Oxidation of Ti_3Al and TiAl Intermetallic Compounds Under Controlled Oxygen Partial Pressures

Zhengwei Li [1], Wei Gao [1*], Yedong He [2] and Sean Li [3]

[1] *Department of Chemical and Materials Engineering, The University of Auckland,*
Private Bag 92019, New Zealand

[2] *Corrosion and Protection Center, University of Science and Technology Beijing, China*

[3] *School of Materials Engineering, Nanyang Technological University, Singapore*

(Received February 26, 2002)

ABSTRACT

In the present study, oxidation of Ti_3Al and TiAl intermetallic compounds was performed at 800°C in the atmosphere of Ar + O_2, with two low oxygen partial pressures, $Po_2 \cong 10^{-17}$ and 10^{-20}atm, which were established and controlled stably using a solid-state electrochemical oxygen-pump system. The oxides formed on the surfaces after various exposures were characterized with field emission gun scanning electron microscopy (FEG-SEM), energy dispersive X-ray spectrometry (EDX), and conventional and glancing angle X-ray diffraction (GAXRD). It was shown that under the present oxidation conditions, selective oxidation of aluminium in the substrate and the preferential formation of alumina scale thereafter were not promoted and realized. The oxide scale formed was still composed of an outer rutile layer, an intermediate alumina-rich layer, a mixed layer of rutile with alumina, and in most cases an oxygen-dissolved zone at the interfacial zone. Based on the results obtained with the elapsing of oxidation time, the evolution of oxidation was discussed briefly.

Key Words: oxidation; intermetallics; Ti_3Al; TiAl; and low oxygen partial pressure.

1. INTRODUCTION

Ti-Al intermetallic compounds, including α_2-Ti_3Al, γ-TiAl, $TiAl_3$ and their alloys, are potential structural materials for applications in aerospace and automobile due to their high specific strength and good mechanical properties at elevated temperatures /1-3/. However, their real uses are largely hindered by the poor ductility/toughness at ambient temperatures and limited creep and oxidation resistance at high temperatures in service /4/. For improving oxidation resistance, alloying with ternary, quaternary or more elements (such as Cr, Nb, Si, W), surface treatments and various coating systems have been widely used, with improvement at various levels /5/. Generally, two types of methods are employed: one is to inhibit the fast growth of rutile (TiO_2) layer, while the microstructure of overall scale does not change significantly; the other is to promote the formation of an alumina (Al_2O_3) layer on the

---

[*] Corresponding author, Tel: +64-9-373-7599-8175;
Fax: +64-9-373-7463; Email: w.gao@auckland.ac.nz
(Wei Gao)

external surface, as alumina has low micro-defects and low growth rate, and can protect the underlying substrate against aggressive environments.

Normally, selective oxidation of a special element in the substrate can be realised by increasing its concentration or diffusion flux, or decreasing the inward diffusion of oxidizing species. Pre-oxidation in vacuum or inert atmospheres, therefore, has been used to form a protective oxide layer on the alloy surface for slowing down or prevention of further oxidation. Pre-oxidation of TiAl-based alloys in sealed Cr_2O_3, SiO_2, and TiO_2 powder packs were carried out by Taniguchi *et al.* /6-8/. Their results showed that with this process, an external layer highly enriched with Al_2O_3 was formed, and contributed to the improvement in cyclic oxidation resistance.

As the standard Gibbs free energy changes (ΔG°) for the formation of TiO, TiO_2, and Al_2O_3 are very close /9/, and the thermodynamic activity of Al in Ti-Al alloys with Al concentration lower than 50at.% is extremely low, selective oxidation of Al, thus, is difficult. In other words, an Al concentration higher than a certain level may always be required for the formation of alumina scale.

As oxidation of Ti-Al alloys was always carried out under high oxygen partial pressures, such as in air or pure oxygen, their oxidation behaviour, especially the possible selective oxidation behaviour, needed to be explored. A solid-state oxygen pump system has been established in our lab, and used successfully in oxidation kinetics studies and to control oxygen partial pressures at extremely low to high levels /10,11/. This paper reports our attempt to use this system to establish two low oxygen partial pressures, and to study their influences on the oxidation behaviour, especially on the selective oxidation behaviour of Al in Ti-Al alloys. By using high-resolution SEM and glancing angle X-ray diffractometer (GAXRD), the oxide formation, especially at the initial stage, was characterised.

2. EXPERIMENTAL

Ti_3Al and TiAl buttons were prepared by vacuum melting and casting with pure Ti (99.999%) and Al (99.9%). The samples were cut into the size of $\sim 10 \times 5 \times 1.5$ mm; all the surfaces were ground to 1200-grit SiC, followed by mechanical polishing down to 1μm diamond finish. The samples were then ultrasonically cleaned in acetone, distilled water, and ethanol, followed by blow drying in warm air. Some samples were checked with an optical microscope and a scanning electron microscope (SEM). The surface was seen to be featureless without obvious scratches or macro-defects. Some samples were also etched with Kroll's solution /12/ for 15-30sec for the microstructural observation. It was revealed that Ti_3Al had a single α_2

Table 1

GAXRD and EDX results of Ti_3Al and TiAl oxidised under low oxygen partial pressures after various time periods

		GAXRD		Ti : Al (atomic)	
		Ti_3Al	TiAl	Ti_3Al	TiAl
~10^{-17} (atm)	0.25hr	Ti_2O, TiO	TiO_2	4 : 1	1.4 : 1
	1.0hr	Ti_2O, TiO, TiO_2	TiO_2	4 : 1	1 : 1
	5hrs	TiO (?), TiO_2	TiO_2, α-Al_2O_3, Z-$Ti_5Al_3O_2$	19 : 1	1.4 : 1
	20hrs	TiO (?), TiO_2	TiO_2, α-Al_2O_3, Z-$Ti_5Al_3O_2$	69 : 1	1.2 : 1
	50hrs	TiO_2	TiO_2, α-Al_2O_3, Z-$Ti_5Al_3O_2$	–	1 : 1
~10^{-20} (atm)	0.25hr	Ti_2O	–	3.1 : 1	1.1 : 1
	1.0hr	Ti_2O	–	3.0 : 1	1 : 1
	5hrs	Ti_2O, TiO	Ti_2O, TiO, α-Al_2O_3 (?)	3.3 : 1	1 : 1
	20hrs	TiO_2	TiO_2, α-Al_2O_3,	–	1 : 1
	50hrs	TiO_2	TiO_2, α-Al_2O_3, Z-$Ti_5Al_3O_2$	–	3 : 1/1 : 1.5

phase with large grain size, while the structure of TiAl was complex, containing two types of grains. One was relatively coarse lamellar colonies of alternating layers of γ and α_2 platelets, containing an average Al content of 47.3at.%; while the other was γ-TiAl with a higher aluminium content of 52.9at.%. These gamma grains were distributed among the lamellar grains.

The cleaned samples (one Ti_3Al and one TiAl) were put into the cold region of the solid-state oxygen pump system. The system was then filled with high-purity argon. Oxygen in the system was then pumped out till the oxygen partial pressure (Po_2) went down to the preset value. After ~1hr stabilisation, the samples were moved into the hot zone of the furnace. After exposure, the samples were withdrawn from the hot zone and cooled to ambient temperature under low Po_2. Before and after oxidation, the mass of samples was measured using an electronic balance with an accuracy of 0.01mg. Curves of mass gain *vs.* time, therefore, could be obtained using several samples under the same oxidation condition.

The surface morphologies and metallographically polished cross-sections of oxidised samples were observed with a high-resolution field emission gun scanning electron microscope (FEG-SEM, Philips XL-30S) and an energy dispersive X-ray spectroscope (EDX) attachment. The oxide phases were characterised using normal wide angle and glancing angle X-ray diffractometer (XRD/GAXRD, Bruker D8) with Cu-Kα radiation.

3. RESULTS

Oxidation mass gain curves for Ti_3Al and TiAl under different Po_2 are shown in Fig. 1. It can be seen that under $Po_2 \doteq 10^{-17}$atm, oxidation of Ti-Al alloys followed approximately a parabolic rate law. As the Po_2 decreased, the mass gains in the first 5hr for Ti_3Al, and 20hrs for TiAl also decreased to a very low level; after which mass gains increased sharply. In general, the lower the Po_2, the lower the mass gains.

3.1. Oxidation of Ti_3Al

After 0.25hr oxidation under $Po_2 \doteq 10^{-17}$ atm, long stick-like oxide grains were formed on the surface (Fig. 2a). GAXRD results indicated that these were probably Ti_2O and TiO. As oxidation time increased to 1hr, growth of these oxide grains could be observed. However, their size was still very small, typically 50 to 300nm (Fig. 2b). At this stage, formation of TiO_2 was revealed by XRD. After 5hr exposure, the outer surface

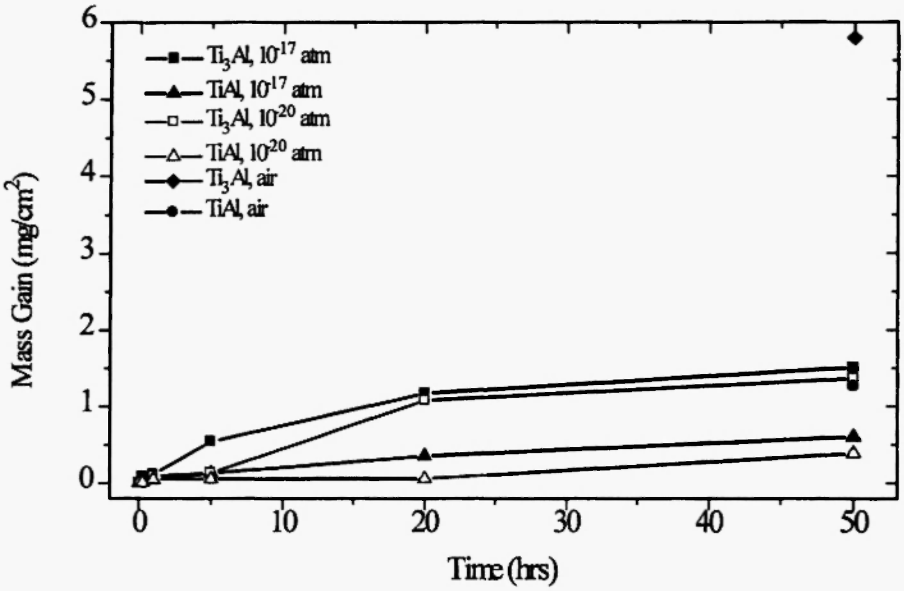

Fig. 1: Oxidation mass gains of Ti_3Al and TiAl *vs.* time at 800°C in air and under low oxygen partial pressures of ~10^{-17} and ~10^{-20}atm.

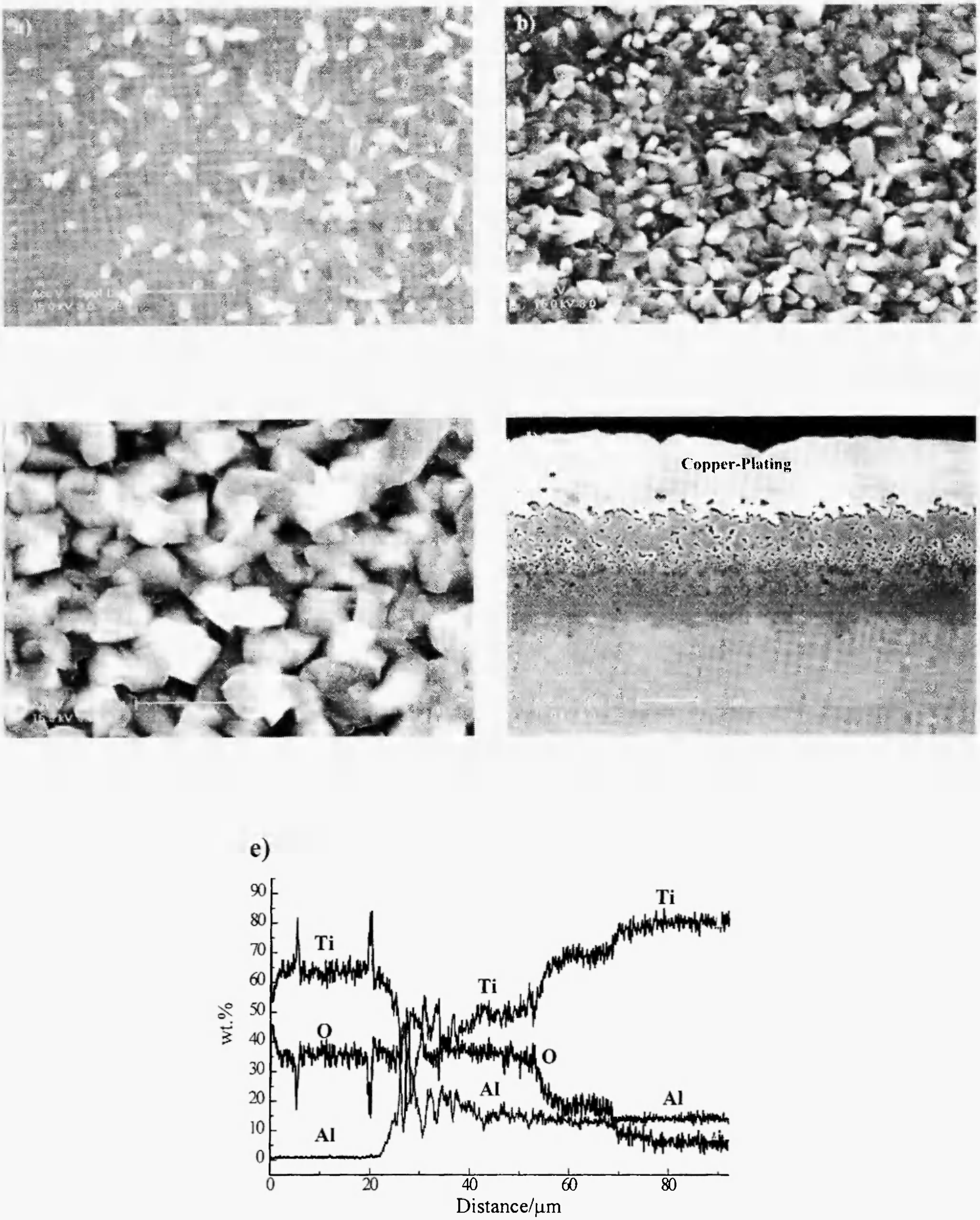

Fig. 2: Surface and cross-section morphologies of Ti_3Al oxidised under $Po_2 \cong 10^{-17}$atm at 800°C, a) 0.25 hr, b) 1 hr, c) 5 hr, d) 50 hr, cross-section, and e) elemental line scanning on d).

was covered with typical rutile crystals as shown in Fig. 2c, which was also proved by XRD results. With increasing time, the size of rutile also increased. Cross-sectional analysis was performed on the samples after 20 and 50hr oxidation. The oxide scale formed after 20hr exposure was about 5 to 7μm thick. Elemental line scanning showed that the outer layer was rutile, underneath which a layer with high concentration of pores was found. The mixed oxide layer was rich in Al near this layer. Close to the interface, a layer ~4μm thick was seen to be mainly composed of rutile. At the interface, a layer about 1μm thick with dissolved oxygen and Al-depletion was detected. After a longer time of oxidation (50hr), the layered structure of the oxide scales developed even further (Fig. 2d), with the same distribution but larger thickness (~50μm) and more pores in the outer rutile layer.

In comparison with the oxidation process under $Po_2 \doteq 10^{-17}$atm, oxidation of Ti_3Al under $Po_2 \doteq 10^{-20}$atm was slower (see Figs. 4a and 4b). After 0.25hr oxidation, small round-shaped grains of ~40nm formed on the surface. GAXRD analysis did not find obvious peaks for any oxides of Ti or Al. As the exposure time increased to 1hr, the surface feature became clearer. Ti_2O was detected by XRD at this stage. After 5hr exposure, long stick-like oxide grains were presented on the outer surface, which were detected as a mixture of Ti_2O and TiO. 20hr later, the surface was entirely covered with rutile crystal. From polished cross-section, it was found that the outer rutile layer was relatively dense. Pores were distributed under this layer. The layout of the multi-layer scale structure was similar to those formed under 10^{-17}atm.

3.2. Oxidation of TiAl

The density of the oxide grains formed on TiAl under $Po_2 \doteq 10^{-17}$atm appeared to be higher than that on Ti_3Al after 0.25hr exposure (Fig. 3a) and with randomly distributed orientations. GAXRD only showed the peaks for TiO_2. As the exposure time increased, the surface morphology showed preferential growth features, which might be related to the original lamellar microstructure of the alloy, and/or the extremely fine polishing lines on the surface. The compositional difference between the protruded oxides and "shadow" areas after 1 or 5hr oxidation could not be measured accurately by EDX analysis due to their limited thickness with respect to the effective volume of X-ray penetration. However, it was still shown that the former had slightly higher Ti content than the latter. Since the EDX results gave out peaks for Ti, Al, and O, while the atomic ratio of Ti to Al was close to 1:1, it was difficult to say that Al oxide was not incorporated into these scales. The size of these protrusions increased with time, finally forming large nodules (Fig. 3d). Cross-sections after 20 and 50hr (Fig. 3f) exposure showed similar layered microstructure: rutile, a mixed layer slightly rich with Al, another layer highly rich with Al, a layer mainly composed of rutile, an Al-depleted and O-enriched layer, detected by XRD as $Z\text{-}Ti_5Al_3O_2$ phase according to the data present in the literature /13,14/.

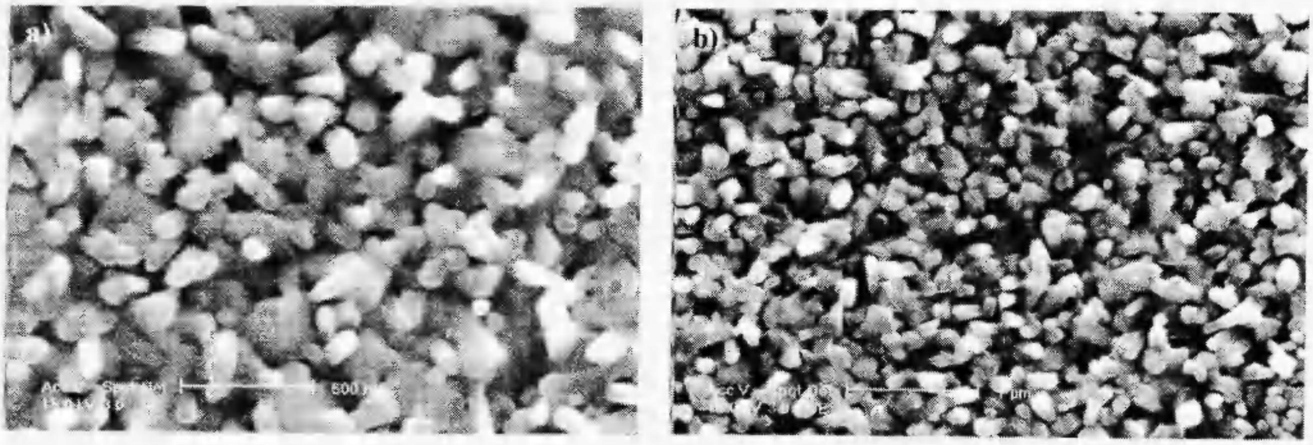

Fig. 3: Surface and cross-section morphologies of TiAl oxidised under $Po_2 \simeq 10^{-17}$atm at 800°C, a) 0.25 hr, b) 1 hr.

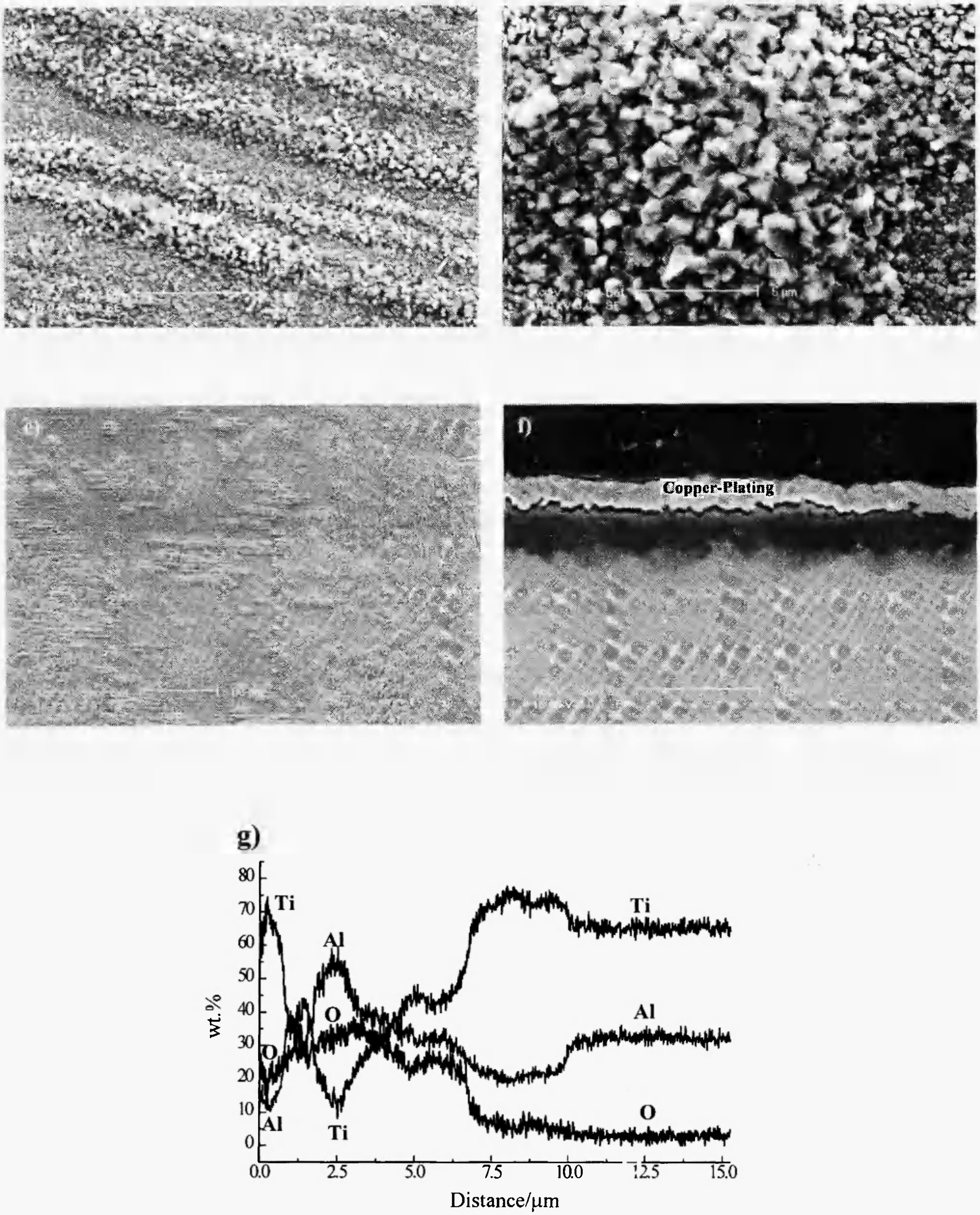

Fig. 3: (continued)
Surface and cross-section morphologies of TiAl oxidised under $Po_2 \doteq 10^{-17}$atm at 800°C, c) 5 hr, d) 20 hr, e) 50 hr, f) 50 hr, cross-section, and g) elemental line scanning on f).

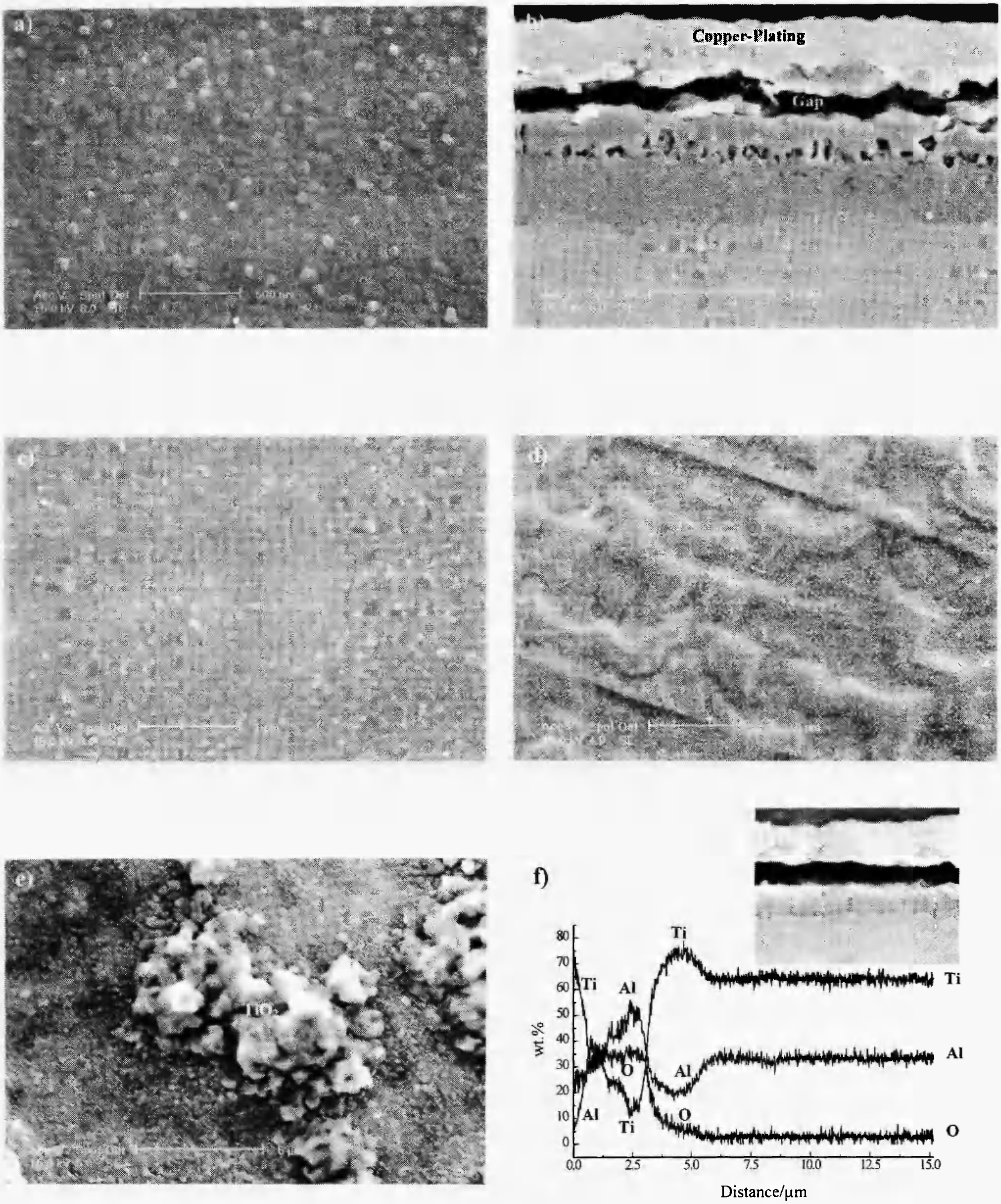

Fig. 4: Surface and cross-section morphologies of Ti_3Al and TiAl oxidised under $Po_2 = 10^{-20}$atm at 800°C, a) Ti_3Al, 0.25 hr, b) Ti_3Al, 20hr, cross-section, c) TiAl, 5 hr, d) TiAl, 20 hr, e) TiAl, 50 hr, and f) TiAl, 50 hr, elemental line scanning.

Oxidation of TiAl under $Po_2 \cong 10^{-20}$atm at 800°C was very slow (see Figs. 4c-e). After 0.25hr exposure, the feature of oxide grains could not be clearly seen with HRSEM. The micrograph after 1hr exposure showed thin plate-stick oxide grains. However, GAXRD analysis on this surface did not show peaks for any Ti or Al oxides. A sample after 5hr exposure indicated the formation of Ti_2O and TiO. The surface morphology after 20hr was different, showing the formation of ridges and wrinkles, which consisted of extremely fine oxide grains with a dense feature. GAXRD detected TiO_2 and α-Al_2O_3 on this sample. After 50hr exposure, rutile nodules formed on the ridges, showing the outward diffusion and growth feature. EDX results indicated that the regions on the ridge have a higher Ti content than that in the lower areas (3:1/1:1.5). Its cross-section morphology of the scale was similar to that oxidised under $Po_2 \cong 10^{-17}$atm, only thinner in total thickness.

3.3. Summary of the Results

Oxidation of Ti_3Al and TiAl under $Po_2 \cong 10^{-17}$ and 10^{-20}atm did not significantly promote the preferential oxidation of Al in Ti-Al intermetallics. The oxide scale formed after a relatively long period of time at 800°C had a multi-layered structure (from outer surface): a layer of rutile, a layer of mixed rutile and alumina (this layer could be further divided into 2 or 3 sublayers with different contents of rutile and alumina), and an Al-depleted and O-dissolved interfacial zone, which has a composition of $Ti_5Al_3O_2$ and is called Z-phase.

Under the testing Po_2 and during the initial oxidation stage (0.25 to 1hr), low valence Ti oxides were identified as Ti_2O and TiO by GAXRD on both Ti_3Al and TiAl. With EDX analysis, it was shown that Ti slightly enriched in the oxide scale, especially on Ti_3Al. As the exposure time prolonged, oxide of Ti with higher valence, i.e., TiO_2, formed, as normally occurs in high Po_2.

Al_2O_3 was not detected by GAXRD in the initial oxidation stages directly, while α-Al_2O_3 could be found on TiAl after at least 5hr oxidation. However, its formation in the initial stages could not be entirely excluded, especially for TiAl, as EDX performed on the outer surface showed that Ti, Al, and O, and the ratio of Ti to Al did not exhibit high enrichment of Ti in the scale.

Oxide scale formed in the first 5 or 20hr seemed to have reasonable protective ability under lower oxygen partial pressure. After that, accelerated oxidation started, as shown in the mass gain *vs.* time curves. Obviously, TiO_2 was the main oxidation product on Ti_3Al under both Po_2 after a long exposure, and TiO_2 nodules grew and developed on the outer surfaces of TiAl. On Ti_3Al alloy, the thickness of the outer layer was about one half of the total oxide scale. At the interface zone between this outer rutile layer and the underlying mixed layer, a large amount of pores were presented. It was also seen that as Po_2 reduced, the thickness of the oxide scale decreased, as did the density of pores. The thickness of outer TiO_2 layer was about 1/10 of the whole oxide scale formed on TiAl; this proportion is much lower than that on Ti_3Al, showing that an increase of Al content in the substrate could decrease the growth of non-protective TiO_2 layer. At the same time, no pores were observed.

4. DISCUSSION

The selective oxidation process is of great importance for engineering alloys used at elevated temperatures. For a typical binary alloy A-B (A is a noble metal and B is an alloying element), selective oxidation means that the oxide BO should form on the alloy surface preferentially when certain conditions are satisfied. Based on Wagner's equation describing the transition from internal to external oxidation of alloy, the following principles can be used to promote selective oxidation /15/:

1) Decrease the oxygen partial pressure in the oxidizing atmosphere using vacuum, inert gas or reducing gas mixture,
2) Increase the outward diffusion flux of B from the substrate through grain refinement, and
3) Addition of third element with a higher affinity to oxygen than A, but lower than B.

Surface-treatment using pre-oxidation under low Po_2 is based on the first principle, and is widely used in industry. Two positive effects could result:

1) If the Po_2 is low enough, exclusive formation of BO

scale on the external alloy surface could be realized,

2) If the BO scale can form externally under the normal oxidation condition, and with a low Po_2, the growth rate of BO could be further reduced; thus the scale compactness and adherence to the substrate could be improved.

The present study of the oxidation behaviour of Ti_3Al and TiAl under decreased Po_2, therefore, was expected to provide information on the possibility of selective oxidation process.

4.1 Effect of Oxygen Partial Pressure

The present results, however, indicated that the preferential oxidation of Al in the Ti-Al system, either Ti_3Al or TiAl, was not improved significantly with low Po_2. This should be related to the thermodynamic activities of Ti and Al in the alloy. At 800°C (1073K), the standard free energy changes (ΔG°) for the formation of Al_2O_3, TiO, and TiO_2, are –212.5, –198.8, and –179.1 kJ/mol, respectively /16/. Correspondingly, their standard dissociation Po_2 is 4.4×10^{-44}, 2.8×10^{-41}, and 2.9×10^{-37}atm. The standard free energy change for the formation of Ti_2O was not available. However, based on the results of TiO and TiO_2, its value should be close to that of Al_2O_3, or even lower. Additionally, if the thermodynamic activities of Al and Ti in the substrate were taken into account, these pressure values would increase, and more importantly, their sequence may change. In other words, Ti oxides may be more stable than Al oxide for Ti-Al substrate. Therefore, the formation order of Ti_2O, TiO, TiO_2 and Al_2O_3 is difficult to control by thermodynamic means. Actually, for the oxidation of pure Ti, it was reported that the formation of TiO_2 is dominant at low temperatures and high Po_2, while at high temperatures, especially above 1000°C, and under low Po_2, Ti oxides with low valences would form /17/. With a long exposure time, Ti_2O and TiO could be oxidized to TiO_2, which is not a thermodynamically stable phase, but formed under most oxidation conditions.

Pre-oxidation tests of TiAl alloys in oxide powder packs by Taniguchi *et al.* showed that very thin, virtually alumina, scales were developed in SiO_2 or TiO_2 packs, while thicker scales, rich in alumina, were produced in Cr_2O_3 powder packs /6-8/. Based on the thermodynamic data, the standard free energy changes (absolute values) of these three oxides are in the sequence of $TiO_2 > SiO_2 > Cr_2O_3$. Their standard dissociation pressures are also much lower than the values in this study. Still, exclusive formation of Al_2O_3 was not fully developed, implying that decrease of Po_2 to a certain level in an oxidising atmosphere has limited influences on the competitive nucleation and growth of Ti and Al oxides in a substrate with a certain amount of Al. In other words, thermodynamic activities of Al and Ti in Ti-Al alloys controlled the oxidation process. Thus increase the content of Al or its activity in the alloy (increase the ratio of a_{Al}/a_{Ti}) should be more effective to the selective oxidation behaviour.

Although the Po_2 used in the present study was not low enough to promote the selective oxidation of Al significantly, it still exerts influence on the growth of oxides. The results indicated that when Po_2 decreased, the mass gains in the first 5 or 20hr exposure were decreased, then increased sharply. It is suggested that with decreasing Po_2, oxide scale showed better protectiveness within a limited time period, perhaps due to the dense scale and small grain size, and the localised alumina enrichment. The former can be verified from the present results, especially on TiAl.

The effects of Po_2 on the microstructure of scales are quite complex. Several factors may play roles. It was observed that the fine lamellae structure of α_2/γ in TiAl substrate could provide a large amount of interfaces with high energy. As the oxygen supplied to the outer surface reduced, absorption and dissolution was slowed down, saturation was limited. Thus, heterogeneous nucleation should be promoted and growth is inhibited, resulting in dense oxide scale with fine oxide grain size /18/.

4.2 Effect of Al Content

The present results indicated that the microstructures of the oxide scales formed on Ti_3Al and TiAl were quite different. As the Al content increased, the percentage of the outer rutile layer in the total thickness decreased significantly, and that of the alumina-rich layer increased. Additionally, on Ti_3Al, only a thin alumina-rich layer was formed, while on TiAl, above this layer, another mixed layer of $TiO_2 + Al_2O_3$ was also presented. It was reported that Al content in $TiAl_2$ or $TiAl_3$ would fulfill the formation of protective alumina external scale as its activity was high enough /19,20/. Ternary addition of Nb in Ti_3Al and TiAl could also greatly improve the oxidation resistance /5/. It was reported that Nb addition increased the ratio of a_{Al} / a_{Ti}, thereby promoting the formation of alumina scale. Our preliminary results, however, showed that the oxidation rate, oxide formation and microstructure on Ti_3Al-11at.%Nb were quite similar to those of Ti_3Al under low Po_2 /21/, which might indicate that, Nb does not improve the ratio of a_{Al} / a_{Ti} directly. The positive influence, thereby, should come from other mechanisms such as doping effect on the growth of rutile /22,23/. In the present study, increase of Al content directly increased the reactive activity and diffusion flux of Al, therefore, thus enriching Al_2O_3 in the mixed scale layer.

4.3. Effect of Alloy Microstructure

For γ-TiAl based intermetallics, microstructural control is an important aspect for the processing and comprehensive properties of materials. Normally, four typical microstructures can be obtained through heat treatment and thermo-mechanical processing: near gamma (NG), duplex (DP), near lamellar (NL), and fully lamellar (FL) structures /24/. It was generally recognized that microstructure has an important influence on the mechanical properties. However, little attention has been paid to its influence on the oxidation behaviour. Gil *et al.* reported that the formation of TiO_2-based scale or alumina layer was strongly dependent on the relative amounts and composition of α_2 and γ phases, and especially on the distribution of these two phases in the alloy /25/. Alumina would form on a fine structure of α_2-phase and γ-TiAl; while coarse α_2-γ eutectoid structure with low Al content led to the formation of fast-growing TiO_2 scale. Similarly, Pérez *et al.* found that for the oxidation of Ti-46Al-1Cr-0.2Si alloy at temperatures ranging from 700 to 900°C, the duplex microstructure presented a higher oxidation rate than the fully lamellar structure /26/. On the other hand, Haanappel *et al.* for the oxidation of Ti-48Al-2Cr at 800°C /27/, and Pérez *et al* for the oxidation of Ti-46Al-1Mo-0.2Si at temperatures from 600 to 900°C /28/, reported that oxidation behaviour was not affected by the microstructure.

In the present study, two phases, α_2 and γ, were present in TiAl alloy, and the local formation of TiO_2, Al_2O_3, and $TiO_2 + Al_2O_3$ scale was believed to be related to the original alloy microstructures. It was found that on the outer surface of TiAl alloy, straight and narrow ridges with fine grains or nodules were formed and mainly composed of rutile. This is probably related to the lamellar structure of the alloy. As the lamellar structure consists of alternating α_2-Ti_3Al and γ-TiAl platelets, formation of Ti and Al oxides is more complex than those from the single-phase structure and under high oxygen pressures. α_2-Ti_3Al is basically a TiO_2 former, while a mixture of alumina and rutile forms on γ-TiAl. Thus, it is supposed that the local scale formed on the α_2-Ti_3Al platelets is less protective than that on γ-TiAl platelets. As the oxidation proceeded, oxygen transported inward, resulting in the local formation of rutile in the region of α_2-Ti_3Al. Rutile grows fast and develops outward, damaging the original outer scale, forming ridges or nodules on the surface. It is believed that with a decrease of Po_2, the difference between the oxidation behaviours of Ti_3Al and TiAl was magnified.

In addition, for TiAl oxidized at 10^{-20} atm for 20hr, crumples of scale formed in comparison with that formed under high Po_2. Similarly, we observed that for the oxidation of pure Cr, plastic deformation of Cr_2O_3 scale increased with decreasing Po_2 /29/. For the oxidation of TiAl in Ar + O_2 atmosphere, Taniguchi *et al.* reported that the crumpled scale was alumina whose deformation behaviour was possibly affected by Po_2 /30/. The convoluted scale fractured, and admitted oxygen into the substrate surface where Al was depleted, resulting in the growth of TiO_2 crystals around the root of the wavy scale. This might be one reason for the present case, as the deformation of TiO_2 or $TiO_2 + Al_2O_3$ layer might also be related to the Po_2.

5. CONCLUSION

1. Controlled low oxygen partial pressures, 10^{-17} and 10^{-20}atm, were established with a solid-state oxygen pump system. Oxidation behaviours of Ti_3Al and TiAl were studied at 800°C in these atmospheres.

2. Special attention was paid to the oxide formation in the initial oxidation stages. The results showed that titanium oxides with low valences were formed, while formation of aluminium oxide was not detected, but could not be excluded. Reducing oxygen partial pressure, therefore, exerted a limited influence on the preferential oxidation of Al in Ti-Al systems.
3. It was shown that Al content and activity was of great importance to the general oxidation behaviour and the scale microstructure, while the influence of alloy microstructure on the scale morphology could also be magnified with lowering of oxygen pressure.

ACKNOWEDGEMENT

The authors would like to thank the technical staff members at the Department and the Research Center for Surface and Materials Sciences for their various help.

REFERENCES

1. G. Sauthoff, *Intermetallics*, Weinheim, New York, VCH, 1995.
2. F.H. Fores, C. Suryanarayana and D. Eliezer, *J. Mater. Sci.*, **27**, 5113 (1992).
3. E.A. Loria, *Intermetallics*, **8**, 1339 (2000).
4. F. Appel, U. Brossmann, U. Christoph, S. Eggert, P. Janschek, U. Lorenz, J. Müllauer, M. Oehring and J.D.H. Paul, *Adv. Eng. Mater.*, **2**, 699 (2000).
5. G. Welsch and P.D. Desal, *Oxidation and Corrosion of Intermetallic Alloys*, Indiana, Purdue University, 1996.
6. S. Taniguchi, T. Shibata, A. Murakami and K. Chihara, *Oxid. Met.*, **42**, 17 (1994).
7. S. Taniguchi, T. Shibata and A. Murakami, *Oxid. Met.*, **41**, 103 (1994).
8. S. Taniguchi, T. Shibata and S. Sakon, *Mater. Sci. Eng.*, **198A**, 85 (1995).
9. G.H. Meier, *Mater. Corros.*, **47**, 595 (1996).
10. Y.D. He, H.Y. Yao, Z.W. Li. H.B. Qi and F.H. Stott, *Oxid. Met.*, **53**, 323 (2000).
11. Z.W. Li, Y.D. He and W. Gao, *Oxid. Met.*, **54**, 47 (2000).
12. R.R. Boyer, in *Metals Handbook*, 9th edn., Vol.9. *Metallography and Microstructures*, OH, ASM, Metals Park, 1985.
13. V. Shemet, P. Karduck, H. Hoven, B. Grushko, W. Fischer and W.J. Quadakkers, *Intermetallics*, **5**, 271 (1997).
14. E.H. Copland, B. Gleeson and D.J. Young, *Acta. Mater.*, **47**, 2937 (1999).
15. C. Wagner, *Z. Elektrochem.*, **63**, 772 (1959).
16. D.R. Lide, *Handbook of Chemistry and Physics*, 71st Edition, Cleveland, Ohio, CRC press, 1990-91.
17. R.Z. Zhu, Y.D. He and H.B. Qi, *High Temperature Corrosion and its Resistant Materials*, Shanghai, Science and Technology Press Shanghai, 1995.
18. Y.D. He, Z.W. Li, H.B. Qi and W. Gao, *Mater. Res. Innov.*, **1**, 157 (1997).
19. J.E. Benci, J.C. Ma and T.P. Feist, *Mater. Sci. Eng.*, **192/193A**, 38 (1995).
20. J.L Smialek and D.L. Humphrey, *Scripta Metall. Mater.*, **26**, 1763 (1992).
21. Z.W. Li and W. Gao, Unpublished result, 2001.
22. Y.S. Chen and C.J. Rosa, *Oxid. Met.*, **14**, 147 (1980).
23. Z.W. Li, W. Gao, S. Li, D. Zhang and Y.D. He, *Oxid. Met.*, **56**, 495 (2001).
24. F. Appel and R. Wagner, *Mater. Sci. Eng.*, **22R**, 187 (1998).
25. A. Gil, E. Wallura, H. Grübmeier and W.J. Quadakkers, *J. Mater. Sci.*, **28**, 5869 (1993).
26. P. Pérez, J.A. Jimenez, G. Frommeyer and P. Adeva, *Oxid. Met.*, **53**, 99 (2000).
27. V.A.C. Haanappel, R. Hofman, J.D. Sunderkotter, W. Glatz, H. Clemens and M.F. Stroosnijder, *Oxid. Met.*, **48**, 263 (1997).
28. P. Perez, J.A. Jimenez, G. Frommeyer and P. Adeva, *Mater. Sci. Eng.*, **284A**, 138 (2000).
29. Z.W. Li, Y.D. He and W. Gao, *Oxid. Met.*, **53**, 577 (2000).
30. S. Taniguchi, Y. Tachikawa and T. Shibata, *Mater. Sci. Eng.*, **232A**, 47 (1997).