JTTEE5 7:64-70

Improvement of the Adhesion of a Ceramic Coating on a Ceramic Substrate

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(Submitted 24 March 1997; in revised form 14 October 1997)

The structure and adhesion of an alumina coating on a ceramic substrate with NiCrAlY alloy bond coating was investigated by heating at 1573 and 1673 K in the air. Phases of NiO, $NiCrO_3$, $NiAl_2O_4$, αAl_2O_3, and Ni were revealed in a 100 μm thick bond coating on heating at 1573 and 1673 K. A veined structure was also detected in the coating heated at 1573 K. The adhesion strength of the coating was improved and reached approximately 20 MPa on heating at 1573 and 1673 K for 14.4 ks in air although the strength of the as-sprayed coating was only 2 MPa. The improvement of adhesion strength may arise from the formation of $NiAl_2O_4$ with a spinel structure at the interfaces of the top coating/bond coating/substrate coating system. The adhesion strength of the coating improved on decreasing the bond coating thickness and reached approximately 45 MPa for a 20 μm thick bond coating which was heated at 1673 K. Only $NiAl_2O_4$ oxide was formed in the bond coating.

Keywords adhesion strength, alumina coating, bond coat, post treating, spinel

1. Introduction

Engineering ceramics of high strength as well as corrosion resistance have been required recently in some industries. Cladding of different ceramics by brazing is one of the technologies (Ref 1-4) to meet this requirement. Thermal spraying is not often used due to the adhesion strength of the ceramic coating being generally low when sprayed directly on ceramics or metallic bond coatings.

The adhesion of a ceramic coating on ceramic substrates with a nickel-base alloy bond coating is able to be improved by heat treatment in air (Ref 5). The strength of the ceramic coating increased by approximately 10 times (~15 MPa) from the as-sprayed condition when heat treated at 1273 K for 7.2 ks in air. This improvement is due to the formation of oxides which have a veined structure and grow into cracks or pores of the ceramic coating substrates. Thus, the improvement of adhesion is attributed to chemical and physical interactions at the interfaces. Therefore, it is anticipated that the adhesion of a ceramic coating will improve with further chemical bonding on both interfaces between the metallic bond coating and the ceramic materials on both sides by heat treatment above 1273 K in air.

The change in strength of the ceramic coating when heat treated above 1273 K was investigated relative to the interface structures through the ceramic and bond coating, as well as the ceramic substrate.

2. Experimental Procedure

A substrate of sintered alumina was plasma sprayed (Table 1) with gray alumina powder (SHOWA DENKO SHOCOAT K-13, 45 to 10 μm diameter) of composition 2.28 TiO_2, 1.07 SiO_2, 0.03 Fe_2O_3, and balance Al_2O_3 (mass%). The bond coat was NiCrAlY alloy (SHOWA DENKO SHOCOAT MA-91, Showa Denko and Minato Tokyo, Japan; 45 to 10 μm diameter, composition of 22.01 Cr, 10.04 Al, 0.88 Y, balance Ni, in mass%). The alumina substrate was 25 mm diameter and 5 mm thick and was grit blasted with silicon carbide of No. 24 mesh prior to spraying the bond coating. The thickness of the top and bond coatings were approximately 300 and 100 μm, respectively, for the research of the strength properties. The thickness of the bond coating was changed from 150 to 20 μm in other samples to investigate this effect on the adhesion strength. The sprayed coatings were heat treated in 1573 and 1673 K for 14.4 ks in air and in vacuum followed by cooling at 5 K/min in the furnace. The observation of the interfaces of top coating, bond coating, and substrate was performed using electron microprobe analysis (EPMA). X-ray diffraction (XRD) (Cu-Kα) was also performed to reveal the phases present at the interface. Strength was measured by a tensile test (JIS H8666).

Table 1 Plasma spraying conditions

Top coating	
Plasma gas	Ar
Powder feed rate, g/min	25
Current, A	800
Voltage, V	28
Spray distance, mm	50
Bond coating	
Plasma gas	Ar
Powder feed rate, g/min	25
Current, A	600
Voltage, V	26
Spray distance, mm	100

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3. Results and Discussion

3.1 *Structure of Coating*

Figure 1 shows a back-scattered electron image of a cross section of an as-sprayed coating on an alumina substrate. There are more pores in the top coating than in the substrate. Pores or cracks in the top coating and the substrate are not impregnated with the metallic bond coating due to polishing. Figure 2 shows a back-scattered electron image of the cross section through the interface between the bond coating and substrate after heat treatment at 1573 K for 14.4 ks. In this case the pores or cracks in the substrate are filled with oxide of the bond coat, and a veined structure has formed. This also pertains to heat treated coating at 1273 K for 7.2 ks (Ref 5).

Figure 3 shows a back-scattered electron and the x-ray images of the heat treated bond coating at 1673 K for 14.4 ks. The bond coating is oxidized and has reacted with alumina on both sides. The width of the reacted layer is thicker at the top coating side than at the substrate side. Nickel is approximately equally distributed in the bond coating, but chromium is less prominent in the reacted layer on both sides of the bond coating. The veined structure, seen in the heat treated coating at 1573 K, is not observed on both sides. The heat treated specimens in vacuum did not form a veined structure or a reacted layer.

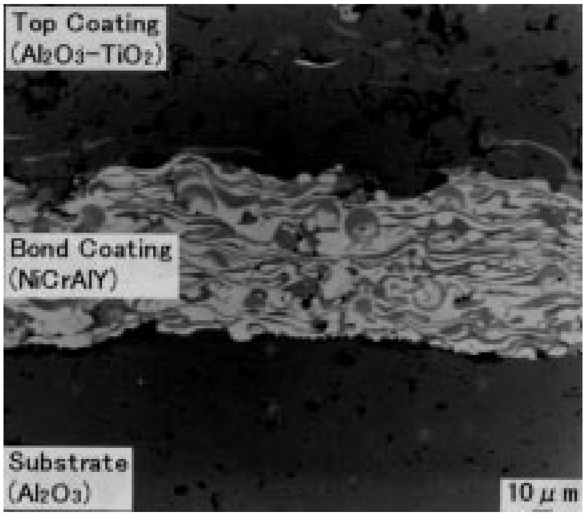

Fig. 1 Back-scattered electron image of coating

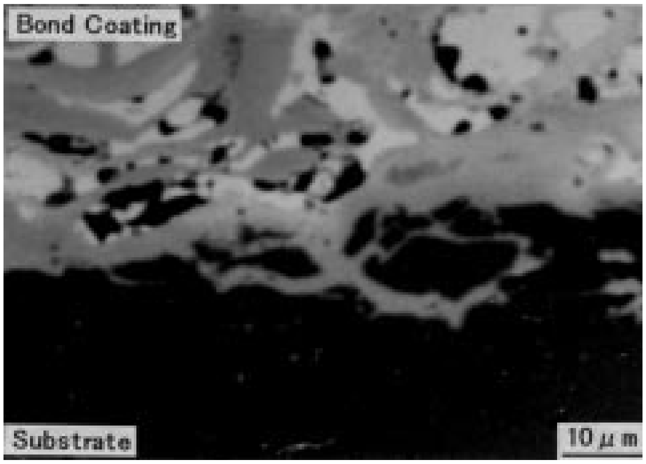

Fig. 2 Back-scattered electron image of coating heat treated at 1573 K for 14.4 ks

Figure 4 shows XRD patterns from the top surface of the NiCrAlY bond coating only without the top coating, as sprayed and heat treated at 1573 and 1673 K for 14.4 ks in air. Broad peaks of Ni solid solution are mainly revealed in the XRD pattern of the as-sprayed coating. Small amounts of αAl_2O_3 and $NiCrO_3$ are formed during thermal spraying. On heating at 1573 K for 14.4 ks, the $NiCrO_3$ concentration increases, and NiO oxide and $NiAl_2O_4$ spinel are formed. The peaks of Ni shift to larger angles and become sharp. This may be due to the decrease of Cr and Al in Ni solid solution which forms $NiAl_2O_4$ and $NiCrO_3$ phases. On heating at 1673 K for 14.4 ks, $NiCrO_3$ and αAl_2O_3 phases diminish, and the amount of $NiAl_2O_4$ and NiO phases increase. Accordingly, NiO and $NiAl_2O_4$ oxides and some Ni phases are present in the heat treated coating at 1673 K for 14.4 ks in air.

Figure 5 shows XRD patterns on the ruptured surface after a tensile test of the gray alumina coating with the bond coating heat treated at 1573 and 1673 K for 14.4 ks. The tensile test specimen failed within the bond coating. The XRD pattern of the specimen heat treated at 1573 K for 14.4 ks is similar to the XRD pattern of the heat-treated bond coating shown in Fig. 4. On heating at 1673 K for 14.4 ks, mainly $NiAl_2O_4$ and NiO oxides exist on the ruptured surface though the volume fraction of $NiAl_2O_4$ oxide in Fig. 5 is larger than the top surface of the bond coating in Fig. 4. This arises because the NiO in the bond coating reacted with Al_2O_3 in the alumina top coating.

3.2 *Adhesion Strength*

Figure 6 shows the adhesion strength of the coatings in the as sprayed and heat treated conditions. The adhesion strength of the coatings is enhanced from 2 MPa by heat treatment at 1573 and 1673 K to approximately 20 MPa. The adhesion strength of the coatings heat treated at 1273 K is approximately 15 MPa (Ref 5).

The formation of $NiAl_2O_4$ oxide by heat treatment in air may enhance the adhesion strength between the top coating and the substrate. The reaction of bond coating with alumina was not completed after the heat treatment at 1673 K for 14.4 ks as shown in Fig. 3. Therefore, the change in the adhesion strength was investigated with respect to the thickness of the bond coating in the range of 150 to 20 μm. Figure 7 shows the strength result as a function of the bond coating thickness. The adhesion strength of the 100 μm and 150 μm thick bond coatings is approximately 20 MPa. The adhesion strength of the coating increases with a decrease in the thickness of the bond coating and reaches approximately 45 MPa in 20 μm thick bond coating.

Figure 8 shows the back-scattered electron and x-ray images of the specimens of 20 μm thick bond coating. The bond coating is composed of one phase, and the width of the reacted phase is approximately twice the original thickness of the bond coat. In the middle of the reacted zone, a layer of voids was indicated by the appearance of the arrows. The position of the layer of voids is not at the center of the reacted phase but deviates to the substrate side (i.e., the reaction between the bond coat and the top coating is faster than between the bond coat and the substrate because the top coat is more porous than the substrate).

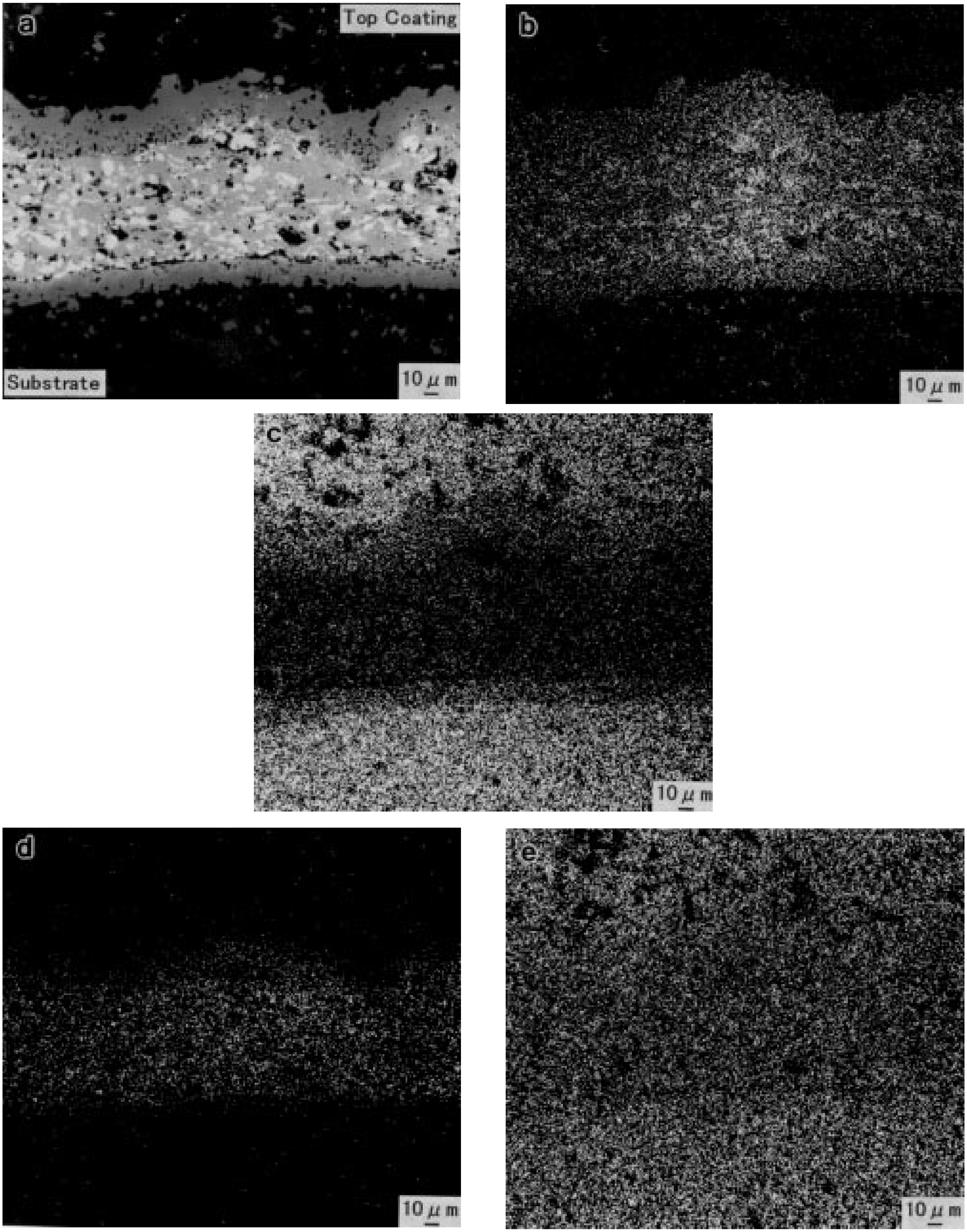

Fig. 3 EPMA images of bond coating heat treated at 1673 K for 14.4 ks. (a) Back-scattered electron image. (b) Ni-Kα. (c) Al-Kα. (d) Cr-Kα. (e) O-Kα

Figure 9 shows the back-scattered electron images of the cross section of ruptured coatings in the specimen with a 20 μm thick bond coating. The coating exhibited a maximum strength of ~45 MPa. Clearly the breakout occurred at the surface of the layer of voids in the reacted zone. Figure 10 shows the XRD patterns of the ruptured surface of the bond coating. The XRD pattern of 20 μm thick bond coating consisted mostly of $NiAl_2O_4$. Peaks of αAl_2O_3 observed may be resultant of the substrate. Whereas in the case of the 100 μm thick bond coating, NiO remains on the ruptured surface in addition to $NiAl_2O_4$. In conclusion, a thinner bond coating is effective in improving the adhesion strength of the coating because it tends to form only $NiAl_2O_4$ phase by the reaction of the bond coating with alumina in the top coating and the substrate.

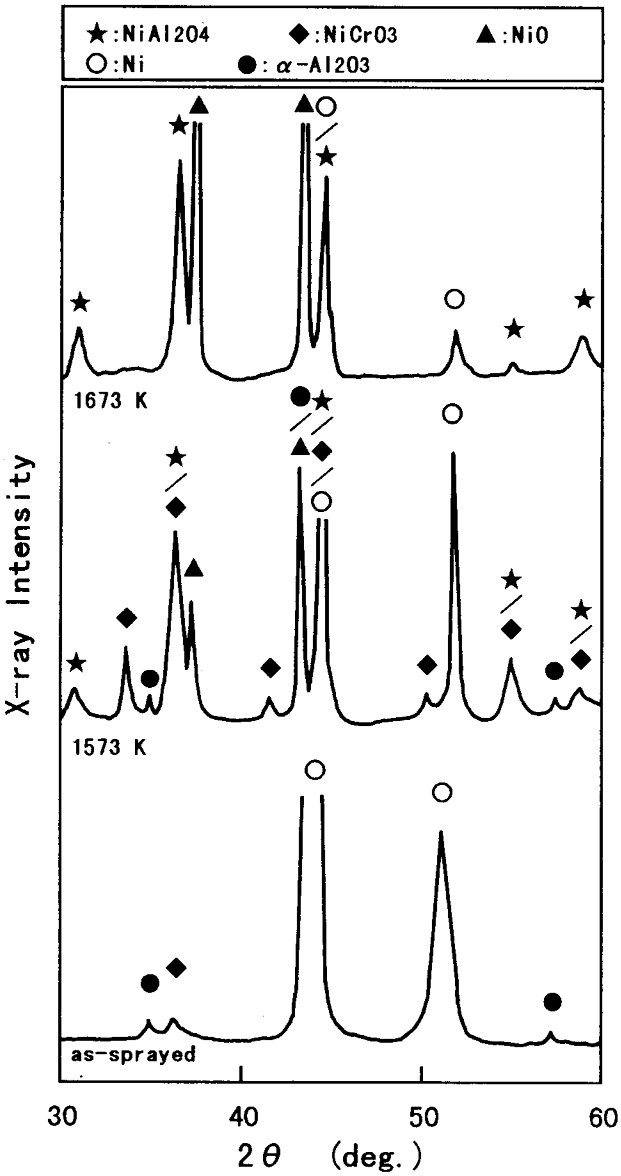

Fig. 4 XRD patterns of bond coating heat treated at various temperatures for 14.4 ks in air

Although alumina base ceramics are important structural materials, they do not exhibit good corrosion resistance to ash. Alumina-chromia ceramics contain a higher ratio of chromia which possess high corrosion resistance to ash (Ref 6). Thus, alumina-50% chromia was thermal sprayed on an alumina-base

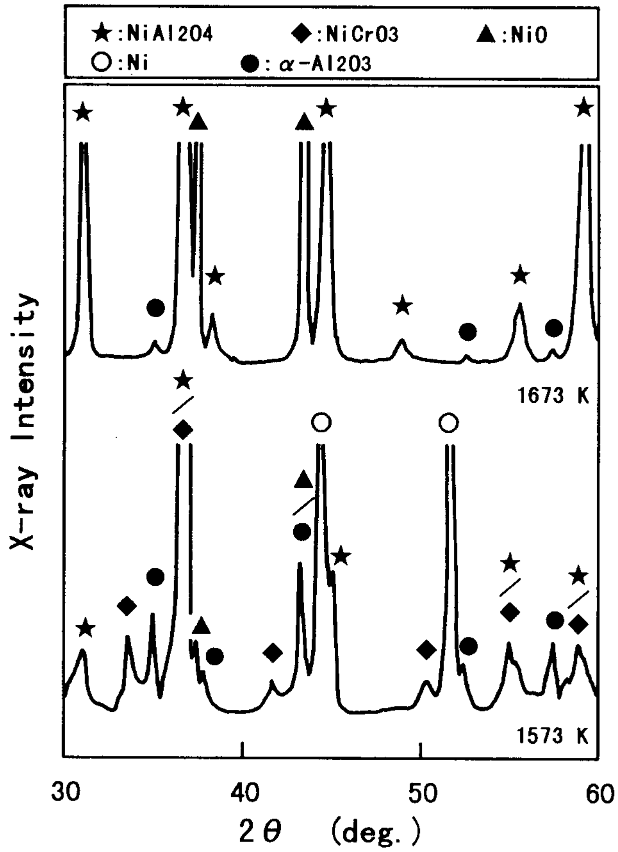

Fig. 5 XRD patterns of the ruptured surface after tensile testing

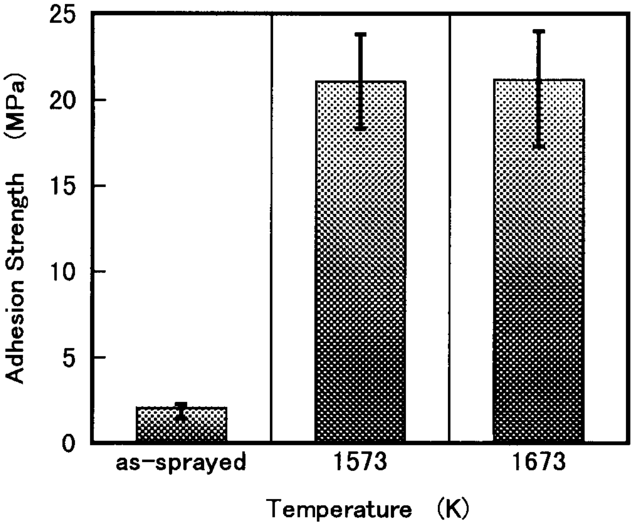

Fig. 6 Adhesion strength of coatings. Coatings were heat treated at 1573 and 1673 K for 14.4 ks in air, except for those in the as-sprayed condition. Longitudinal bars show maximum and minimum strength of three samples.

ceramic with a NiCrAlY bond coating followed by heat treatment at 1673 K for 36 ks in air. Figure 11 shows the back-scattered electron image micrograph by EPMA at the interface between the alumina-base substrate and alumina-50% chromia coating after heat treatment. The adhesion of the coating was adequate for practical use, and the removal of the coating did not occur during heating and cooling of the furnace.

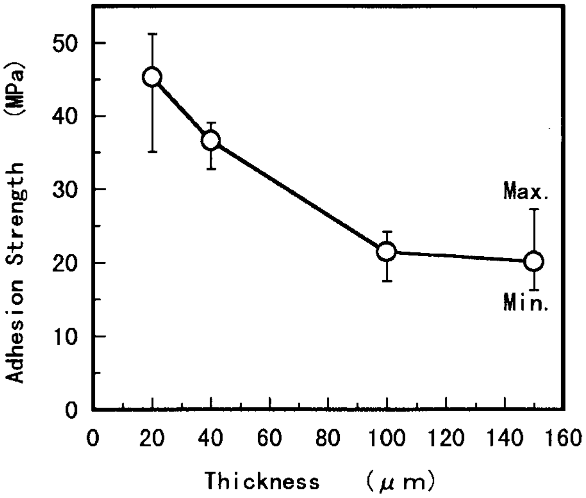

Fig. 7 Change in adhesion strength as a function of bond coating thickness after heat treating at 1673 K for 14.4 ks in air

4. Conclusions

The change in the structure and strength of plasma sprayed gray alumina coatings on a high purity alumina substrate with NiCrAlY alloy bond coating by heating at 1573 and 1673 K in air was investigated. The results obtained are summarized as follows.

- A veined structure forms at the interfaces between the bond coating and top coating and the substrate on heat treatment at 1573 K for 14.4 ks.
- The adhesion strength of the coating enhanced and exhibited a strength of ~20 MPa on heat treatment at 1573 and 1673 K whereas the strength of the as sprayed coating was ~2 MPa.
- The enhancement of strength arises due to physical joining by the veined structure and chemical joining by the formation of $NiAl_2O_4$ oxide at the interfaces.
- The adhesion strength of the coating increases on decreasing the bond coating thickness. In the 20 μm thick bond coating, the strength exhibited ~45 MPa, and only $NiAl_2O_4$ oxide was formed in the bond coating on heating at 1673 K.

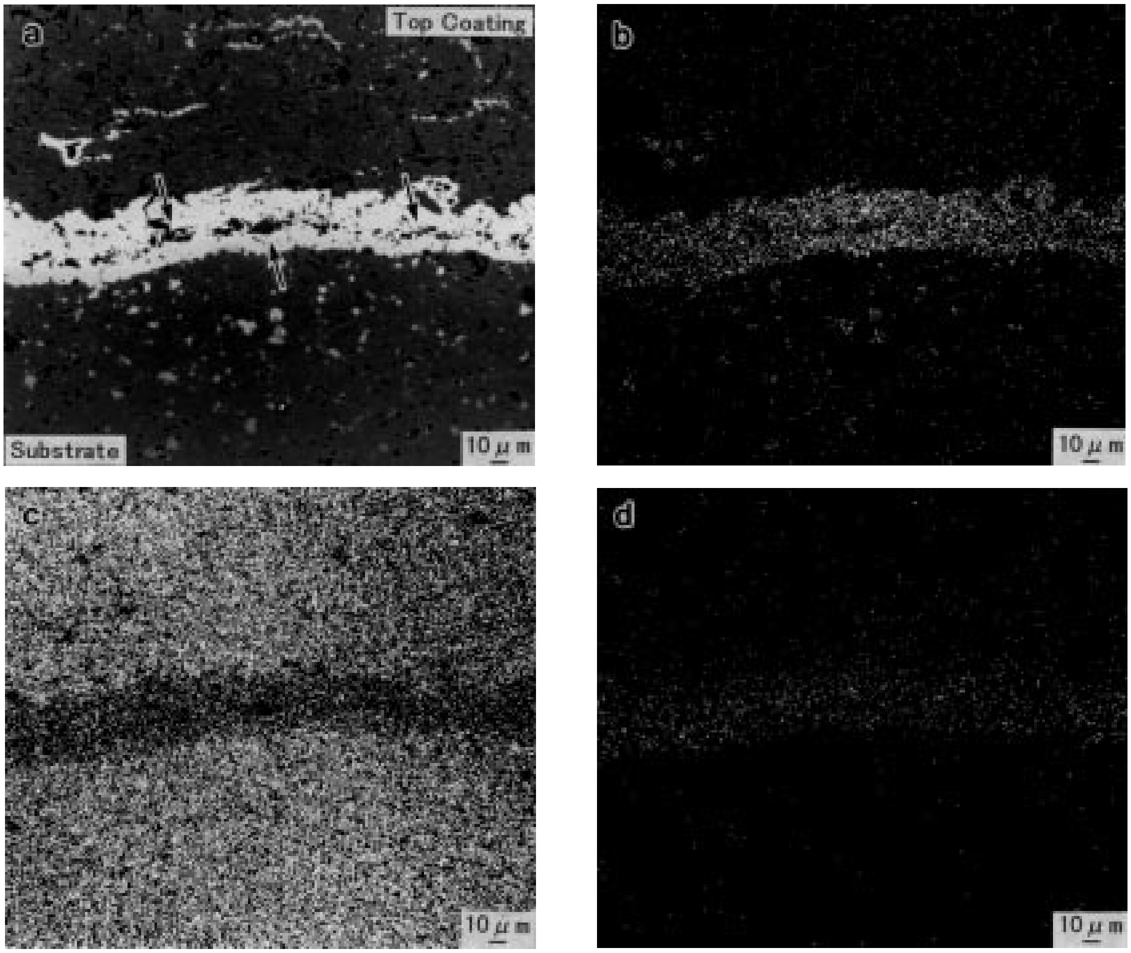

Fig. 8 EPMA images of 20 μm thick bond coating heat treated at 1673 K for 14.4 ks. (a) Back-scattered electron image. (b) Ni-Kα. (c) Al-Kα. (d) Cr-Kα

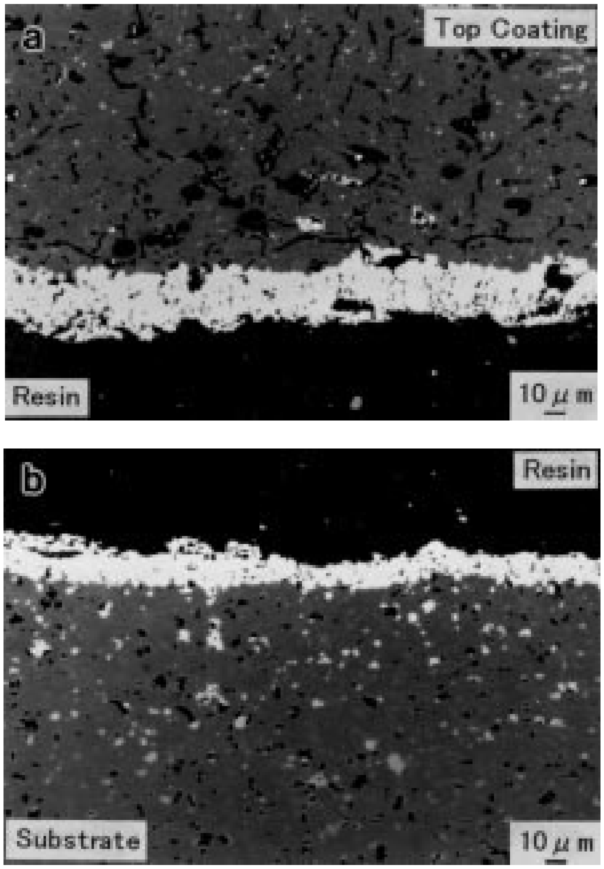

Fig. 9 EPMA images of 20 μm thick bond coating heat treated at 1673 K for 14.4 ks after tensile testing

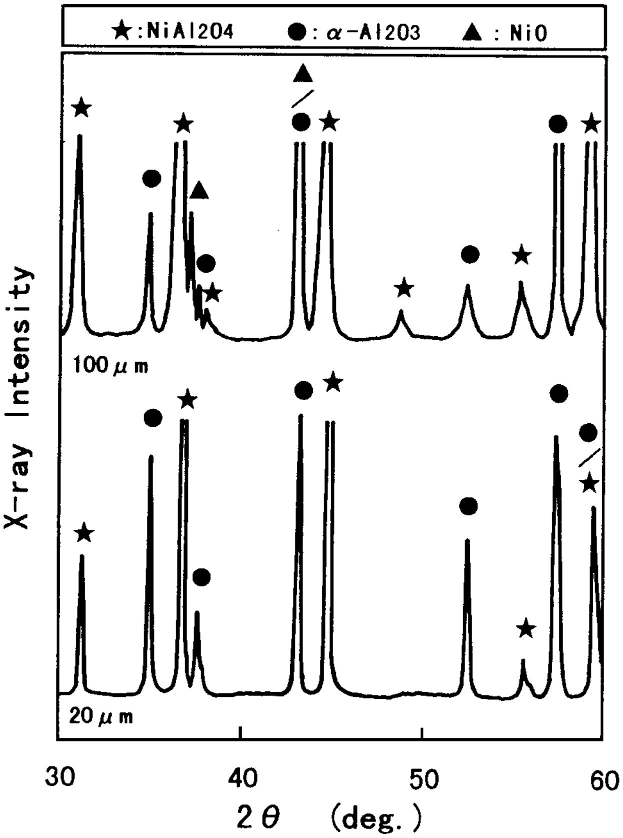

Fig. 10 XRD patterns on ruptured surface of 100 and 20 μm thick coatings heat treated at 1673 K 14.4 ks

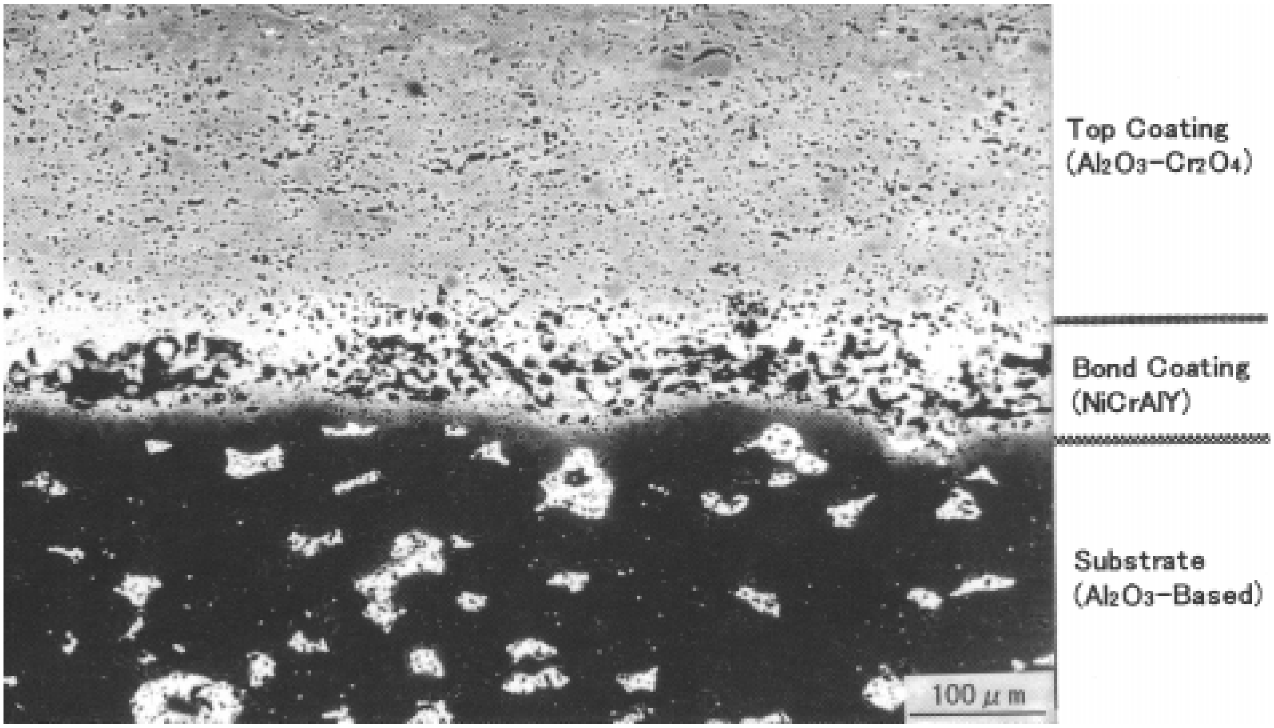

Fig. 11 Back-scattered electron image at interface between sprayed alumina-50% chromia and alumina-base substrate with NiCrAlY bond coating heat treated at 1673 K for 36 ks in air

Acknowledgments

The authors wish to acknowledge the Center for Instrumental Analysis, Kyushu Institute of Technology for EPMA measurements and x-ray analysis.

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