Interdiffusion and Oxidation Behaviour of Two Phase α_2-Ti_3Al/γ-TiAl Titanium Aluminide Alloys

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Abstract

Titanium aluminide base materials are considered as one of promising materials for higher operating temperatures due to their higher melting points compared to superalloys. However, these materials are normally brittle at ambient temperatures and relatively low in oxidation resistance due to the high rate of TiO2. Improvement on the oxidation resistance could be obtained through coating application or/and alloy modification to promote more protective scale of Al_2O_3. This paper reports the results of interdiffusion test on coated α_2-Ti_3Al/γ-TiAl alloy and oxidation test on ternary Ti-Al-Cr and quaternary Ti-Al-Cr-Ag α_2-Ti_3Al/γ-TiAl alloys. Degradation of $TiAl_3$ layer in coated α_2-Ti_3Al/γ-TiAl based samples occurred during exposure at 900°C due to inward diffusion of aluminium and outward diffusion of titanium, followed by increasing of interdiffusion zone ($TiAl_2$ layer) thickness. Experimental results also indicated that 2 at.% Cr addition into binary Ti-Al α_2-Ti_3Al/γ-TiAl alloy reduced the growth rate of TiO_2 and increased the formation of Al_2O_3 at the outer layer of the scale. Furthermore, addition of 2 at.% Ag into ternary Ti-Al-Cr α_2-Ti_3Al/γ-TiAl alloy formed Laves and Z phases which believed as the resources of Al elements for protective Al_2O_3 scale.

Introduction

Materials used in high temperature applications must posses both strength and corrosion resistance. These requirements, however, are often incompatible and the solution is either to apply a corrosion-resistance coating or alloy modification. An example of this is provided by the high strength, nickel base superalloy components used in aero gas turbine engines. Such components are usually protected by a coating based on the intermetallic compound, β-NiAl [1,2]. This type of coating is very resistance to oxidation owing to its ability to form exclusively the slow-growing oxide, Al_2O_3. However, superalloys have reached the highest performance up to about 0.9 of their melting points through applications of single crystals, alloy modifications and Pt-modified aluminide coatings. Therefore, higher temperature resistance materials should be developed for higher temperature applications. One of the most promising materials is intermetallic base materials of aluminide systems such as β-NiAl and γ-TiAl.

TiAl based materials have lower density compared to NiAl systems. These materials are principally binary alloys of Ti and Al with the phase diagram shown in Figure 1. The most promising intermetallic phases in TiAl-based alloys are α_2-Ti_3Al with the crystal structure of order DO_{19} hexagonal, Figure 2, and γ-TiAl having LI_o face centered tetragonal crystal structure, Figure 3. Compared to α_2-Ti_3Al, γ-TiAl-based materials have better oxidation resistance due to their higher in aluminum content. However, γ-TiAl-phase has high brittleness at ambient temperature. Several efforts have been made to improve the brittleness of γ-TiAl-based materials, mainly by alloying elements additions. These additions have also normally been inline with the effort to increase the oxidation resistance of the materials due to the fact that the formation rate of TiO_2 is higher than that of Al_2O_3 in both α_2-Ti_3Al and γ-TiAl materials [3].

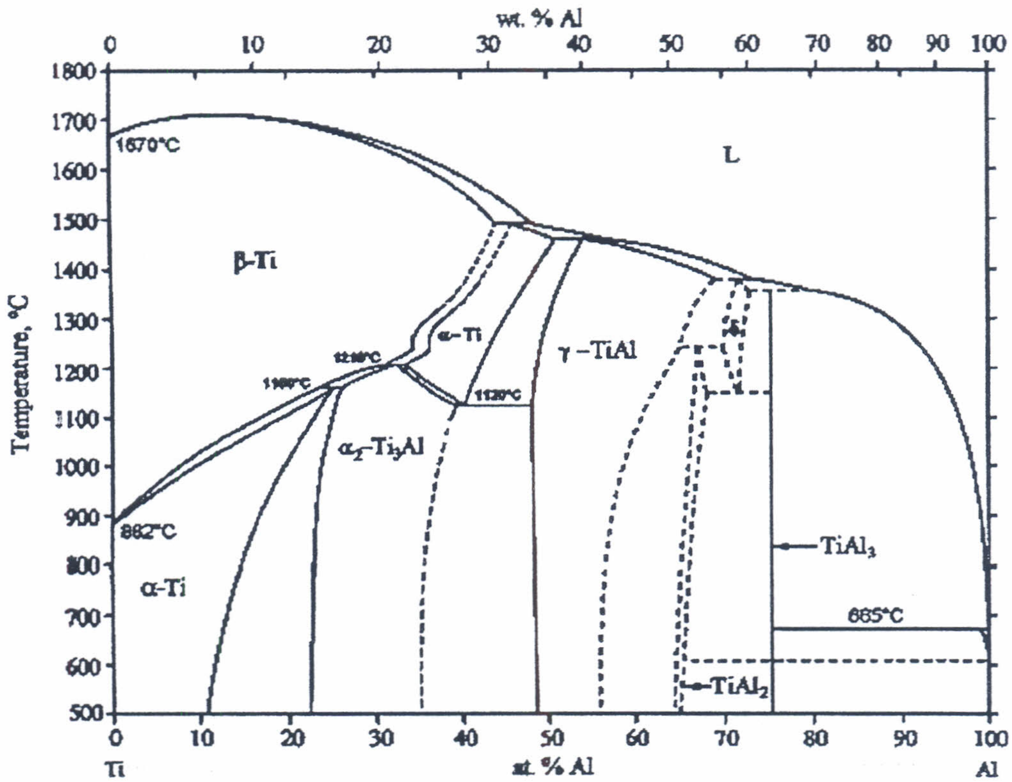


Figure 1. Phase diagram of binary Ti – Al alloys[3]

It is generally accepted that the brittleness of the Ti-Al systems decrease with the decreasing in aluminium content. Two phase intermetallic α_2-Ti_3Al/γ-TiAl based alloys would have better mechanical properties compared to single γ-TiAl-based alloys. To increase the oxidation resistant of these two phase alloys, coatings based on titanium aluminide of γ-TiAl could be applied on these alloys. Aluminium is required to form protective Al_2O_3 scale in the outer part of the material.

Pack cementation has been well established to developed aluminide coatings. Metals to be coated are put in a retort containing pack materials of halide salts activator, inert materials alumina and aluminium containing master alloy. The coatings are developed when the retort is then heated at high temperatures in an inert or reducing atmosphere, due to interdiffusion between deposited aluminium and titanium from the substrate.

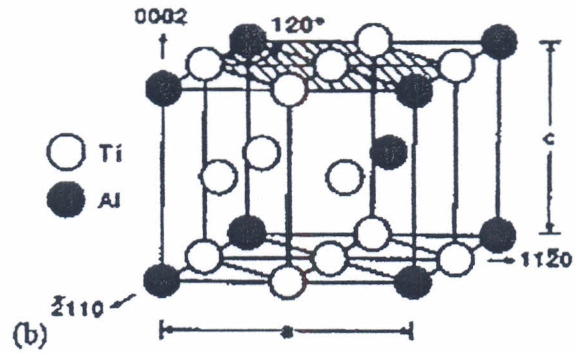


Figure 2. Crystal structure of order DO_{19} hexagonal for α_2-Ti_3Al[4]

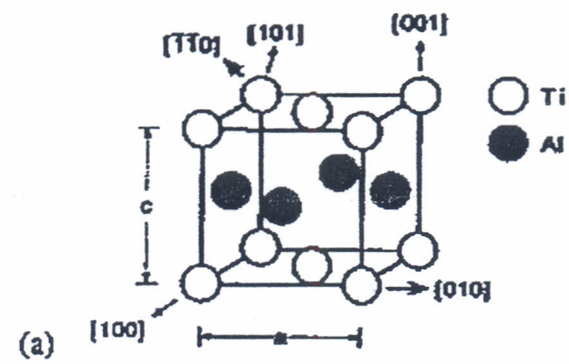


Figure 3. Crystal structure of LI_o face centered tetragonal for γ-TiAl[4].

During applications at high temperatures, degradation of γ-TiAl coatings could occur through two main modes, *i.e.*, interdiffusion between elements in the coating and in the substrate, and oxidation of the coatings. Due to the different in chemical potentials of aluminium and titanium in the coating and in the substrate., the aluminium content in the coating decreases with time of high temperature exposure due to the interdiffusion of Ti and Al. This causes the oxidation resistance of the coating decreases and an intermixed of TiO_2 and Al_2O_3 might occur in the scale.

Ternary alloying addition such as chromium was considered to improve Al_2O_3 and Cr_2O_3 oxide formation, and to reduce the growth rate of TiO_2 [5]. However, at relatively high content, this element makes the brittleness of TiAl material increase significantly. It was reported that the oxidation resistance of TiAl based materials increase with formation of Z-phase ($Ti_5Al_3O_2$) and Laves phase [$Ti(Cr, Al)_2$] [6].

The effect of Cr and Ag additions on the oxidation behaviour of two phase α_2-Ti_3Al/γ-TiAl based alloys have not been investigated. This study investigate the interdiffusion behaviour of coated α_2-Ti_3Al/γ-TiAl based alloys and the oxidation behaviour of Cr and Ag modified α_2-Ti_3Al/γ-TiAl based alloys at high temperatures.

Experimental Procedures

This study covers three parts of experimental work, i.e., (i) interdiffusion behaviour of coated two phase binary Ti-Al α_2-Ti_3Al/γ-TiAl model alloy, (ii) oxidation behaviour of Cr- modified ternary Ti-Al-Cr α_2-Ti_3Al/γ-TiAl model alloy, and (iii) oxidation behaviour of Ag-modified quarternary Ti-Al-Cr-Ag α_2-Ti_3Al/γ-TiAl model alloys. The two phase binary α_2-Ti_3Al/γ-TiAl model alloy was made by melting of 42.5 at.% Al dan 57.5 at% Ti in a single arc furnace within argon atmosphere. The buttons of the alloys were then homogenized in a horizontal tube furnace at 1100oC for 24 hours in argon atmosphere. The homogenized alloys were then cut to obtain coupon samples prepared for aluminide coating.

Pack aluminizing was carried to develope aluminide coating on these samples. Powders of 20%-wt Al, 2%-wt NH_4Cl, and 78%-wt Al_2O_3 were thoroughly mixed and put in a retort in which four sample coupons were inserted, Figure 4. The retort was then heated in a horizontal tube furnace at 900^0C for 10 hours. Interdiffusion test was carried out by heating the coated samples at temperatures of 900^0C for 5, 10 and 25 hours in argon atmosphere to avoid from oxidation. The microstructures of the as coated and the heated samples were then analyzed using energy dispersive x-ray analysis (EDAX) to obtain the concentration profiles of the samples.

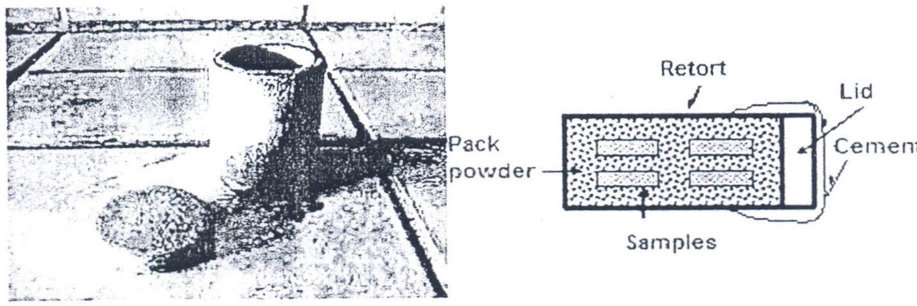


Figure 4. Retort used for pack aluminizing

Ternary Cr-modified α_2-Ti_3Al/γ-TiAl alloy was made by addition of 2 at.% Cr in 50 at.% Ti-Al alloys, while quaternary Cr and Ag modified α_2-Ti_3Al/γ-TiAl alloy was prepared to obtain three alloys, as shown in Table 1. The melting of these two model alloys was carried out in single arc furnace in Ar atmosphere. The alloys were homogenized at 1000°C for 24 hours. The oxidation test was done at 900°C for 2, 10 and 25 hours in a vertical tube furnace in air atmosphere, Figure 5. The oxidized samples were analyzed based on the weight changes and microstructure and x-ray analysis results.

Table1. Chemical composition of quaternary 2 fasa $\gamma-TiAl$ and α_2-Ti_3Al model alloys

Alloy	Atomic %				
	Ti	Al	Ag	Cr	Total
I	48	50	1,5	0,5	100
II	48	49	1,5	1,5	100
III	48	47,5	1,5	3	100

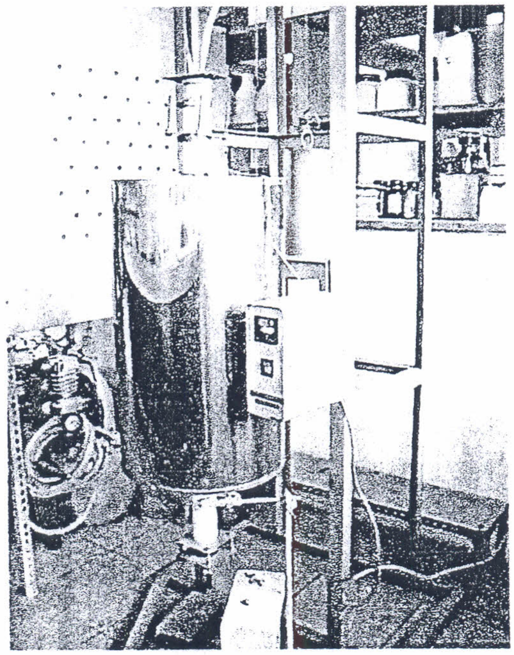


Figure 5. Vertical tube furnace used for high temperature oxidation tests.

Experimental Results and Discussion

Figure 6 shows the microstructure of binary α_2-Ti_3Al/γ-TiAl based model alloy. It indicates clearly the phases of α_2-Ti_3Al and γ-TiAl with Widmanstatten morphology being γ-TiAl. The Cr-modified and Cr+Ag-modified α_2-Ti_3Al/γ-TiAl based alloys were basically had similar microstructure, which might be due to relatively low content of Cr and Ag in the alloys.

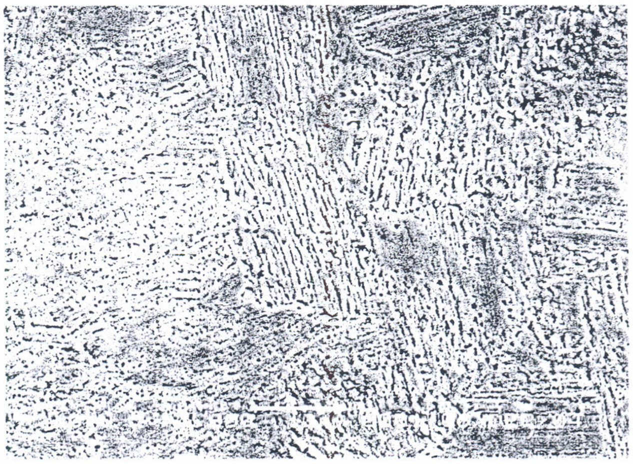


Figure 6. Microstructure of α_2-Ti_3Al/γ-TiAl based model alloy.

Figure 7 shows the microstructure and concentration profiles of Ti and Al of coated binary α_2-Ti_3Al/γ-TiAl alloy. The coating of about 40 micron thick is essentially $TiAl_3$ phase at the outer layer, under which a thin layer of $TiAl_2$ for about 4 μm thick is considered as an interdiffusion zone. Collumnar grains developed in the $TiAl_3$ layer indicates that the growth of the coating was essentially induced by the outward diffusion of Ti from the substrate of α_2-Ti_3Al/γ-TiAl.

Microstructures and concentration profiles of coated binary α_2-Ti_3Al/γ-TiAl alloy heated at 900°C for 5, 10 and 25 hours are shown in Figures 8, 9 and 10 respectively. These experiment results showed that the interdiffusion between coating and substrate alloy at 900°C causing degradation of coating ($TiAl_3$ layer) with time of exposure, by decreasing the thickness of $TiAl_3$. On the other hand, interdiffusion zone ($TiAl_2$ layer) thickness increased with time of exposures. The growth kinetics of $TiAl_2$ layer at 900°C followed general kinetics equation of $x = kt^{1/n} + C$ with the value of n being 2,7, as shown in Figure 11.

Experimental results indicated that oxidation in air atmosphere for unmodified binary α_2-Ti_3Al/γ-TiAl alloy gave external scale of essentially TiO_2, as shown in Figure

12. Only small amount of Al_2O_3, being about 0.3 wt.%, observed in the outer part of the scale. However, addition of 2% chromium on α_2-Ti_3Al/γ-TiAl alloy can reduce the growth rate of TiO_2 and increase Al_2O_3 at interface and oxidation layers, as indicated by the surface analysis shown in Figure 10. The outer part of the scale is composed of intermixed of Al_2O_3, TiO_2 and Cr_2O_3 for about 74 wt.%, 21 wt.% and 5 wt.% respectively. This addition of Cr in the ternary Ti-Al-Cr reduces the outward diffusion of Ti and increase the outward diffusion of Al.

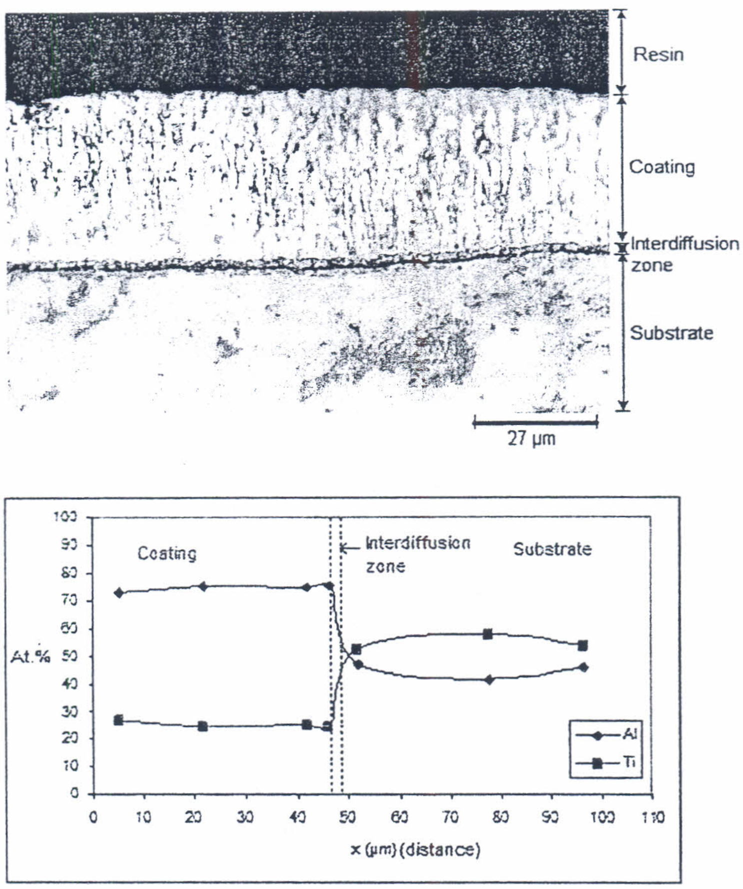
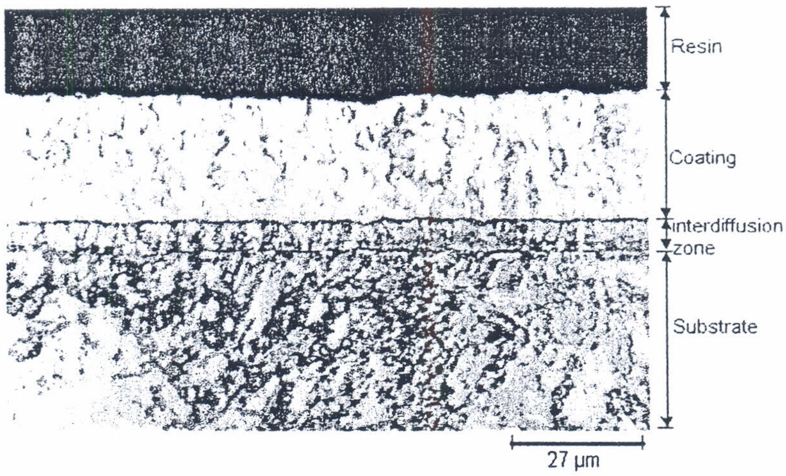


Figure 7. Microstructure and concentration profiles of Ti and Al of as coated binary α_2-Ti_3Al/γ-TiAl alloy.



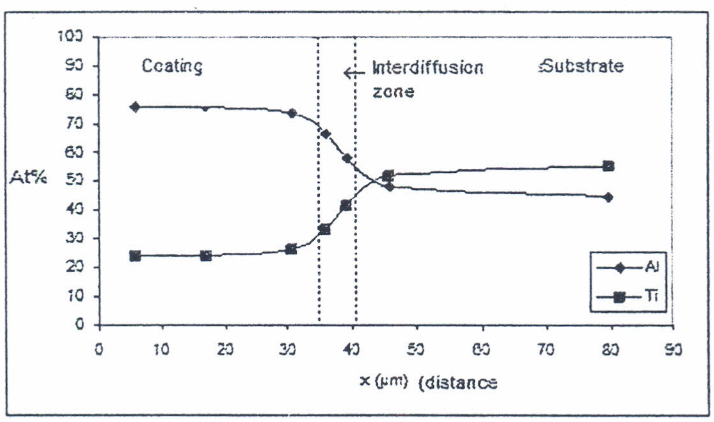


Figure 8. Microstructure and concentration profiles of Ti and Al of coated binary α_2-Ti_3Al/γ-TiAl alloy heated at 900°C for 5 hours.

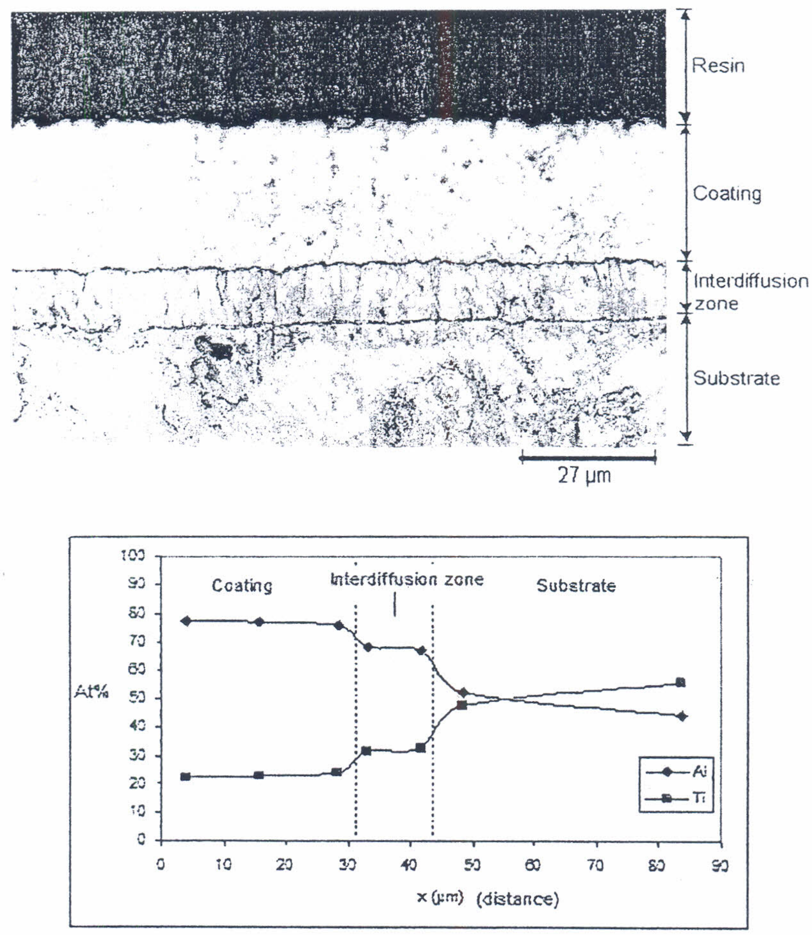
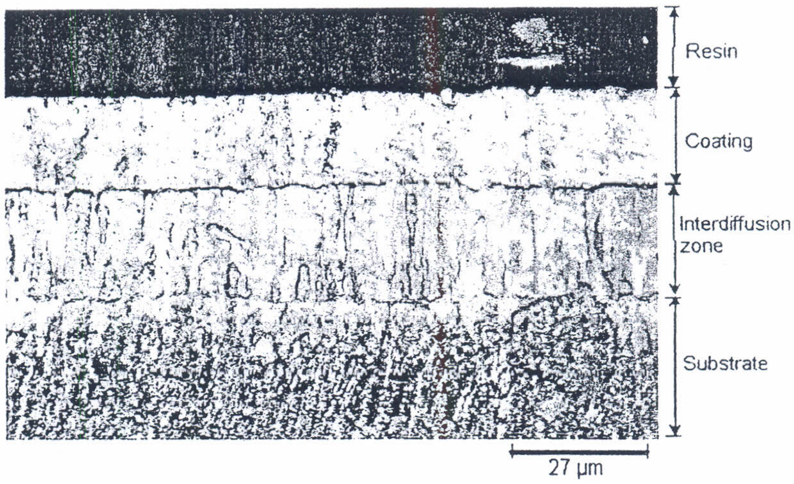


Figure 9. Microstructure and concentration profiles of Ti and Al of coated binary α_2-Ti_3Al/γ-$TiAl$ alloy heated at 900°C for 10 hours.



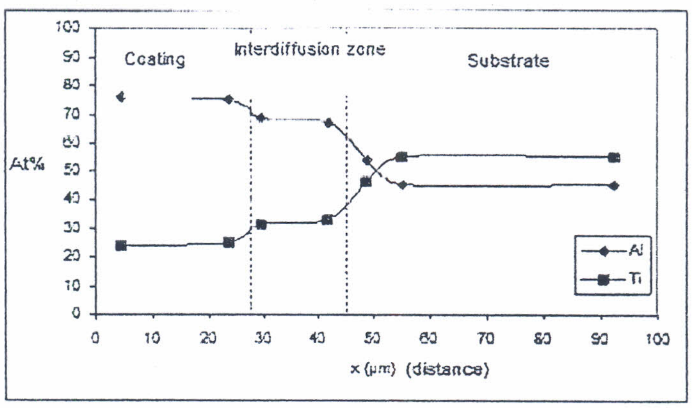


Figure 10. Microstructure and concentration profiles of Ti and Al of coated binary α_2-Ti_3Al/γ-TiAl alloy heated at 900°C for 25 hours.

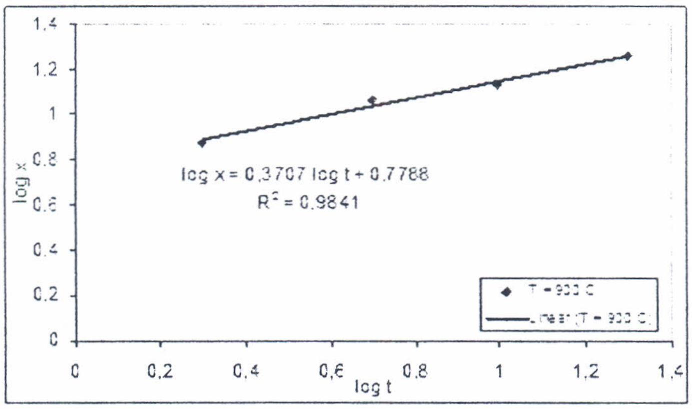


Figure 11. Kinetic of the enlargement of interdiffusion zone of the coated samples heated at 900°C for various times.

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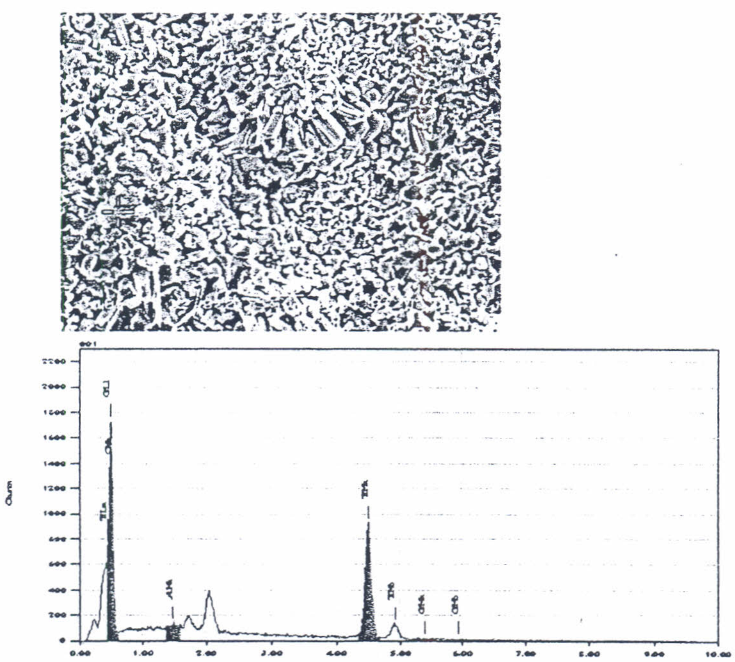
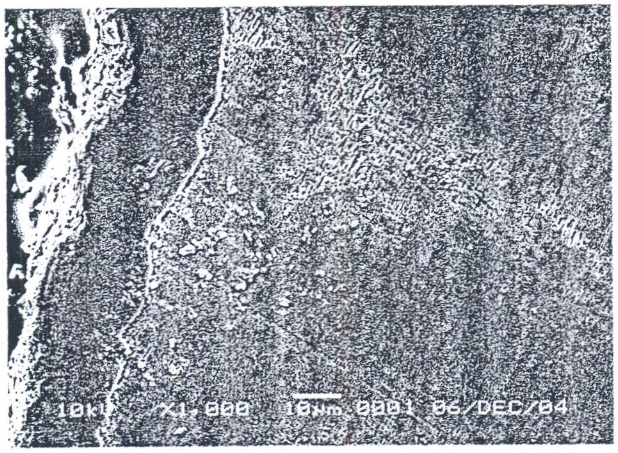


Element		(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O			40.07							
Al K	*	1.486	0.15	0.16	0.22	Al2O3	0.28	0.05	0.6905	
Ti K		4.508	59.78	0.66	99.78	TiO2	99.72	11.96	300.5775	
Cr K	*									
Total			100.00		100.00		100.00	12.01		

Figure 12. Surface analysis of uncoated binary α_2-Ti_3Al/γ-TiAl alloy heated at 900°C for 25 hours.



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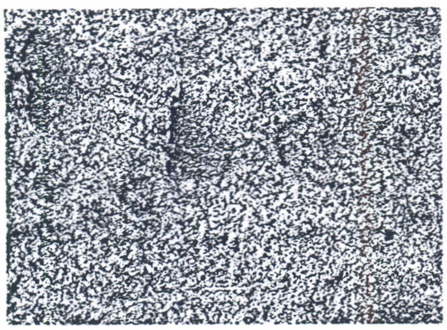

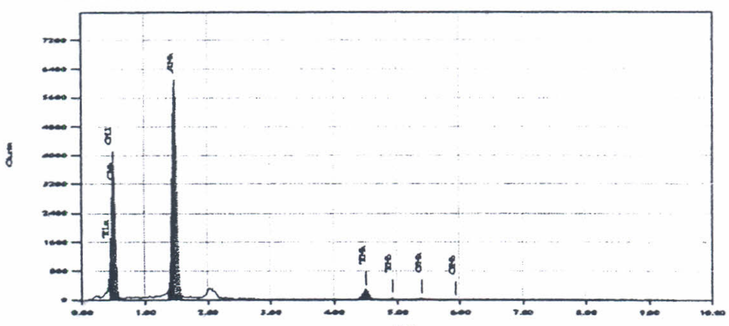

Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation K
O		44.84						
Al K	1.486	39.12	0.23	70.83	Al2O3	73.82	12.42	160.6612
Ti K	4.508	12.82	1.04	26.15	TiO2	21.38	2.29	50.8489
Cr K	5.411	3.21	1.84	3.02	Cr2O3	4.69	0.53	12.3785
Total		100.00		100.00		100.00	15.24	

Figure 13. Microstructure and surface analysis results of Cr-modified α_2-Ti_3Al/γ-TiAl alloy heated at 900°C for 25 hours

Oxidation of Ag-modified Ti-Al-Cr-Ag α_2-Ti_3Al/γ-TiAl alloys produced the formation of intermixed of Laves ($Ti(Al,Cr)_2$) phase, Z ($Ti_5Al_3O_2$) phase and Ag-rich precipitates as shown in Figure 18. However, above these intermixed phases, TiN and TiO_2 minor phases were also found in the matrix of Al_2O_3. The TiO_2 is expected also formed from TiN phase. The outer layer of the scale was essentially consisted of Al_2O_3 and TiO_2. The kinetics behaviour of oxidation of Ag modified Ti-Al-Cr α_2-Ti_3Al/γ-TiAl alloy is shown in Figure 20. Alloy III which has the highest Cr content, which is 3 at.%, shows the best oxidation resistance among the three model alloys. It was also observed from the microstructure that cracks or voids that formed as the result of Kirkendal effect underneath the scale were rehealed by TiN and Ti(Al,Cr)2. The Laves and Z phases were also considered as the barrier for further outward diffusion of Ti from the substrate, and therefore reduce the formation of unprotective TiO_2 and stabilize the protective oxide of Al_2O_3.

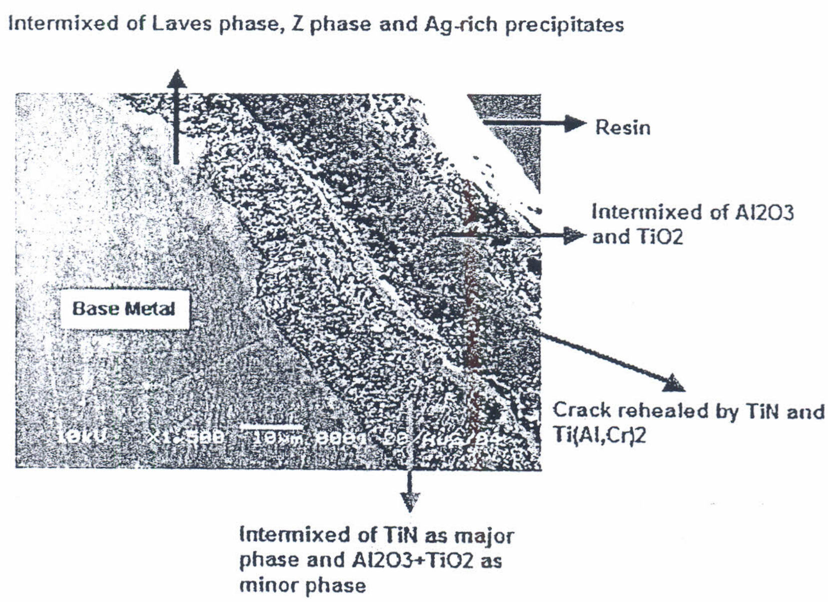

Figure 14. Microstructure of alloy II oxidized at 900°C for 25 hours.

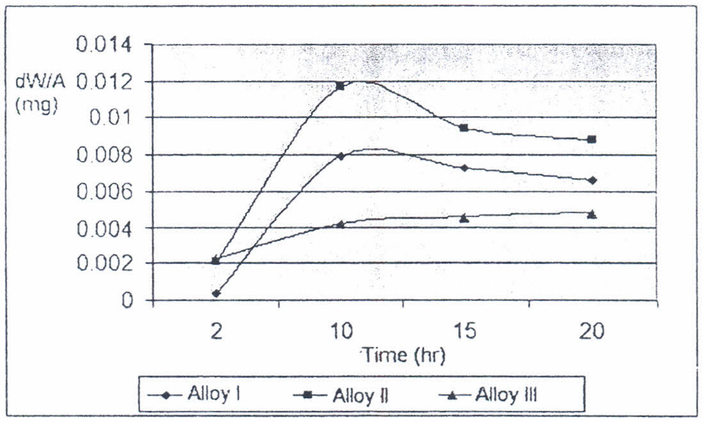

Figure 20. Weight change (gr/cm2) with times of alloys I, II and III oxidized at 900°C for 25 hours.

Conclusions

The investigation into the interdiffusion and oxidation behaviour of binary, ternary and quaternary α_2-Ti_3Al/γ-TiAl based alloys at high temperature revealed the following conclusions.

1. Degradation of $TiAl_3$ layer in coated α_2-Ti_3Al/γ-TiAl based samples occurred during exposure at 900°C due to inward diffusion of aluminium and outward diffusion of titanium. This was followed by increasing of interdiffusion zone ($TiAl_2$ layer) thickness.
2. Addition of 2 at.% Cr into α_2-Ti_3Al/γ-TiAl based alloy reduced the growth rate of TiO_2 and increases the formation of Al_2O_3 at the outer layer of the scale.
3. Addition of Ag for 1.5 at.% in ternary α_2-Ti_3Al/γ-TiAl (Ti-Al-Cr) alloy formed Laves and Z phases which are believed as the resources of Al elements for protective Al_2O_3 scale.
4. Among three quaternary α_2-Ti_3Al/γ-TiAl model alloys, the Ti-Al-Cr-Ag alloy with 3 at.% Cr has the best oxidation resistance.

Acknowledgement

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