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Ceramic Coating on Ceramic with Metallic Bond Coating

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The change in structure and adhesion strength of the interface by heating in air has been investigated for a plasma-sprayed alumina coating on a ceramic substrate with a 50Ni-50Cr alloy bond coating. A veined structure composed of NiO, $NiCr_2O_4$, and $NiAl_2O_4$ oxides grew from the bond coating into cracks or pores in the top coating and the alumina substrate after heating at 1273 K for 20 h in air. The $NiAl_2O_4$ spinel may have formed by the oxidization of nickel, which subsequently reacted with the alumina coating or the substrate. The mechanism of the penetration of the spinel oxides into the cracks or pores is not clear. The adhesion strength of the coating is increased to about 15 MPa after heating at 1273 K for 20 h in air, compared to an as-sprayed coating strength of only 1.5 MPa.

Keywords adhesion strength, alumina coating, bond coating, plasma spraying, veined oxide

1. Introduction

Engineering ceramics are used for their heat and wear resistance. However, industry is demanding increasingly severe property requirements for ceramics. For instance, high-strength ceramics with corrosion resistance to ash is needed by the iron and steel industries. Joining of high-strength ceramics and corrosion-resistant ceramics by brazing is thus far the most effective means of satisfying this requirement (Ref 1-4).

Ceramic coating of ceramic substrates by thermal spraying is rarely applied since the resulting adhesion strength is very low. It has been reported (Ref 5) that the adhesion strength of Ni-Al composite powder coating on alumina ceramic increases when heat treated in air due to the formation of $NiAl_2O_4$ on the alumina substrate/coating interface. Accordingly, the adhesion strength of ceramic coatings on ceramics may be enhanced by using a metallic bond coating and heat treating the coatings in air.

This paper describes work to improve the adhesion strength of ceramic coatings on a ceramic substrate with a bond coating of nickel-base alloy by heating in air. In this study, the substrate and coating materials were alumina and gray alumina, respectively.

2. Experimental Procedure

Gray alumina powder (SHOWA DENKO SHOCOAT K-13 (Showa Denko, Minato Tokyo, Japan), +45-10 μm particle size range) was sprayed onto a sintered alumina substrate with a bond coating of 50Ni-50Cr (SHOWA DENKO SHOCOAT MA-71M; Showa Denko, Minato Tokyo, Japan, +45-10 μm particle size range) alloy using a 40 kW conventional plasma spray apparatus (Bay State PG 100) under the conditions shown in Table 1. The chemical composition of the gray alumina powder (in mass percent) is 2.28 TiO_2, 1.07 SiO_2, 0.03 Fe_2O_3, and the remainder Al_2O_3. Alumina disks measuring 25 mm in diameter and 5 mm thick were made of high-purity alumina by sintering. The sintered alumina substrate was blasted with 24-grit silicon carbide before spraying the bond coating. The top and bond coatings were about 300 and 100 μm thick, respectively. The sprayed coatings were heat treated at 1273 K for up to 40 h in air and in vacuum, followed by cooling at 5 K/min in the furnace. The top coating/bond coating/substrate interfaces were studied by means of electron microprobe analysis (EPMA) and transmission electron microscopy (TEM). The adhesion strength of the coatings was measured by tensile testing (JIS H8666).

3. Results and Discussion

3.1 *Structure of Coating and Interface*

Figure 1 shows a backscattered electron image of a cross section of the as-sprayed coating by EPMA. A number of microcracks are present in the surface of the alumina substrate, and the top coating contains many pores.

Figure 2 shows backscattered electron images of the cross section through the top coating/bond coating/substrate interfaces. Figure 2(a) shows the as-sprayed coating; Fig. 2(b) and (c) show the interfaces of the bond coating with the top coating and with the substrate, respectively, in the coating heat treated at 1273 K for 20 h. A veined structure formed through the cracks and the pores in the top coating (Fig. 2b). This structure also formed along the cracks of the alumina substrate (Fig. 2c). Figure 3 shows backscattered electron images of the veined structure at the interface with the top coating under high magnification. The veined structure grows through the pores from the bond coating (Fig. 3a). It is clear that only nickel and

Table 1 Plasma spraying conditions

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

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chromium exist in this structure, as shown in Fig. 3(b) to (d), and that it initiates from the bond coating and grows along the cracks (Fig. 4a). Figures 4(b) to (d) verify that mainly nickel and little chromium are contained in the structure. Accordingly, it is concluded that the veined structure is composed of oxides and grows from the bond coating through the cracks and pores in the top coating and the cracks in the substrate when heat treated at 1273 K in air for 20 h.

Observation by TEM was performed to investigate the veined structure in detail. Figure 5(a) shows a bright-field image of the alumina substrate heat treated at 1273 K for 40 h. The area indicated by arrows c to f is the veined structure. The diffraction patterns in Fig. 5(c) to (f) are taken from the locations of the corresponding arrows in Fig. 5(a). These diffraction patterns reveal that the veined structure is composed of NiO, $NiCr_2O_4$, and $NiAl_2O_4$ oxides. It is clear that spinel oxides, such as $NiCr_2O_4$ and $NiAl_2O_4$, are formed in the veined structure, as shown in Fig. 5(b).

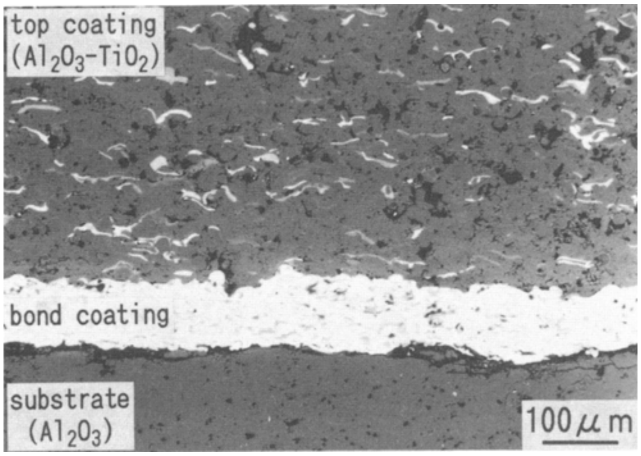

Fig. 1 Backscattered electron image of as-sprayed coating with metal bond coating

Based on the results obtained from EPMA and TEM, it is concluded that $NiAl_2O_4$ spinel is formed by the reaction of alumina and NiO formed by the oxidization of the bond coating. The veined structure was not found when the coating was heat treated at 1273 K in vacuum for 40 h. Thus, the veined oxide forms by oxidization of the metal in the bond coating. It is not clear how NiO penetrates into cracks or pores and forms the $NiAl_2O_4$ spinel.

3.2 *Adhesion Strength*

Figure 6 shows the change in the tensile adhesion strength of the coating as a function of holding time at 1273 K. The adhesion strength of the as-sprayed coating is low, 1.5 MPa. However, the adhesion strength of the coating after heat treating at 1273 K for 20 or 40 h is about 15 MPa. In the case of the heat treatment in vacuum, the top coating flaked because of the difference in the thermal expansion ratio between the top coating/bond coating/substrate. Therefore, the adhesion strength of the coating decreased compared to the as-sprayed coating.

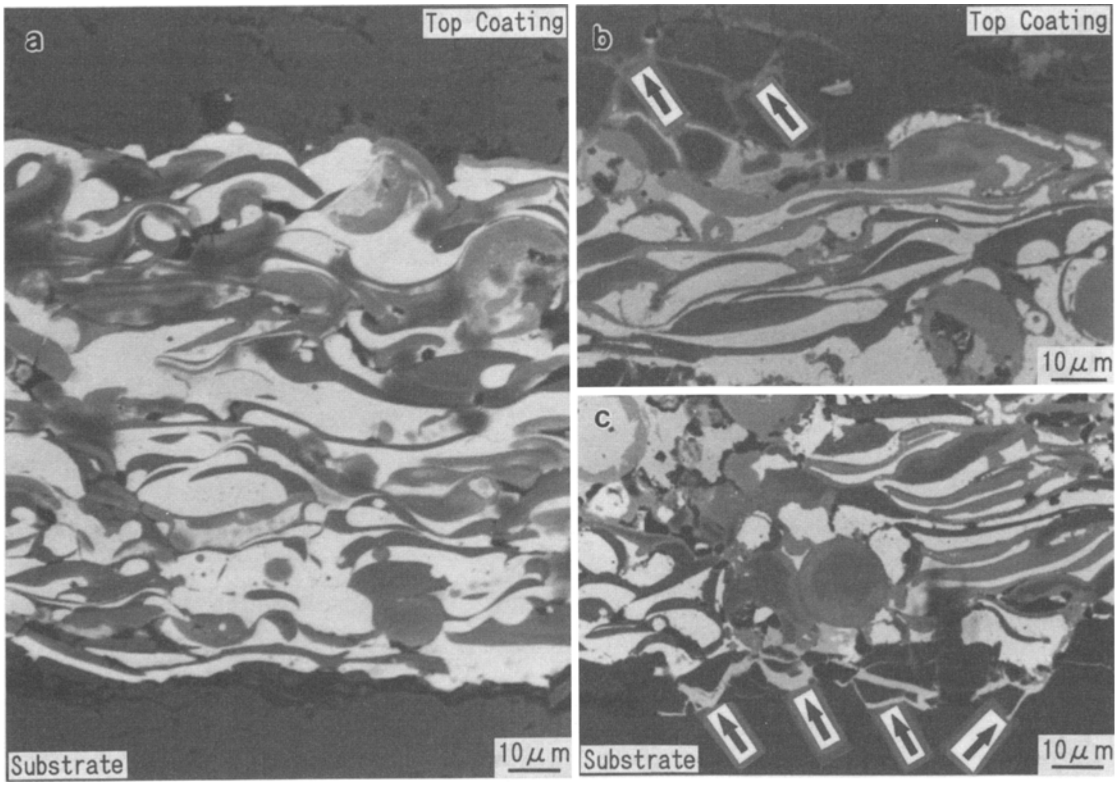

Fig. 2 Backscattered electron images of bond coating. (a) As-sprayed. (b) Bond coating/top coating interface, heated at 1273 K for 20 h. (c) Bond coating/substrate interface, heated at 1273 K for 20 h. Arrows in (b) and (c) show the veined structure.

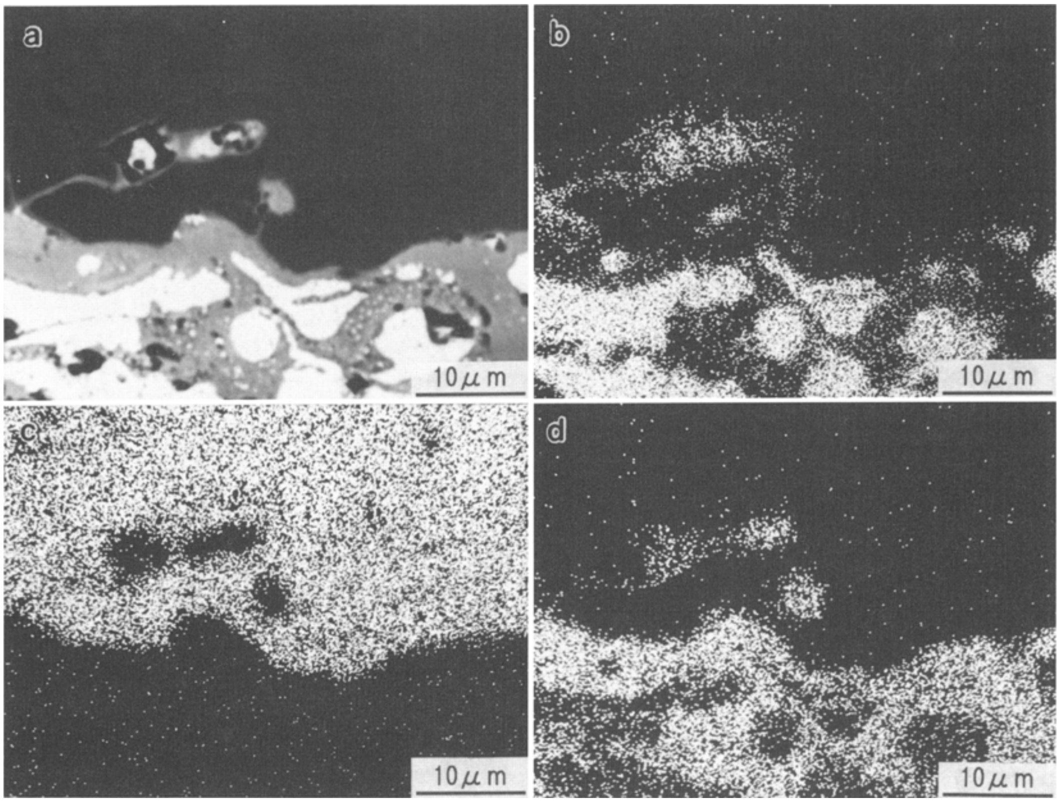

Fig. 3 EPMA images of top coating/bond coating interface, heat treated at 1273 K for 20 h. (a) Backscattered electron image. (b) Ni-Kα. (c) Al-Kα. (d) Cr-Kα

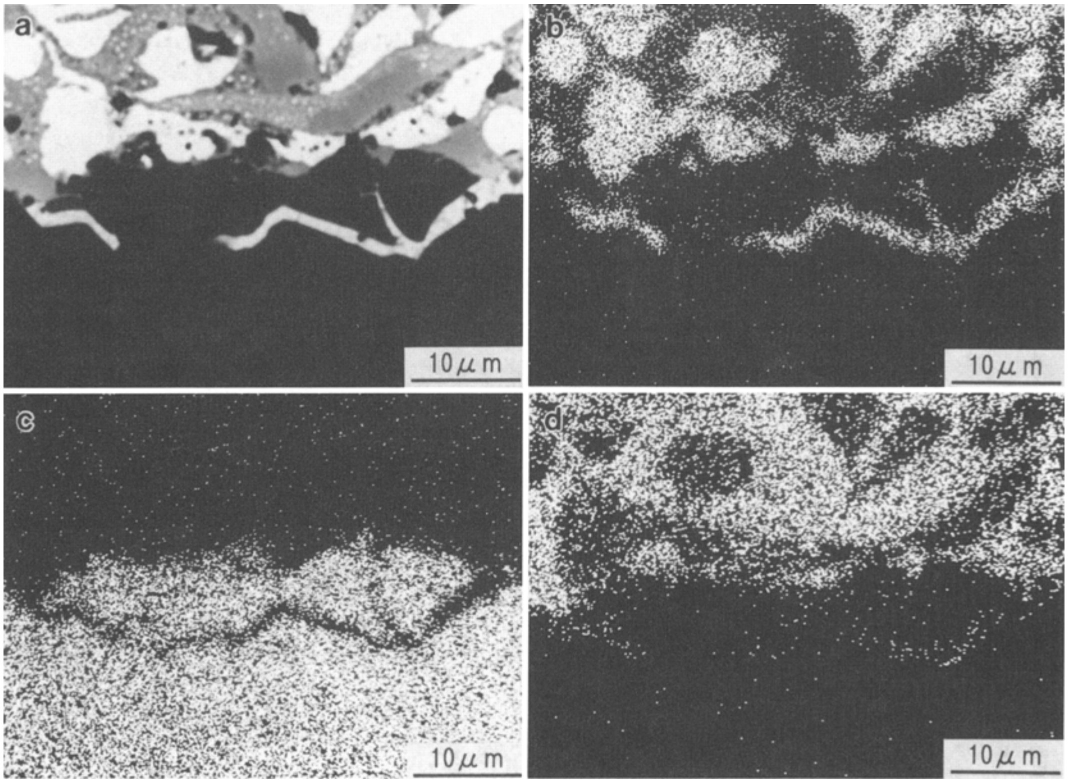

Fig. 4 EPMA images of bond coating/substrate interface, heated at 1273 K for 20 h. (a) Backscattered electron image. (b) Ni-Kα. (c) Al-Kα. (d) Cr-Kα

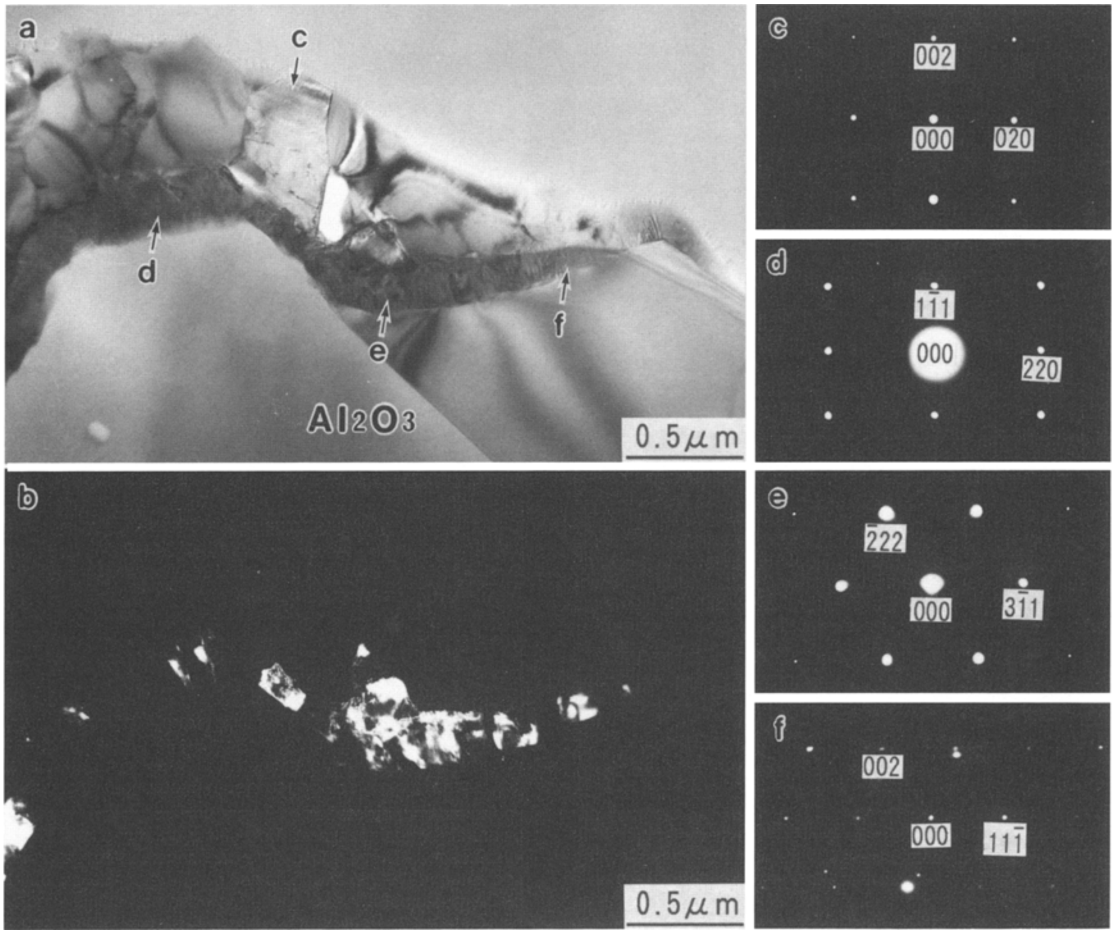

Fig. 5 TEM images of veined oxide formed from bond coating in substrate. (a) Bright-field image. (b) Dark-field image obtained by $[\bar{1}3\bar{3}]$ reflection of $NiCr_2O_4$ and/or $[\bar{4}\bar{4}0]NiAl_2O_4$. (c) to (f) Diffraction patterns obtained from regions indicated by arrows c to f, respectively, in (a). (c) $B \parallel [\bar{1}00]$NiO. (d) $B \parallel [\bar{1}12]NiCr_2O_4$. (e) $B \parallel [\bar{1}\bar{2}1]NiCr_2O_4$. (f) $B \parallel [1\bar{1}0]NiAl_2O_4$

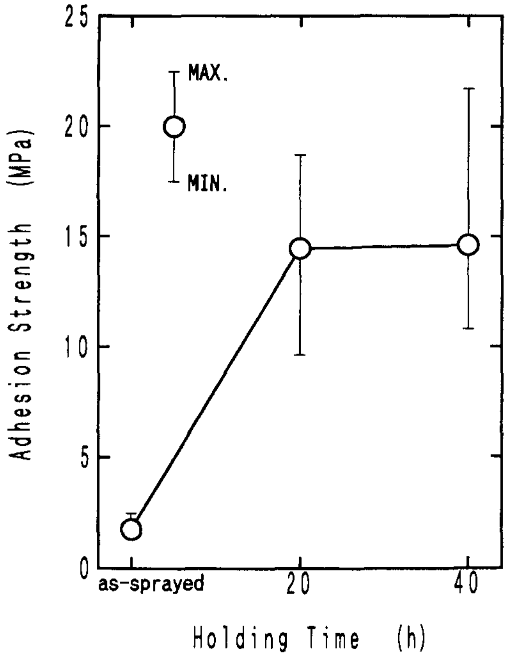

Fig. 6 Change in adhesion strength as a function of holding time at 1273 K in air

The increase in the adhesion strength of the coating heat treated in air is thought to be caused by the formation of veined oxides through cracks and pores in the top coating, bringing about densification of the top coating structure at the interface, and cracks in the substrate. Also, the enhanced interlamellar bonding strength and/or bonding strength between the substrate and the bond coating probably contributes to the increased adhesion strength of the top coating.

4. Conclusions

An investigation was conducted of the change in structure and adhesion strength of gray alumina coatings on high-purity alumina substrates with a 50Ni-50Cr alloy bond coating by heat treating at 1273 K up to 40 h in air. The results are summarized as follows:

- A veined structure formed in the substrate and the top coating from the bond coating after heat treating at 1273 K for 20 h in air.
- The veined structure consisted of NiO, $NiCr_2O_4$, and $NiAl_2O_4$ oxides.
- The as-sprayed coating exhibited a low adhesion strength of about 1.5 MPa. The adhesion strength of the coating in-

creased up to approximately 15 MPa when heat treated at 1273 K in air.

The enhanced adhesion strength of the top coating after heat treatment occurred due to the formation of the veined oxide in the alumina substrate and the top coating and the increased interlamellar bonding strength and/or bonding strength between the substrate and the bond coating. It is expected that ceramic/ceramic composites formed by thermal spray can be further developed from the results of this work.

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References

1. T. Iseki and M.G. Nicholas, The Elevated Temperature Strengths of Alumina-Aluminum and Magnesium-Aluminum Samples, *J. Mater. Sci.,* Vol 14, 1979, p 687-692
2. M. Naka, Y. Hirono, and I. Okamoto, Joining of Alumina/Alumina Using Al-Cu Filler Metal and Its Application to Joining of Alumina/Aluminum, *Trans. JWRI,* Vol 16 (No. 2), 1987, p 301-307
3. H. Okamura, M. Sakamoto, and T. Shida, Bonding of Silicon Carbide Ceramics by Using Active Brazing Metal, *Q. J. Jpn. Weld. Soc.,* Vol 8, 1990, p 272-279 (in Japanese)
4. A. Watanabe, H. Kato, and K. Yoshikawa, Properties of Alumina/Al/Alumina Joints Produced in Air Atmosphere, *Mater. Sci. Technol.,* Vol 9, 1993, p 155-160
5. N. Murakami, K. Kishitake, M. Hasebe, T. Kobayashi, and K. Murashige, Joining between Alumina and Metal by Use of Plasma Sprayed Ni-Al Coating on Alumina, *J. Jpn. Therm. Spray. Soc.,* Vol 30 (No. 2), 1993, p 11-17 (in Japanese)