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# Comments on the high temperature oxidation characteristics of Ti<sub>3</sub>SiC<sub>2</sub> in air

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The high temperature oxidation characteristics of  $Ti_3SiC_2$  have been studied extensively before. However, we believe that there are still the ambiguous points concerning the scale structure and oxidation mechanism of  $Ti_3SiC_2$ . Hence, the oxide scales formed, the distribution and roles of Ti, Si and C in the scale, and the oxidation mechanism are discussed based on the results obtain from this and previous studies. In this study,  $Ti_3SiC_2$  compounds were produced via a powder metallurgical process, oxidized between 900 and 1200 °C in air for up to 100 h, and the oxidation characteristics are discussed.

Key words: Ti<sub>3</sub>SiC<sub>2</sub>, Titanium, Silicon, Carbon, Oxidation.

## Introduction

 $Ti_3SiC_2$  is a remarkable material for a myriad of applications, because of its unique combination of metallic and ceramic properties [1]. Like metals, it has excellent electrical and thermal conductivities, high toughness, a high fatigue-crack growth threshold, low hardness, machinability, and high thermal-shock resistance. Like ceramics, it displays excellent chemical resistance, high Young's modulus, high temperature strength, and a high melting point. It is usually synthesized via powder metallurgical routes such as hot pressing or hipping. In order to use  $Ti_3SiC_2$  as high-temperature structural components, the oxidation behavior of  $Ti_3SiC_2$  was studied extensively at temperatures ranging from 900 °C to 1500 °C in air [1-17].

Most of these oxidation studies were conducted using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectrometry (EDS). However, to accurately trace the carbon in  $Ti_3SiC_2$ during oxidation, it is imperative to utilize electron probe microanalysis (EPMA), because of its ability to detect carbon. Yet, the previous oxidation studies on  $Ti_3SiC_2$  still need further discussion, owing to an inadequate interpretation of experimental data. The aim of this study is to critically discuss the high-temperature oxidation characteristics of  $Ti_3SiC_2$  proposed by other researchers, based on this and previous studies.

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## **Experimental**

Powders of TiC<sub>0.67</sub> (< 45  $\mu$ m) and Si (< 70  $\mu$ m) were mixed in a molar ratio of 3 to 1 in a SPEX shaker mill for 10 minutes, and hot pressed at 1400 °C under an Ar pressure of 25 MPa for 90 minutes to prepare a bulk Ti<sub>3</sub>SiC<sub>2</sub> sample with dimensions of 19 mm $\phi \times 10$  mm. After being cut into pieces  $10 \times 5 \times 5$  mm<sup>3</sup> in size, the Ti<sub>3</sub>SiC<sub>2</sub> specimens were ground to a 1000 grit finish, ultrasonically cleaned in acetone and methanol, and oxidized isothermally at 900, 1000, 1100 and 1200 °C in atmospheric air for 100 h. Following oxidation, the specimens were investigated by means of scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectrometry (EDS), X-ray diffraction (XRD) and EPMA.

#### **Results and Discussion**

It is known that the oxidation of  $Ti_3SiC_2$  results in the formation of rutile-TiO<sub>2</sub>, SiO<sub>2</sub>, and CO [2, 4, 7, 10] or CO<sub>2</sub> [3, 8, 11, 13], as shown in eq. (1).

$$Ti_3SiC_2(s) + O_2(g) \rightarrow TiO_2(s) + SiO_2(s) + (CO(g) \text{ or } CO_2(g))$$
(1)

In reality, no one has proved the formation of CO and CO<sub>2</sub>, which would be experimentally difficult. The SiO<sub>2</sub> formed was amorphous (Barsoum et al. [2]; oxidation at 900-1200 °C for 10 h, Li et al. [8]; oxidation at 1000-1500 °C for 20 h, Chen et al. [10]; oxidation at 800-1300 °C for 48 h, Racault et al. [13]; oxidation at 850-1050 °C for 6 h), tridymite (Sun et al. [4]; oxidation at 900-1300 °C for 20 h), or cristobalite (Barsoum et al. [2]; oxidation at 1240-1400 °C for 12 h, Gao et al. [11]; oxidation at 1100-1300 °C for 30 h, Racault et al. [13]; oxidation at 1050-1250 °C for 6 h). It is seen that, even

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**Fig. 1.** XRD pattern of oxide scale formed on  $Ti_3SiC_2$  after oxidation for 100 h in air. (a) scale formed at 900 °C, (b) outer scale formed at 1000 °C, (c) inner scale formed at 1000 °C, (d) outer scale formed at 1200 °C, (e) inner scale formed at 1200 °C.

under the same oxidation conditions, SiO<sub>2</sub> has different structures. This discrepancy may have originated from the different microstructure, density and purity of each sample tested. Our XRD tests for the oxidized specimens indicated that the SiO<sub>2</sub> formed at 900-1100 °C for up to 100 h was amorphous. For example, rutile-TiO<sub>2</sub> and amorphous SiO<sub>2</sub> formed on the Ti<sub>3</sub>SiC<sub>2</sub> matrix, as shown in Fig. 1(a). In Fig. 1(b), Ti<sub>3</sub>SiC<sub>2</sub> was not visible, because the X-rays could not penetrate beyond the oxide scale. Hence, the inner scale was X-rayed after grinding off the outer  $TiO_2$  scale, as shown in Fig. 1(c). Here, rutile-TiO<sub>2</sub> and the Ti<sub>3</sub>SiC<sub>2</sub> matrix were detected, because the SiO<sub>2</sub> formed was amorphous. The crystallization of  $SiO_2$  occurred when  $Ti_3SiC_2$  was oxidized at 1200 °C for 100 h, as shown in Fig. 1(d) and (e). The outer  $TiO_2$  scale was detected in Fig. 1(d), whereas the inner (TiO<sub>2</sub>, SiO<sub>2</sub>)-mixed scale was detected in Fig. 1(e). However, when Ti<sub>3</sub>SiC<sub>2</sub> was oxidized at 1200 °C for 20 h, only rutile was detected thoughout the scale. Hence, it is suggested that the  $SiO_2$  that formed below the outer TiO<sub>2</sub> scale transformed from amorphous into cristobalite, as oxidation progressed at 1200 °C.

Gao et al. [14] proposed that Ti<sub>3</sub>SiC<sub>2</sub> tended to

decompose above 600 °C in air, according to the eq. (2)

$$Ti_3SiC_2 \rightarrow TiC_x(s) + Si(s)$$
 (2)

They explained that, above 1100 °C, Ti<sub>3</sub>SiC<sub>2</sub> decomposed severely owing to the oxidation of  $TiC_x(s)$  and the vapor phase reaction;  $Si(g)+O_2 \rightarrow SiO(g)$ . However, their explanation is based on thermogravimetricdifferential thermal analyses (TG-DTA), which cannot see  $TiC_x(s)$  and Si(s), which will be  $TiO_2$  and  $SiO_2$ , respectively. It is known that Ti<sub>3</sub>SiC<sub>2</sub> decomposes to  $TiC_{x}(s)$  and Si(s or g) at temperatures of 1300-1600 °C under an inert atmosphere or vacuum [11, 13, 15]. This can happen because Ti<sub>3</sub>SiC<sub>2</sub> has strong Ti-C bonds and weak bonds between the Si layers and Ti<sub>3</sub>C<sub>2</sub> octahedrons. However, the reaction (2) is unlikely to occur in air, because Ti<sub>3</sub>SiC<sub>2</sub> would be oxidized readily to form the thermodynamically stable TiO<sub>2</sub> and SiO<sub>2</sub>. Furthermore, the reaction proposed by Gao et al. requires the following eq. (3).

$$Si(s)=Si(g)$$
 (3)

For eq. (3), the standard free energy changes,  $\Delta G^{\circ}$ , are given as follows;

 $\Delta G^{\circ} = -RT \ln (P_{Si(g)}/a_{Si(s)})_{eq} = -RT \ln (P_{Si(g)})_{eq} = 276,224$ (J at 900 °C), 232,781 (J at 1200 °C)

Thus, the equilibrium vapor pressure of Si(g),  $P_{Si(g)}$ , at 900 and 1200 °C can be calculated as  $5 \times 10^{-13}$  and  $5 \times 10^{-9}$  atm, respectively. These low vapor pressures indicate that the amount of Si(g) that will form is too small to account for the amount of SiO<sub>2</sub> that was present in the scale. Ti<sub>3</sub>SiC<sub>2</sub> would be oxidized according to eq. (1), without forming TiC<sub>x</sub>(s) and Si(s). Since TiC<sub>x</sub>(s) has poor oxidation resistance and Si is an active element, they cannot be precursors of the oxide scale.

On the other hand, Yang et al. [12], based on the Ti-Si-O phase diagram calculated by Lutha [18], suggested that TiO<sub>2</sub> should form preferentially when a thermodynamic equilibrium has been established between Ti<sub>3</sub>SiC<sub>2</sub> and the gas phase at the their oxidation test temperature of 1000 °C. However, Lutha studied the oxidation of the Ti-Si binary system at 800 °C. Moreover, the activities of Ti and Si in Ti<sub>3</sub>SiC<sub>2</sub> are still unknown. Hence, Yang et al.'s explanation is wrong. One cannot tell which oxide would form preferentially between TiO<sub>2</sub> and SiO<sub>2</sub> because of the lack of thermodynamic data.

Previously, Feng et al. [15] measured the activation energy for the oxidation of  $Ti_3SiC_2$  (Q=312.5 kJ/mol in the range 950-1100 °C) from the weight gain versus oxidation time curves. However, they could not explain the physical meaning of the Q value from the diffusion process though the TiO<sub>2</sub> and SiO<sub>2</sub> oxides. Therefore, they suggested that another unknown step might be involved in the oxidation process of  $Ti_3SiC_2$ . At least, they should have taken into account the vaporization of



Fig. 2. Thickness of the oxide layer formed on  $Ti_3SiC_2$  after oxidation at 900-1200 °C for 5-100 h in air.

carbon to explain the oxidation of  $Ti_3SiC_2$ . Other factors that can affect the oxidation rates, and, as a resultant, the Q value are the oxidation conditions (i.e., time/temperature/atmosphere), the microstructure, the sample purity and density. In particular for  $Ti_3SiC_2$ , no samples were 100% pure and dense [2, 4, 7, 8, 11]. The most frequently found impurity is TiC [2, 14, 15], which increases the oxidation rates and decreases the activation energy, Q [2,5,10]. SiC is another impurity in  $Ti_3SiC_2$ [3].

The oxidation kinetics of  $Ti_3SiC_2$  were generally evaluated based on the weight gain versus oxidation time curves using thermogravimetric analyzers (TGA) [3-5, 8, 10, 11, 13-16]. It is generally suggested that the air-oxidation resistance of  $Ti_3SiC_2$  is acceptable up to 1050-1100 °C owing to the formation of dense scales [5, 9, 13, 14]. However, Radhakrishnan et al. [16] questioned the potential utility of  $Ti_3SiC_2$  at elevated temperatures in air, because of big weight gains at their oxidation test temperature of 1000 °C. This difference in opinion came from the fact that the oxidation kinetics

**Table 1**. Thickness of the scale formed on pure Ti, TiAl-2Cr-2Nb, and SUS 430 after oxidation at 900-1200 °C for 100 h in air

Sample	µm at 900 °C	µm at 1000 °C	µm at 1100 °C	µm at 1200 °C
Ti	630	745	1000	2525
TiAl-2Cr-2Nb	2.8	12	40	980
SUS 430	13	25	145	523

of Ti<sub>3</sub>SiC<sub>2</sub> are strongly influenced by the impurities, density, and also by the vaporization of carbon that lowers the weight gain curves. This vaporization may be one of the reasons for the unusual TGA results obtained by Racault et al. in air [13]. They found that the weight gain obtained at 1150 °C is lower than that obtained at 1050 °C. In this study, the oxidation resistance of Ti<sub>3</sub>SiC<sub>2</sub> was evaluated by measuring the scale thickness, as shown in Fig. 2. For comparison, Ti alloy (99.9% pure), TiAl-2Cr-2Nb intermetallic compound (Ti-47Al-2Cr-2Nb, in wt.% hereafter), and stainless steel (SUS 430; Fe-17Cr alloy) were also tested, and their scale thicknesses are listed in Table 1. As the oxidation progressed, the scale thickened, as expected in Fig. 2 and Table 1. Ti<sub>3</sub>SiC<sub>2</sub> displayed better oxidation resistance than pure Ti, because of the SiO<sub>2</sub> existing in the inner oxide scale. But, Ti<sub>3</sub>SiC<sub>2</sub> displayed worse oxidation resistance than TiAl-2Cr-2Nb and SUS 430, due partly to the evaporation of carbon that disrupts the continuity of the oxide layer. However, it is noted that TiAl-2Cr-2Nb oxidizes rapidly at 1200 °C.

Figure 3 shows the SEM morphology and EDS spectra of the surface scale formed on  $Ti_3SiC_2$ . Numerous, fine rutile crystallites were seen in the area 'X' (Fig. 3(a) and (b)). But, such small crystallites were not visible at the given magnification in the area 'Y' (Fig. 3(a)). Oxide grains in this area were exceedingly small due mainly to the simultaneous growth of TiO<sub>2</sub> and SiO<sub>2</sub>



**Fig. 3.** Oxide scale formed on  $Ti_3SiC_2$  after oxidation for 100 h in air. (a) SEM top view at 900 °C, (b) EDS spectrum of area X, (c) EDS spectrum of area Y, (d) SEM top view at 1000 °C, (e) EDS spectrum of (d), (f) SEM top view at 1100 °C, (g) SEM top view at 1200 °C.



Fig. 4. EPMA analysis on the scale formed on  $Ti_3SiC_2$  after oxidation at 1100 °C for 20 h in air. (a) cross-sectional image, (b) Ti map, (c) Si map, (d) carbon map, (e) oxygen map.

(Fig. 3(c)). The inhomogeneous nucleation of the surface oxides is due mainly to the anisotropy of the layered matrix grains. It is noted that the standard free energies of formation of oxides per mole  $O_2$  ( $\Delta G_f^{o}$ ), for example at 1000 °C, are as follows [19]; TiO = -842 (kJ), SiO<sub>2</sub>= -682 (kJ), CO=-453 (kJ), and CO<sub>2</sub>=-396 (kJ). To form TiO<sub>2</sub>, TiO should form first. Although the activities of Ti and Si in Ti<sub>3</sub>SiC<sub>2</sub> are unknown, the large amount of Ti in Ti<sub>3</sub>SiC<sub>2</sub> and highly negative  $\Delta G_f^o$  value of TiO may imply that Ti is more active than Si in  $Ti_3SiC_2$ , favoring the easier formation of TiO<sub>2</sub> when compared to SiO<sub>2</sub>. Rutile progressively grew to coarse oxide grains, as the oxidation temperature increases, covering the oxide surface (Fig. 3(d)-(g)). In Fig. 3(g), TiO<sub>2</sub> has grown into the characteristic pillar-like rutile crystals. Since the lattice defect concentration of the nonstoichiozmetric TiO<sub>2</sub> is high, TiO<sub>2</sub> grows much faster than the highly stoichiometric SiO<sub>2</sub>. Clearly, TiO<sub>2</sub> cannot act as an effective barrier to oxidation. Previously, Li et al. [7] indicated that the formation of a dense  $TiO_2$  film on the surface acted as a diffusion barrier that retarded the diffusion of oxygen below 1300 °C. However, the oxidation resistance of Ti<sub>3</sub>SiC<sub>2</sub> would depend mainly on the continuity and compactness of not TiO<sub>2</sub> but SiO<sub>2</sub>.

It is generally accepted that the oxidation of  $Ti_3SiC_2$ from 900 °C up to 1500 °C in air results in the formation of a duplex scale that consists of an outer rutile-TiO<sub>2</sub> layer and an inner (TiO<sub>2</sub>,SiO<sub>2</sub>)-mixed layer [2-4, 8, 10-12, 15, 16]. Figure 4 shows the cross-sectional images and the corresponding EPMA mappings of  $Ti_3SiC_2$ after oxidation at 1100 °C for 20 h. There is negligible carbon in the oxide scale, owing to the escape of C as CO or CO<sub>2</sub> into the air. Around the interface of the outer rutile-TiO<sub>2</sub> layer and the inner (TiO<sub>2</sub>,SiO<sub>2</sub>)-mixed layer, microscopic voids existed (Fig. 4(a)).

Figure 5 shows the cross-sectional images and the corresponding EPMA line profiles of  $Ti_3SiC_2$  after

oxidation at 1100 °C for 100 h. The overall scale morphology and elemental distribution of Fig. 5 did not differ from those of Fig. 4. Voids were seen below the outer rutile-TiO<sub>2</sub> layer. In particular, an array of voids was seen at the interface between the outer TiO<sub>2</sub> layer and the inner (TiO<sub>2</sub>,SiO<sub>2</sub>)-mixed layer in Fig. 5. According to Li et al. [8, 9], these voids would diffuse into both the inner layer and the outer layer, leading to the formation of a porous oxide layer. It appears as though they confused voids with vacancies. Vacancies can move according to their concentration gradient. However, the



**Fig. 5.** EPMA analysis on the scale formed on  $Ti_3SiC_2$  after oxidation at 1100 °C for 100 h in air. (a) cross-sectional image, (b) line profiles of Ti, Si, carbon, and oxygen.

fact that voids were formed indicates that favorable conditions were established for the accumulation of vacancies. Voids would tend to keep growing, once they were formed, as can be seen in Fig. 4 and 5. The reverse reaction, that is, the dissipation of voids suggested by Li et al. [8, 9] would not occur under normal oxidation conditions. The formation of the porous oxide layer in the later stage of oxidation is considered due to the increased extent of oxidation, which leads to the nucleation and growth of more voids. As the oxidation progresses, the outward diffusion of Ti continuously accumulates Kirkendall voids around the interface of the outer TiO<sub>2</sub> layer and the inner (TiO<sub>2</sub>,SiO<sub>2</sub>)-mixed layer. Also, voids continuously grow owing to the ensuing escape of carbon. At the same time, the anisotropic, fast growth of TiO<sub>2</sub> would accentuate the mismatch in volume expansion between TiO<sub>2</sub> and SiO<sub>2</sub>, facilitating the formation of voids.

On the other hand, Feng et al. [15] found colonies of titanium silicide, probably TiSi2, in and around the oxide scale, when Ti<sub>3</sub>SiC<sub>2</sub> was oxidized at 1100 °C for 100 minutes in air. However, this is an exceptional case, because such TiSi2 colonies were not found in other oxidation studies. Recently, Chen and Zhou [17] found Ti<sub>5</sub>Si<sub>3</sub> at the interface of the oxide scale and the  $Ti_3Al_{1-x}Si_xC_2$  matrix, which is the mixture of  $Ti_3SiC_2$ and another isostructural Ti<sub>3</sub>AlC<sub>2</sub> compound. This was attributed to the precipitation of Ti<sub>5</sub>Si<sub>3</sub> from the Ti<sub>3</sub>Al<sub>1-x</sub>-Si<sub>x</sub>C<sub>2</sub> matrix during oxidation. Similarly, TiSi<sub>2</sub> colonies may have precipitated from the Ti<sub>3</sub>SiC<sub>2</sub> matrix. Another possibility for the TiSi<sub>2</sub> colonies may be due to the heterogeneity of their powder metallurgically synthesized sample. The extremely oxidation-resistant TiSi<sub>2</sub>, once formed, would resist oxidation [20] and could therefore stay within the oxide scale of Ti<sub>3</sub>SiC<sub>2</sub>.

Sun et al. [4, 5] previously reported that there was a discontinuous SiO<sub>2</sub> layer inside the coarse, outer TiO<sub>2</sub> layer when Ti<sub>3</sub>SiC<sub>2</sub> was oxidized at temperatures between 1100 and 1200 °C in air. No such discontinuous  $SiO_2$  layer was observed in other studies [7, 8, 11, 14]. The presence of  $SiO_2$  inside the outer  $TiO_2$  layer may occur via the following 2 routes. Firstly, Si ions also diffuse outwards to a certain extent, as Ti ions do to form the outer TiO<sub>2</sub> layer. Secondly, Si ions were pushed upwards toward the surface by the outwardly moving Ti ions. It is worthwhile noting that Si ions in SiO<sub>2</sub> are relatively immobile, because of the higher bonding energy of Si<sup>+4</sup>-O (443 kJmol<sup>-1</sup>) as compared with Ti<sup>+4</sup>-O (305 kJmol<sup>-1</sup>) [21]. Hence, the second route is the more likely occur, resulting in the incorporation of some SiO<sub>2</sub> particles inside the outer TiO<sub>2</sub> layer.

## Conclusions

 $Ti_3SiC_2$  oxidized according to the eq.;  $Ti_3SiC_2+O_2 \rightarrow$ 

 $TiO_2+SiO_2+(CO \text{ or } CO_2)$ , without forming  $TiC_x(s)$  and Si(s).  $Ti_3SiC_2$  displayed better oxidation resistance than pure Ti, but worse oxidation resistance than TiAl-2Cr-2Nb and SUS 430. The oxidation resistance of  $Ti_3SiC_2$  depends mainly on the continuity and compactness of not rutile- $TiO_2$  but  $SiO_2$ , which crystallized into cristobalite after oxidation at 1200 °C for 100 h. Microscopic voids formed below the outer  $TiO_2$  layer, which grew to pillar-like grains. Carbon escaped from  $Ti_3SiC_2$  during oxidation.

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