JTTEE5 4:353-357

Tensile Strength of Plasma-Sprayed Alumina and/or Zirconia Coatings on Titanium

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The heat treatment effect on the characteristics and tensile strength of plasma-sprayed alumina, yttria-stabilized zirconia (YSZ), and mixtures of alumina and YSZ coatings on titanium was investigated. The as-sprayed structures of alumina and YSZ coatings consists of α and γ alumina phases, and cubic and tetragonal zirconia phases, respectively. The tensile strength of the coatings containing a large amount of YSZ is increased from 25 to 50 MPa by heat treatment at 800 °C. The 60%YSZ-Al_2O_3 coating showed the highest tensile strength. The tensile strength increase of the YSZ-containing coating by heat treatment is caused by formation of 10 to 100 nm wide microcracks. The interface adhesion strength between the heat-treated titanium substrate and the alumina-containing coating is increased by chemical reaction at the interface. Thus, a heat-treated alumina and zirconia mixture coating may be favorable in obtaining high tensile strength due to microcrack formation in the coating and the chemical reaction at the interface.

1. Introduction

TITANIUM and its alloys possess characteristics, such as relatively low specific gravity, good corrosion resistance, and high strength, so the alloys are often used in aircraft and chemical industries. Although titanium alloys have excellent properties, they are inferior to wear resistance and high-temperature oxidation (Ref 1, 2). Alumina and zirconia ceramic coatings are widely used to improve wear resistance and heat insulation of steel and other metals, respectively. Reports of ceramic coatings on titanium, however, are few (Ref 3, 4).

The zirconia thermal expansion coefficient is very close to that of titanium in a wide temperature range. Therefore, the zirconia adhesion on titanium should be very good, and the thermal shock resistance should be excellent. This characteristic is favorable to the heat treatment of a zirconia coating on titanium.

In the present work, the ceramic coating was applied to titanium by plasma spraying, and the coating strength and structure were investigated with respect to the heat treatment.

2. Experimental Procedure

Plasma spraying was carried out using powders of white alumina, 8 wt% yttria-stabilized zirconia (YSZ), and mixtures of alumina and YSZ. The YSZ weight fraction in the mixtures was 0.2, 0.4, 0.6, and 0.8. The mixtures were obtained after being mixed in a ball mill for 2 h. Titanium substrates of 6 mm thickness were treated by blasting with alumina grit before spraying. Coatings of 0.2 mm thickness were obtained by use of plasma spray equipment (AVCO, H-1003) under operating parameters of 22.4 kW power, 50 mm spraying distance, and argon carrier gas. Coated samples were heat treated at 600, 800, and 1000 °C for 1 h in a vacuum, followed by air cooling.

Keywords ceramic coatings, interface reaction, microcrack, tensile strength, titanium substrate

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Phase composition of the as-sprayed and heat-treated coatings was investigated by x-ray diffraction (XRD) analysis using Cu-K_α radiation. Structure of the coatings was observed by transmission electron microscopy (TEM) at an acceleration voltage of 300 kV. Distribution of chemical elements was evaluated by an electron probe microanalysis (EPMA). Tensile tests were carried out following the Japanese standard (JIS-H8664) by use of a 30 mm diam specimen. Results of tensile tests were obtained as the average of three specimens.

3. Results and Discussion

3.1 *Tensile Strength*

Figure 1 shows the relationship between the tensile strength and the YSZ content in the as-sprayed condition. Tensile strength increases linearly with an increase in YSZ content from 7 MPa for a pure Al_2O_3 coating to 25 MPa for the coating containing 60% YSZ or more.

Figure 2 shows the effect of heat treatment on the tensile strength of the specimens. Tensile strength of all the specimens increases slightly after heat treatment at 600 °C and largely after heat treatment at 800 °C. Note that the coatings containing 60% or more YSZ exhibit a maximum value of 45 MPa or more after

Table 1 Location of fracture in tensile test

		Heat treatment temperature, °C		
Coating	**As-sprayed**	**600**	**800**	**1000**
Al_2O_3	*I*	*I*(*C*)	*C*	*C*
20 wt% ZrO_2-40 wt% Al_2O_3	*I*	*I*(*C*)	*C*	*C*
40 wt% ZrO_2-60 wt% Al_2O_3	*C*	*C*	*C*	*C*
60 wt% ZrO_2-80 wt% Al_2O_3	*C*	*C*	*C*	*C*
80 wt% ZrO_2-20 wt% Al_2O_3	*C*	*C*(*I*)	*C*(*I*)	*C*
ZrO_2	*C*	*C*(*I*)	*C*	*C*

C is fractured in coating (cohesive mode) *I* is fractured at interface (adhesive mode). Parentheses indicate the minor component of the fracture mode.

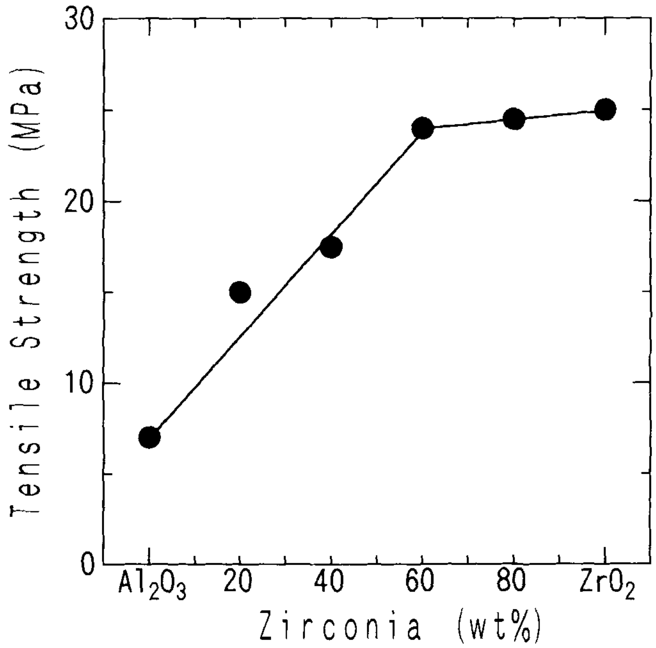


Fig. 1 Coating tensile strength in the as-received condition as a function of YSZ content

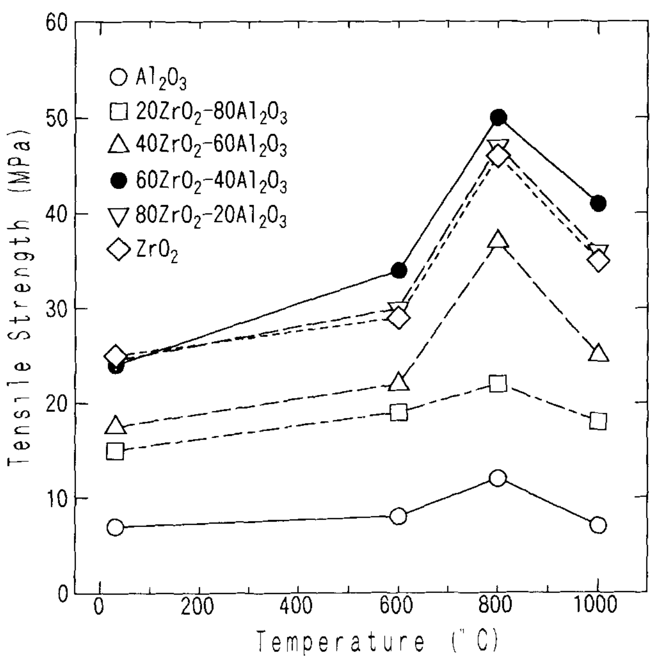


Fig. 2 Tensile strength change as a function of heat-treatment temperature. Material compositions are in wt%.

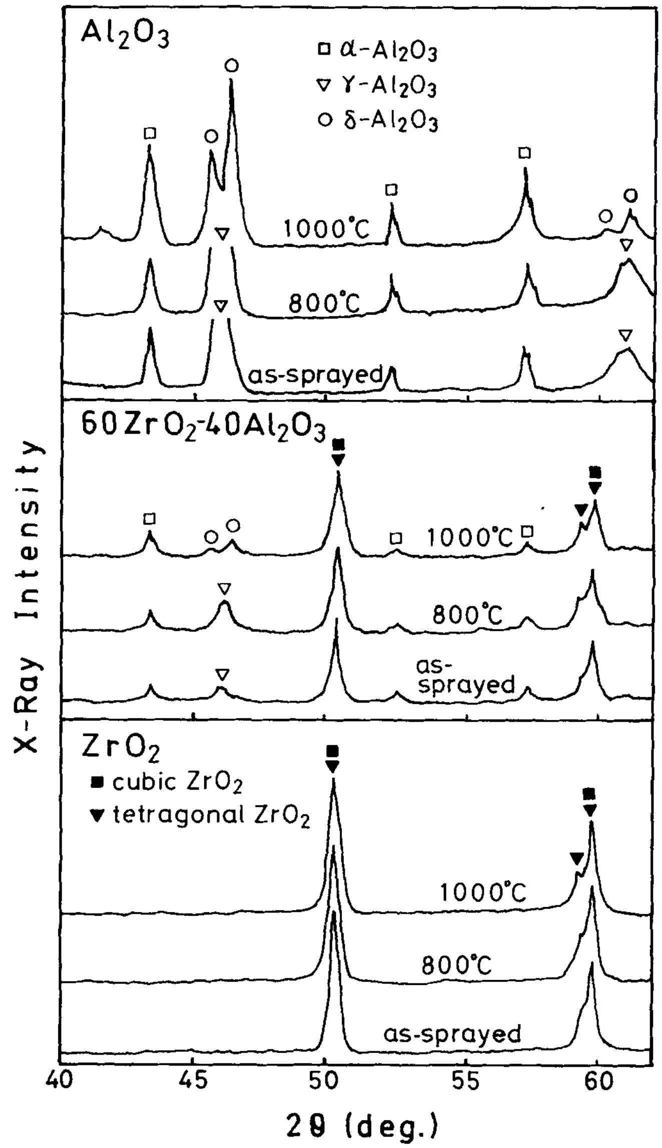


Fig. 3 XRD profiles of the different as-sprayed and heat-treated coatings

heat treatment at 800 °C. Tensile strength is decreased on the 1000 °C heat treatment.

The location of fracture in each specimen after the tensile test is summarized in Table 1, where *I* and *C* mean that the location of fracture is at the interface or in the coating, respectively. In the as-sprayed specimens containing 20% or less YSZ, debonding occurs at the interface of the coating and the substrate (i.e., the adhesive failure) whereas in the specimens containing 40% or more YSZ, fracture takes place in the coatings (i.e., cohesive failure). Adhesion strength is higher than cohesion strength in the specimens containing 40% or more YSZ.

In the alumina coatings containing 20% or less YSZ, the location of fracture mode changes from adhesive to cohesive as the heat-treatment temperature elevates and the tensile strength increases slightly up to 800 °C. This indicates that the alumina-rich coating adhesion strength is increased by heat treatment. On the other hand, the location of fracture in the YSZ-rich coatings (80%YSZ-Al_2O_3 and YSZ coatings) changes from cohesive to adhesive by heat treatment up to 800 °C. Furthermore, tensile strength of all specimens shows markedly high values at 800 °C. When heat treated at 1000 °C, cohesive fracture occurs in all specimens, and tensile strength decreases. This may be caused by the thermal expansion difference through the transformation of the titanium substrate from α (hcp) phase to β (bcc) phase.

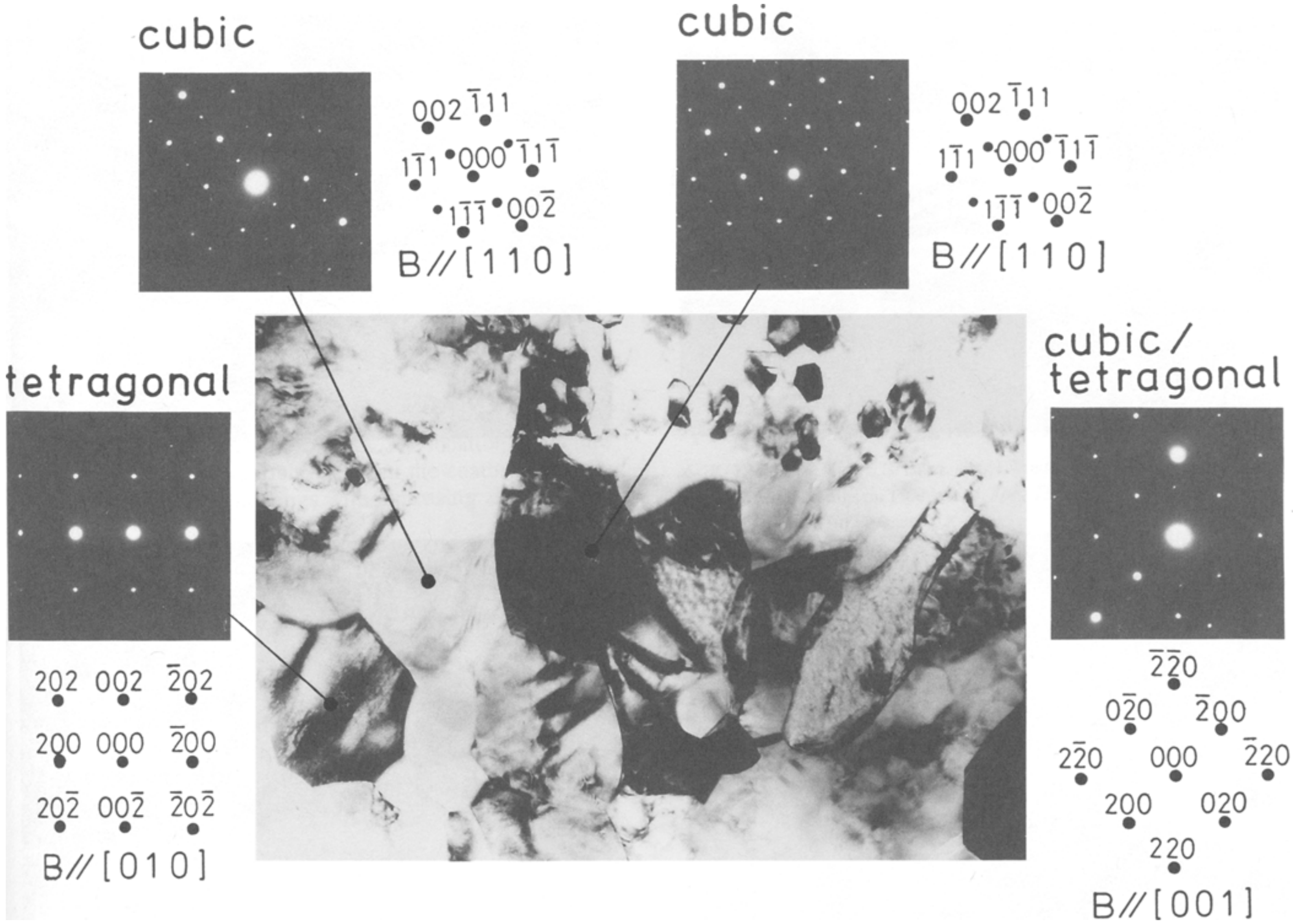


Fig. 4 TEM micrographs of the as-sprayed YSZ coating

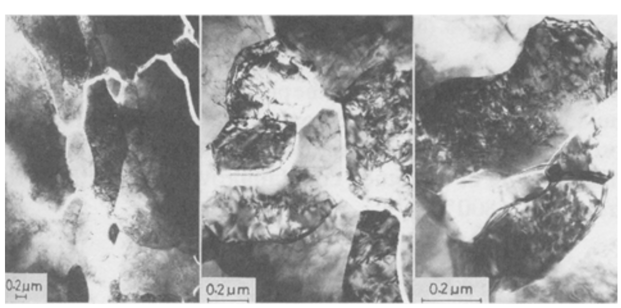


Fig. 5 TEM micrographs of the YSZ coating heat treated at 800 °C

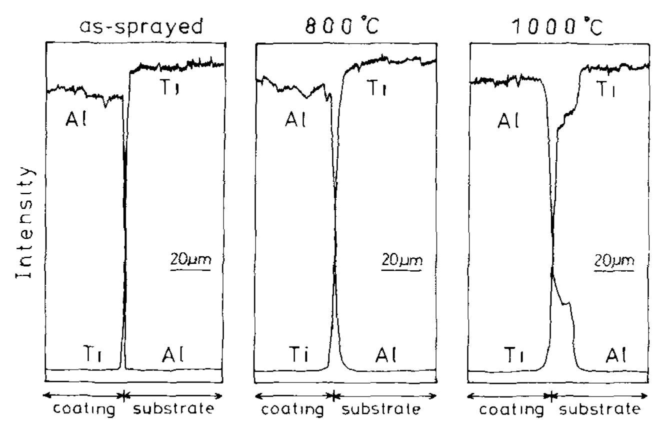
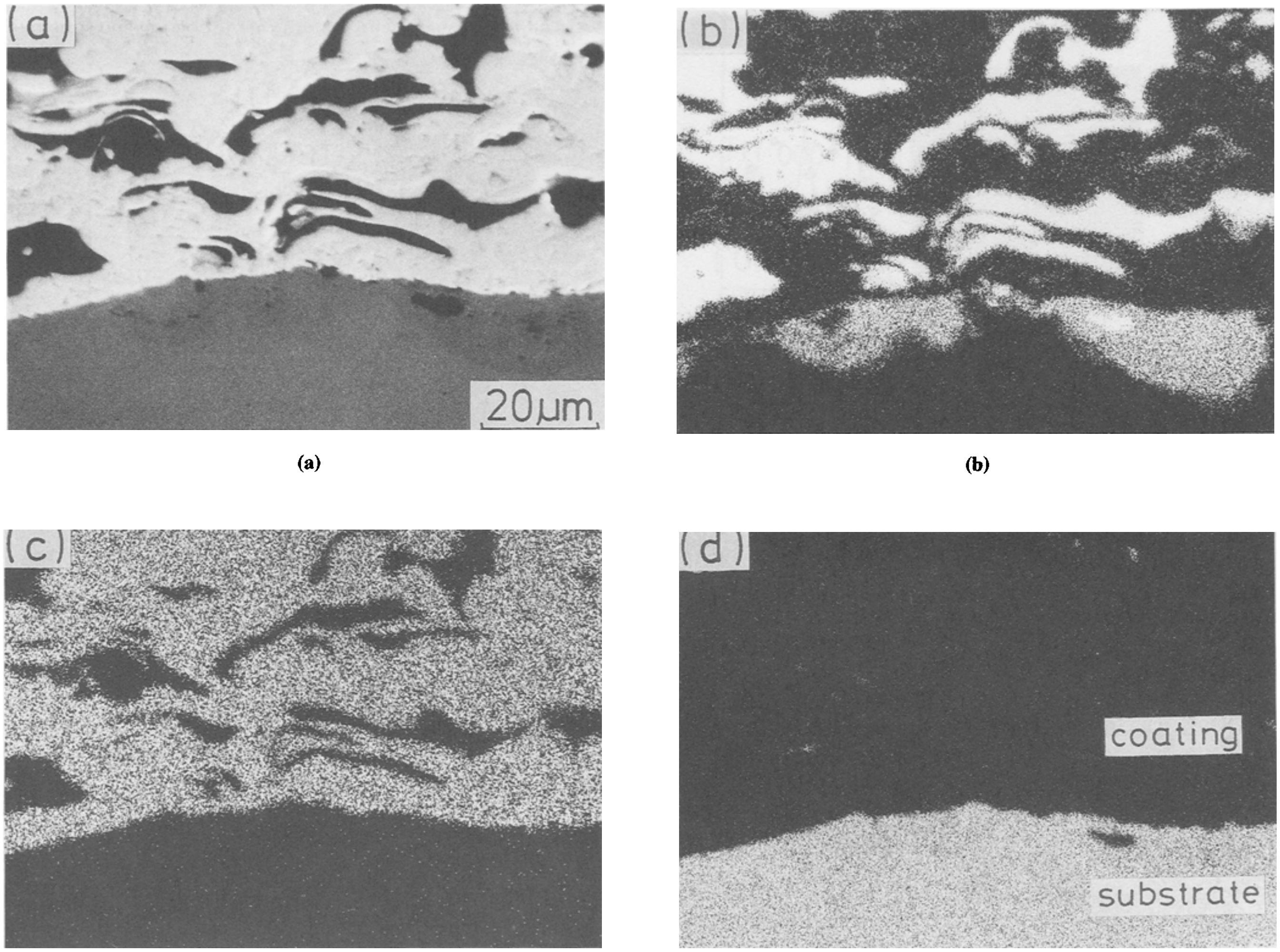


Fig. 6 Line analyses of Al-K_α and Ti-K_α of the as-sprayed and heat-treated alumina coating

3.2 *Structure of Coating*

Plasma-sprayed coatings consist of rapidly solidified nonequilibrium phases. Figure 3 shows XRD patterns of alumina, 60%YSZ-40%Al_2O_3, and YSZ coatings heat treated at 800 and 1000 °C. The as-sprayed alumina coating consists of α and γ alumina phases. The nonequilibrium γ phase shows little change during heat treatment up to 800 °C and transforms to δ phase at 1000 °C, leaving the α phase unchanged. A volume expansion due to the transformation of γ phase to δ phase may bring about the cohesive failure mode (Table 1) and, as a result, the low tensile strength (Fig. 2) after heat treatment at 1000 °C.

The 60%YSZ-40%Al_2O_3 coating consists of cubic and tetragonal zirconia phases in addition to α and γ alumina phases in the as-sprayed condition. Diffraction peaks of the zirconia



(a) (b) (c) (d)

Fig. 7 EPMA images of the 60%YSZ-40%Al_2O_3 coating heat treated at 1000 °C. (a) Composition. (b) Al-K_α. (c) Zr-K_α. (d) Ti-K_α images

phases are changed insignificantly by heat treatment up to 1000 °C. Decomposition behavior of the alumina phases is similar to that of the alumina coating. Accordingly, the 60%YSZ-40%Al_2O_3 coating may be deteriorated by the transformation of γ alumina to δ alumina.

For the YSZ coating, diffraction peaks of cubic and tetragonal zirconia phases are observed in the as-sprayed condition. Little change in the diffraction peaks is observed by heat treatment. Note, however, that peak separation of the cubic and tetragonal phases becomes clear and the broadening of the peaks decreases as the heat-treatment temperature elevates. A microstructural change probably occurs through heat treatment.

Figure 4 shows transmission electron micrographs of the as-sprayed YSZ coating. Small grains, less than 1.5 μm, are observed. The selected area diffraction patterns show that the grains are of cubic and tetragonal zirconia phases. Notice that no microcracks exist in the grains and/or at the grain boundaries. Microcracks of 10 to 100 nm in width, however, are observed along grain boundaries when heat treated at 800 °C, as shown in Fig. 5. The microcracks may be caused by a partial transformation of tetragonal to cubic phase and thermal expansion differences between the phases (Ref 5). Microcracks in bulk, partially stabilized zirconia are known to inhibit crack propagation to improve fracture toughness (Ref 6). Thus, the YSZ coating of this study could improve in strength by heat treatment at 800 °C.

3.3 *Interface Reaction*

The strength of the interface of the alumina-rich coatings was improved by heat treatment. EPMA was carried out, focusing on the interface of the alumina coating and titanium substrate. Figure 6 shows EPMA line profiles of aluminum and titanium. The profiles of both elements in the as-sprayed condition exhibit steep responses at the interface while the profiles at the interface become sluggish by heat treatment at 800 and 1000 °C. This suggests that aluminum atoms diffused into the titanium substrate. Figure 7 shows the specific x-ray images of 60%YSZ-40% Al_2O_3 coating; the diffusion of aluminum was also found in the specimen (Fig. 7b) whereas diffusion of zirconium and titanium was difficult to detect (Fig. 7c and d). These analyses indicate that alumina is chemically reduced by titanium, and as a result, aluminum atoms diffuse into the titanium substrate under heat treatment. Oxygen may also diffuse into the titanium substrate (Ref 3). Thus, a chemical reaction occurs at the interface in the alumina-rich coatings, and the interface strength increases due to such heat treatment.

4. Conclusions

The tensile strength and the structure of plasma-sprayed ceramic coatings of alumina, YSZ, and these mixtures, when sprayed on to titanium, were investigated. The results are:

- The tensile strength in the as-sprayed condition increases with the increase of zirconia content to 60% and reaches 25 MPa for the zirconia-rich coatings. The location of fracture changes from the interface between the coating and substrate to within the coatings with increasing zirconia content.
- The tensile strength of the zirconia-rich coatings increases from 25 to 45 MPa or above by heat treatment at 800 °C.
- Microcracks are observed in the zirconia phase after heat treatment at 800 °C. This may cause the increase of the coating strength with a high zirconia content.
- Aluminum reacts with titanium at the coating and substrate interface at high temperatures. This may increase the interface adhesion strength.

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