

High Temperature Oxidation of Ti_3Al/SiC_p Composites in Oxygen

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In order to improve the oxidation resistance of Ti_3Al , Ti -25at.%Al composites containing dispersed particles of 15wt.%SiC were prepared by a tubular mixing-spark plasma sintering method. The sintered composites had Ti_3Al , SiC, Ti_5Si_3 and TiC. The presence of Ti_5Si_3 and TiC indicates that some of SiC particles reacted with Ti to form more stable phases. From oxidation tests at 800, 900 and 1000°C under 1 atm of pure oxygen, it was found that the oxidation rate of Ti_3Al was effectively reduced by the addition of SiC. The scale was primarily composed of an outer TiO_2 layer having some Al_2O_3 islands, an intermediate relatively thick Al_2O_3 layer, and an inner $TiO_2+Al_2O_3+SiO_2$ mixed layer. Beneath the scale, Kirkendall voids were seen.

Key words : Intermetallics, Ti_3Al , Silicon carbide, Oxidation

I. Introduction

Titanium aluminides based on monolithic α_2-Ti_3Al have attracted a great deal of attention from the aerospace and automobile industries for high temperature applications, because of their low density, high specific strength and good creep rupture strength.¹ However, their applications have been limited due to the poor fracture toughness and impact resistance at low temperature, and poor oxidation resistance and oxygen embrittlement at high temperature.

Alloy compositions of Ti_3Al with current engineering significance are based on Ti -(20-25at%)Al-(10-30at%)Nb with and without (0.5-5at%)(V, Mo).² By alloying with Nb, V and Mo, mechanical properties such as ductility, strength and creep resistance have been improved to a greater extent. In order to improve the oxidation resistance of Ti_3Al , several techniques including alloying additions and surface treatments have been employed. However, it should be noted that the alloying additions have not resulted in continuous alumina scale formation, though the oxidation rate decreased to some extent. The scale primarily consisted of an outer TiO_2 layer and inner $TiO_2+Al_2O_3$ mixed layer, which were separated by an intermediate Al_2O_3 layer which was not sufficiently continuous to become a protective layer. Approximately 60-70at%Al was needed for binary Ti-Al alloys to form a continuous alumina scale in air.³ Regarding the surface treatment, oxidation resistant TiAl₃ coating has been successfully applied on Ti_3Al +Nb alloys by conventional pack aluminizing.^{4,5} The coating displayed excellent cyclic oxidation resistance at 1000°C for at least 40 hr by the formation of a primarily protective alumina scale. However, the inherently brittle coating was susceptible to local fracture,

revealing multiple coating cracks during thermal cycling.

In this study, in order to improve the intrinsic resistance to oxidation, Ti_3Al composites containing dispersed SiC particles were prepared and their high temperature oxidation behavior was investigated. Recently, the present authors⁶ reported that TiAl composites containing dispersed particles of 5, 10, 15wt%SiC had excellent oxidation resistances during both isothermal and cyclic oxidation tests between 1000 and 1200°C in air. The thin scales primarily consisted of a single layer of Al_2O_3 mixed with randomly distributed TiO_2 . This was a sharp contrast with other conventional TiAl alloys where thick multiple layers of $TiO_2/Al_2O_3/TiO_2+Al_2O_3$ scales from the oxide-gas interface formed.^{7,8} The purpose of this paper is to find the feasibility of employing dispersed SiC particles in Ti_3Al alloys and, if any, to present the beneficial effects of SiC particles in Ti_3Al alloys.

II. Experimental Procedure

Powders of Ti (10 μm size, 99.9% pure), Al (3 μm size, 99.9% pure) and SiC(2-3 μm size, >99% pure) were weighed in appropriate ratios and mixed in a tubular mixer for 75hr under Ar+1%N₂ atmosphere to make 75% Ti-25%Al-15wt% SiC alloys. The mixer (Switzerland, Willy A. Bachofer Co., Type T2C) uses no mixing media and has tubular plastic container which performs three-dimensional rotational mixing. The composition is given in terms of atomic percent for metallic components, based only on the metallic components, while the dispersed phase of SiC is given in weight percent based upon the total weight of the alloy. The mixed powders were discharged into a graphite mold positioned in a specially designed uniaxial die, evacuated, and then plasma

sintered at 1050°C for 10 min. under the pressure of 57 MPa. The prepared cylindrical specimen was approximately 30 mm in diameter and 4.7 mm high. The obtained sintered density was 97.9%. After cutting into appropriate sizes to have about 2 g in weight, the specimens were sanded to a 1200 grit SiC paper to remove any oxide that may have formed and finally were oxidized.

Oxidation tests were performed at 800, 900 and 1000 °C under 1atm of pure oxygen atmosphere. Weight changes during oxidation were continuously measured using Shimadzu TGA-51H automatic recording microbalance. Morphologies of the base composite and the scale were examined by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA), electron probe micro-analysis (EPMA) and X-ray diffraction (XRD) analysis.

III. Results and Discussion

Fig. 1 shows the morphology of Ti, Al and SiC powders mixed to manufacture Ti₃Al-15wt%SiC specimens. Individual particles of angular-shaped Ti, round Al and partially fragmented SiC are seen, indicating that no considerable solid state reactions among particles occurred



Fig. 1. Scanning electron micrography of Ti, Al and SiC powders after mixing.

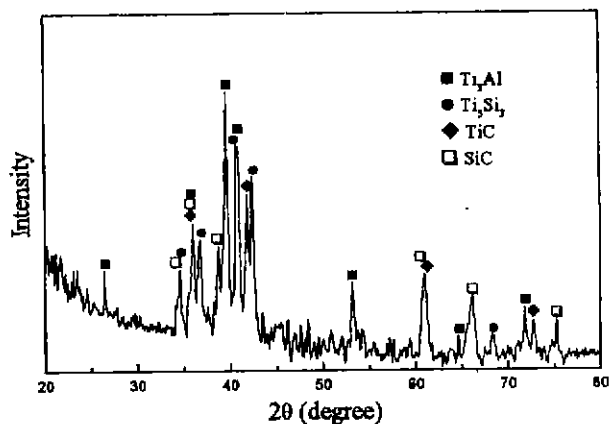


Fig. 2. X-ray diffraction pattern of sintered Ti₃Al-15wt%SiC composite.

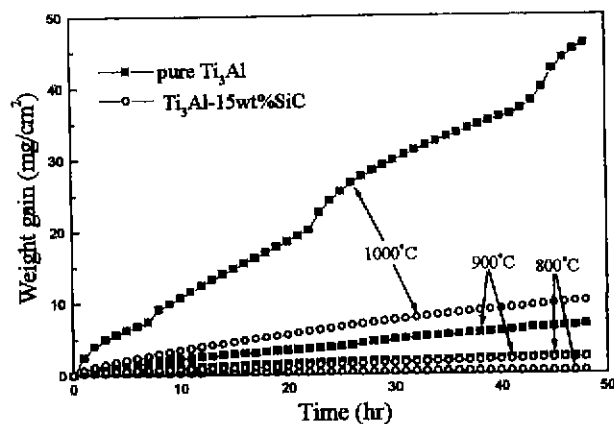


Fig. 3. Weight gain vs. time curves of pure Ti₃Al and Ti₃Al-15wt%SiC during oxidation in oxygen.

during mixing. However, the XRD pattern of a sintered specimen shown in Fig. 2 clearly shows that the matrix consisted of α-Ti₃Al, SiC, Ti₅Si₃ and TiC. The presence of Ti₅Si₃ and TiC indicates that the some of SiC particles have reacted during sintering with Ti to form thermodynamically more stable Ti₅Si₃ and TiC phases.

The oxidation kinetics of Ti₃Al-15wt%SiC specimen between 800 and 1000°C are shown in Fig. 3. For comparison, the oxidation kinetics of SiC-free Ti₃Al alloy manufactured by the identical sintering process are included. As expected, the weight gains of both alloys increased as the oxidation temperature increased. In contrast with SiC-free alloy which displays repetitive scale breakdown at 1000°C, the SiC-containing specimen exhibits less weight gains and generally follows the parabolic

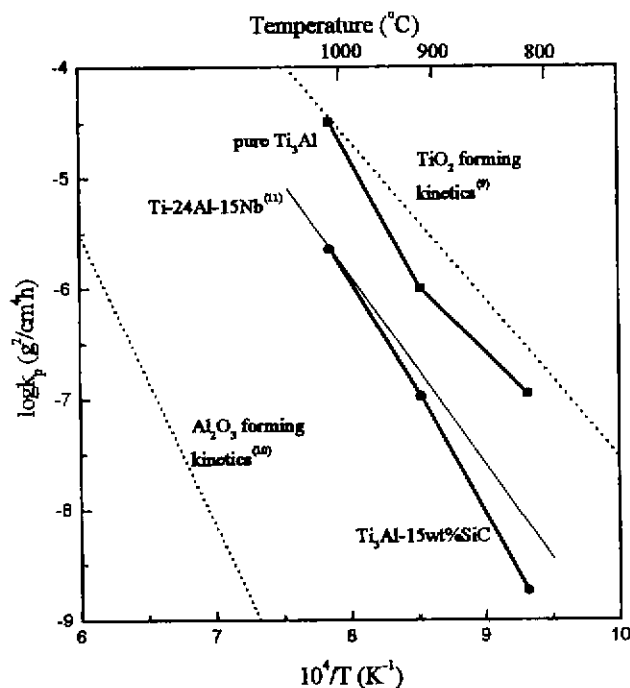


Fig. 4. Plot of k_p values in oxygen as a function of $1/T$.

rate law. This indicates that the kinetics is controlled by a diffusion process. Strictly, the curves of SiC-free specimen at 1000°C is parabolic only in time intervals between discontinuities. But, for the sake of simplicity, all the curves were fitted to a single parabolic equation, $\Delta W = k_p t^{1/2}$, where ΔW is the weight gain per unit area and t is the oxidation time. The derived parabolic rate constants, k_p , for the two specimens at each temperature were presented in Fig. 4. Also, superimposed are the kinetics for the formation of TiO_2 ⁹⁾ and Al_2O_3 .¹⁰⁾ Although the k_p values of the SiC-containing specimen lie a little closer to that of the formation of TiO_2 than that of the formation of Al_2O_3 , the SiC addition has effectively increased the oxidation resistance of Ti_3Al . The oxidation rate of $\text{Ti}_3\text{Al-15wt\%SiC}$ is comparable to that of Ti-24Al-15Nb .¹¹⁾

A typical X-ray diffraction pattern of $\text{Ti}_3\text{Al-15wt\%SiC}$ after oxidation is shown in Fig. 5. The oxides formed on both SiC-containing and SiC-free specimens primarily consisted of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$. The only difference between these two specimens is that, under the identical oxidation condition, the SiC-free specimen had stronger TiO_2 peaks

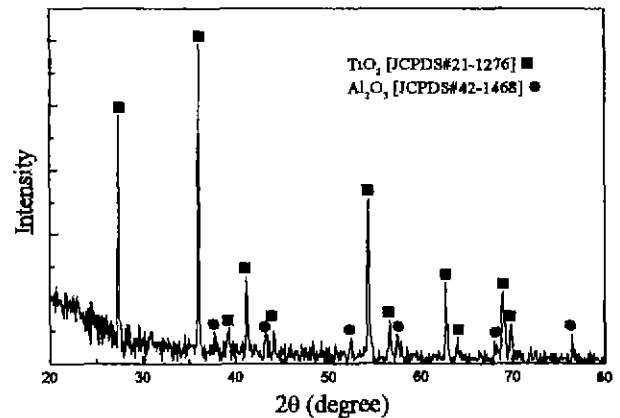


Fig. 5. X-ray diffraction pattern of $\text{Ti}_3\text{Al-15wt\%SiC}$ after oxidation in oxygen for 48 hr at 1000°C.

or weaker Al_2O_3 peaks compared to SiC-containing specimen. This indicates that SiC dispersoids help the alumina formation to some degrees. It is well known that in Ti_3Al alloys^{2,12)} an outer layer of fast-growing TiO_2 develops as

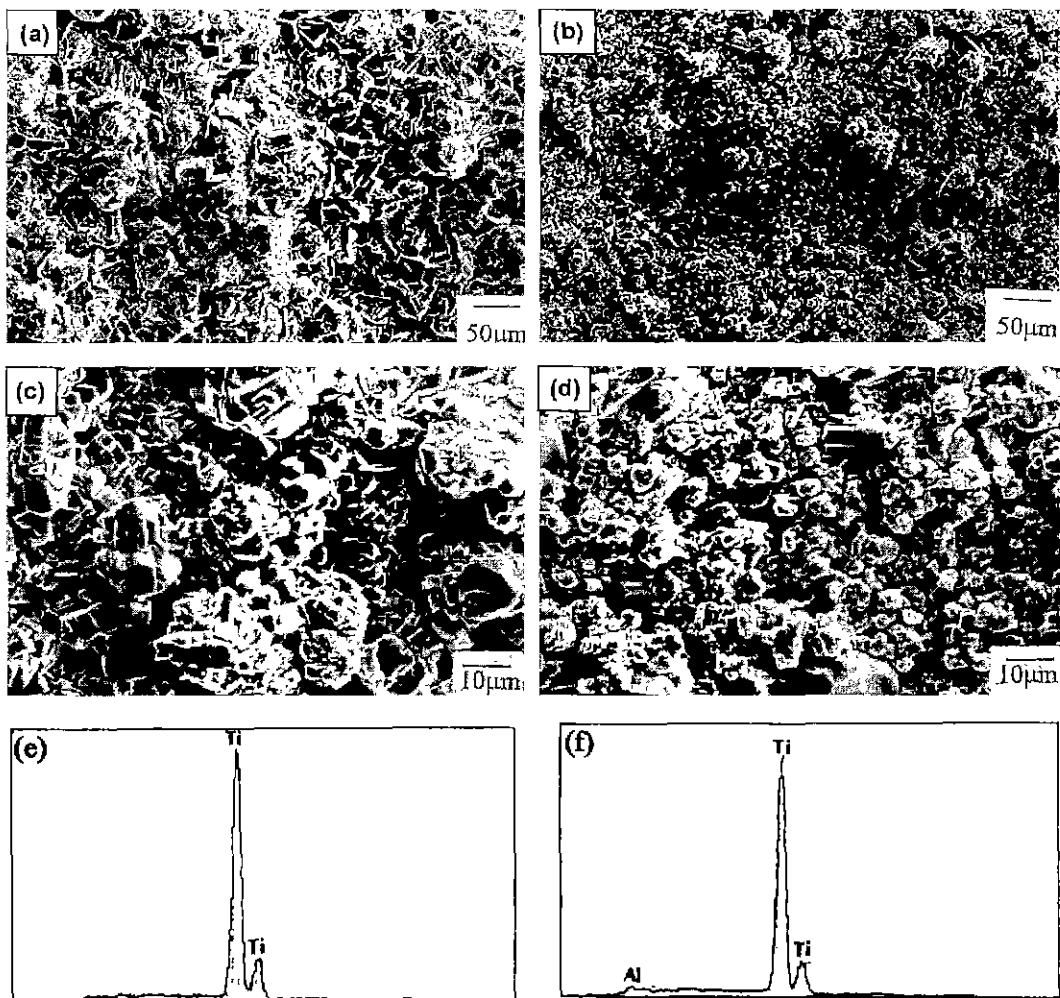


Fig. 6. Scales after oxidation in oxygen at 1000°C. (a) top view of pure Ti_3Al , 15 hr, (b) top view of $\text{Ti}_3\text{Al-15wt\%SiC}$, 15 hr, (c) top view of pure Ti_3Al , 48 hr, (d) top view of $\text{Ti}_3\text{Al-15wt\%SiC}$, 48 hr, (e) EDXA spectrum of (c) and (f) EDXA spectrum of (d).

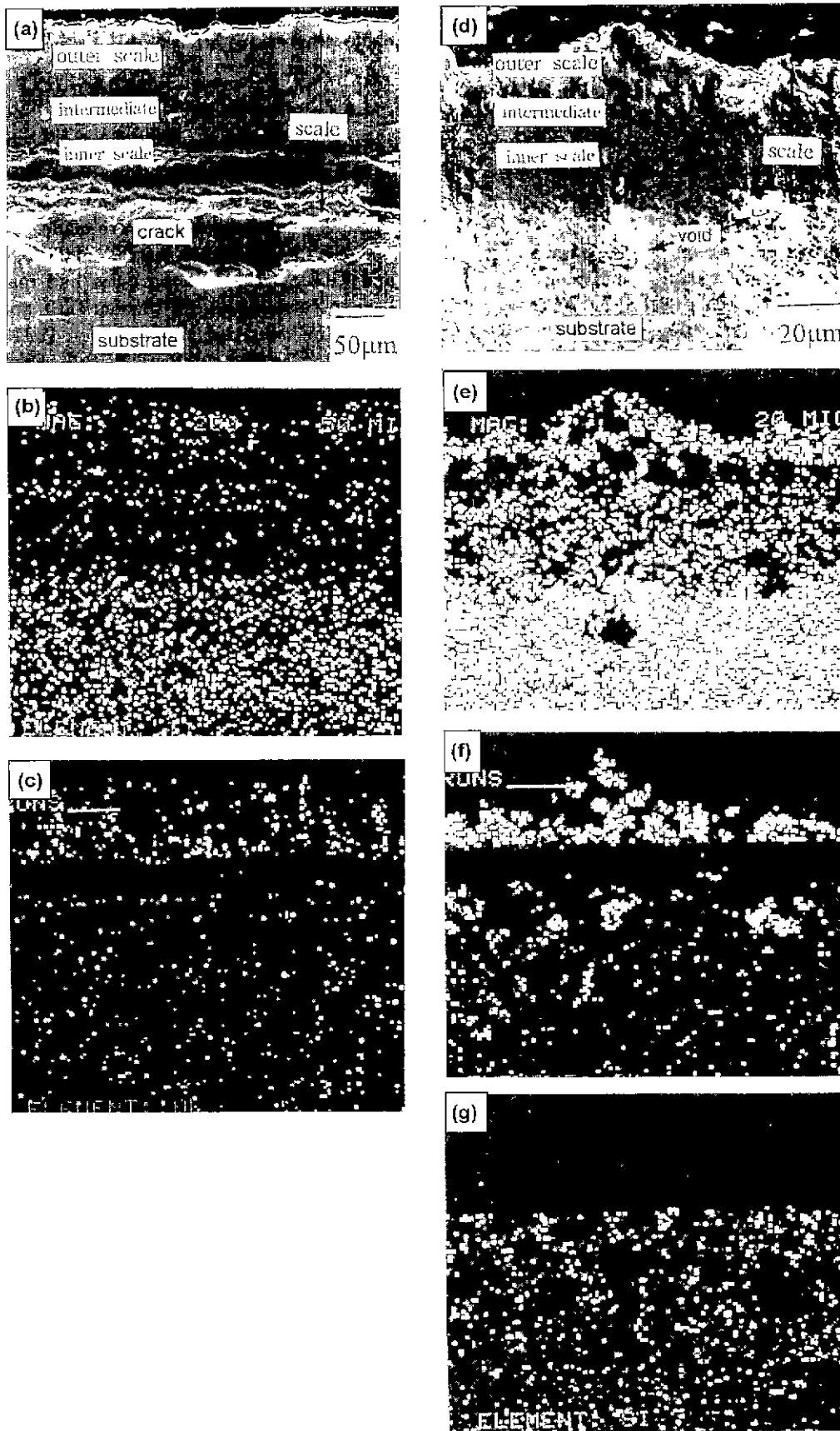


Fig. 7. Scales after oxidation in oxygen for 48 hr at 1000°C. (a) cross section of pure Ti_3Al , (b) Ti image, (c) Al image, (d) cross section of $Ti_3Al-15wt\%SiC_p$, (e) Ti image, (f) Al image and (g) Si image.

the reaction progresses. Immediately beneath this layer, the outward diffusion of Ti to form TiO_2 leaves Kirkendall voids. Also, the selective oxidation of Ti at the outer surface depletes Ti leading to the increase of Al concentration so that an alumina layer forms underneath the TiO_2 layer. Once outer TiO_2 and intermediate Al_2O_3 layers form, the outward diffusion of Ti and Al is retarded and, thereby, inward diffusion of oxygen plays a role when inner $\text{TiO}_2+\text{Al}_2\text{O}_3$ mixed layer forms.¹²⁾

The surface microstructures and EDXA spectra of oxide films produced on SiC-free and SiC-containing Ti_3Al are given in Fig. 6. The oxide scale formed on SiC-free Ti_3Al had randomly oriented essentially pure TiO_2 crystals, the growth rate of which always increased as the oxidation time or temperature increased. On the other hand, the scale on $\text{Ti}_3\text{Al-15wt}\%\text{SiC}$ had always a fine microstructure and a smooth surface, the composition of which was composed of TiO_2 and some Al_2O_3 . The fact that the scale formed on SiC-containing specimens had finer oxide grains may indicate that unreacted SiC dispersoids are acting as oxide nucleation sites leading to a decrease in oxide grain size, similar to the other dispersoid oxides¹³⁾ and nitrides.¹⁴⁾ This increase in nucleation rate allows for a more rapid formation of a protective scale and a lower total mass gain.

Fig. 7 shows the cross sections of the scales formed on both SiC-free and SiC-containing specimens after oxidation for 48 hr at 1000°C. The scales on both specimens were basically composed of an outer TiO_2 layer having some Al_2O_3 islands, an intermediated Al_2O_3 layer which is known to provide the necessary oxidation protection in Ti_3Al , and an inner $\text{TiO}_2+\text{Al}_2\text{O}_3$ mixed layer. Such morphologies were frequently observed in Ti_3Al alloys.^{15,16)} The major differences of Fig. 7(d) from Fig. 7(a) are as follows.

Firstly, the thickness of the scale is much thinner. This obviously indicates that the oxidation resistance was effectively increased through the incorporation of SiC dispersoids in Ti_3Al . Secondly, the intermediate Al_2O_3 layer is thicker, though this layer is not continuous enough to prevent the further oxidation of the base matrix. Thirdly, elemental distribution of Si within the inner $\text{TiO}_2+\text{Al}_2\text{O}_3$ mixed layer is noticed. This phenomenon is in principle quite similar to that observed in TiAl+Si alloys,^{16,17)} where an amorphous SiO_2 layer which would not show-up in XRD patterns was present at the inner $\text{TiO}_2+\text{Al}_2\text{O}_3$ layer. Fourthly, the Kirkendall void formation owing to the outward diffusion of the substrate elements, which occurs simultaneously with the inward diffusion of oxygen during oxidation in Ti-Al alloys,¹⁵⁾ is seen beneath the oxide scale. The voids would generally decrease the scale adherence. However, it should be noted that in SiC-free alloys the serious outward diffusion of the substrate elements as well as the inward diffusion of oxygen due to the poorer oxidation resistance led to the formation of interconnected numerous voids, resulting in local spalla-

tions or cracking at the oxygen-affected zone below the oxide-substrate interface.

IV. Conclusions

A composite of $\text{Ti}_3\text{Al-15wt}\%\text{SiC}$ was powder metallurgically prepared and its oxidation behavior at 800, 900 and 1000°C under 1 atm of pure oxygen was studied. The following observations were made.

(1) The sintered composites had Ti_3Al , SiC, TiAl, Ti_3Si_3 and TiC. Some of SiC particles had reacted with Ti to form more stable phases such as Ti_3Si_3 and TiC.

(2) The oxidation resistance of Ti_3Al was effectively increased by the addition of SiC. Dispersoids of SiC appear to facilitate the alumina formation and oxide grain refinement.

(3) The scale was primarily composed of an outer TiO_2 layer having some Al_2O_3 islands, an intermediate relatively thick Al_2O_3 layer, and an inner $\text{TiO}_2+\text{Al}_2\text{O}_3+\text{SiO}_2$ mixed layer. The formation of an amorphous SiO_2 phase within the inner mixed layer increases the oxidation resistance further. Beneath the scale, Kirkendall voids were seen.

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