Oxidation of Metals, Vol. 48, Nos. 5/6, 1997

Effect of A Sputtered TiAlCr Coating on the Oxidation Resistance of TiAl Intermetallic Compound

Zhaolin Tang,* Fuhui Wang,* and Weitao Wu*

Received February 12, 1997; revised April 22, 1997

The effect of a sputtered TiAlCr coating on the oxidation resistance of TiAl intermetallic compound was investigated in static air. The bare TiAl alloy exhibited poor isothermal and cyclic-oxidation resistance at 800–1000°C due to the formation of TiO_2-base scales which tend to spall during cooling. A sputtered Ti–50Al–10Cr coating remarkably improved the oxidation resistance of TiAl, due to the formation of an adherent Al_2O_3 scale at 800–1000°C. After long-term oxidation (at 900°C for 1000 hr), TiAlCr coating still provided excellent protection for the TiAl alloy. Minor interdiffusion occurred due to the inward diffusion of Cr, while no Kirkendall voids were found at the coating/substrate interface. In contrast, NiCrAlY and CoCrAlY coatings reacted extensively with the TiAl alloys. Moreover, the TiAlCr coating alloy is based on γ-TiAl and TiAlCr Laves phases, which may offer improved mechanical properties. The TiAlCr coating exhibited a better combination of oxidation resistance and substrate compatibility than conventional aluminide and MCrAlY coatings.

KEY WORDS: TiAl intermetallic compound; isothermal/cyclic oxidation; TiAlCr coating; MCrAlY coating; interdiffusion.

INTRODUCTION

TiAl intermetallic compounds have been receiving considerable interest as high-temperature structural materials due to their low density, high specific strength, and low cost, compared to currently used Nickel-base superalloys.[1,2] However, poor oxidation resistance of TiAl must be overcome

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*State Key Laboratory for Corrosion and Protection, Institute of Corrosion and Protection of Metals, Academia Sinica, Shenyang 110015, China.

before it may be used in practice at elevated temperatures because it does not form a continuous Al_2O_3 scale, but a nonprotective $TiO_2 + Al_2O_3$ mixed scale.[3,4]

In order to solve the poor oxidation resistance of TiAl intermetallics, several kinds of coatings have been investigated, including aluminide coatings,[5–7] MCrAl(Y) overlay coatings,[8–11] nanocrocrystalline TiAl coating,[12,13] and Si_3N_4,[14] SiO_2,[15] and Al_2O_3[16,17] ceramic coatings. Improvement of the oxidation resistance of TiAl intermetallics has been achieved with these coatings, but they still encountered some problems. The ideal coating for TiAl intermetallics should form an adherent Al_2O_3 scale and exhibit excellent compatibility with the substrate. Aluminizing forms a $TiAl_3$ layer, which is very brittle[5]; MCrAlY overlay coatings could form $AlCo_2Ti$ or $AlNi_2Ti$ brittle phase and Kirkendall voids between the coating and substrate, which are very harmful to the mechanical properties and the long-term oxidation resistance[11]; ceramic coatings may crack and spall during thermal cycling due to the mismatch of thermal coefficients[14–17]; nanocrystalline TiAl coating offers limited improvement in the oxidation resistance because a protective Al_2O_3 scale still failed to form.[12,13] Recently, a new class of Ti–Al–Cr coatings have been proposed and they provide excellent oxidation protection for TiAl intermetallics, but few data have been published.[18–20]

In this paper, the effect of a sputtered Ti–50Al–10Cr coating on oxidation resistance of γ-TiAl was investigated, because this coating alloy, with limited composition deviation from γ-TiAl, possesses excellent isothermal and cyclic oxidation resistance at 800–1100°C in air.[21]

EXPERIMENTAL PROCEDURES

Specimen Preparation

The TiAl and TiAlCr alloys (nominal composition Ti–50Al and Ti–50Al–10Cr at.%, respectively) were melted by using a vacuum-induction furnace with a CaO crucible. The TiAl ingot was cut into 20 × 10 × 3 mm specimens and ground down to 600-SiC paper, peened, and ultrasonically cleaned in ethanol. The TiAlCr target, 380 × 126 × 8 mm, was prepared for magnetron-sputtering. Sputtering parameters were as follows: argon pressure 0.2 Pa, power density about 4.2 w/cm^2, and substrate temperature 250–300°C. NiCrAlY and CoCrAlY coatings were also prepared with magnetron sputtering. Their nominal compositions were Co–31Cr–11Al–0.3Y and Ni–32Cr–11Al–0.3Y (at.%), respectively. The thickness of these coatings is about 30 μm.

Oxidation Tests

Isothermal-oxidation tests were carried out at 800, 900, and 1000°C in static air. For bare TiAl, an electronic thermal-balance was used to record the mass change continuously because of the severe spallation of oxides scales during cooling; for TiAl with TiAlCr coating, the specimens were placed in alumina crucibles oxidized at the desired temperatures and cooled to room temperature at regular intervals of 20 hr for mass measurement. The sensitivity of the balance used in the study was 10^{-4} g.

Cyclic-oxidation tests were conducted at 900 and 1000°C in static air. The specimens were kept at the desired temperature for 1 hr and cooled down to room temperature for 10 min as a cycle.

Metallographic Examination

The original and oxidized specimens were examined by X-ray diffractometery (XRD) using Cu–Kα radiation at 40 kv and 30 μm. The composition of the outer surfaces and cross-section of the specimens were examined by scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDAX). Concentration profiles of metallic elements along the cross-section were obtained using EDAX. Microhardness measurements (Hv) were carried out on mechanically-polished samples. The load of the test diamond was 25 g and the loading time was 15 sec.

RESULTS

Coating Structure

Figure 1 shows the surface morphology and cross-section fractograph of the sputtered TiAlCr coating. The coating possesses a columnar structure

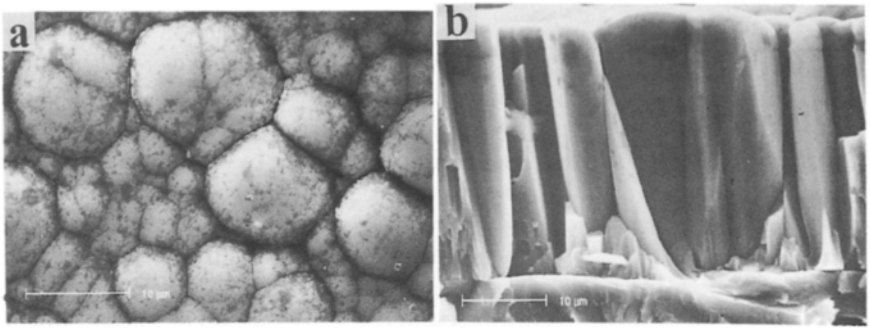

Fig. 1. TiAl with TiAlCr coating before oxidation: (a) surface morphology, (b) cross-sectional fractograph.

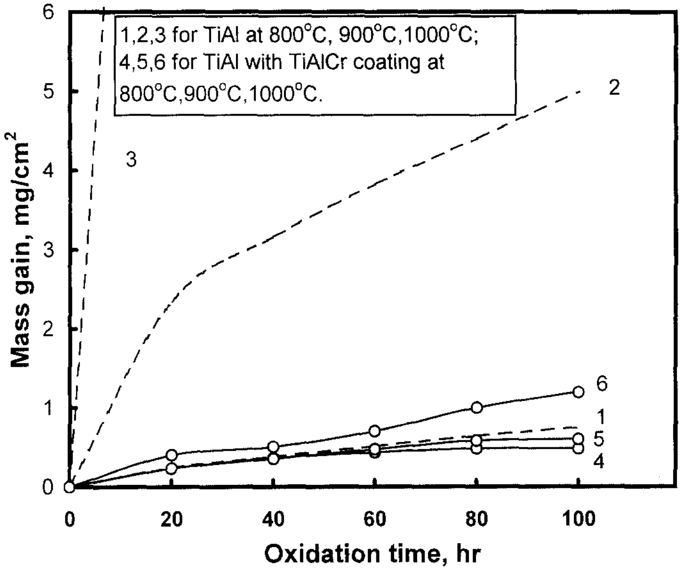

Fig. 2. Isothermal-oxidation kinetics of specimens.

with a spherical surface. XRD analysis indicated the coating was composed of γ-TiAl and TiAlCr Laves phases.

Isothermal Oxidation

Figure 2 shows the isothermal-oxidation kinetics. The bare TiAl alloy shows much higher mass gains. However, TiAlCr coatings decrease the oxidation rate of TiAl alloy by about one order of magnitude. At 800 and 900°C, the mass gains for TiAl with TiAlCr coating are very small; however, an obvious increase occurs after 40 hr at 1000°C.

Figure 3 shows the surface morphology and cross-section of TiAl alloy after 100 hr oxidation at 900°C. The scale exhibits a typical layered structure. The outer layer(I) is mainly TiO_2. the inner one(III) is the $TiO_2+Al_2O_3$ mixed layer, and between the two layers is an Al_2O_3-rich layer(II). The scale structures after 100 hr at 800 and 1000°C are similar to that at 900°C except that the Al_2O_3-rich layer at 1000°C is not so obvious as that at 800 and 900°C. The scale structure agrees with that described in the literature[3] (The EDAX techniques used in the present work are not sensitive to the presence of nitrides, which may also be present in the scale). The Al_2O_3 barrier is not stable and will dissolved and reprecipitate in the outer TiO_2 layer, which will result in breakaway oxidation after 300 hr oxidation at 900°C. However, at 1000°C the breakaway oxidation may come after a short transition period,

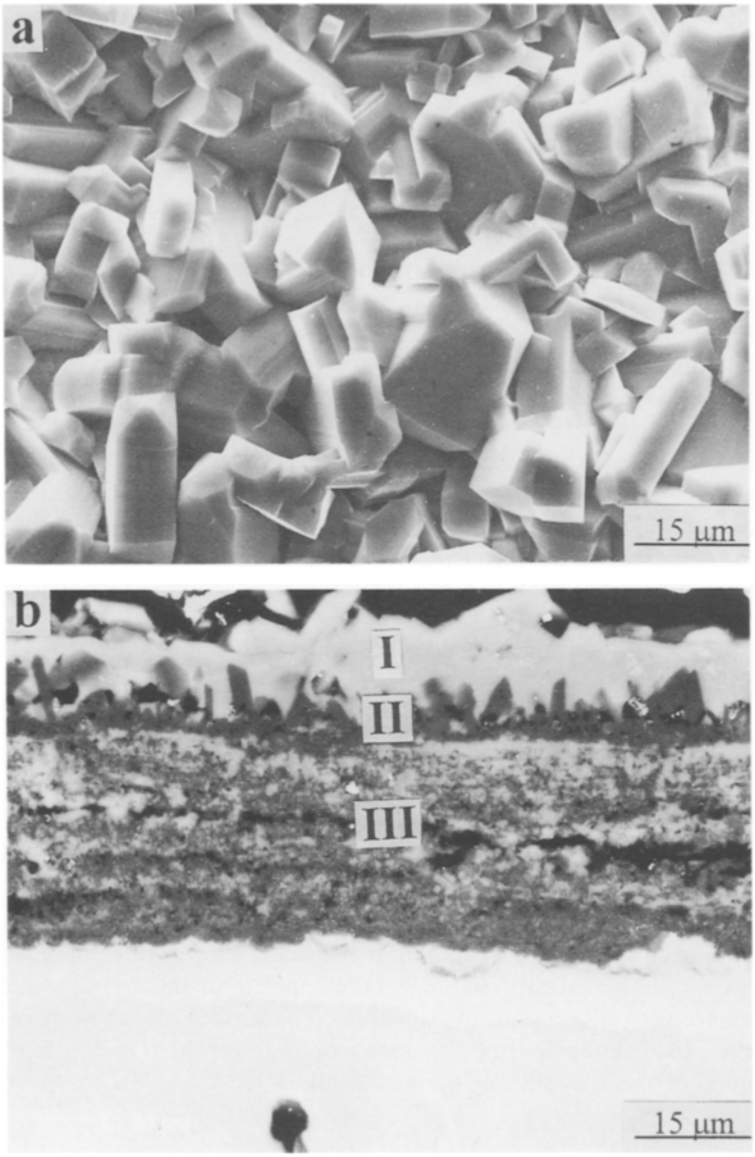

Fig. 3. TiAl after 100 hr oxidation at 900°C: (a) Surface morphology, (b) cross-sectional microstructure.

maybe no more than 100 hr and the kinetics quickly followed a linear law. Failure to form a protective Al_2O_3 scale results in the poor oxidation resistance.[3]

The TiAlCr coating, just like the TiAlCr alloy,[21] forms an adherent Al_2O_3 scale, so it provides excellent protection for TiAl alloy at 800–1000°C. Figure 4 shows the surface morphology and cross-section of TiAl with a TiAlCr coating after 100 hr oxidation at 1000°C. EDAX analysis indicated that a uniform and adherent Al_2O_3 scale formed on the TiAlCr coating. The surface morphology and the cross-section of TiAl with a TiAlCr coating after 100 hr oxidation at 800 and 900°C are similar to that at 1000°C except that occasional TiO_2 nodules appear at 1000°C (Fig. 5) which may contribute to the higher mass gains at this temperature.

Figure 6 shows a cross-section microstructure of TiAl with TiAlCr coating after 1000 hr oxidation at 900°C. It is seen that a uniform and adherent Al_2O_3 scale still provides good protection. The coating is adherent to the substrate, and no Kirkendall voids appear in the coating/substrate interface. Figure 7 show the results of EDAX analysis and microhardness test along the cross-section. It is seen that mainly a little Cr diffusion is found. Compared with the original coating thickness, the interdiffusion after 1000 hr at 900°C was approximately 12 μm. The microhardness results also show the inward diffusion of Cr. No microcracks around indents occurred.

Cyclic Oxidation

Figure 8 shows the cyclic-oxidation kinetics. For bare TiAl, a mass loss was found only after ten cycles at 900°C, and a more severe mass loss was found at 1000°C. However, the TiAlCr coating remarkably improves the cyclic-oxidation resistance of the TiAl alloy.

Figure 9 shows the surface morphology and cross-section of TiAl with a TiAlCr coating after 100-cycle oxidation at 1000°C. An adherent Al_2O_3 scale forms on the coating (Fig. 9a), also with occasional TiO_2 nodules (similar to that in Fig. 5) which are more numerous and larger than those formed during isothermal oxidation at the same temperature; these contribute to the higher mass gain. No cracks appear in the coating, and the coating are very adherent to the substrate. The surface morphology of TiAl with the TiAlCr coating after 100-cycle oxidation at 900°C is similar to that at 1000°C except that smaller nodules form at 900°C.

MCrAlY Coatings

MCrAlY(M = Co,Ni) coatings remarkably decrease the oxidation rate of TiAl.[11] However, these coatings react extensively with TiAl. Figure 10 shows a cross-sectional microstructure of TiAl with a NiCrAlY coating after

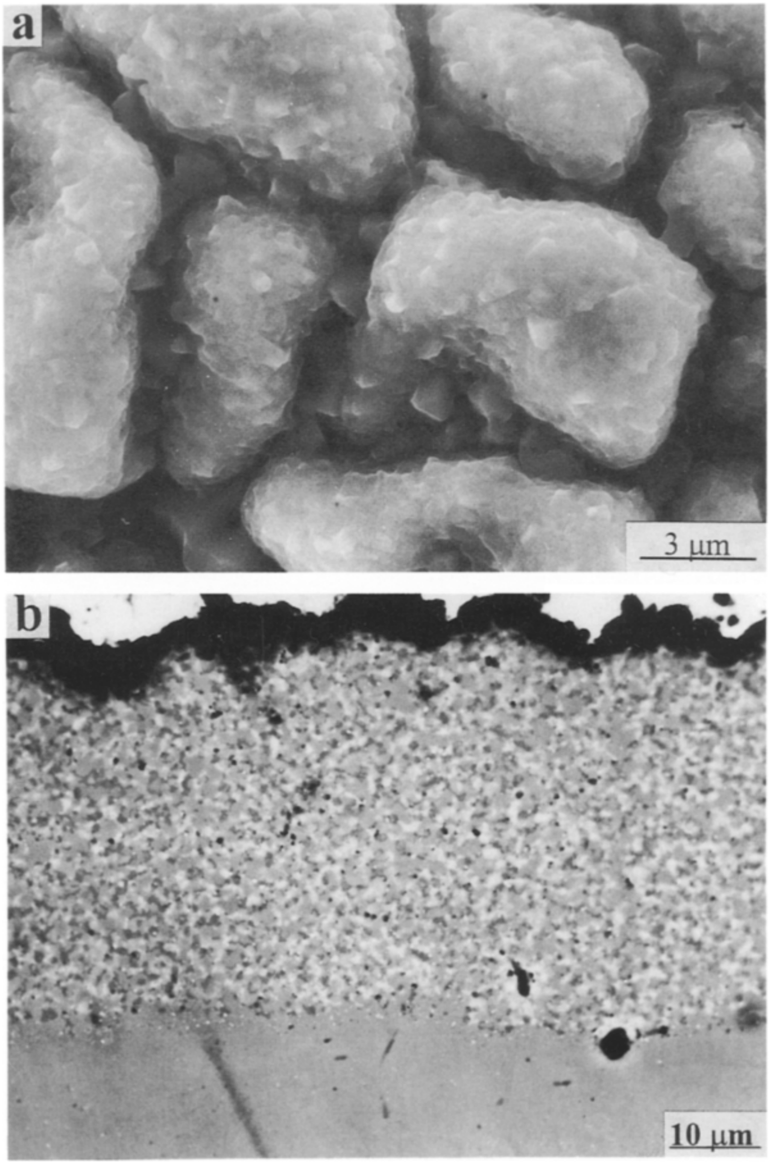

Fig. 4. TiAl with TiAlCr coating after 100 hr oxidation at 1000°C: (a) Surface morphology, (b) cross-sectional microstructure.

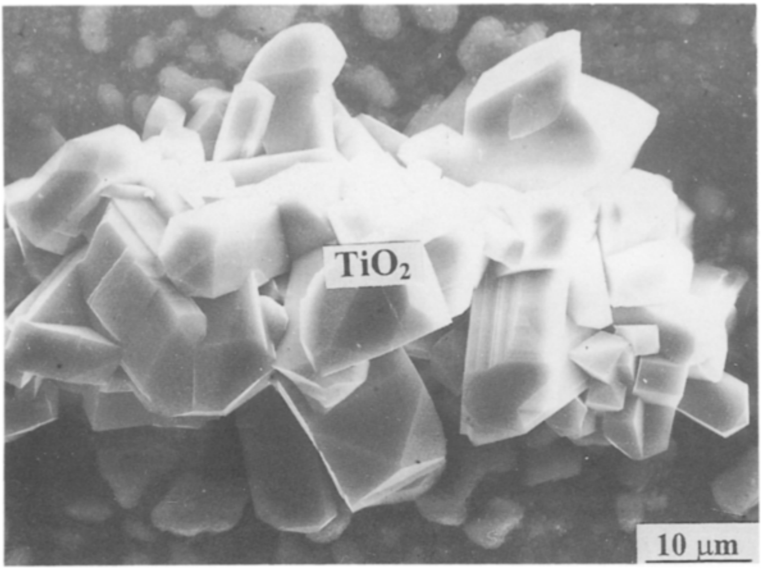

Fig. 5. TiO_2 nodule on TiAlCr coating ater 100 hr oxidation at 1000°C.

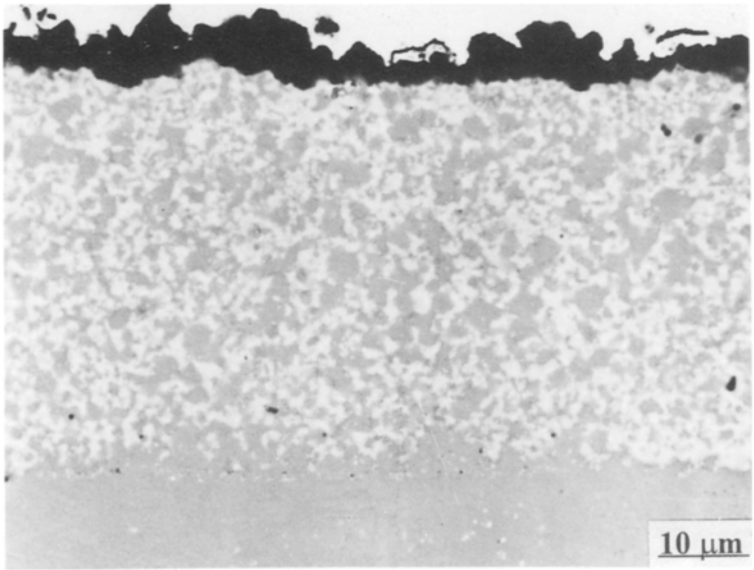

Fig. 6. Cross-sectional microstructure of TiAl with TiAlCr coating after 1000 hr oxidation at 900°C.

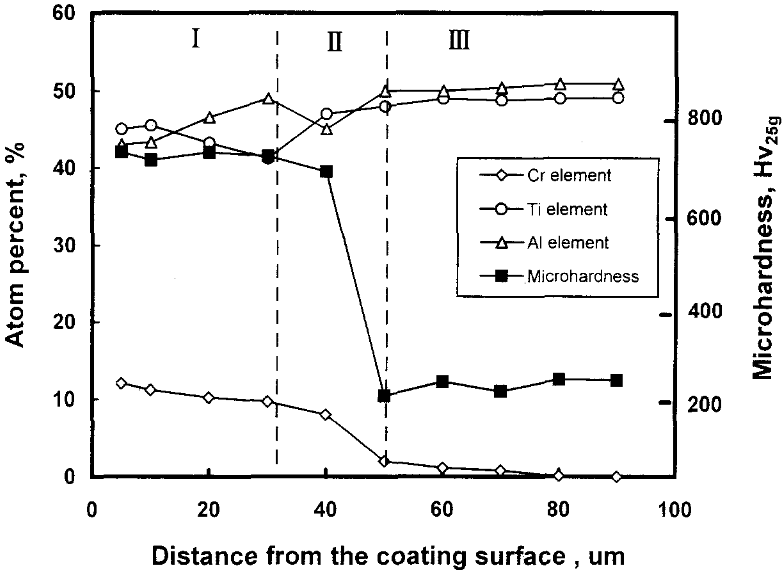

Fig. 7. Element and microhardness profile across the coating-substrate interface for TiAl and TiAlCr coating after 1000 hr oxidation at 900°C: (I) coating; (II) diffusion layer; (III) substrate.

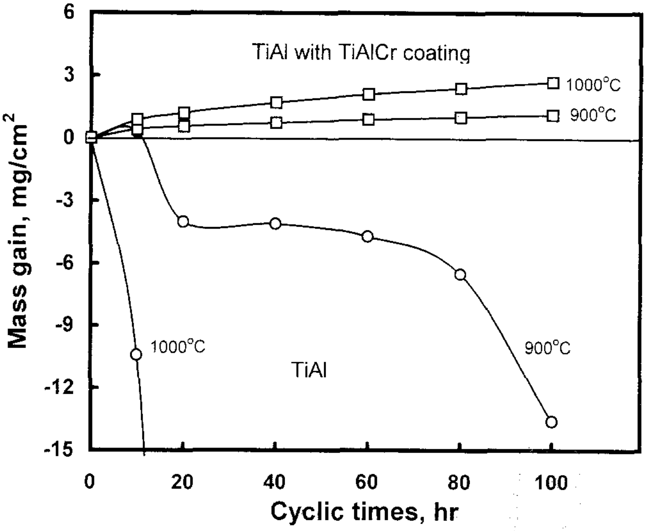

Fig. 8. Cyclic-oxidation kinetics of specimens.

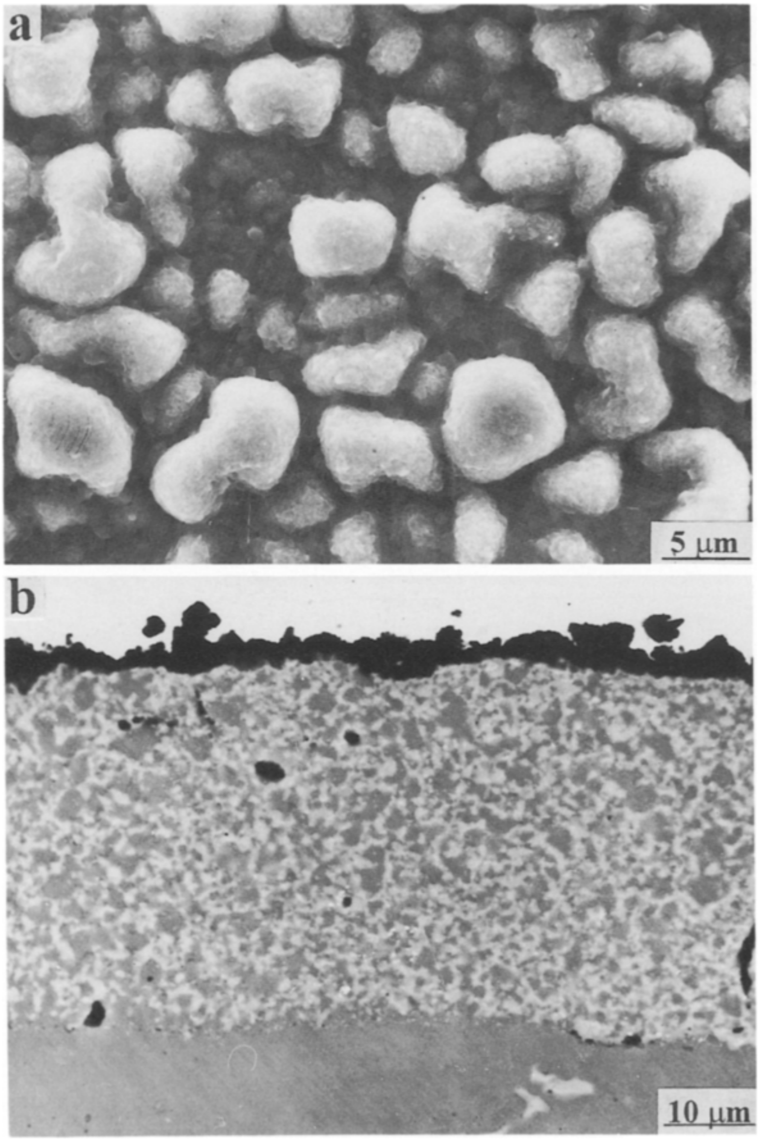

Fig. 9. TiAl with TiAlCr coating after 100-cycle oxidation at 1000°C: (a) Surface morphology, (b) cross-sectional microstructure.

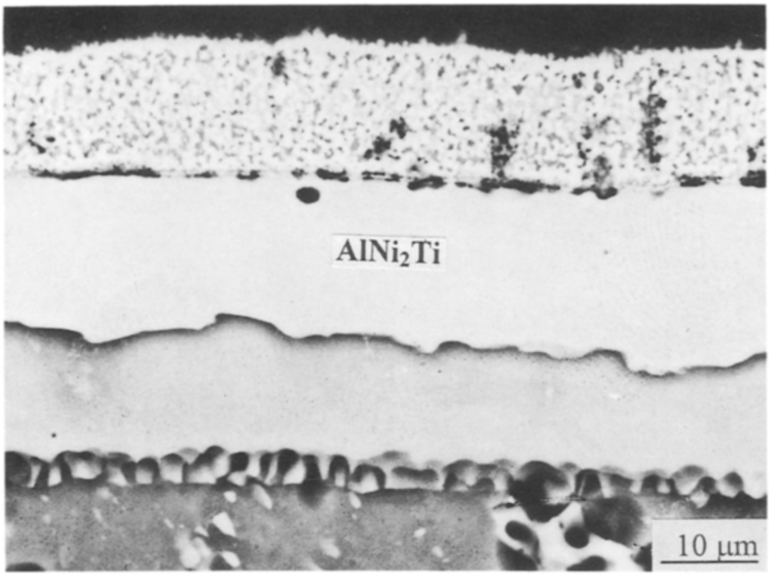

Fig. 10. Cross-sectional microstructure of TiAl with NiCrAlY coating after 100 hr oxidation at 900°C.

100 hr oxidation at 900°C. Two diffusion layers exist, and Kirkendall voids form at the coating/substrate interface. Figure 11 shows the composition and microhardness profiles across the NiCrAlY coating/substrate interface. Severe Ni diffusion occurred, and the diffusion depth is about 40 μm. Also some Ti diffuses into the coating, but Cr diffusion is negligible. XRD results indicated that the outer diffusion layer is composed mainly of the $AlNi_2Ti$ ternary intermetallic. Microhardness results show that the diffusion layer is much harder than the substrate. Moreover, many microcracks around indents were found in the diffusion layers, which indicated that the diffusion layers were also very brittle. This is similar for CoCrAlY-coated TiAl, as shown in Fig. 12 and 13. Two diffusion layers and Kirkendall voids formed at the coating/substrate interface and mainly the inward diffusion of Co occurred. XRD results indicated that the outer diffusion layer was composed mainly of the $AlCo_2Ti$ ternary intermetallic, which is also very hard and brittle.

DISCUSSION

It is now generally accepted practice to protect high-temperature materials against oxidation with coatings, such as diffusion coatings and

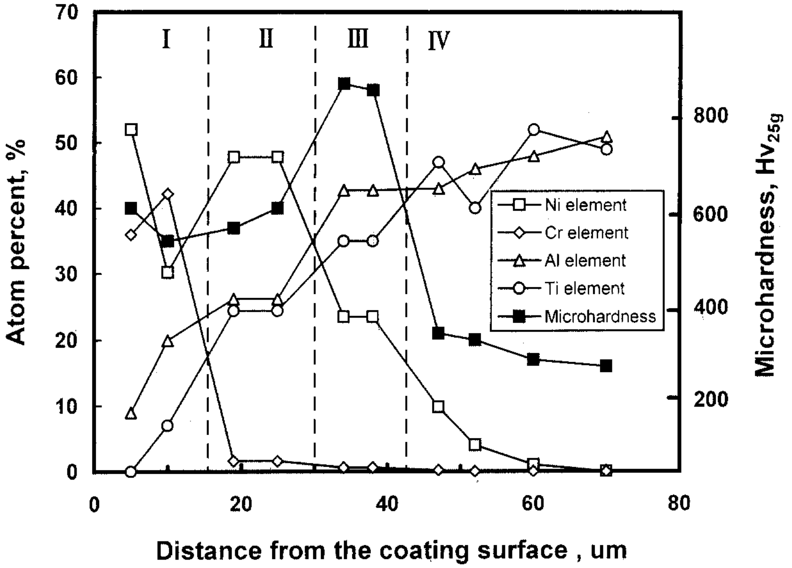

Fig. 11. Element and microhardness profile across the coating–substrate interface for TiAl with NiCrAlY coating after 100 hr oxidation at 900°C: (I) coating; (II) outer diffusion layer; (III) inner diffusion layer; (IV) substrate.

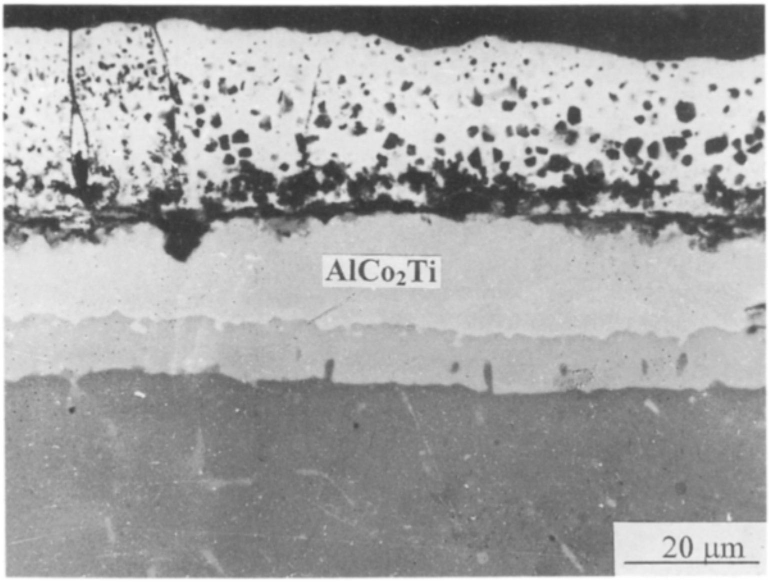

Fig. 12. Cross-sectional microstructure of TiAl with CoCrAlY coating after 100 hr oxidation at 900°C.

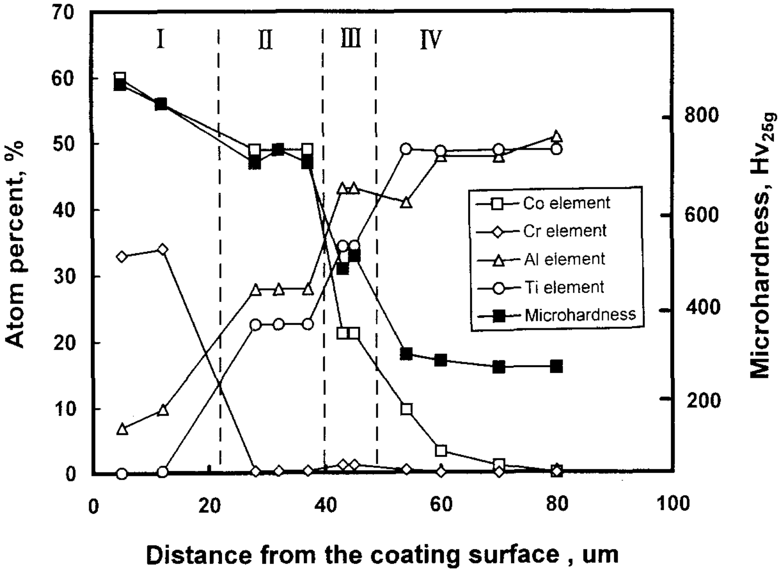

Fig. 13. Element and microhardness profile across the coating–substrate interface for TiAl with CoCrAlY coating after 100 hr oxidation at 900°C: (I) coating; (II) outer diffusion layer; (III) inner diffusion layer; (IV) substrate.

*M*CrAlY overlay coatings.[22,23] Aluminizing provides a simple technique to obtain a $TiAl_3$ coating on Ti_3Al and TiAl alloys so the oxidation resistance is improved remarkably due to the formation of a protective Al_2O_3 scale. However, $TiAl_3$ is very brittle, and cracks normal to the surface may occur during cooling after aluminizing. This will be detrimental to the long-term and cyclic-oxidation resistance.[5]

*M*CrAlY coatings, successfully used to protect Ni-, Fe-, and Co-base superalloys, can remarkably decrease the oxidation rate of TiAl. However, the severe interdiffusion may result in several problems. First, the interdiffusion make the coatings thinner quickly, which would influence the long-term oxidation resistance. Second, the diffusion layer is hard and brittle and this will be harmful to the mechanical properties of TiAl. Third, maybe the most severe effect, many Kirkendall voids formed at the coating/substrate interface, and the voids developed into cracks, which will deteriorate the coating adherence to substrate.

These studies suggest that conventional aluminide and *M*CrAlY coatings may not be suitable for the protection of TiAl against high-temperature oxidation, and a protective coating especially designed for TiAl alloy is needed. The ideal protective coating for TiAl alloy should form an adherent Al_2O_3 scale and exhibit excellent compatibility to the substrate so that thermal-expansion mismatch and interdiffusion are minimized. In order to achieve this, the coating alloy should have a similar composition to the TiAl alloy, namely a coating alloy based on TiAl is preferred. Nanocrystalline (microcrystalline) coatings represent an entirely new concept, because these coatings have the same composition as those of substrates and exhibited excellent compatibility to the substrate.[24] However, nanocrystalline TiAl coatings improved the oxidation resistance only to a limited degree, because a protective Al_2O_3 scale still failed to form.[12,13] This indicated that a third element is still needed to promote the formation of a continuous Al_2O_3 scale on nanocrystalline TiAl coatings.

To date, many studies dealing with the effects of ternary alloying elements on oxidation resistance of TiAl alloy showed that Cr can exhibit the best effect under certain conditions.[18,21,25–27] Thus, recent work has emphasized the protection of TiAl by Ti–Al–Cr alloys.[18–20]

A recent study showed that Ti–50Al–10Cr alloy possesses excellent isothermal and cyclic-oxidation resistance at 800–1100°C in air.[21] This composition is in the range described in Refs. 18–20. In this study, a sputtered Ti–50Al–10Cr coating not only effectively protect TiAl from oxidation, but also exhibited excellent thermal and chemical compatibility with the substrate. Slight interdiffusion occurs due to the inward diffusion of Cr, while no Kirkendall voids were found at the coating/substrate interface. These results indicated that the diffusion coefficient of Cr in TiAl is much lower than that of Co and Ni. Moreover, the coating alloys are based on γ-TiAl and TiAlCr Laves phases and the TiAlCr Laves phase is surrounded by the continuous γ-TiAl, the same as described in Refs. 19 and 28. Therefore, the TiAlCr coating offered the necessary mechanical properties and substrate compatibility such that no cracks were found after cyclic oxidation or around microhardness indentations.

It is seen that the TiAlCr coating not only remarkably improved the oxidation resistance of TiAl intermetallics but also exhibited better compatibility between the substrate and coating than any other conventional aluminide and *M*CrAlY coatings. This coating may become a realistic protective coating for TiAl alloys. Future research should evaluated the effect of TiAlCr coatings on mechanical properties of engineering γ-TiAl.

CONCLUSIONS

1. The sputtered Ti–50Al–10Cr coating possesses a columnar structure consisting γ-TiAl and TiAlCr Laves phases.

2. The sputtered Ti–50Al–10Cr coating provides excellent oxidation protection for TiAl alloy due to the formation of an adherent Al_2O_3 scale. After long-term oxidation (900°C for 1000 hr), inward diffusion of Cr is

estimated to be just 12 μm, and no Kirkendall voids were found at the coating/substrate interface.

3. A TiAlCr coating exhibits a better combination of oxidation resistance and compatibility between the substrate and coating than conventional *M*CrAlY Coatings. This coating may become a realistic protective coating for engineering γ-TiAl.

ACKNOWLEDGMENTS

This project was supported by the National Natural Sciences Foundation of China (NSFC) for Outstanding Young Scientists and by the National Advanced Material Committee of China.

REFERENCES

1. Y. M. Kim, *J. Met.* **42**, 24 (1989).
2. Y. W. Kim, *J. Met.* **47**, 38 (1995).
3. S. Becker, A. Rahmel, M. Schorr, and M. Schutze, *Oxid. Met.* **38**, 425 (1992).
4. K. L. Luthra, *Oxid. Met.* **36**, 475 (1991).
5. J. Shen, Z. Teng, Z. Jiang, L. Zhou, and T. Li, *J. Uni. Sci. Technol. Beijing* **S13**, 624 (1991).
6. A. Takei and A. Ishida, *7th APCCC, Int. Acad. Publ., China* **2**, 718 (1991).
7. H. Mabuchi, T. Asai, and Y. Nakayama, *Scripta Metall.* **23**, 685 (1989).
8. T. Simizu, T. Iikubu, and S. Isobe, *Mater. Sci. Eng.* **A153**, 602 (1992).
9. S. Taniguchi, T. Shibada, N. Asanuma, H. Lou, F. Wang, and W. Wu, *Oxid. Met.* **39**, 457 (1993).
10. S. Taniguchi, N. Asanuma, T. Shibada, F. Wang, H. Lou, and W. Wu, *J. Jpn. Inst. Met.* **57**, 781 (1993).
11. Z. Tang, F. Wang, and W. Wu, *J. Chin. Soc. Corros. Prot.* **17**, 116 (1997).
12. F. Wang, H. Lou, and W. Wu, *Oxid Met.* **43**, 395 (1995).
13. Z. Tang, F. Wang, and W. Wu, *Trans. Nonferro. Met. Soc. Chin.* **7**, 103 (1997).
14. S. Taniguchi, T. Shibada, T. Yamada, X. Liu, and S. Zou, *ISIJ Int.* **33**, 869 (1993).
15. S. Taniguchi, T. Shibada, and N. Katoh, *J. Jpn. Inst. Met.* **57**, 666 (1993).
16. S. Taniguchi, T. Shibada, and K.Takeuchi, *Mater. Trans. JIM* **32**, 299 (1991).
17. Z. Tang, F. Wang, and W. Wu, *Chin. J. Mater. Res.* (to be published).
18. R. L. McCarron, J. C. Schaeffer, G. H. Meier, D. Berztiss, R. A. Perkins, and J. Cullinan, *Titanium '92*, F. H. Froes and I. Caplan eds. (TMS, Warrendale, PA, 1993), p. 1971.
19. M. P. Brady, W. J. Brindley, J. L. Smialek, and I. E. Locci, *JOM* **48**, 46 (1996).
20. M. P. Brady, J. L. Smialek, and W. J. Brindley, U.S. Patent Office (1996) (submitted).
21. F. Wang, Z. Tang, and W. Wu, *Oxid. Met.* **48**, 509 (1997).
22. T. N. Rhys-Jones, *Corros. Sci.* **29**, 623 (1989).
23. R. Sreiff, *J. Phys. IV* **3**, 17 (1993).
24. F. Wang, PhD dissertation, Institute of Corrosion and Protection of Metals, Shenyang, China (1993).
25. Y. Shida and H. Anada, *Corros. Sci.* **35**, 945 (1993).
26. Y. Shida and H. Anada, *Oxid. Met.* **45**, 197 (1996).
27. D. W. McKee and S. C. Huang, *Corros. Sci.* **33**, 1899 (1992).
28. M. P. Brady, J. L. Smialek, and F. Terepka, *Scripta Metall.* **32**, 1659 (1995).