Long-time Oxidation of $\text{Ti}_3(\text{Al,Si})\text{C}_2$ Carbides at 400-800 °C

Junhee Hahn¹, Sang Whan Park², and Dong Bok Lee^{3,*}

¹Center for Energy Materials Metrology, Korea Research Institute of Standards and Science, Daejeon 34113, Republic of Korea

²Materials Architecturing Research Center, KIST, Seoul 02792, Republic of Korea

³School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

Abstract: Quaternary carbides of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ ($x=0.3, 0.5$, and 0.7) were oxidized at 400, 600, and 800 °C for 0.5-6 months in order to study their long-time oxidation behavior in air. When they were oxidized at 400-600 °C for 0.5-3 months, oxidation proceeded relatively slowly with moderate weight gains. However, further oxidation at 400-600 °C for 6 months resulted in the oxidation-induced microcracking of oxide scales due to large volume expansion and large stress induced owing to the formation of Al_2O_3 , SiO_2 , TiO_3 , and TiO_2 in oxide scales. However, at 800 °C, microcracking of oxide scales, which could lead to pulverization of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$, did not occur due to stress relaxation in oxide scales. Instead, at 800 °C, $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ oxidized rapidly to form thick, somewhat porous oxide scales, which consisted primarily of an outer TiO_2 layer with some Al_2O_3 , an intermediate Al_2O_3 layer with some TiO_2 , and an inner TiO_2 layer with some ($\text{SiO}_2+\text{Al}_2\text{O}_3$). The overall long-time oxidation resistance of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 400-800 °C was considered to be poor. Factors that determined the oxidation rates of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ were; (1) How fast titanium oxidized to semi-protective titanium oxides, (2) How fast Al and Si oxidized to Al_2O_3 and SiO_2 barrier oxides, and (3) Whether oxidation-induced microcracking occurred in oxide scales or not. The ratio of Al/Si in $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ and the matrix grain size were apparently not dominant factors, because the basic oxidation mode of $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$, $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, and $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ was similar under the identical oxidation condition.

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1. INTRODUCTION

Ternary carbides such as Ti_3AlC_2 and Ti_3SiC_2 consist of edge-sharing Ti_3C_2 layers, which are separated by hexagonal nets of Al and Si atoms, respectively [1]. Like metals, they have good thermal and electrical conductivity, high toughness, and good machinability. Like ceramics, they display excellent chemical resistance, high Young's moduli, high temperature strength, and high melting points. Ti_3AlC_2 and Ti_3SiC_2 form $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ solid solutions, which have attracted enormous interest for a number of applications because of their high strength, hardness, and good oxidation resistance [2-4]. To utilize $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ quaternary carbides as structural components, a comprehensive understanding of their oxidation properties over a wide range of temperatures

is essential. Previously, $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ carbides with various compositions were synthesized via powder metallurgical routes, and their oxidation behavior was studied at 900-1300 °C [3-10]. Zhou *et al.* reported that $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ ($x=0.05-0.15, 0.75-0.95$) displayed good oxidation resistance at 900-1100 °C, because of formation of a continuous, protective $\alpha\text{-Al}_2\text{O}_3$ layer, in addition to the less protective TiO_2 [3-5]. The oxidation resistance of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ decreased at 1200-1350 °C owing to additional formation of Al_2TiO_5 through the reaction of $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 [4]. Besides $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 , the formation of a small amount of protective SiO_2 in oxide scales during oxidation at 900-1100 °C was also reported by Liu *et al.* [6]. Lee *et al.* reported that the oxidation of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 900-1200 °C led to formation of oxide scales that consisted of an outer (rutile- TiO_2 , $\alpha\text{-Al}_2\text{O}_3$)-mixed layer, a thin, intermediate Al_2O_3 layer, and an inner (rutile- TiO_2 , amorphous SiO_2)-mixed layer [7-10]. They suggested that the formation of semi-protective TiO_2 and the escape of carbon deteriorated the oxidation resistance. However,

- Junhee Hahn, Sang Whan Park: 연구원, Dong Bok Lee: 교수

*Corresponding Author: Dong Bok Lee

[Tel: +82-2-290-7355, E-mail: dlee@skku.ac.kr]

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further studies on the oxidation of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ are needed, because the purity and size of the starting powders, the sintering temperature/time/method, and the composition (x in $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$) in the powder metallurgically synthesized samples greatly influence the oxidation kinetics, mechanism, and scale structures. This study aimed to characterize the oxidation behavior of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ ($x=0.3, 0.5, 0.7$) at 400–800 °C for 6 months, which has not yet been adequately investigated. In this study, the oxidation characteristics of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ were compared with those of pure titanium.

2. EXPERIMENTAL

Polycrystalline $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$, $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, and $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ were synthesized by mixing TiC_x ($x=0.6$, $<45\text{ }\mu\text{m}\phi$), Al ($<45\text{ }\mu\text{m}\phi$, 99.9% purity), and Si ($<70\text{ }\mu\text{m}\phi$, 99.9% purity) powders at molar ratios of 3:0.7:0.3, 3:0.5:0.5, and 3:0.3:0.7, respectively, in a shaker mill for 10 min, and hot pressing into $19\text{ mm}\phi \times 10\text{ mm}$ pellets at 1400 °C under a pressure of 25 MPa for 60 min in flowing Ar gas [7–10]. Hot pressed pellets were cut into the required dimensions of $10 \times 10 \times 5\text{ mm}^3$, ground with 1000 grit SiC paper, ultrasonically cleaned in acetone and methanol, and oxidized at 400, 600, and 800 °C for 0.5–6 months in air atmosphere using a muffle furnace. For comparison purposes, pure titanium coupons were simultaneously oxidized. The specimens were analyzed using a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS), a field-emission electron probe microanalyzer (EPMA), and a high-power X-ray diffractometer (XRD) with Cu-K α radiation at 40 kV and 150 mA.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM microstructures of synthesized $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$. These specimens consisted of lamellar or somewhat equiaxed grains of micrometer size, which was typical in isostructural Ti_3SiC_2 [1,11], Ti_3AlC_2 [12], and $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ [7–10]. Average grain size was about 7.5 μm in length and 2.5 μm in thickness for $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$, 4 μm in length and 2 μm in thickness for $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, and 3 μm in length and 1.5 μm in thickness for $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$.

Fig. 1. SEM microstructure of (a) $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$, (b) $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, and (c) $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ (etchant; $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}=1:2:4$).

Apparently, grains refined with the addition of Si, which might be closely related with the reactivity and diffusivity of starting materials during hot pressing. Using the image analyzer, the volume fraction of pores was measured as 1.5% for $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$, 1.3% for $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, and 1% for $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ respectively, which suggested that the average density of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ was 98.7%.

In general Ti_3AlC_2 , $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$, and Ti_3SiC_2 have a layered hexagonal structure. Silicon atoms partially substituted into the Al sites in Ti_3AlC_2 to form $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$. Monolithic $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ was successfully synthesized, without any impurities under the detection limit of the XRD

Fig. 2. XRD patterns of Ti_3AlC_2 , $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$, $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$, and Ti_3SiC_2 between 5° and 80° .

technique, as shown in Fig. 2. Minor impurities in synthesized carbides are usually Ti_2AlC and Al_4C_3 in case of Ti_3AlC_2 , TiC , Ti_5Si_3 and SiC in case of Ti_3SiC_2 , and unreacted raw materials such as SiC and graphite [13-16].

Figure 3 shows long-time oxidation curves of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$, which were obtained by measuring weight gains due to

Fig. 3. Oxidation curves of $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$, $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, and $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ at 400, 600, and 800 °C for 0.5-6 months.

oxidation using a microbalance. Each data point was obtained from one specimen. Generally, weight increased more with the increment of oxidation time and temperature. At 400 °C, $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ displayed the smallest weight gains for 0.5-3 months, but oxidized completely to powder at 6 months. At 600 °C, $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ displayed modest weight gains for 0.5-3 months, but again oxidized to powder at 6 months. As such, pulverization of $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ during oxidation at (400, 600 °C)/(6 months) resulted from oxidation-induced microcracking of oxide scales, as will be explained later. When microcracking of oxide scales and subsequent pulverization of samples were absent during oxidation at

Fig. 4. Oxidation curves of Ti at 400, 600, and 800 °C for 0.5-6 months.

Fig. 5. XRD patterns of $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$ after oxidation for 3 months at 400, 600, and 800 °C.

(400-600 °C)/(6 months), simply the thickening of oxide scales proceeded, being similar to the oxidation of common metals. At 800 °C, all $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ oxidized relatively fast at similar rates, without pulverization. $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ oxidized faster at 400 °C than at 600 °C. Such anomalous oxidation was also observed during oxidation of Ti_3AlC_2 at 400-900 °C [17,18], Ti_2AlC at 500-900 °C [19], $\text{Ti}_3\text{AlC}_2/\text{TiC}$ composites at 550-950 °C [20], and Ti_3SiC_2 at 650 °C [21].

Basically, the oxidation behavior of $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$,

Fig. 6. XRD patterns of Ti after oxidation for 3 months at 400, 600, and 800 °C.

$\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$, and $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ at each test temperature of 400, 600, and 800 °C is considered to be similar, considering anomalous oxidation kinetics, and experimental error that arouse owing to the diverse size and alignment of matrix grains and density difference in each specimen (Fig. 1). $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ oxidizes according to the following equation [7-10].

The protectiveness of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ mainly depends on the continuity and compactness of extremely slow-growing Al_2O_3 and SiO_2 . These oxides could not grow fast enough to suppress the growth and transformation of titanium oxides, and the microcracking of oxide scales at 400-600 °C (*see* Figs. 7b and 11b). The origin of oxidation-induced microcracking is the large volume expansion arisen owing to the eq. (1), which yielded large stress that could disintegrate $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ into powder at 400-600 °C. At 800 °C, $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ did not suffer microcracking due to the stress relaxation (*see* Figs. 8 and 9). These figures show that $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ formed thick TiO_2 -rich oxide scales due mainly to fast oxidation of titanium, although Al_2O_3 and SiO_2 still

Fig. 7. SEM top view after oxidation at 400, 600, and 800 °C for 3 months. (a) Ti, (b) $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$.

grew slowly at 800 °C. The result obtained Fig. 3 may be summarized as follows. The long-time oxidation resistance of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ was poor due to microcracking of oxide scales and subsequent pulverization of samples at 400-600 °C as well as fast oxidation of titanium in $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 800 °C.

For comparison, titanium was subjected to the same oxidation conditions given in Fig. 3, and the weight gains due to oxidation were measured as shown in Fig. 4. Each data point was obtained from one sample. Titanium oxidized quite slowly at 400 °C, moderately at 600 °C, and extensively at 800 °C. Hence, the oxidation limit of Ti is known to be 600 °C [22]. Oxidation kinetics of Ti changed from parabolic to linear at 600-1000 °C, transitioning earlier with the increment of temperature [23,24]. Titanium, which forms semi-protective TiO_2 , is not oxidation-resistant. It displayed better oxidation behavior than $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 400 and 600 °C without pulverization. However, it oxidized much faster than $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 800 °C (Figs. 3 and 4).

Figure 5 shows XRD patterns of $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$ after (400-800 °C/3 months)-oxidation. At 400 °C, strong matrix peaks and weak (rutile- TiO_2 , Ti_3O)-peaks were detected, because of the thin scale formation. At 600 °C, Ti_3O disappeared while rutile- TiO_2 peaks became slightly stronger, implying that transient Ti_3O transformed to stable rutile- TiO_2 . At 600 °C, matrix peaks were strong, because the scale was still thin. Alumina and silica, which formed according to eq. (1), were undetected due to their small amount or amorphous nature. When oxidized further at 800 °C, matrix peaks were no longer detectable because a thick rutile- TiO_2 scale covered the surface [17,18].

For comparison, titanium was oxidized under the same conditions given in Fig. 5, and XRD data were acquired, as shown in Fig. 6. When oxidized at 400 °C, strong α -Ti matrix peaks and a faint anatase- TiO_2 peak were detected, indicating that oxidation progressed so slowly that a superficial oxide scale formed. Under the same 400 °C-oxidation, oxide peaks shown in Fig. 5 were a little stronger than those shown in Fig. 6, which suggested that $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$ oxidized a little faster than Ti, as is noticeable from Figs. 3 and 4. Also, anatase-to-rutile transformation occurred slightly faster in $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$ than in Ti. Such an increased oxidation rate and enhanced anatase-to-rutile transformation of $\text{Ti}_3\text{Al}_{0.5}\text{Si}_{0.5}\text{C}_2$ at 400 °C might be affected by the simultaneous oxidation of Al, Si, and carbon. At 400 °C, TiO_2 grew slowly, Al_2O_3 and SiO_2 grew much more slowly, and $\text{CO}_2(\text{g})$ liberated, which could affect the oxidation kinetics and TiO_2 -transformation in $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$. The 600 °C-oxidation revealed strong (rutile- TiO_2 , α -Ti)-peaks and relatively weak Ti_3O peaks (Fig. 6),

which indicated that the oxide scale was relatively thin, and metastable anatase that was detected at 400 °C transformed to stable rutile at 600 °C [25,26]. Transient Ti_3O was absent, and a thick scale consisting of rutile- TiO_2 formed after 800 °C-oxidation (Fig. 6).

Surfaces of $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ after (400-800 °C/3 months)-oxidation were compared with those of Ti, as shown in Fig. 7. For Ti at 400 °C, grinding grooves that formed during the sample preparation stage were visible because of the slow oxidation rate. Titanium oxides on Ti grew to micrometer sized round grains at 600 °C. Rutile- TiO_2 grains that formed at 800 °C on Ti were still fine despite lengthy oxidation, because they continued to nucleate at the surface through outward diffusion of Ti^{4+} ions from the matrix [23-25]. By contrast, $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ suffered from the microcracking of the oxide scale at 400 °C. The oxide scale that formed at 600 °C on $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ was thin; however, short microcracks were visible. Unlike Ti, $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ was prone to microcracking and subsequent pulverization at 400-600 °C (Fig. 3). Oxidation-induced microcracking was similarly observed during the oxidation of Ti_2AlC at 500-600 °C for 20 h [19], Ti_3SiC_2 at 650 °C for 10 h [21], and $\text{Ti}_3\text{AlC}_2/\text{TiC}$ composites at 500-660 °C for 20-40 h [17,20]. At 800 °C, rutile- TiO_2 on $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ grew to characteristic coarse, pillar-like grains, because not nucleation but grain growth of TiO_2 dominated owing to partial deterrence of the outward diffusion of Ti^{4+} ions from the matrix by simultaneously formed Al_2O_3 and SiO_2 [7-10]. The absence of Al_2O_3 and SiO_2 was the reason for the much faster oxidation of Ti compared to $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 800 °C (Figs. 3 and 4).

Figure 8 shows EPMA results of $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ after (800 °C/3 months)-oxidation. The oxide scale consisted primarily of an outer TiO_2 layer having a small amount of Al_2O_3 , an intermediate Al_2O_3 layer having a small amount of TiO_2 , and an inner TiO_2 layer having a small amount of ($\text{SiO}_2+\text{Al}_2\text{O}_3$). There was sufficient Ti in $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ to form outer and inner TiO_2 -rich layers. Since silicon oxidizes roughly *in situ* due to the high bonding energy of $\text{Si}^{4+}\text{-O}^{2-}$ [27], SiO_2 can be treated as a marker to understand the oxidation mechanism [11,28]. Hence, it is seen that the flat interface between the intermediate Al_2O_3 -rich layer and inner TiO_2 -rich layer corresponds to the original sample surface. The thickness of the oxide scale was $\sim 140\ \mu\text{m}$, which varied to a certain

Fig. 8. $\text{Ti}_3\text{Al}_{0.7}\text{Si}_{0.3}\text{C}_2$ after oxidation at 800 °C for 3 months. (a) EPMA cross-sectional secondary electron (SE) image, (b) EPMA line profiles along A-B.

extent depending on the location. Voids formed more in the thicker part of the oxide scale. They formed due to the Kirkendall effect caused by the outward diffusion of Ti^{4+} and Al^{3+} ions, the evolution of CO_2 , and anisotropic volume expansion during scaling [7-10]. Voids could act as easy-diffusion paths and stress concentrators.

Figure 9 shows EPMA results of $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ that oxidized under the same condition given in Fig. 8. The oxide scale with a thickness of $\sim 125\ \mu\text{m}$ consisted primarily of the outer TiO_2 layer having some Al_2O_3 , the intermediate Al_2O_3 layer having some TiO_2 , and the inner TiO_2 layer having some Al_2O_3 and SiO_2 . The oxide scales shown in Figs. 8 and 9 formed through the follow process.

Upon exposure to oxygen, titania, alumina, and silica formed competitively on $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$, according to eq. (1). Nonstoichiometric TiO_2 soon overgrew highly stoichiometric

Fig. 9. $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ after oxidation at 800 °C for 3 months. (a) EPMA cross-sectional SE image, (b) EPMA maps of Ti, Si, Al and O.

Al_2O_3 and SiO_2 , and constituted the outer scale. This process depleted Ti underneath, and thereby enriched Al, leading to formation of the intermediate Al_2O_3 scale, which in turn depleted Al and thereby enriched Ti underneath, resulting in formation of the inner TiO_2 scale. It is noted that TiO_2 grew by either outward diffusion of interstitial Ti^{4+} ions or inward diffusion of O^{2-} ions via oxygen vacancies [29]. The outer oxide layer grew by outward diffusion of Ti^{4+} ions plus a small amount of Al^{3+} ions, the intermediate oxide layer grew by outward diffusion of Al^{3+} ions plus a small amount of Ti^{4+} ions, and the inner oxide layer containing some SiO_2 grew by inward diffusion of O^{2-} ions.

On the other hand, oxide scales that formed on Ti_3SiC_2 consisted of an outer TiO_2 layer, an intermediate SiO_2 layer, and an inner $(\text{TiO}_2+\text{SiO}_2)$ -mixed layer [11], whereas those that formed on Ti_3AlC_2 consisted of an outer TiO_2 layer, an intermediate Al_2O_3 layer, and an inner $(\text{TiO}_2+\text{Al}_2\text{O}_3)$ -mixed layer [12]. In this study, the intermediate layer consisted of not SiO_2 but Al_2O_3 , because of the low dissociation pressure of Al_2O_3 when compared to SiO_2 .

For comparison, titanium was oxidized under the same condition given in Figs. 8 and 9, and the SEM result is shown in Fig. 10. A laminated rutile- TiO_2 oxide layer was seen. Its thickness varied in the range of 0.8-1.3 mm, depending on

Fig. 10. SEM cross-sectional SE image of Ti after oxidation at 800 °C for 3 months.

Fig. 11. $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ after oxidation at 400 °C for 3 months. (a) EPMA cross-sectional SE image, (b) EPMA cross-sectional back-scattered electron (BSE) image, (c) EPMA maps of Ti, Si, Al and O.

the location. Titanium gained the weight about six time more than $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 800 °C, because it could not form Al_2O_3 and SiO_2 (Figs. 3 and 4).

Figure 11 shows EPMA results of $\text{Ti}_3\text{Al}_{0.3}\text{Si}_{0.7}\text{C}_2$ after (400 °C/3 months)-oxidation. This specimen displayed the weight gain of 1.8 mg/cm^2 (Fig. 3). Its surface displayed oxidation-induced microcracks (Fig. 7b). The oxide scale was 9 μm -thick (Fig. 11a), and had microcracks, which could facilitate the inward diffusion of oxygen (Fig. 11b). At 400 °C, $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ oxidized relatively slowly for 0.5-3

months (Fig. 3). Unlike Figs. 8 and 9, the oxide scale shown in Fig. 11c could not develop into the triple-layered oxide scale, because of the slow diffusion and oxidation reaction. Additionally, the outward diffusion of cations was negligible, which could be recognizable from the location of SiO_2 in the oxide scale (Fig. 11c). Such resulted in the formation of the TiO_2 -rich oxide scale having rather uniformly distributed SiO_2 and Al_2O_3 , which was plausible considering that the ratio of Ti:Al:Si was 3:0.3:0.7.

4. CONCLUSIONS

The oxidation behavior of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ at 400–800 °C for 0.5–6 months was studied. During (400–600 °C/6 months)-oxidation, oxidation-induced microcracking could lead to pulverization of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$, because oxidation of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ to Ti_2O_3 , (anatase or rutile)- TiO_2 , Al_2O_3 , SiO_2 , and $\text{CO}_2(\text{g})$ induced a large volume expansion and thereby high stress in the oxide scales. During (800 °C/0.5–6 months)-oxidation, microcracking and subsequent pulverization of $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ did not occur due to stress relaxation; however, $\text{Ti}_3\text{Al}_x\text{Si}_{1-x}\text{C}_2$ formed thick oxide scales consisting of an outer TiO_2 -rich layer, an intermediate Al_2O_3 -rich layer, and an inner TiO_2 -rich layer owing to enhanced oxidation and diffusion rates.

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