DIFFRACTION STUDY ON THE THERMAL STABILITY OF Ti$_3$SiC$_2$/TiC/TiSi$_2$ COMPOSITES IN VACUUM


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ABSTRACT

Titanium silicon carbide (Ti$_3$SiC$_2$) 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 paper, the effect of high vacuum annealing on the phase stability and phase transitions of Ti$_3$SiC$_2$/TiC/TiSi$_2$ composites at up to 1550°C was studied using in-situ neutron diffraction. The role of TiC and TiSi$_2$ on the thermal stability of Ti$_3$SiC$_2$ during vacuum annealing is discussed. TiC reacts with TiSi$_2$ between 1400-1450°C to form Ti$_3$SiC$_2$. Above 1400°C, decomposition of Ti$_3$SiC$_2$ into TiC commenced and the rate increased with increased temperature and dwell time. Furthermore, the activation energy for the formation and decomposition of Ti$_3$SiC$_2$ was determined.

KEYWORDS: Ti$_3$SiC$_2$, thermal stability, in-situ 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$_3$SiC$_2$ and Ti$_2$AlC$_2$, 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$_3$SiC$_2$ 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$_3$SiC$_2$ in vacuum has attracted little attention [10, 14-16]. Emmerlich et al. [14] investigated the thermal stability of Ti$_3$SiC$_2$ thin films and reported that the rapid decomposition of Ti$_3$SiC$_2$, associated with Si out-diffusion and de-twinning of as-released Ti$_3$C$_2$ slabs into oriented TiC layers, is observed when annealing at 1100-1200°C. Radhakrishnan et al. [16] reported similar results for the decomposition of Ti$_3$SiC$_2$ in vacuum and stated that Ti$_3$SiC$_2$ did not dissociate up to 1800°C but was found susceptible to carburation and oxidation. Oo et al. [15] studied the thermal stability of Ti$_3$SiC$_2$ in argon with low oxygen partial pressure and reported that Ti$_3$SiC$_2$ decomposed into TiC and Ti$_2$SiC$_2$. Sun et al. [10] reported the occurrence of transformation between $\alpha$- and $\beta$- Ti$_3$SiC$_2$, and that $\alpha$-Ti$_3$SiC$_2$ is more stable than $\beta$- Ti$_3$SiC$_2$.

It is difficult to synthesize Ti$_3$SiC$_2$ 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$_3$SiC$_2$ only occupies a small area which is intersected by the boundaries of TiC, SiC, and TiSi$_2$. In this study, two Maxthal Ti$_3$SiC$_2$ 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$_3$SiC$_2$ was investigated using in-situ high-temperature neutron diffraction. Furthermore, synchrotron radiation diffraction (SRD) was used to characterize the surface composition in as-received and vacuum-annealed samples.

EXPERIMENTAL SAMPLE PREPARATION

Maxthal Ti$_3$SiC$_2$ 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$_3$SiC$_2$ 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 $\lambda$ = ~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), R-weighted pattern (Rwp), R-expected (Rexp), and the goodness-of-fit (χ²), were evaluated. In Rietica, χ² is defined as the square of Rwp to Rexp. 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.

RESULTS AND DISCUSSION

Phase Transition during Vacuum Annealing

Results in Figures 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, TiSi₂ reacted with TiC during vacuum annealing to form Ti₃SiC₂ at temperatures above 1300°C as follows:

\[
\text{TiSi}_2 \text{(s)} + 2\text{TiC(s)} \rightarrow \text{Ti}_3\text{SiC}_2 \text{(s)} + \text{Si(g)}
\]

This reaction resulted in the increased amounts of Ti₃SiC₂. By 1500°C, TiSi₂ was fully consumed to form Ti₃SiC₂, and at the same time, a pronounced decrease in Ti₃SiC₂ content from 65.4 ±1.22 to 58.3 ±1.22 mol % was observed. The reduction of Ti₃SiC₂ with a complementary increase in TiC suggests that the decomposition of Ti₃SiC₂ into TiC occurs (via the sublimation of Ti and Si gaseous) as follows:

\[
\text{Ti}_3\text{SiC}_2 \text{(s)} \rightarrow 2\text{TiC(s)} + \text{Ti(g)} + \text{Si(g)}
\]

On the other hand, Sample B, consisting of more TiC than Sample A, showed better stability in vacuum. Here, Ti₃SiC₂ also formed from the reaction of TiSi₂ and TiC at 1400-1500°C. Once TiSi₂ was depleted, there was only a small decrease in Ti₃SiC₂ content from 1500 to 1550°C. However, within experimental and/or calculation errors, the Ti₃SiC₂ decomposition was not clearly observed, which implies better thermal stability for Sample B in vacuum at up to 1550°C.

A comparison of phase abundances between Samples A and B before and after vacuum annealing is summarized in Table 1. It shows that the consummation of TiSi₂ did not contribute to the increase of Ti₃SiC₂ in Sample A, but did increase the amount of Ti₃SiC₂ in Sample B. In other words, Sample A underwent more decomposition, even though the relative molar fraction of Ti₃SiC₂ content remained 58.3±1.19 mol%.

Figures 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 Ti₃SiC₂ 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.

Figures 1 and 2: Ti-Si-C ternary phase diagram at isothermal section at 1250 °C [17].
Table 1: Phase abundances before and after vacuum treatment for samples A and B.

<table>
<thead>
<tr>
<th>Phase abundance (rel. mol%)</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Ti&lt;sub&gt;3&lt;/sub&gt;SiC&lt;sub&gt;2&lt;/sub&gt;</td>
<td>58.2±1.48</td>
<td>58.3±1.19</td>
</tr>
<tr>
<td>TiC</td>
<td>34.8±1.40</td>
<td>41.8±1.41</td>
</tr>
<tr>
<td>TiS&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7.0±1.28</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 3: Phase abundance as a function of temperature during vacuum annealing for (a) Sample A and (b) Sample B. Errors bars indicate two estimated standard deviations ±2σ.

Fig. 4: Phase abundance as a function of dwell time at (a) 1400, (b) 1450, (c) 1500, and (d) 1550°C for sample A. Errors bars indicate two estimated standard deviations ±2σ.
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. Errors bars indicate two estimated standard deviations ±2σ.

Fig. 6: Comparison of surface composition in (a) Sample A and (b) Sample B before and after vacuum annealing. (Legends: X: Ti₃SiC₂)
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 Ti₃SiC₂ occurring at these temperatures, respectively. Assuming that the decomposition of Ti₃SiC₂ commenced at ≤1400°C, the increased Ti₃SiC₂ content for Sample B implies that the reformation and decomposition of Ti₃SiC₂ appeared rapidly and that the reaction rate for the decomposition was smaller.

For Sample B, only the formation of Ti₃SiC₂ was clearly observed. At 1500 and 1550°C, TiC and Ti₃SiC₂ were in an equilibrium state, no decomposition or reformation was observed. The ratio of TiC: Ti₃SiC₂ = ~1:1 may infer that the concentration of TiC affects the rate of Ti₃SiC₂ decomposition and a compound with 50 mol% Ti₃SiC₂ and 50 mol% TiC may be stable in vacuum up to 1550°C.

**Comparison of surface composition in as-received and as-annealed Samples A and B**

Fig. 6 shows the comparison of near-surface composition (diffraction pattern) in Samples A and B before and after vacuum annealing up to 1550°C. Certain unknown peaks were observed in the annealed samples. These unknown peaks cannot be identified by the “DIFFRA” EVA program, which may be not reported in the current ICSD or PDF database system. This suggests that the thermal dissociation process is more complex than anticipated. More future works will be required to dig out the truth of the thermal dissociation of Ti₃SiC₂ composites.

**CONCLUSIONS**

A comparative study on the thermal stability of Ti₃SiC₂ with various contents of TiC and TiSi₂ was conducted using in-situ neutron diffraction. When annealed in vacuum at an elevated temperature, TiC and TiSi₂ reacted to form Ti₃SiC₂, but at the same time Ti₃SiC₂ decomposed into TiC via the sublimation of Ti and Si. We find here that the reformation of Ti₃SiC₂ is more rapid than its decomposition and that Ti₃SiC₂ with a higher content of TiC and TiSi₂ is less susceptible to thermal decomposition in vacuum at up to 1550°C. SRD results show that the thermal dissociation process of Ti₃SiC₂ is much more complicated than expected. More work is required to understand the mechanism of phase dissociation in Ti₃SiC₂.

**ACKNOWLEDGEMENTS**

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**REFERENCES**