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Oxidation resistance of intermetallic compounds Al_3Ti and TiAl

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The oxidation kinetics and morphological features of Al_3Ti and TiAl were investigated. The oxidation resistance of Al_3Ti is much better than that of TiAl, for example, by a factor of about 30 at 1000° C for 48 h. The big difference in the oxidation resistance is related to the characteristics of the external oxide scales of a protective Al_2O_3 or a mat of crystalline TiO_2 formed on Al_3Ti or TiAl, respectively. Sufficient aluminium transport from Al_3Ti assists the formation of the Al_2O_3 scale which acts as a protective film against oxidation. The poor aluminium content of TiAl produces Ti_3Al phase at the interface of TiAl and oxide scales and increases the diffusivity of titanium in the Al_2O_3 scale. The external crystalline TiO_2 scale produced by the diffusion of titanium through the Al_2O_3 scale enhances oxidation of TiAl.

1. Introduction

Considerable attention has recently been given to the mechanical and oxidation properties of the aluminides with transition metals which have been used as high-temperature materials of superior strength-to-weight ratio in aircraft and/or automobile parts [1]. One of the candidates for low density–high strength intermetallic compounds used at high temperatures exists in the Al–Ti system. In this system there are three intermetallic compounds or ordered alloys such as Ti_3Al, TiAl and Al_3Ti. The deformation behaviour of these compounds have been extensively investigated and the difficulty for industrial application is overcome by improvement of their ductility [2–11].

Recently, Al_3Ti has been expected to be a potential candidate for a low-density high-temperature structural material itself, and also a good coating material, because its greater aluminium content gives a lower density and probably better oxidation resistance than TiAl [10, 12]. TiAl and Ti_3Al have been reported to exhibit on poor resistance to oxidation at high temperatures above about 800° C, because the external layer of those compounds is not a protective Al_2O_3 film, but TiO_2 or a mixture of TiO_2 and Al_2O_3 [12]. When the surface is coated with Al_3Ti, a protective Al_2O_3 film can be expected to form and increase the oxidation resistance.

In this paper we present the isothermal oxidation kinetics and resistance of the intermetallic compounds Al_3Ti and TiAl. The morphology of the oxides and the alloy formed on the compounds are also reported.

2. Experimental details

Pure titanium (99.9%) and aluminium (99.99%) were melted in a high-purity argon plasma furnace to prepare intermetallic compounds TiAl containing 35 wt % Al and Al_3Ti containing 37.3 wt % Ti. Al_3Ti single-phase specimens were carefully prepared by remelting and solidification of the master ingot in Ar–10% H_2 gas atmosphere because of its narrow composition. Thin sheets (10 mm × 10 mm × 1 mm) were cut from the cast ingot and their surfaces were electrically polished after grinding with metallographic polishing papers. Isothermal oxidation tests were carried out at temperatures between 800 and 1000° C in pure oxygen gas flowing at a rate of $200\,\mathrm{ml\,min^{-1}}$ at atmospheric pressure. Weight gains due to oxidation were examined by thermogravimetric analysis. The microstructure of the oxide scales and/or the alloy formed at the interface was observed by scanning electron microscopy and the microanalyses of the principle elements (Al, Ti) were also done by energy-dispersive X-ray (EDX) analyses. Crystal structure was confirmed by X-ray diffractometry measurement.

3. Results and discussion

Fig. 1 shows the variation of weight gain per unit area of TiAl compounds with the oxidation time at various temperatures. In the early stages of oxidation, the curves show a parabolic shape indicating formation of a protective oxide thin scale against oxidation, probably Al_2O_3 scale. After the initial transient period, the curves become linear and the slope of the curves increases with increasing temperature. In particular, weight gain increases at great speed at 1000° C. The transient period from the parabolic to the linear part is shortened with increasing temperature.

For comparison with the oxidation kinetics of Al_3Ti and TiAl, the weight gain–oxidation time curves of both compounds at 900 and 1000° C are shown in Figs 2 and 3. It is obvious that the oxidation resistance of Al_3Ti is much better than that of TiAl. The tendency

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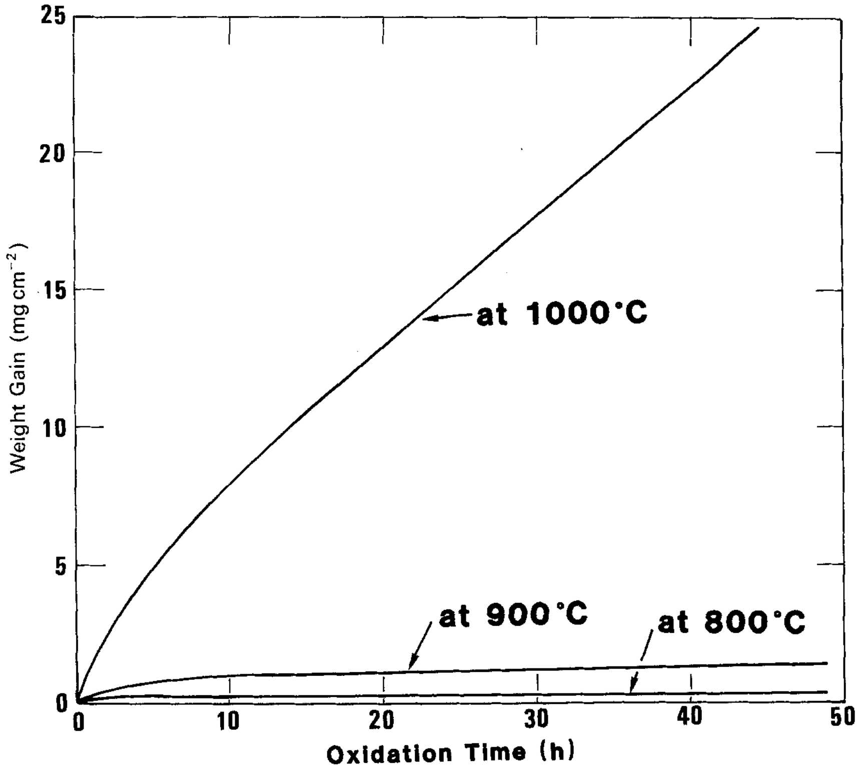

Figure 1 Thermogravimetric results for weight gain per unit area of TiAl as a function of annealing time, when exposed to oxygen at various temperatures.

becomes more remarkable at higher temperatures. The oxidation of Al_3Ti is much slower than that of TiAl, for example, roughly by a factor of 30 at 1000° C for 48 h. The weight gain–time relationship of Al_3Ti was proved to be still controlled by a parabolic rate law in the form of parabolic plots even at 1000° C. Thus, the big difference in the kinetics of oxidation of Al_3Ti and TiAl can be attributed to the morphology and the characteristics of the oxide scales.

Fig. 4 shows a scanning electron micrograph and the EDX analyses of a cross-section of oxide scales formed on the TiAl exposed to oxygen at 1000° C for 48 h. The external layer of the oxide scales is TiO_2 and the mixture of Al_2O_3 and TiO_2 can be observed under the TiO_2 layer. Large numbers of voids and pores are formed in the phase of the mixture of Al_2O_3 and TiO_2. In the early stages of oxidation of TiAl, Al_2O_3 film must be formed on the surface but it does not effectively as a protective oxide scale against further oxidation because of the high diffusivity of titanium in the Al_2O_3 scale, and the nucleation and growth of TiO_2 phase in the Al_2O_3 scale produces many pores. Numerous pores and oxide scales which were embedded as a diffusion marker are observed at the initial surface of TiAl, indicated by a white arrow in Fig. 4. Under the initial surface of TiAl, oxide scales are also observed

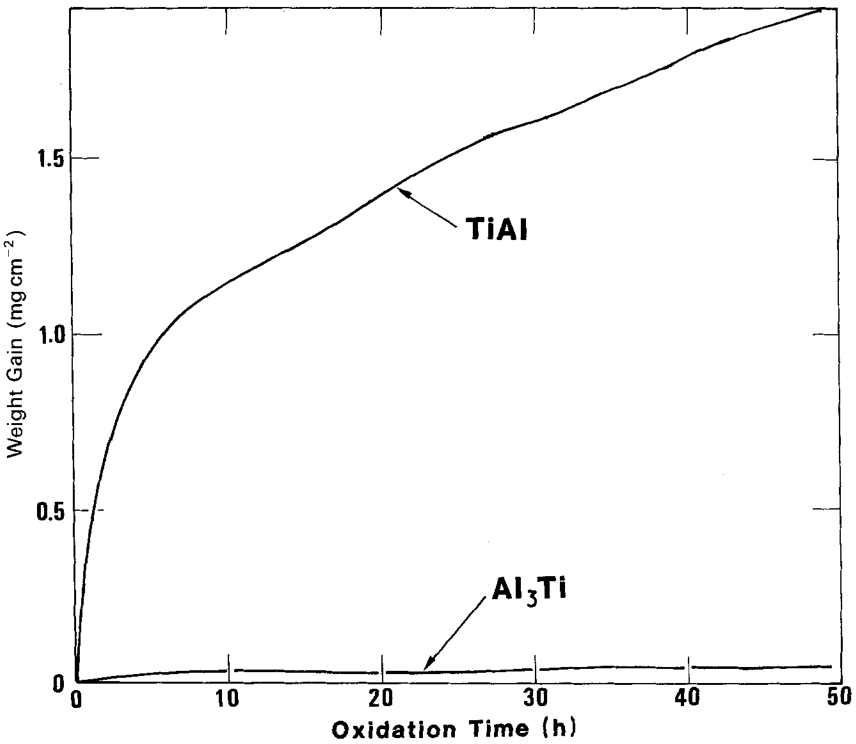

Figure 2 Variation of weight gain per unit area with oxidation time of Al_3Ti and TiAl oxidized in oxygen at 900° C.

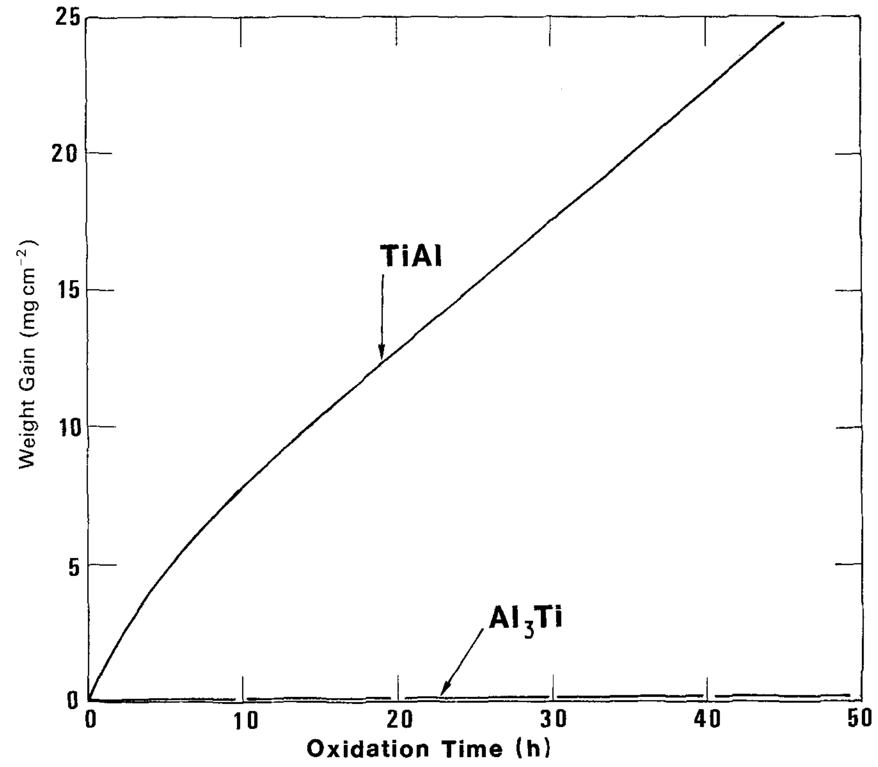

Figure 3 Variation of weight gain per unit area with oxidation time of Al_3Ti and TiAl oxidized in oxygen at 1000° C.

which shows oxygen can also diffuse to the TiAl compound. The poor aluminium content in TiAl during oxidation produces Ti_3Al at the oxide/metal interface. Even after short periods of oxidation, Ti_3Al can be observed. The existence of Ti_3Al may accelerate the penetration of titanium in the Al_2O_3 phase and therefore the oxidation resistance of TiAl will fall. The general microstructural and morphological features of the oxide scales and the Ti_3Al phase at the interface, are almost the same at the test temperatures, although there is a difference in the growth rate of the oxide scales and the Ti_3Al phase.

The crystal structure of the oxide scales and the intermetallic compounds for the TiAl specimen annealed in oxygen at 1000° C for 48 h was examined (Fig. 5). Al_2O_3 and TiO_2 scales have $D5_1$(α-Al_2O_3) and C4-type structure, respectively, and Ti_3Al phase has $D0_{19}$-type ordered structure. Although the surface of the oxidized TiAl sheet was X-ray irradiated, all the oxidation products could be examined because the substrate TiAl was confirmed to have an $L1_0$ type ordered structure from the diffraction patterns. The average composition of the mixture of Al_2O_3 and TiO_2 scales observed in Fig. 4 corresponded to that of the complex oxide Al_2TiO_5 but the X-ray diffraction patterns did not show any evidence of the presence of Al_2TiO_5.

The morphology of the surface oxide films because its affect on adherence and spallation is very important in maintaining the nature of the oxide film as a

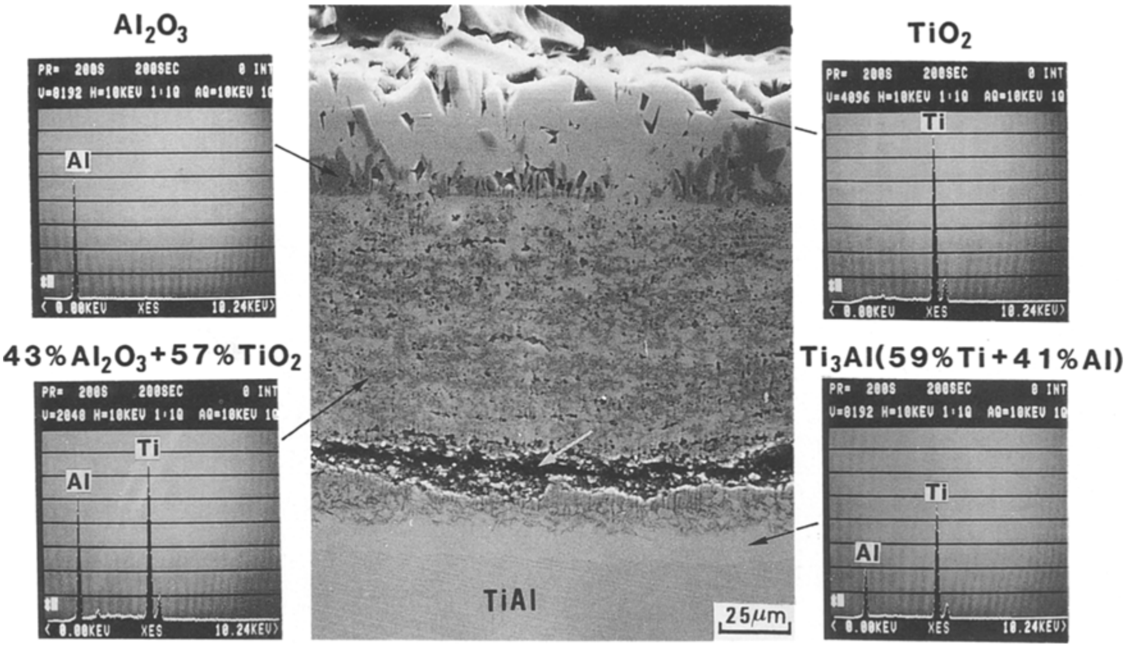

Figure 4 Scanning electron micrograph and energy-dispersive X-ray analyses of a cross-section of TiAl oxidized in oxygen at 1000° C for 48 h.

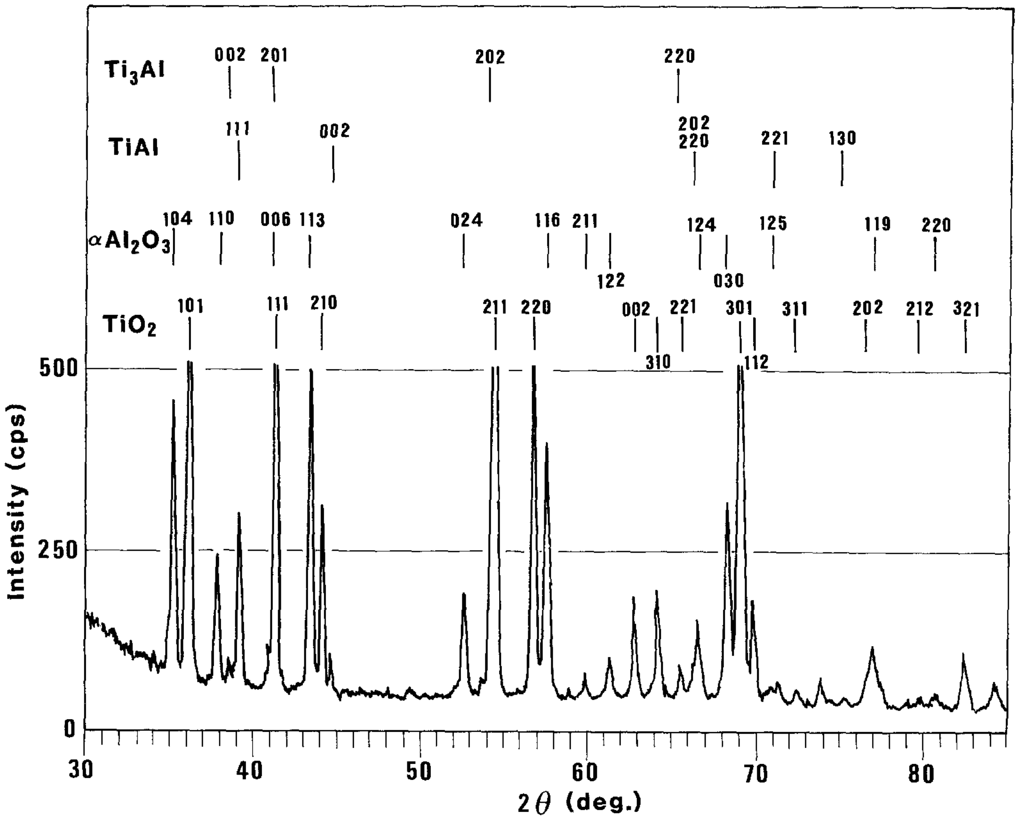

Figure 5 X-ray diffraction spectra of the TiAl specimen oxidized in oxygen at 1000° C for 48 h.

protective diffusion barrier. The surface microstructure of oxide films produced on TiAl and Al_3Ti compounds is given in Fig. 6. The oxide scale formed on Al_3Ti has a fine microstructure and a smooth surface. Even during the cooling and heating process, the good adherence of the oxide film to Al_3Ti was maintained. On the other hand, the external surface of TiAl was covered with a mat of fine crystals of TiO_2. The crystal growth of randomly oriented rod-like grains of TiO_2 leads to the formation of numerous voids and pores at the grain boundaries which trigger crack initiation and spallation of oxide films from the alloy substrate. The spallation of the crystalline TiO_2 layer is enhanced by the thermal cycling, resulting in the acceleration of oxidation.

Al_3Ti has been shown in Figs 2 and 3 to exhibit much better oxidation resistance than TiAl. Fig. 7 shows a scanning electron micrograph of a cross-section of Al_3Ti exposed to oxygen at 1000° C for 48 h. The results of EDX analyses are also given in the figure. The external oxide scale consists of almost all α-Al_2O_3 and no intermetallic compound can be observed at the interface between Al_3Ti and oxide scale, although a crevice induced during preparation of the EPMA specimen is seen. Because of its greater aluminium content, sufficient aluminium transport from Al_3Ti takes place for the growth of a protective Al_2O_3 layer to occur even during a long period of annealing at high temperatures. Low titanium content in the Al_2O_3 layer hinders the nucleation of TiO_2 phase and the formation of voids and pores. The absence of the high titanium content Ti_3Al compound at the interface with Al_3Ti causes a big difference in the oxidation resistance between Al_3Ti and TiAl.

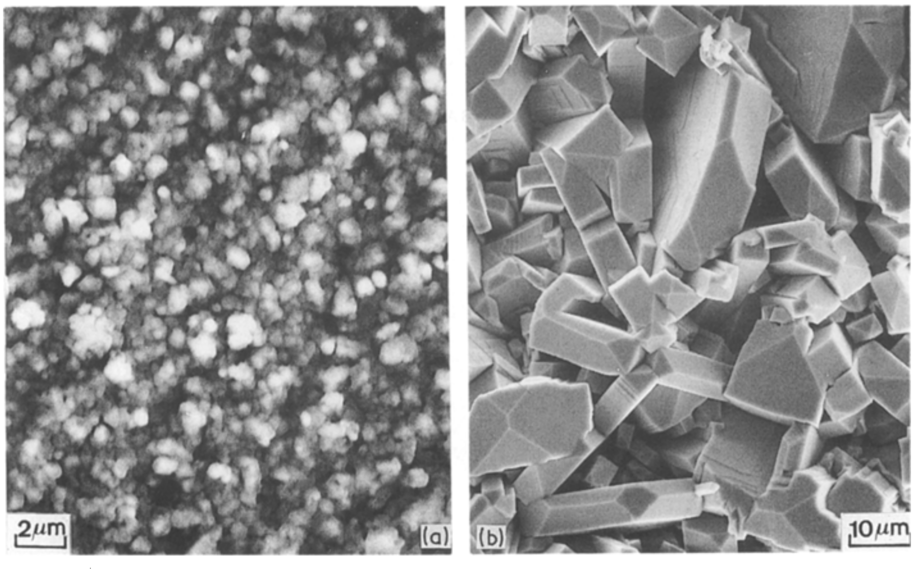

Figure 6 Scanning electron micrographs of the surface oxide scales formed on Al_3Ti and TiAl. (a) α-Al_2O_3 scale formed on Al_3Ti exposed to oxygen at 1000° C for 48 h. (b) TiO_2 scale formed on TiAl exposed to oxygen at 1000° C for 48 h.

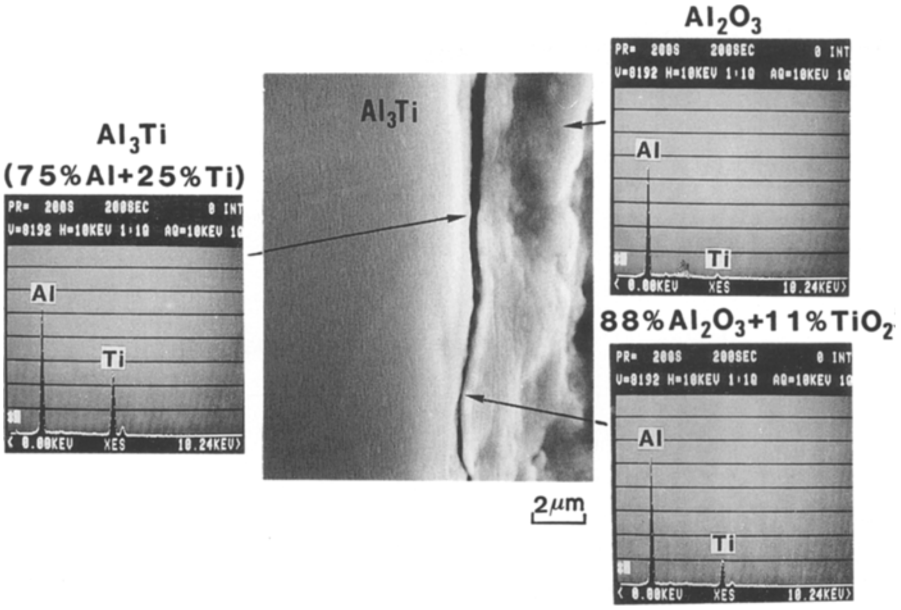

Figure 7 Scanning electron micrograph and energy-dispersive X-ray analyses of Al_3Ti oxidized in oxygen at 1000° C for 48 h.

Therefore, Al_3Ti can be used as a good coating material for the compound TiAl and some dilute alloys with a TiAl-base, similar to other aluminides used as coating materials such as NiAl and FeAl. The Al_3Ti coating would be effective for protecting the titanium- and TiAl-based alloys against oxidation at high temperatures. Aluminizing of titanium and titanium–aluminium alloys can be accomplished by conventional methods which include slurry spraying, molten dipping and pack cementation. A well-adhering coating layer of Al_3Ti can be obtained without difficulty because of the much faster diffusivity in Al_3Ti than in other aluminides of titanium.

4. Conclusions

1. The weight gain–time curves of Al_3Ti oxidation show a parabolic relation even at 1000° C.

2. In the early stages of oxidation, Al_2O_3 scale may be formed on TiAl but it cannot act as a protective film in further stages because of the high diffusivity of titanium in the Al_2O_3 scale, resulting in the formation of TiO_2 crystalline phase as an external scale.

3. Ti_3Al was formed at the interface of TiAl and oxide scale during oxidation, because of the poor aluminium content of TiAl. The penetration of titanium and the formation of TiO_2 in the Al_2O_3 scale may be accelerated by the existence of Ti_3Al. Numerous pores in the mixture of Al_2O_3 and TiO_2 scales also hinder the oxidation resistance.

4. The oxidation resistance of Al_3Ti is much better than that of TiAl, and the tendency becomes more remarkable with increasing test temperatures.

5. Al_3Ti can be used as a good coating material against oxidation for the titanium- and TiAl-based alloys.

Acknowledgements

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