Sample B. In other words, Sample A underwent more decomposition, even though the relative molar fraction of Ti_3SiC_2 content remained 58.3±1.19 mol%.

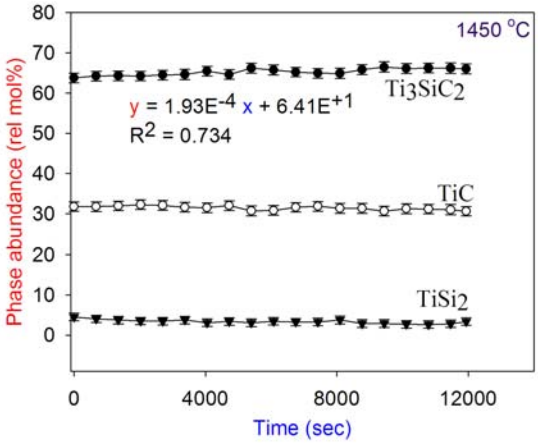
Figs. 4 and 5 show the isothermal phase transition at 1400, 1450, 1500, and 1550°C for Sample A and Sample B, respectively. The results show that phase abundance varies as a linear function of dwell time (< 200 minutes). The slope of Ti_3SiC_2 regression lines can be treated as the rate for either decomposition (negative) or reformation (positive). It is noted that the decomposition rate increases with temperature.

For Sample A, the plots show slopes with positive values at 1400 and 1450°C and negative at 1500 and 1550°C, consistent with reformation and decomposition of Ti_3SiC_2 occurring at these temperatures, respectively. Assuming that the decomposition of Ti_3SiC_2 commenced at ≤1400°C, the increased Ti_3SiC_2 content for Sample B implies that the reformation and decomposition of Ti_3SiC_2 appeared rapidly and that the reaction rate for the decomposition was smaller.

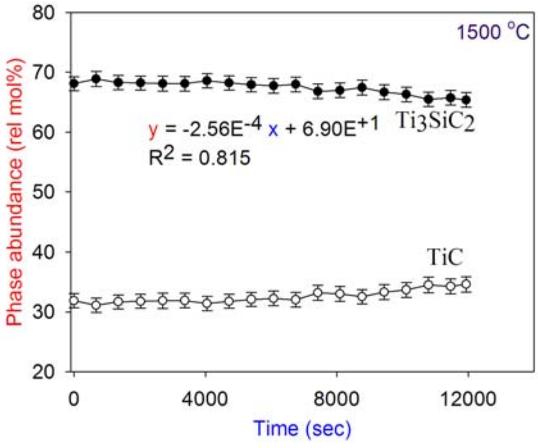
For Sample B, only the formation of Ti_3SiC_2 was clearly observed. At 1500 and 1550°C, TiC and Ti_3SiC_2 were in an equilibrium state, no decomposition or reformation was observed. The ratio of TiC: Ti_3SiC_2 = ~1:1 may infer that the concentration of TiC affects the rate of Ti_3SiC_2 decomposition and a compound with 50 mol% Ti_3SiC_2 and 50 mol % TiC may be stable in vacuum up to 1550 °C.



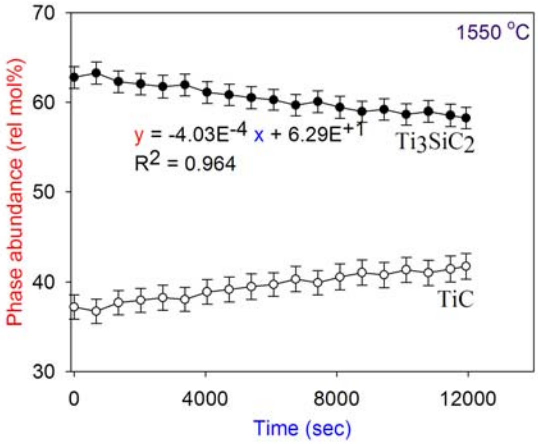
(a)



(b)

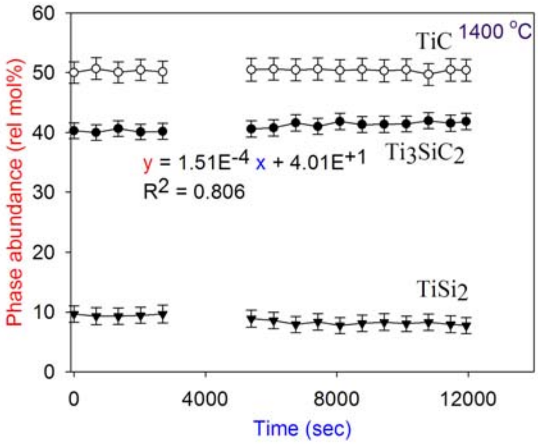


(c)

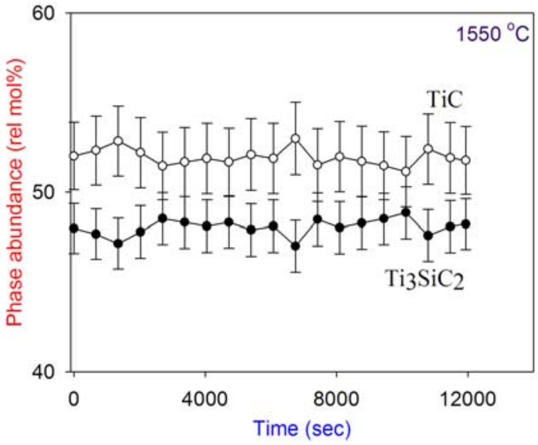


(d)

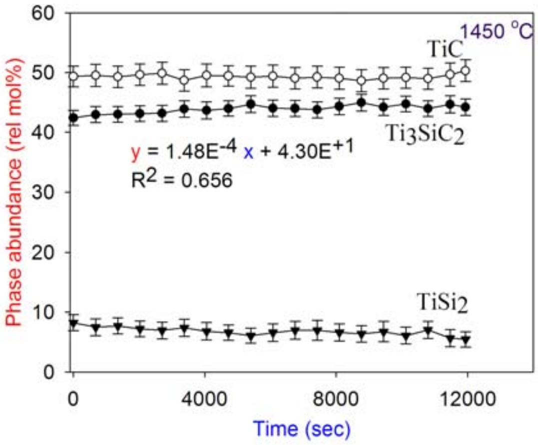
Fig. 4: Phase abundance as a function of dwell time at (a) 1400, (b) 1450, (c) 1500, and (d) 1550°C for sample A.



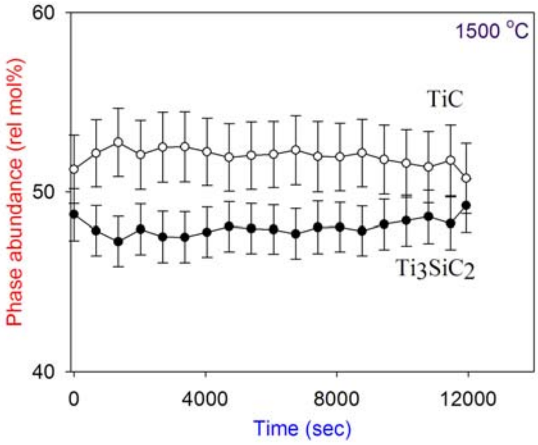
(a)



(d)



(b)

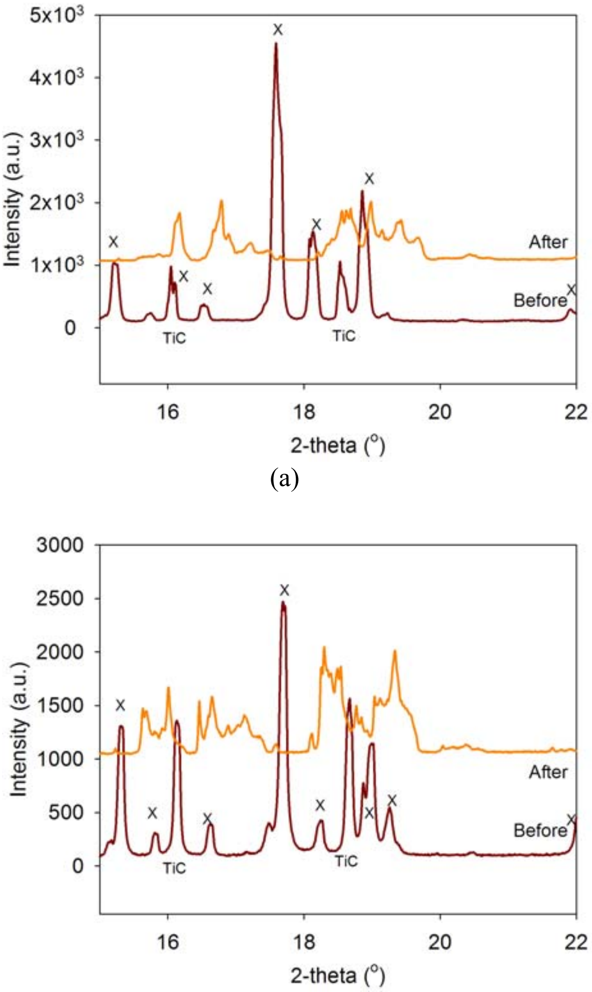


(c)

Fig. 5: Phase abundance as a function of dwell time at (a) 1400, (b) 1450, (c) 1500, and (d) 1550°C for sample B. Note that sections of data in (a) were not obtained due to equipment malfunction.

Comparison of near-surface composition in samples before and after thermal decomposition

Fig. 6 shows the comparison of near-surface composition in Samples A and B before and after vacuum-annealing at up to 1550°C. Several unknown peaks were observed in the annealed samples. These unknown peaks could not be identified by the "*DIFFRA*^{plus} EVA" program, which suggests that the unknown phase formed is not in the current ICSD or PDF database. This implies that the thermal dissociation process is more complex than has been anticipated. Further work will be required to ascertain the actual chemistry of the thermal dissociation of Ti_3SiC_2 containing $TiSi_2$ and TiC as second phases.



(a)

(b)

Fig. 6: Comparison of near-surface composition in (a) Sample A and (b) Sample B before and after vacuum annealing. (Legend: X: Ti_3SiC_2)

CONCLUSIONS

A comparative study on the thermal stability of Ti_3SiC_2 with various contents of TiC and $TiSi_2$ was conducted using *in-situ* neutron diffraction. When annealed in vacuum at an elevated temperature, TiC and $TiSi_2$ reacted to form Ti_3SiC_2, but at the same time Ti_3SiC_2 decomposed into TiC (*via* the sublimation of Ti and Si). We find here that the reformation of Ti_3SiC_2 is more rapid than its decomposition and that Ti_3SiC_2 with a higher content of TiC and $TiSi_2$ is less susceptible to thermal decomposition in vacuum at up to 1550°C. SRD results show that the thermal dissociation process of Ti_3SiC_2 is much more complicated than expected. Further work is required to understand the actual mechanism of high-temperature thermal decomposition in Ti_3SiC_2.

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