

Cyclic Oxidation and Hot Corrosion Behaviour of Ti-48Al-2Cr with Aluminide Coatings

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ABSTRACT

Aluminide coating was directly applied onto Ti-48Al-2Cr alloy using electro-spark deposition (ESD) technique. The coating has a thickness of 15-20 μm , a gradient composition, and a metallurgical bonding to the substrate. Cyclic oxidation and hot corrosion tests were carried out at 800°C to evaluate the protective ability of the coating under relatively severe corrosion environments. It was shown that under both test conditions, a uniform and compact external scale mainly composed of $\alpha\text{-Al}_2\text{O}_3$ formed on the coated specimens. This scale exhibited excellent spallation and hot corrosion resistance. While the scale with multi-layered structure formed on Ti-48Al-2Cr under cyclic oxidation condition consisted of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$, which suffered severe cracking and spallation after extended oxidation. During hot corrosion test, this layer spalled away extensively and dissolved partially into the molten salt. These results showed that aluminide coated Ti-48Al-2Cr could undergo severe oxidation and hot corrosion conditions.

Key Words: titanium aluminide; cyclic oxidation; hot corrosion; scale spallation; electro-spark deposited coating

1. INTRODUCTION

Recently, Ti-Al intermetallic compounds have been considered as attractive structural materials for applications in aerospace and automobile industries due to their high specific strength, high melt point, and reasonably good mechanical properties at high temperatures [1,2]. Their real application, however, was hindered by their low ductility and toughness at room temperature, poor creep resistance and strength at elevated temperatures, and relatively low oxidation resistance at high temperatures.

The poor oxidation resistance of TiAl intermetallics is mainly due to the formation of non-protective and fast-growing TiO_2 (rutile). To improve the high temperature oxidation resistance, two main methods have been practiced. One is to decrease the growth rate of rutile; the other is to promote the formation of external alumina scale. For these purposes, micro- and macro-alloying are extensively used [3]; surface treatments and various coating systems are also developed [4]. Improvements at various levels are obtained.

Generally, it is accepted that coating is a relatively simple, effective and economical way to improve the oxidation resistance. TiAl_3 coatings have been applied

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onto TiAl by traditional pack cementation /5/ and magnetron sputtering /6/ with significant improvement. However, the coatings prepared by pack cementation often degraded quickly due to the presence of micro-cracks caused by the thermal mismatch between the coating and substrate. Thereby, coating and substrate should be always treated as an integrated system.

Electro-spark deposition technique was developed in our labs, and has been applied to stainless steels /7/ and Ti₃Al-Nb alloy /8/ with promising results in reducing oxidation rate and improving scale spallation resistance. In this study, aluminide coating was deposited onto a Ti-48Al-2Cr alloy. Tests under severe conditions including cyclic oxidation and hot corrosion at 800°C were carried out to evaluate the protective ability of this coating.

2. EXPERIMENTAL

The substrate material used was a cast Ti-48Al-2Cr (at.%) alloy. The specimens were all cut into the size of 12×10×2 mm with a diamond saw. All surfaces were ground to 500 grit SiC paper, followed by ultrasonic cleaning in acetone and alcohol, and blow dry.

The principle and apparatus of the electro-spark deposition technique were described in detail elsewhere /7/. The electrode material used in the present study was industrially pure aluminium (Al>99.0%), and cut into a disk of ~40 mm in diameter. The deposition was performed three times on each surface. During each run, the impact force, moving speed, and output energy in each spark were carefully programmed and controlled. The processing parameters were chosen to obtain a relatively thick coating with gradually changed Al and Ti compositions, thereby, improving the match and bonding between the coating and substrate, and also making the outer surface as flat and smooth as possible.

Cyclic oxidation test was carried out at 800°C in ambient atmosphere. Each cycle contained 60min heating at 800°C and 10min cooling in ambient temperature, and was automatically controlled by a timer-step-controlling unit. Specimens were put separately in crucibles, which were preheated at 850°C till their masses were stable. After a certain amount of cycle, the mass of specimen with and without crucible was measured with an electronic balance with an

accuracy of 0.01mg. Therefore, the total mass gain and scale spallation could be obtained.

NaCl (melting point = 801°C) and Na₂SO₄ (m.p. 884°C) were used as the corrosive sources for the hot corrosion test, and were mixed with a ratio of 1:9 in weight. Specimens were held in alumina crucibles separately. About 10g of the mixed salt powder was packed in a large alumina crucible with a lid. The crucibles with samples were put in the large crucible, which was positioned in the hot zone of a vertical furnace at 800°C (as shown in Fig. 1). After a certain time period of exposure, the specimens with crucibles were withdrawn from the furnace, and cooled in ambient air for about 15 min. Before measuring the mass change, the specimens were washed in hot water, cool water, and alcohol, and then dried in hot air.

The surfaces and cross-sections of the specimens before and after exposure were examined with optical microscope (OM), scanning electron microscope (FEG-SEM, Philips XL-30S) and X-ray diffractometer (Bruker D8) with Cu-K_α radiation.

3. RESULTS

3.1 Coating

Fig. 2 shows the typical cross-section and elemental line scanning of the aluminide coating formed on Ti-48Al-2Cr by the electro-spark deposition (ESD) technique. From the metallographically polished cross-section, it can be seen that the coating covers the whole surface. The contrast between the coating and substrate

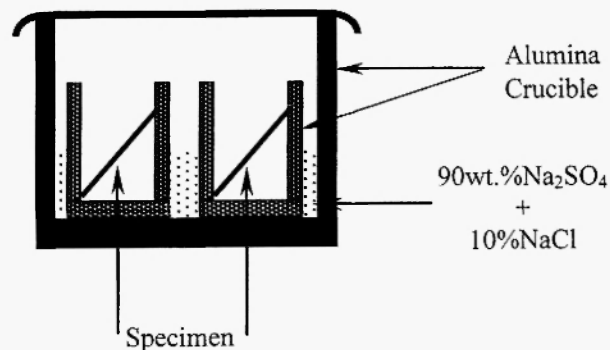


Fig. 1: Experimental set up for the hot corrosion test at 800°C with Na₂SO₄ + NaCl as the corrosive agents.

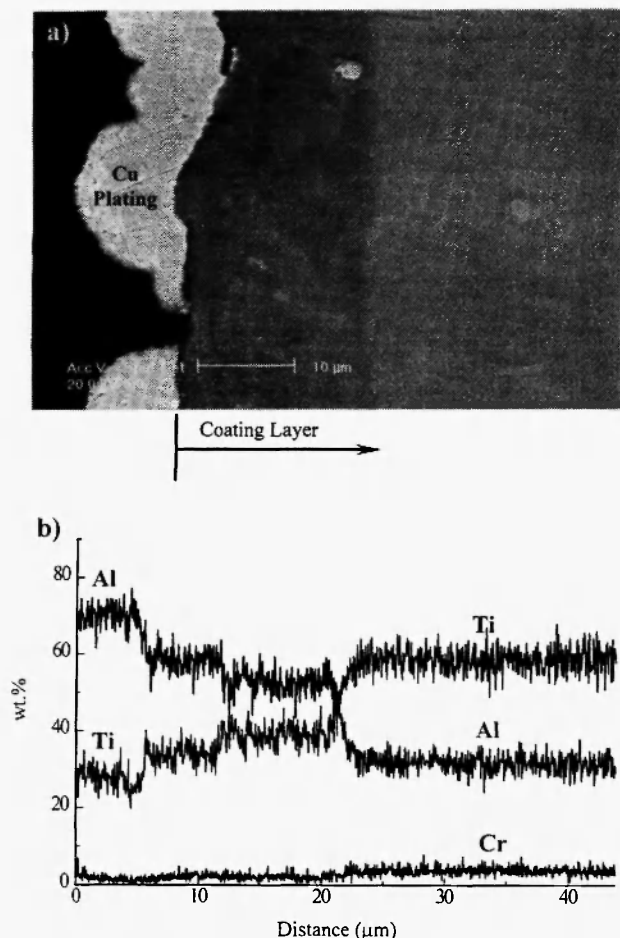


Fig. 2: Aluminide coating formed on Ti-48Al-2Cr using electro-spark deposition (ESD) technique: a) cross-section morphology, and b) elemental line scanning, showing the formation of three sub-layers and a total thickness of about 20μm.

is relatively weak, and no obvious defects, such as pores and cracks, could be observed. The interface, therefore, is difficult to distinguish from the SEM image. Based on the elemental line scanning result, it can be clearly seen that Al and Ti were the main elements in the coating, which has a typical thickness of about 20μm. The concentration of Cr in the coating is relatively low in comparison with that in the substrate (~2at.%). It was also found that the coating could be further divided into three sub-layers according to the concentrations of Al and Ti: the first sub-layer is about 5μm, with an average Al concentration of ~70wt.%, close to the Al

concentration of stoichiometric TiAl_3 ; the second layer is about 7μm thick, with an Al content of ~56 wt.%; and the third layer is about 9μm, and has an Al content of ~51wt.%. In comparison with our previous results, the interfacial zone is relatively narrow, about 2μm. XRD analysis showed that TiAl_3 is the main phase present in the coating layer.

3.2 Cyclic Oxidation

Fig. 3 shows the cyclic oxidation kinetics of Ti-48Al-2Cr with and without coating at 800°C in air. The curve for the mass gain vs. time for cast Ti-48Al-2Cr could be divided into several linear sections with different slopes, showing that the oxide scale had relatively poor protective ability, Fig. 3(a). After about 100 cycles, scale spallation started, mainly on the corners and along the edges, where stress concentration may exist. Surface morphologies of this sample after different exposure time are shown in Fig. 4. After 1

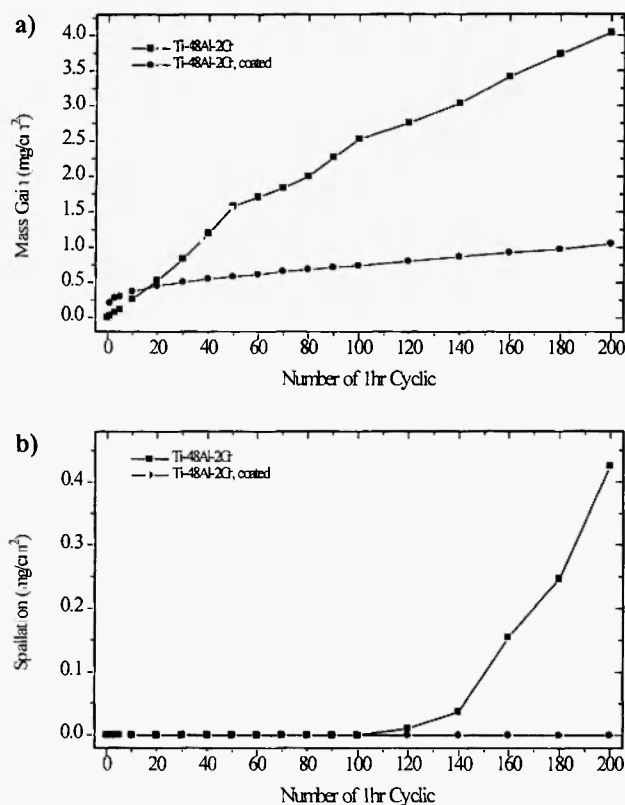


Fig. 3: Cyclic oxidation of Ti-48Al-2Cr with and without aluminide coating at 800°C in air: a) oxidation mass gain, and b) scale spallation.

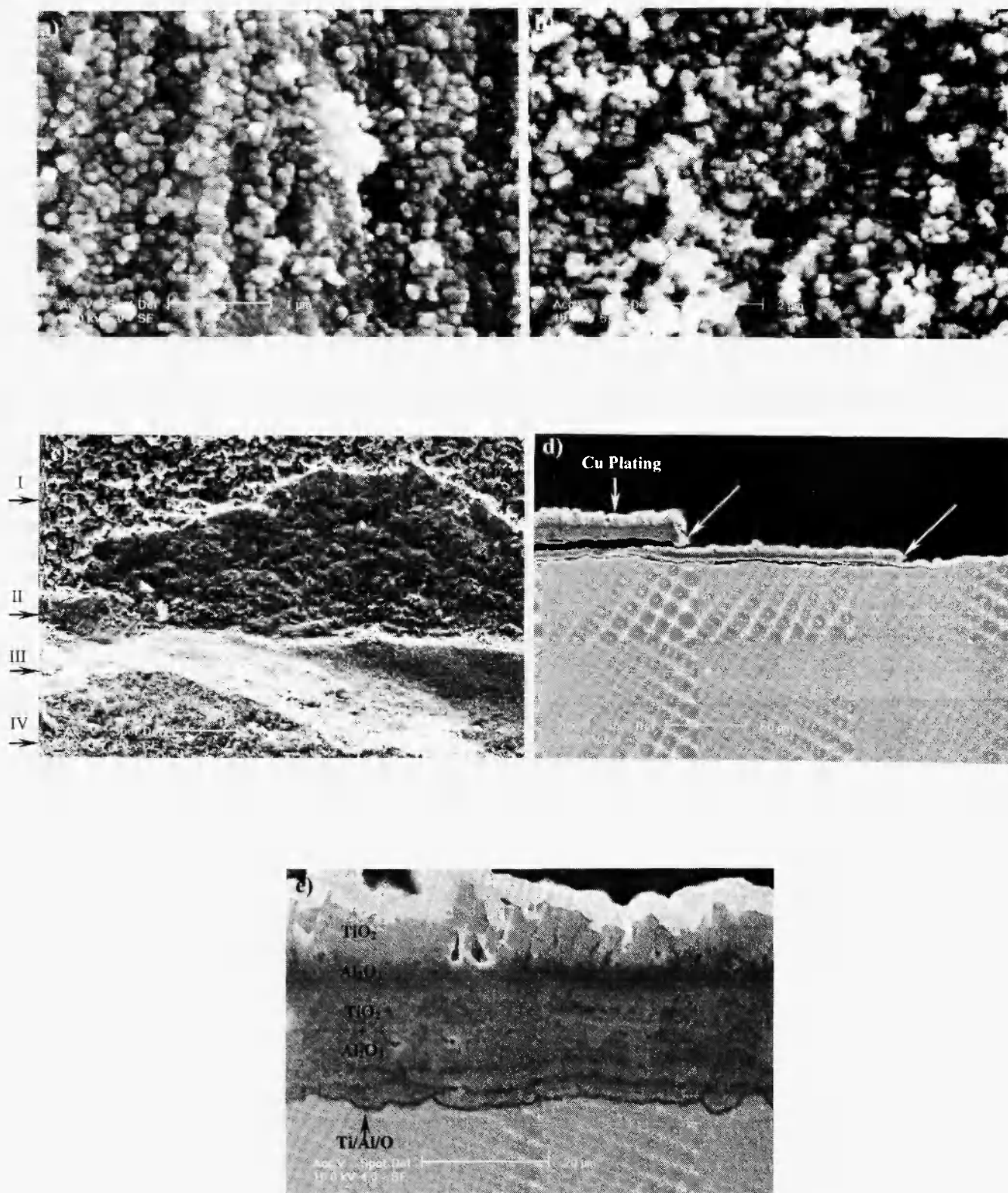


Fig. 4: Surface morphologies and cross-sections of Ti-48Al-2Cr with and without aluminide coating after cyclic oxidation at 800°C in air: a) Ti-48Al-2Cr, 1 cycle, b) Ti-48Al-2Cr, 10 cycles, c-e) Ti-48Al-2Cr, 200 cycles,

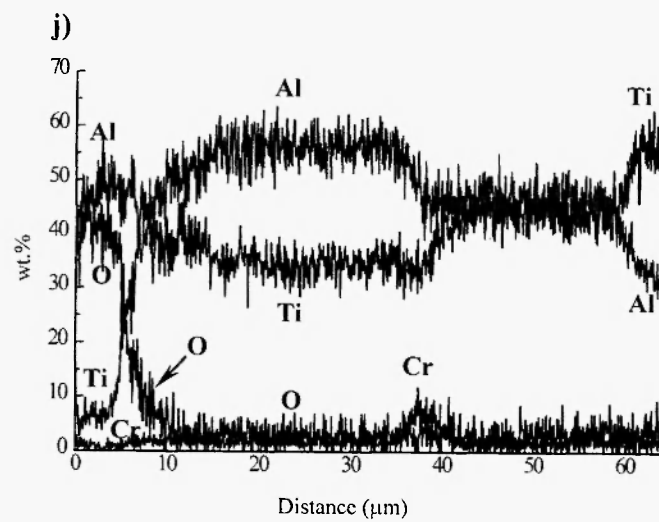
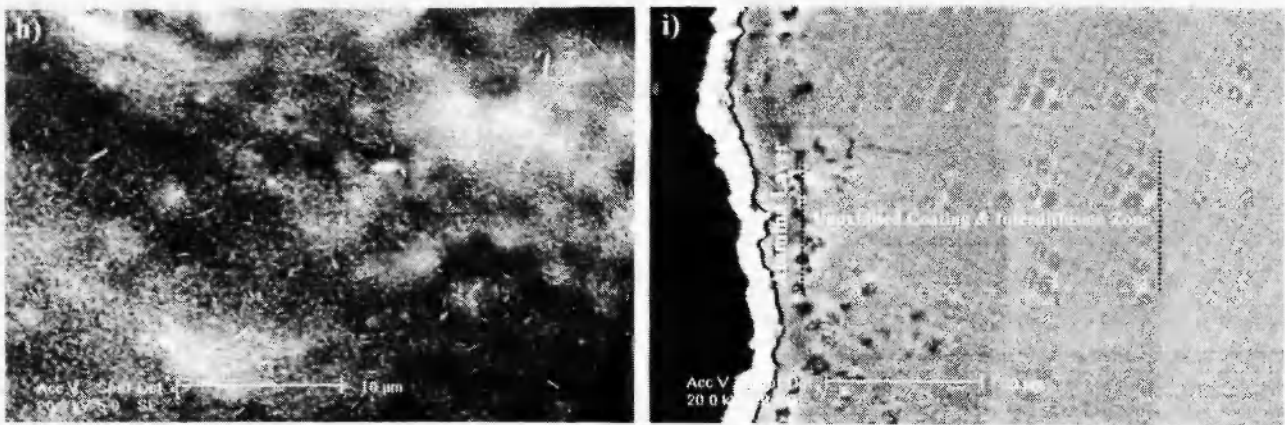
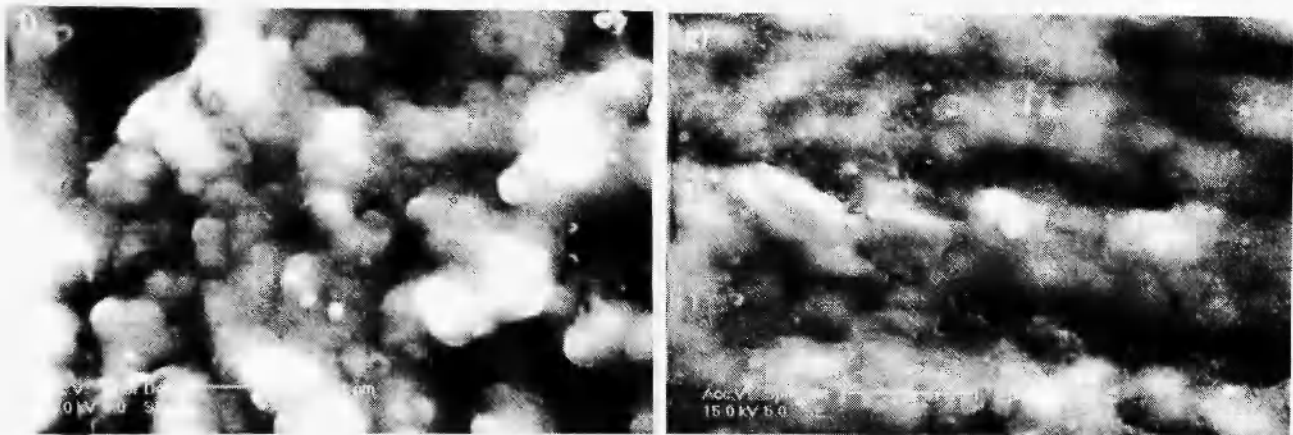


Fig. 4 (continued)
 (f) coated, 1 cycle, (g) coated, 10 cycles, and (h-j) coated, 200 cycles

cycle, small oxide particles were found on the outer surface, Fig. 4(a). With conventional XRD, however, no peaks for the oxides of Ti and Al could be found; this might be due to the limited thickness of the oxide scale. After 10 cycles, the scale formed was still composed of small particles (Fig.4b); XRD only revealed the formation TiO_2 at this stage. After longer exposure, typical rutile crystals were observed on the outer surface. Cross-sectional analysis showed that a multi-layered oxide scale was formed on this specimen, including an outer rutile, an alumina rich layer, a thick layer with rutile and alumina, and an oxygen-dissolved and Al-depleted interfacial layer (Fig. 4e). On some locations, scale spalled away severely with vertical fracture profile (Fig. 4c and d).

The coated Ti-48Al-2Cr specimen showed a different behaviour. Mass gain in the first 5 cycles was relatively high, then slowed down quickly, following an approximately parabolic rate law to the end of test. No cracking or spallation was observed and recorded during the whole test, as shown in Fig. 3. The surface morphology revealed that, after 1 cycle, small oxide particles were formed on the surface (Fig. 4f). It was still difficult to analysis the exact phase of these particles with XRD. The morphology of this oxide, however, is not like metastable alumina, which often shows whisker-type morphologies. After 10 oxidation cycles, these particles became a continuous layer with a quite compact feature (Fig. 4g). From the polished cross-section micrograph, it can be seen that an oxide layer with a thickness of 5 to $7\mu\text{m}$ covered the whole surface after 200 cycles (Fig. 4i). XRD showed that this oxide scale was mainly composed of $\alpha\text{-Al}_2\text{O}_3$; TiO_2 with weak intensity was also found. Just underneath this layer, small pores, however, could be found. A layer with different contrast was also seen between the un-oxidized coating and substrate.

3.3 Hot Corrosion

Hot corrosion reaction kinetics of Ti-48Al-2Cr with and without aluminide coating at 800°C in $\text{Na}_2\text{SO}_4 + \text{NaCl}$ containing environment was present in Fig. 5. Since the specimens were cleaned in hot water after every exposure, the curves showed the result of mass gain due to the formation of the reaction products and

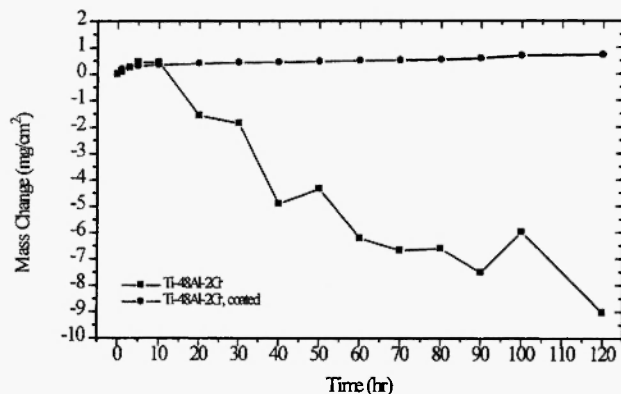


Fig. 5: Hot corrosion kinetics of Ti-48Al-2Cr with and without aluminide coating at 800°C . Corrosive agents: 90wt.% $\text{Na}_2\text{SO}_4 + 10\text{wt.}\%\text{NaCl}$.

mass loss due to scale spallation. Hot corrosion kinetics of Ti-48Al-2Cr with ESD coating exhibited protective behaviour; no scale spallation could be found. On the contrary, Ti-48Al-2Cr sample suffered severe oxidation and scale spallation. Scale spallation commenced after only 1hr of corrosion. During each cooling and washing time, part of the oxide scale detached and spalled away.

The morphology of the corroded surface was examined using SEM. It was found that on some parts, whisker-type oxide covered the surface (Fig. 6c), while on other parts, the scale was not continuous, and a feature of lamellae, islands, and pits could be seen (Fig. 6a and b). From the polished cross-section, thick oxide scales could still be found on some locations (Fig. 6d). However, this scale contains pores and fissures in its main body, and has apparently poor bonding with the substrate. At the interface, a small amount of sulphur could be detected with EDS; but it is not sure whether or not the sulphur is in the form of titanium sulphide, aluminium sulphide, or more complex compounds.

The surface of the coated Ti-48Al-2Cr was wholly covered with a dense scale showing a nodule-like morphology (Fig. 6e). A continuous oxide layer with a thickness of $\sim 5\mu\text{m}$ was observed from the cross-section (Fig.6f), which was detected as alpha-alumina by XRD. No chloride, sulphide or sulphate was detected in the scale, coating and specimen.

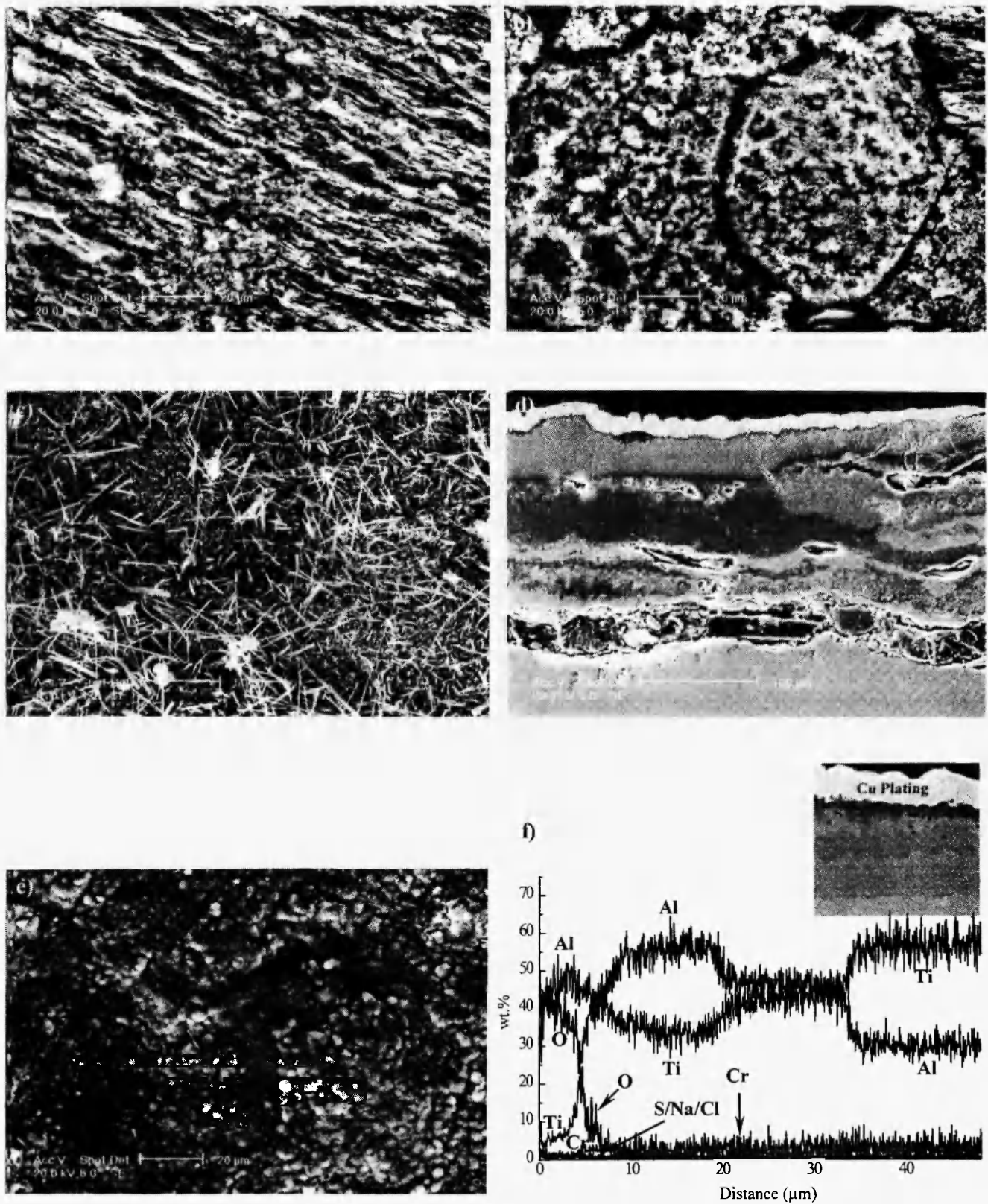


Fig. 6: Surface morphologies and cross-sections of Ti-48Al-2Cr with and without aluminide coating after hot corrosion test at 800°C: a-d) Ti-48Al-2Cr, and e-f) coated.

4. DISCUSSION

4.1 Coating

Electro-spark deposition (ESD) is a simple technique for metal surface hardening and/or toughening by applying hard or wear-resistant coatings [9,10]. Our previous work on the development of this technique showed that with the addition of Al or oxidation resistant alloys into the surface layer of substrate, a coating formed through this micro-metallurgical process, leading to dramatically improved oxidation resistance. Studies on ESD with pure aluminium electrode also showed that with the addition of Al in the outer region of a Ti₃Al-Nb alloy, an intermetallic phase TiAl₃ could form directly. The coating formed had gradually changed composition profiles of Al, Nb, and Ti, and, more importantly, a metallurgical bonding to the substrate. Improved oxidation and scale spallation resistance were obtained.

In the present study, processing parameters were carefully controlled in each step (three steps in total), including the output energy in each spark, moving speed and contact force. As expected, a coating layer composed of three sub-layers formed on Ti-48Al-2Cr substrate. Al concentration increased from the inner to the outer sub-layer. XRD analysis showed the formation of TiAl₃ phase, consistent with the EDS elemental line scanning. The exact phase structures of the inner sub-layers were not clear. They are probably the Al-enriched TiAl₂ or TiAl phases according to the phase diagram.

4.2 Cyclic Oxidation

It is well known that on TiAl-based alloys, a layered scale structure consisting of TiO₂ and α -Al₂O₃ will form after relatively long thermal exposure [11,12]. The outer layer was basically composed of typical TiO₂ crystals (rutile) with random orientation, leading to numerous pores and voids near their grain boundaries. This outer TiO₂ layer normally formed through the outward diffusion of Ti ions while the inner layer, consisting of a mixture of rutile and alumina, was believed to form from the inward penetration of oxygen. Meanwhile, the simultaneous countercurrent diffusion of Ti and O may also result in the formation of TiO₂ in the middle part of

the oxide scale. This may in turn lead to the development of large compressive stresses in the scale and the degradation of the inner Al₂O₃ layer. In the present study, the formation of the oxide scale probably followed the above mechanism; and the scale provided limited protection to the underlying substrate as TiO₂ has high growth rate and cannot withstand temperatures above 700°C.

Although the oxidation kinetics of the cast Ti-48Al-2Cr alloy followed a slightly decreasing rate, in each section, it exhibited linear behaviour, indicating that the scale is permeable to the reactants. After about 100 cycles, scale spallation was observed; and detachment at the scale/substrate interface and in the scale was observed. It is supposed that during each cooling/heating time period, cyclic stresses were developed, which might lead to the generation of micro-cracks. These micro-cracks may partially relieve the stresses, but provide additional paths for the transportation of oxygen, resulting in a high oxidation rate. As the stress exceeded a critical value (or the scale reached a critical thickness), spallation occurred (partially aided by micro-cracks) [13,14].

Oxidation of Ti-48Al-2Cr with aluminide coating is somewhat different. TiAl₃ is reported as an excellent Al₂O₃-former in the binary Ti-Al systems as it has a high Al content [15]. With the SEM and XRD results obtained in the present study, it was shown that the cyclic oxidation of the coated Ti-48Al-2Cr was basically controlled by the formation and growth of α -Al₂O₃. The oxidation behaviour in the initial 10-cycles is different, and the rate is high. For the oxidation of cast TiAl₃ alloy at temperatures below 1000°C, Smialek *et al.* reported this similar behaviour and ascribed this as the internal oxidation of a second phase enriched in Al [15]. The present case may also follow this mechanism. Another mechanism is, we believe, that the surface roughness after ESD may play a role, i.e., the actual area for initial reaction is larger than the measured area, resulting in a high calculated oxidation rate. As the exposure proceeded, the surface became flat; and the reaction area was relatively stable.

For the spallation resistance, the following aspects can be ascribed:

1) α -Al₂O₃ was the main oxidation product on the

coated samples. It is generally accepted that this scale has a slow-growing rate, and may survive in service even when cracks occur due to thermal shock.

- 2) It is observable that the oxide scale formed on the coated samples consisted of fine grains, which favor stress relief during oxidation or cooling, then resist cracking and spallation /16/.
- 3) The coating surface has a certain degree of roughness. The oxide scale formed, thereby, has a rugged character. Thus the growth and thermal stresses may be applied to different directions in the scale. Some of the stress components may cancel each other out, reducing the stress parallel or normal to the substrate surface. This reduces the probability of scale cracking.
- 4) The interface of coating and substrate also has a certain degree of roughness and inhomogeneity. Inward-growth of oxide occurs locally, thereby resulting in a complex oxide scale-metal interface after oxidation, enhancing the adhesion of the oxide scale to the alloy surface.
- 5) The impact applied by the rotating electrode may develop a high level of surface tension in the coating layer. Thus the scale formed could withstand higher elastic deformation /17/.

4.3 Hot Corrosion

Hot corrosion is a form of severe environmental attack for the engineering materials. The key feature for this type of degradation at high temperature (825-950°C) is that sulphur released from the sulphate could penetrate deeply into the scale and/or the substrate through oxidation/reduction along various paths to form metal sulphides, while at lower temperatures (600-750°C), mixed salts (e.g. sulphates and sulphur trioxide) melt, and flux away the surface oxides, reducing the protective ability of surface oxides /18/. In the present case, the attack might be a mixture of these two types. Moreover, the addition of NaCl could accelerate the corrosion process. It was generally agreed that chlorides could trigger the breakdown of the protective scales, resulting in scale spallation. It was also known that Al and Ti, etc., could react with chlorine readily to form aluminium and titanium chloride, weakening the

mechanical stability of the scale and causing scale cracking and spallation, and depleting the elements responsible for the formation of protective oxide scale. More importantly, generation and reaction of chlorine is a self-catalytic process. Therefore, a small amount of chlorine could exert great influence on the corrosion process, increasing the corrosion rate /19/. In comparison with the cyclic oxidation test results at the same temperature, it is believed that S and Cl (in the form of Cl⁻, Cl or Cl₂) attack the Ti-Al substrate severely. Scale spallation was initialised just after 5hrs; high mass loss was recorded. Dissolution of the scale and/or the substrate could be observed in the form of pits and lamellae. Whisker-type oxides formed on the outer surface, which is highly related to the generation of chlorides.

Diffusion coating of aluminide with or without further modification (such as platinum doping or Pt-Al phases) have been used for hot corrosion protection /20/. In the present study, aluminide coating was fabricated directly on a Ti-48Al-2Cr alloy substrate using a simply designed electro-spark deposition (ESD) apparatus. Significant improvement in hot corrosion resistance has been obtained. In comparison with the oxidation process in air, the formation of salt vapour near or on the substrate surface could reduce the oxygen partial pressure, promoting the selective oxidation of Al in the Al-rich coating layer further, resulting in the quick formation of alumina on the outer surface. Continuous and dense α -Al₂O₃ definitely can prohibit the inward transportation of S and/or Cl, preventing their attack to the alloy substrate.

5. CONCLUSIONS

1. Aluminide coating was directly produced on a Ti-48Al-2Cr alloy using a simple electro-spark deposition (ESD) apparatus with pure aluminium electrode. The coating has a typical thickness of 20µm with a gradient composition and a strong metallurgical bonding to the substrate. The main phase of the coating is TiAl₃. With careful processing control, three sub-layers were formed in the coating with increased Al content from inside to outside.

2. Cyclic oxidation and hot corrosion tests were performed at 800°C up to 200hrs. The results showed that α -Al₂O₃ was formed on the outer surface of all coated samples. It is believed that the formation of α -Al₂O₃ layer with a fine-grained structure and dense feature slows down the oxidation rate, improves the scale spallation resistance, and reduces the inward transportation and attack of S and Cl.

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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. G. Welsch and P.D. Desal, *Oxidation and Corrosion of Intermetallic Alloys*, Purdue University, Indiana, 1996.
4. S. Taniguchi, *MRS Bull.*, **15**, 31 (1994).
5. H. Mabuchi, T. Asai and Y. Nakayama, *Scripta Metall.*, **23**, 685 (1989).
6. C. Leyens, M. Peters and W.A. Kaysser, *Adv. Eng. Mater.*, **2**, 265 (2000).
7. Z.W. Li, W. Gao, P.M. Kwok, S. Li and Y.D. He, *High Temp. Mater. Proc.*, **19**, 443 (2000).
8. Z.W. Li, W. Gao and Y.D. He, *Scripta. Mater.*, **45**, 1099 (2001).
9. R.N. Johnson, in *Elevated Temperature Coatings: Science and Technology 1*, edited by N.B. Dahotre, J.M. Hampikian, and J.J. Striglich, The Minerals, Metals and Materials Society, 1995; p265.
10. Z. Chen, *Electro-Spark Toughening Technique* (in Chinese), The Mechanical Industry Press, 1985.
11. S. Becker, A. Rahmel, M. Schorr and M. Schütze, *Oxid. Met.*, **38**, 425 (1992).
12. M. Schmitz-Niederau and M. Schütze, *Oxid. Met.*, **52**, 225 (1999).
13. S. Becker, M. Schütze and A. Rahmel, *Oxid. Met.*, **39**, 93 (1993).
14. M. Schmitz-Niederau and M. Schütze, *Oxid. Met.*, **52**, 241 (1999).
15. J.L. Smialek and D.L. Humphrey, *Scripta Metall. Mater.*, **26**, 1763 (1992).
16. R.L. Coble, *J. Appl. Phys.*, **34**, 1679 (1963).
17. H.E. Evans, *Int. Mater. Rev.*, **40**, 1 (1995).
18. R.Z. Zhu, Y.D. He and H.B. Qi, *High Temperature Corrosion and the Corrosion-Resistant Materials*, Shanghai Science and Technology Publishing House, Shanghai, 1995.
19. I. Gurrappa, *Oxid. Met.*, **51**, 353 (1999).
20. I. Gurrappa, *Corrosion Prevention & Control*, 151, Dec, 1997.