High-temperature oxidation behaviour of $\text{Ti}_3\text{Si}_{(1-x)}\text{Al}_x\text{C}_2$ in air

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Abstract. The oxidation behaviours of bulk $\text{Ti}_3\text{Si}_{(1-x)}\text{Al}_x\text{C}_2$ prepared by hot pressing were investigated. The results showed that the isothermal oxidation behaviour of Ti_3SiC_2 obeyed a parabolic law between 900 and 1100°C, and followed a two-step parabolic rate law between 1200°C and 1300°C. The cyclic oxidation behaviour of material is assumed to obey a three-step parabolic rate law at 1100°C and 1200°C. The calculated activation energy of isothermal oxidation is 101.43 kJ·mol⁻¹. The oxide layers consisted of a mass of $\alpha\text{-Al}_2\text{O}_3$ and little TiO_2 and SiO_2 are observed on Ti_3SiC_2 as a dense and adhesive protect scale. The oxidation mechanism varies with the additive aluminum that greatly improves the oxidation resistance of Ti_3SiC_2 .

Keywords. Ti_3SiC_2 ; isothermal oxidation; cyclic oxidation; oxidation kinetics.

1. Introduction

Recently, many researchers have put their focus on a nanolaminate compound, Ti_3SiC_2 , which combines the merits of metals and ceramics. Like metals, it is thermally and electrically conductive, easy to machine with ordinary tools, and well resistant to thermal shock. Like ceramics, it has high strength, high melting point (>3000°C) and resistant to oxidation (Barsoum and El-Raghy 1996; El-Raghy *et al* 1997, 1999; Barsoum *et al* 1999). All these merits are due to its special layered microstructure. Ti_3SiC_2 has hexagonal crystal structure with a space group of $P6_3/mmc$ (Barsoum and El-Raghy 1996). The theoretical gravity, measured Young's modulus and Vickers hardness are 4.53 g·cm⁻³, 320 GPa and 4 GPa, respectively (Barsoum and El-Raghy 1996; El-Raghy *et al* 1997). As an excellent oxidation-resistance material, the oxidation behaviours of Ti_3SiC_2 or Ti_3SiC_2 -based composite material had been investigated by several researchers. Since the characters of studied materials, such as contents, microstructure and synthesized methods, were different with each other, varied oxidation behaviours were reported (Racault *et al* 1994; Tong *et al* 1995; Barsoum and El-Raghy 1997; Feng *et al* 1999; Sun *et al* 2001).

In this paper, the isothermal oxidation and cyclic oxidation at high temperature of bulk Ti_3SiC_2 sintered by hot pressing with the starting mixture powders of TiC:Ti:Si:Al = 2:1:1:0.2 in molar were investigated. The additive aluminum, which did favour to the fabrication of

Ti_3SiC_2 , also improves the high-temperature oxidation resistance.

2. Experimental

2.1 Material preparation

In our last work, a novel fabrication method of Ti_3SiC_2 was introduced with the aluminum addition. The mixture powders with a designed composition of TiC:Ti:Si:Al = 2:1:1:0.2 in molar ratio was mixed in ethanol for 24 h. Then the mixture powders were placed in a graphite die, 50 mm in diameter, with a layer of BN previously brushed on the inner surface. The samples were sintered in a hot pressing system at 1350°C in an Ar atmosphere for 2 h with a pressure of 30 MPa. The density and purity of the sintered products were 4.49 g·cm⁻³ and 98.2% in weight fraction, as measured by Archimedes method, XRD analysis and SEM observation. EDS and EPMA results revealed the additive aluminum still exists in the matrix, though the loss of aluminum is much more than that of silicon at high temperature. The compound can be described by the formula, $\text{Ti}_3\text{Si}_{(1-x)}\text{Al}_x\text{C}_2$ ($0 < x < 0.16$) (Zhu and Mei 2009). In the following study, the formula is abbreviated as TSAC. Further investigation demonstrates that Ti, Al, Si are uniformly distributed in the matrix.

2.2 Oxidation experiments

The rectangular bars with $4 \times 4 \times 10$ mm³ were cut by the electrical discharge method for oxidation experiments.

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The surfaces were ground down to the 800-grit SiC paper. The isothermal oxidation experiments were performed from 900–1300°C in air for 20 h with an interval of 100°C. All samples were put in the Al_2O_3 crucibles and held at the oxidation temperature in a furnace to requisite time. The cyclic oxidation experiment was also performed in the furnace at the temperature of 1100°C and 1200°C. The samples were held at the temperature for an hour and cooled to room temperature in half an hour, which was called a cycle. The weight gains were measured by a microbalance with $\pm 10^{-4}$ g accuracy.

The X-ray diffraction (XRD) was used to determine the phases of oxide using a rotating anode X-ray diffractometer (Model D/MAX-RB, RIGAKU Corporation, Japan). The microstructures of oxide scales were investigated with scanning electron microscopy (SEM, Model JSM-5610LV, JEDL Ltd, Japan) coupled with energy-dispersive spectroscopy (EDS, Model Phoenix, EDAX, USA) for composition analysis.

3. Results and discussion

3.1 Oxidation kinetics

The dependence of weight gain per unit surface area on oxidation time at 900–1300°C is shown in figure 1(a). It was seen that the specific mass gains were relatively small at these several temperatures. The value, 2.48×10^{-2} kg/m², which was obtained at 1300°C for 20 h is much smaller than the values of Ti_3SiC_2 and Ti_3AlC_2 ,

75×10^{-2} kg/m² and 3.5×10^{-2} kg/m², under similar condition reported by Sun *et al* (2001). The results indicated that TSAC had good high-temperature oxidation resistance.

Correspondingly, the data shown in figure 1(b), was the dependence of the square of weight gain per unit area against oxidation time. The curves of 900 and 1100°C are in agreement with the linear law, and there is almost no difference for the weight gain between 900°C and 1000°C. The curves of 1200 and 1300°C were rather complicated. The two-step parabolic oxidation process was supposed to explain the oxidation kinetics (Sun *et al* 2009). So we suggested the oxidation of TSAC generally obeyed the parabolic rate law, which can be expressed as

$$(\Delta W/S)^2 = k_p t + c, \quad (1)$$

where $\Delta W/S$ is the weight gain per unit surface, k_p the parabolic rate constant and t the time, c is a constant. The parabolic rate constants at different temperatures, which are listed in table 1 were calculated according to figure 1(b). At 1200°C, the parabolic rate constants are 3.57×10^{-9} kg² m⁻⁴ s⁻¹ for 1–5 h and 8.08×10^{-10} kg² m⁻⁴ s⁻¹ for 6–20 h; at 1300°C, the parabolic rate constants are 2.48×10^{-8} kg² m⁻⁴ s⁻¹ for 1–4 h and 5.71×10^{-9} kg² m⁻⁴ s⁻¹ for 5–20 h, which suggests that a protect scale that prevents further oxidation was formed on the surface in the first 5 h at 1200°C and first 4 h at 1300°C.

In order to get more information of the oxidation process of TSAC, the activation energy, Q , was calculated in terms of the Arrhenius-type formula:

$$k = k_0 \exp(-Q/RT), \quad (2)$$

where k_0 is the pre-exponential factor, Q the effective activation energy, R the universal gas constant, and T the absolute temperature. The temperature dependence of the parabolic rate constants is shown in figure 2. According to the slope of the line shown in figure 2, a value of Q was calculated as 110 ± 10 kJ·mol⁻¹, however, the value of Ti_3SiC_2 consisting of 2 vol% TiC is 370 ± 20 kJ·mol⁻¹ (Barsoum and El-Raghy 1997) and the value of Ti_3AlC_2 is 175 kJ·mol⁻¹ (Wang and Zhou 2003). But the much lower

Figure 1. (a) Weight gain per unit area vs time for Ti_3SiC_2 oxidized at different temperatures and (b) dependence of the square of weight gain with time for Ti_3SiC_2 oxidized at different temperatures.

Figure 2. Arrhenius-type plot for k_p at 900–1300°C.

parabolic rate constant values resulted in the excellent oxidation behaviour.

The cyclic oxidation behaviour of TSAC at 1100–1200°C for 40 cycles was also investigated. The dependence of mass gain per unit surface area against number of cycles is shown in figure 3(a). Correspondingly, the square of the mass gain per unit surface area vs number of cycles is shown in figure 3(b).

A three-step cyclic oxidation process is obtained by carefully analysing the two curves. In the first step, i.e. at the first 6 cycles for 1100°C and the first 4 cycles for 1200°C, a sharp oxidation process is observed. In the second step, i.e. from 7 to 33 cycles for 1100°C and 4 to 31 cycles for 1200°C, the oxidation rate is much slower. In the third step, i.e. after 33 cycles at 1100°C and 31 cycles at 1200°C, nearly no mass gain is observed. Obviously, the formation and densification of the dense oxide scale occur in the first and second steps, while in the third step the dense oxide scale prevents the TSAC from fur-

ther oxidizing. It takes more time to densify the oxide scale at 1100°C due to lower temperature. No macro crack and spallation were observed at the oxidized surface.

3.2 Phase composition and microstructure of scale

To study the excellent oxidation resistance of TSAC samples, XRD and SEM were used to analyse the phase composition and surface morphology of the oxide scales, respectively. The XRD patterns of the samples oxidized at different temperatures for 20 h are shown in figure 4. Peaks from reflection on α - Al_2O_3 , TiO_2 (rutile) and Ti_3SiC_2 can be seen, and there are no peaks of SiO_2 and other carbides. It was also seen that the main peaks belonged to Ti_3SiC_2 even at a temperature of 1200°C, and its intensities decreased as oxidized temperature increased, which indicated the oxide scales were very thin and proved good oxidation resistance of samples from the other point. The composition of cyclic oxide scale was also analysed by X-ray diffraction (figure 5). The reaction products, α - Al_2O_3 and TiO_2 , and Ti_3SiC_2 are also observed. The peaks of Ti_3SiC_2 , whose intensities decreased with increased temperatures, are also present. The intensities of the α - Al_2O_3 and TiO_2 peaks are strengthened with increased temperature.

Table 1. Parabolic rate constants at 900–1300°C.

Temperature (°C)	Parabolic rate constants, K_p ($kg^2 m^{-4} s^{-1}$)
900	2.45×10^{-10}
1000	2.46×10^{-10}
1100	5.21×10^{-10}
1200	$3.57 \times 10^{-9}/8.08 \times 10^{-10}$
1300	$2.48 \times 10^{-8}/5.71 \times 10^{-9}$

Figure 3. (a) Plots of mass gain per unit surface area against number of cycles and (b) dependence of the square of the weight gain with number of cycles for Ti_3SiC_2 oxidized at 1100°C and 1200°C.

Figure 4. Results of X-ray diffraction analysis on the scale surface for 20 h at different temperatures.

Figure 5. XRD patterns of the scale surface after cyclic oxidation for 40 cycles at 1100°C and 1200°C.

The SEM micrographs of scales oxidized at 1200°C and 1300°C for 20 h are shown in figures 6(a) and (b). The thicknesses of oxide scales are 4–7 μm at 1200°C and 8–10 μm at 1300°C, respectively. Figures 7(a), (b) show the oxide-surface micrographs of samples cyclic-oxidized at 1100°C and 1200°C for 40 cycles, respectively. The thicknesses of dense oxide scales are about 6–8 μm . The large micro-crack can be observed between matrix and oxide scale. As shown in table 2, the results from EDS spectra indicated the oxide scales consisted of dense $\alpha\text{-Al}_2\text{O}_3$, and accompanied with little TiO_2 and SiO_2 , which prevent Ti_3SiC_2 from further oxidizing at high temperature. However, there are no peaks of SiO_2 in XRD patterns. It might be attributed to the fact that the SiO_2 content is so low that XRD do not detect it.

3.3 Oxidation mechanism

In order to understand the excellent resistance to oxidation of TSAC, further, it is important to appreciate the

primary oxidation mechanism. Many researchers have reported the oxidation of Ti_3SiC_2 which was controlled by the outward diffusion of titanium and inward diffusion of oxygen (Tong *et al* 1995). However, the oxidation product mainly consisted of $\alpha\text{-Al}_2\text{O}_3$ in our work, which suggests the oxidation mechanism has completely varied with the addition of aluminum.

At initial oxidation stage, the *in situ* oxidation of TSAC occurred. TiO_2 and SiO_2 were formed, and $\alpha\text{-Al}_2\text{O}_3$ was also formed with the addition of aluminum. The total reaction is summarized in the following equation

Table 2. Approximate weight fraction and bulk fraction of products in oxidized scale after cyclic oxidation at 1200°C.

	$\alpha\text{-Al}_2\text{O}_3$	TiO_2	SiO_2
Weight fraction (%)	88.37	6.53	5.10
Bulk fraction (%)	86.51	7.51	5.98

Figure 6. SEM micrographs of samples after oxidation for 20 h at (a) 1200°C and (b) 1300°C.

Figure 7. Secondary electron micrographs of samples after cyclic oxidation for 40 cycles at (a) 1100°C and (b) 1200°C.

Table 3. Bulk modulus, Young's modulus, density and thermal-expansion coefficients of Ti_3SiC_2 , $\alpha-Al_2O_3$, TiO_2 and SiO_2 .

Composition	Bulk modulus (GPa)	Young's modulus (GPa)	Density (g/cm ³)	TEC ($\times 10^{-6} K^{-1}$)	
				Normal to <i>c</i> axis	Parallel to <i>c</i> axis
$\alpha-Al_2O_3$	228	390	3.98	7.9	8.8
TiO_2	15.02	27	4.25	6.8	8.3
SiO_2	98.98	86.8	2.648	14	9
TiC	243	448	4.93		7.4
Ti_3SiC_2	206	320	4.53		9.1

Table 4. Thickness, thermal-expansion coefficient, and Young's modulus of oxide scale and matrix.

	Thickness (μm)	TEC ($\times 10^{-6} K^{-1}$)	Young's modulus (GPa)	Stress (MPa)
Oxide scale	8.05	8.44	344.61	-212.88
Matrix	4034.1	9.1	320	425.75

As the addition of aluminum, further oxidation of TSAC is not controlled by the outward diffusion of titanium and inward diffusion of oxygen, but by the outward diffusion of aluminum and inward diffusion of oxygen. As the densification of oxide scales, the two diffusion processes were held back. It is why TSAC has better oxidation resistance than Ti_3SiC_2 .

3.4 Discussion

From the above experimental results, the TSAC has excellent resistance to isothermal oxidation and cyclic oxidation. As the oxidation of Ti_3SiC_2 was controlled by the diffusion, the growth stresses should be rather small. Only the thermal stresses in the scale and matrix cyclic-oxidized at 1200°C resulting from the thermal-expansion mismatch are calculated in the following discussion.

Given the force balance, the thermal stress in oxide scale and matrix can be calculated by the following equations

$$\sigma_1 = \frac{(\alpha_1 - \alpha_2)E_1E_2d_2\Delta T}{2E_1d_1 + E_2d_2}(1 - \nu),$$

$$\sigma_2 = \frac{2(\alpha_2 - \alpha_1)E_1E_2\Delta T}{2E_1d_1 + E_2d_2}(1 - \nu),$$

where σ_1 , σ_2 ; α_1 , α_2 ; E_1 , E_2 ; d_1 , d_2 ; ν_1 , ν_2 are the stresses, thermal-expansion coefficients, appropriate Young's

modulus, average thickness and Poisson ratio of the oxide scale and matrix, $\Delta T = (T_{ox} - T_0)$. It is assumed that the modulus and thermal-expansion coefficients are independent of temperature. The total thermal-expansion coefficient was calculated by the Turner equation (Wang and Zhou 2003)

$$\alpha = \frac{\alpha_1K_1F_1/\rho_1 + \alpha_2K_2F_2/\rho_2 + \alpha_3K_3F_3/\rho_3}{K_1F_1/\rho_1 + K_2F_2/\rho_2 + K_3F_3/\rho_3},$$

where α_i , K_i , F_i and ρ_i are the thermal-expansion coefficients, bulk modulus, weight fraction and density of phase *i*. Crude results of weight fraction and bulk fraction calculated by EDS are listed in table 2. The thermal-expansion coefficients of different compositions are listed in table 3. The Young's modulus were calculated by the following equation

$$E = E_1V_1 + E_2V_2 + E_3V_3,$$

where E_i and V_i are the Young's modulus and bulk fraction of phase *i*. The values of Young's modulus of $\alpha-Al_2O_3$, TiO_2 and SiO_2 are listed in table 3. The Poisson ratio of oxide scale and matrix is 0.3 and 0.2, respectively. The average thickness of oxide scale and matrix was measured under SEM observation, which is given in table 4. The stresses produced in the oxide scale and matrix during cooling are -186.27 and 425.75 MPa. These crude data give us much important comparisons. The negative value shows that the oxide scale comes under compressive stress during cooling, while the positive value indicates tensile stress in the matrix. The enough compressive in-plane stresses in oxide scales make the loss of adherence to occur. Though the weight loss was not observed in the 40 cycles, the big crack was clearly shown in the micrograph (figure 7).

4. Conclusions

It is found that the oxidation kinetics of monolithic TSAC prepared by hot pressing generally obeys a parabolic law. The dense and adhesive oxide scales formed on TSAC consisted of a great deal of α -Al₂O₃ and little TiO₂ and SiO₂, which could greatly improve the high-temperature oxidation resistance of Ti₃SiC₂. The additive aluminum varies the oxidation mechanism of Ti₃SiC₂ with the outward diffusion of aluminum and inward diffusion of oxygen. A compressive stress was calculated in oxide scale cyclic-oxidized at 1200°C, which make the scales tend to craze.

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References

- Barsoum M W and El-Raghy T 1996 *J. Am. Ceram. Soc.* **79** 1945
- Barsoum M W et al 1999 *J. Phys. Chem. Solids* **60** 429
- Barsoum M and El-Raghy T 1997 *J. Electrochem. Soc.* **14** 2508
- El-Raghy T et al 1997 *J. Am. Ceram. Soc.* **80** 513
- El-Raghy T et al 1999 *J. Am. Ceram. Soc.* **82** 2855
- Feng A, Orling T, Yano T and Munir Z A 1999 *J. Mater. Res.* **14** 925
- Racault C, Langlais F and Naslain R 1994 *J. Mater. Sci.* **29** 3384
- Tong X, Okano T, Iseki T and Yano T 1995 *J. Mater. Sci.* **30** 3087
- Sun Z, Zhou Y and Li M 2001 *Corros. Sci.* **43** 1095
- Wang X H and Zhou Y 2003 *Corros. Sci.* **45** 891
- Zhu J and Mei B 2009 *Scr. Mater.* **36** 1742