



Title	Electric Field Assisted Treatment of Various Plasma Sprayed ZrO <sub>2</sub> Coatings(Physics, Process, Instruments & Measurements)
Author(s)	Ohmori, Akira; Aoki, Katsuyuki; Sano, Saburo et al.
Citation	Transactions of JWRI. 1991, 20(2), p. 181-188
Version Type	VoR
URL	<a href="https://doi.org/10.18910/6899">https://doi.org/10.18910/6899</a>
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# Electric Field Assisted Treatment of Various Plasma Sprayed $\text{ZrO}_2$ Coatings

Akira OHMORI\*, Katsuyuki AOKI\*, Saburo SANO\*, Yoshiaki ARATA\*\*, Katsunori INOUE\* and Nobuya IWAMOTO\*

## Abstract

*A systematic experimental investigation was carried out to clarify the phenomena which occur during the electric field assisted treatment of various  $\text{ZrO}_2$  coatings sprayed on copper or SS41 steel substrates; and the possibility of improving the adhesive strength between substrate and coating by the electric field assisted treatment was examined. It was found that the occurrence of a Zr-Cu-O layer was clearly recognized at the interface between the ceramic coating and the copper substrate, which was arranged as the cathode in the experiment. But the formation of Zr-Cu-O layer was greatly depended on the kinds of  $\text{ZrO}_2$  coatings. It was revealed that the adhesive strength of a coating can be raised by the electric field assisted treatment to over a three times of that as for a sprayed  $\text{ZrO}_2$  (8wt%  $\text{Y}_2\text{O}_3$ ) coating. The electric field assisted treatment was also applied to  $\text{ZrO}_2$  (8wt%  $\text{Y}_2\text{O}_3$ ) sprayed onto mild steel but no improvement in adhesive strength resulted. However, when the coated steel was heated in air to form an Fe oxide at the coating/substrate interface, the adhesive strength was nearly doubled by a subsequent electric field treatment.*

**KEY WORDS :** (Electric Field Assisted Treatment) ( $\text{ZrO}_2$  Coating) (Cu Substrate) (SS41 Steel Substrate) (Plasma Spraying) (Adhesive Strength)

## 1. INTRODUCTION

Plasma sprayed ceramic coatings have been widely applied in many industrial fields because of an excellent wear and erosion resistance, heat resistance, and corrosion resistance which ceramics possess themselves. The  $\text{ZrO}_2$  coatings are well known as thermal barrier coatings.<sup>1-2)</sup> However, the adhesive strength of ceramics coatings to the substrate is one of the most important properties and can sometimes limit their application. In the coating substrate system, the mechanisms which contribute to adhesive strength are mechanical interlocking, adhesion and absorption, chemical reaction, diffusion, electrostatic force, epitaxy etc. at the interface between coating and substrate.<sup>3-4)</sup> In the case of ceramic coatings, less effective wetting of the substrate by the ceramics results in a smaller area of real contact,<sup>5)</sup> so that the adhesive strength might largely depend on mechanical interlocking. Diffusion, which would greatly improve the adhesive strength, cannot usually be recognized. To improve the adhesive strength of ceramic coatings, a bond coating of metals is commonly applied. However, in order to make greater use of ceramic coatings, it is necessary to develop more effective post-treatment methods.

In the case of bonding between metals and solid electrolyte ceramics such as glasses<sup>6)</sup>, beta-alumina<sup>7)</sup> and

$\text{ZrO}_2$ <sup>8)</sup>, the mobile ions in these materials are utilized to form a strong bond because diffusion occurs at the interface between the metal and ceramics with the assistance of an electric field. It was thought that this phenomenon could also be applied to improve the adhesive strength of  $\text{ZrO}_2$  ceramic coatings.

## 2. MATERIALS AND EXPERIMENTAL PROCEDURES

### 2.1 Materials

The substrates were an industrial-grade pure copper bar or a SS41 mild steel bar, each with a diameter of 10mm, cut into 12mm lengths. The surface to be sprayed was polished with # 600 emery paper, then grit-blasted prior to spraying.

Commercially available three kinds of  $\text{ZrO}_2$  containing 24wt% MgO (shoden NWDT), 8wt%  $\text{Y}_2\text{O}_3$  (shoden K-30) and 25wt%  $\text{CeO}_2$ -3wt%  $\text{Y}_2\text{O}_3$  (METCO, 205NS) as a stabilizer were used as the spraying powders as shown in **Table 1**. Electrodes for the electric field treatment were of industrial-grade pure copper plate and SUS304 steel plate, both 15 mm  $\times$  25 mm  $\times$  2 mm. Plasma spraying was carried out in the air and the three kinds of  $\text{ZrO}_2$  coatings with a thickness of 150-200  $\mu\text{m}$  was produced by employing the spraying conditions shown in **Table 2**.

† Received on Nov. 12, 1991

\* Associate Professor

\*\* Graduate Student

\*\*\* Emeritus Professor

\*\*\*\* Professor

Transactions of JWRI is published by Welding Research Institute, Osaka University, Ibaraki, Osaka 567, Japan

## 2.2 Method of electric field assisted treatment (FAT)

Figure 1 shows a schematic diagram of the FAT equipment. For FAT, a copper plate placed on the  $ZrO_2$  sprayed coating was used as an electrode, on top of which SUS 304 steel plate was fixed. On the copper or SS41 steel side of the substrate, a SUS 304 steel plate was fixed for use as the other electrode. In order to prevent

**Table 1** Chemical compositions of  $ZrO_2$  powders used for spraying

No.	Chemical compositions (wt%)			
	MgO	CeO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>
1	24	—	—	76
2	—	—	8	92
3	—	25	3	72

**Table 2** Plasma spraying conditions

Plasma gas (Ar)	$4.2 \times 10^4$ kg/m <sup>2</sup>
Auxiliary gas (He)	$4.2 \times 10^4$ kg/m <sup>2</sup>
Powder carrier gas (Ar)	$5.6 \times 10^4$ kg/m <sup>2</sup>
Hopper setting	$0.05s^{-1}$
Spraying current	800 A
Spraying voltage	35 V
Spraying distance	100 mm
Cooling air pressure	$2.0 \times 10^4$ kg/m <sup>2</sup>

oxidation of the test piece, the FAT was done in a vacuum of  $1.33 \times 10^{-3}$  Pa. DC constant-voltage and constant-current power was used as the power source for FAT, which was done after reaching the required temperature, the holding time being varied under a constant current. The FAT treatment conditions used in this study are shown in Table 3.

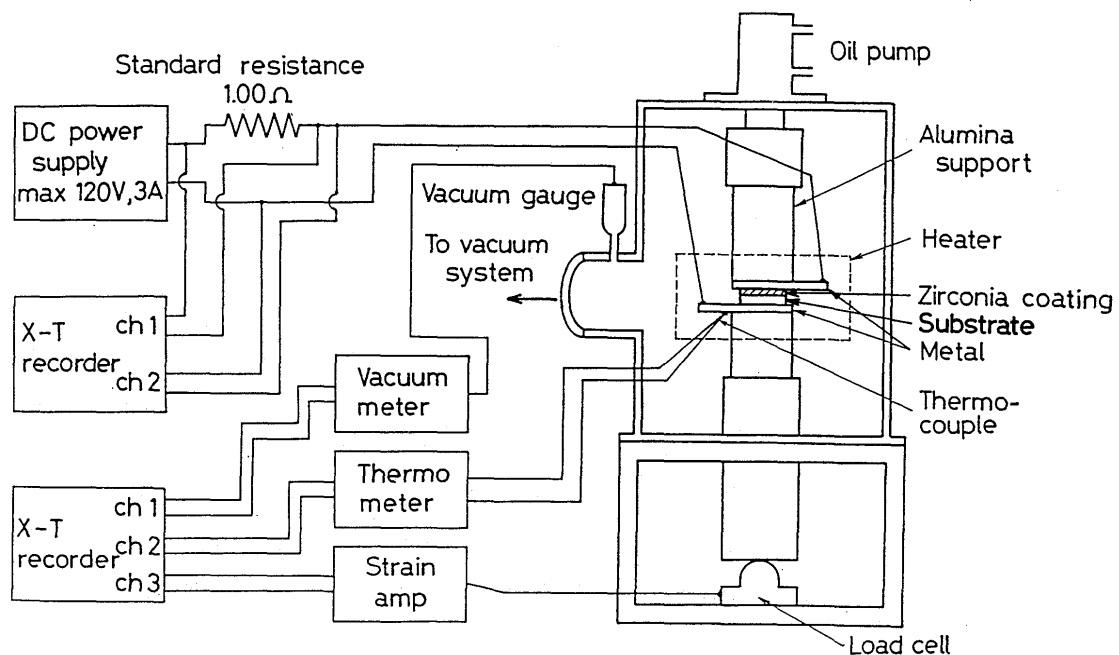
## 2.3 Method of analysis of interface between substrate and $ZrO_2$ coating

Cross section of sprayed test pieces and heat-treated test pieces were examined with an optical microscope and a scanning electron microscope (SEM), and changes in elemental composition of the interface between substrate metal and sprayed coating were studied by means of Energy Dispersive X-ray analyzer (EDX) (20kV-100 A). For the measurement of adhesive strength between substrate metal and sprayed coating, an Instron-type tensile tester was used; the tensile test was repeated three times at a cross-head speed of 1mm per 60 s, and the mean value was taken as the adhesive strength. In Fig. 2, the schematic diagram of tensile test specimens is shown.

## 3. RESULTS AND DISCUSSION

### 3.1 $ZrO_2$ coatings sprayed on Cu substrate

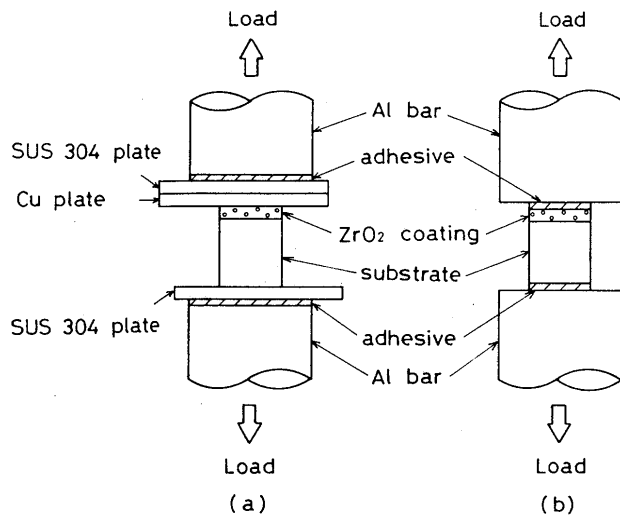
FAT was carried out under the conditions shown in Table 2. Holding time was 1.2ks was and current was 1000mA. Figure 3 shows examples of voltage and current change in time during FAT for  $ZrO_2$  coatings on Cu



**Fig. 1** Schematic diagram of apparatus for electric field assisted treatment (FAT)

**Table 3** Electric field assisted treatment conditions

Temperature	773K - 1073K
Time	60-12.6×10 <sup>3</sup> s
Pressure	9.3×10 <sup>-4</sup> kg/m <sup>2</sup>
Voltage	10V
Current	0-2000mA
atmosphere	1.33 ×10 <sup>-3</sup> Pa

**Fig. 2** Schematic diagram of tensile test specimens  
a) After FAT  
b) As-coated or after heat-treatment

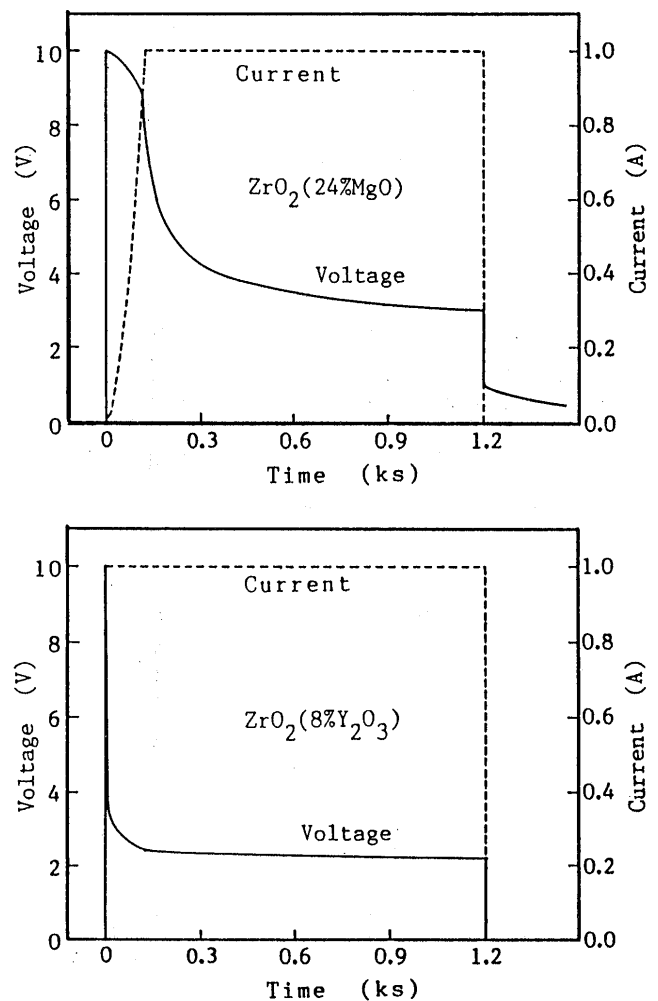
substrate at 1073 K.

**Figure 4** shows some examples of the results of optical microscope observation, SEM observation and line analysis by means of EDX for ZrO<sub>2</sub> (24 wt% MgO) (a), ZrO<sub>2</sub> (25wt% CeO<sub>2</sub>-3wt% Y<sub>2</sub>O<sub>3</sub>) (b) and ZrO<sub>2</sub> (8wt% Y<sub>2</sub>O<sub>3</sub>) (c) coatings sprayed on Cu substrate before and after FAT. New phases, which were not seen in the as-coated examples, formed at both interfaces on the cathode and anode sides; as a result of line analysis by EDX, formation of the diffusion zone of Cu and Zr was observed continuously over a wide range on the cathodic interface for ZrO<sub>2</sub> (8wt% Y<sub>2</sub>O<sub>3</sub>).

However, for both ZrO<sub>2</sub> (24wt% MgO) and ZrO<sub>2</sub> (25wt% CeO<sub>2</sub>-3wt% Y<sub>2</sub>O<sub>3</sub>), the diffusion zone of Cu and Zr was formed discontinuously at the cathodic interface.

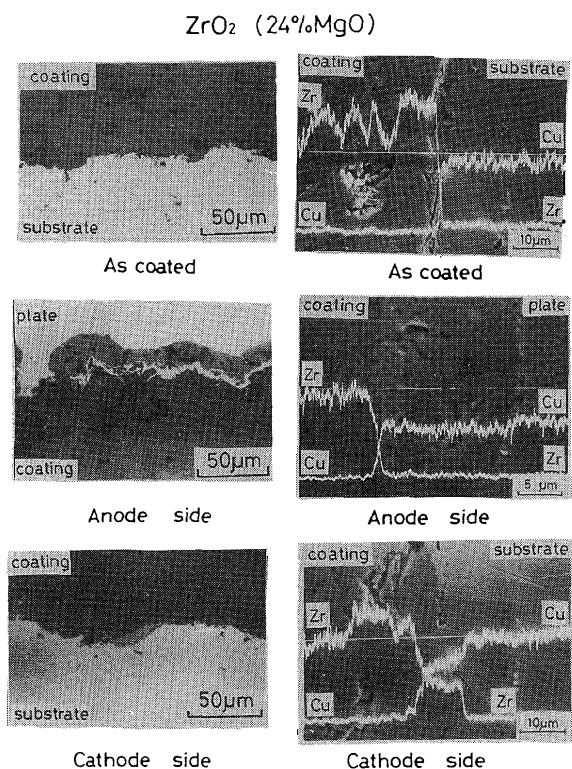
The phase formed at the anodic interface, through analysis by X-ray diffraction, was recognized to be Cu oxide, mainly comprising Cu<sub>2</sub>O. **Figure 5** is a schematic drawing of the change at the interface of both anode and cathode sides following FAT for the ZrO<sub>2</sub> coatings sprayed on Cu substrate.

In Fig. 4, a metallic band is seen on the anodic interface of ZrO<sub>2</sub> sprayed coatings and Cu<sub>2</sub>O has also

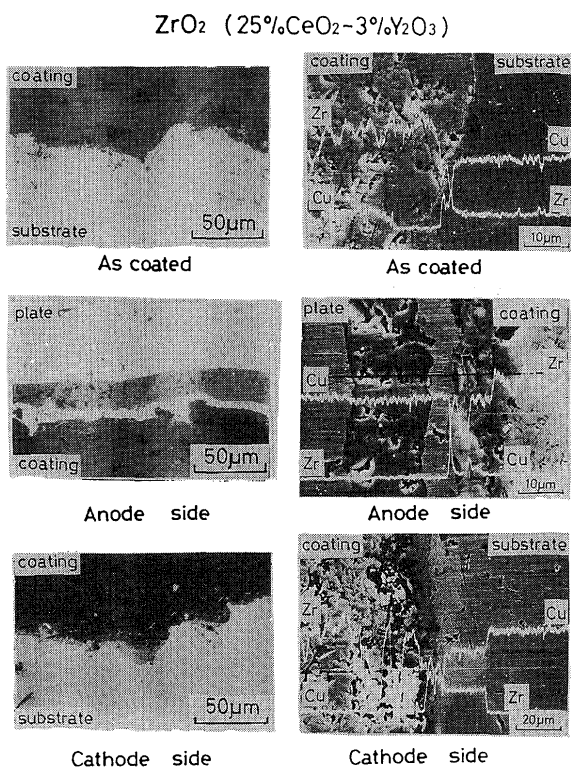
**Fig. 3** Examples of voltage and current change in time during FAT for ZrO<sub>2</sub> coatings on Cu substrate at 1073 K

formed. The metal is Cu caused by the chemical reduction of Cu<sub>2</sub>O at 1073 K when the FAT voltage was switched off. In order to confirm this phenomenon, the application of voltage was continued during cooling after FAT. **Figure 6** (a) is an optical micrograph of the anodic interface for ZrO<sub>2</sub> (8 wt% Y<sub>2</sub>O<sub>3</sub>) coating, Fig. 6 (b) shows the results when the voltage was off during the cooling stage. From Fig 6 (a), when the voltage was on during cooling, the formation of reduced metallic Cu was not seen at the anodic interface, but Cu<sub>2</sub>O had formed intermittently. It is believed that this resulted from a patchy contact between the copper electrode plate and the rough ZrO<sub>2</sub> surface which gave rise to current flow solely between the partial contact surfaces where Cu<sub>2</sub>O was subsequently formed.

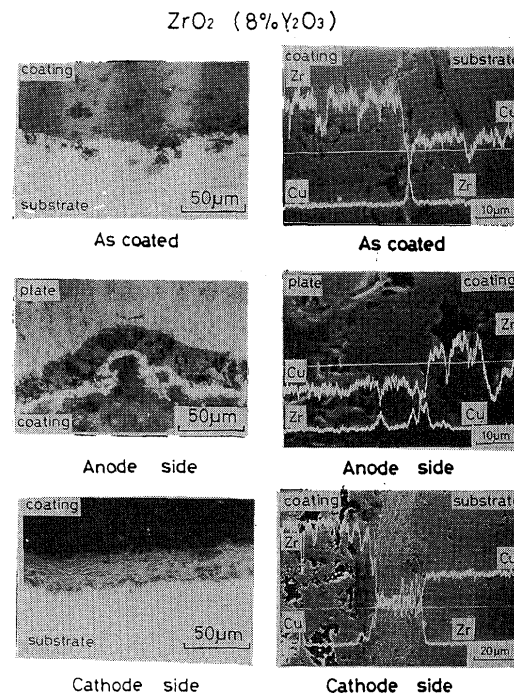
On the other hand, the continuous layer of Cu-Zr-O at the cathode side suggests that there was a uniform current flow between the Cu substrate and the ZrO<sub>2</sub> (8 wt%) coating during FAT. However, the discontinuous layers of Cu-Zr-O at the cathode side for another ZrO<sub>2</sub> coatings is



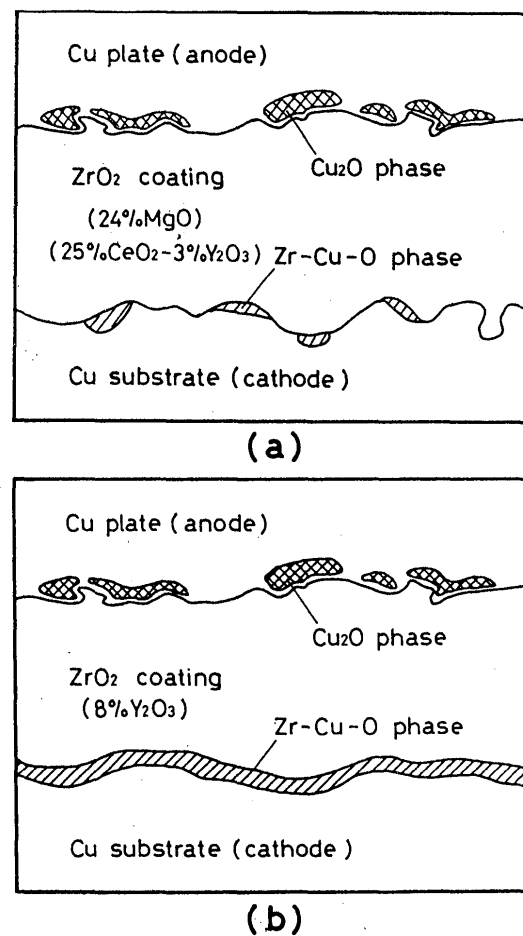
**Fig. 4** (a) Microphotographs and EDX analysis results of electric field treated  $\text{ZrO}_2$  (24% MgO) coating sprayed on Cu substrate



**Fig. 4** (b) Microphotographs and EDX analysis results of electric field treated  $\text{ZrO}_2$  (25 wt%  $\text{CeO}_2$ -3 wt%  $\text{Y}_2\text{O}_3$ ) coating sprayed on Cu substrate



**Fig. 4** (c) Microphotographs and EDX analysis results of electric field treated  $\text{ZrO}_2$  (8%  $\text{Y}_2\text{O}_3$ ) coating sprayed on Cu substrate



**Fig. 5** Illustration of formation of reaction layer at interface for electric field treated  $\text{ZrO}_2$  coating (a: 24 wt% MgO and 25 wt%  $\text{CeO}_2$ -3 wt%  $\text{Y}_2\text{O}_3$ ) (b: 8 wt%  $\text{Y}_2\text{O}_3$ )

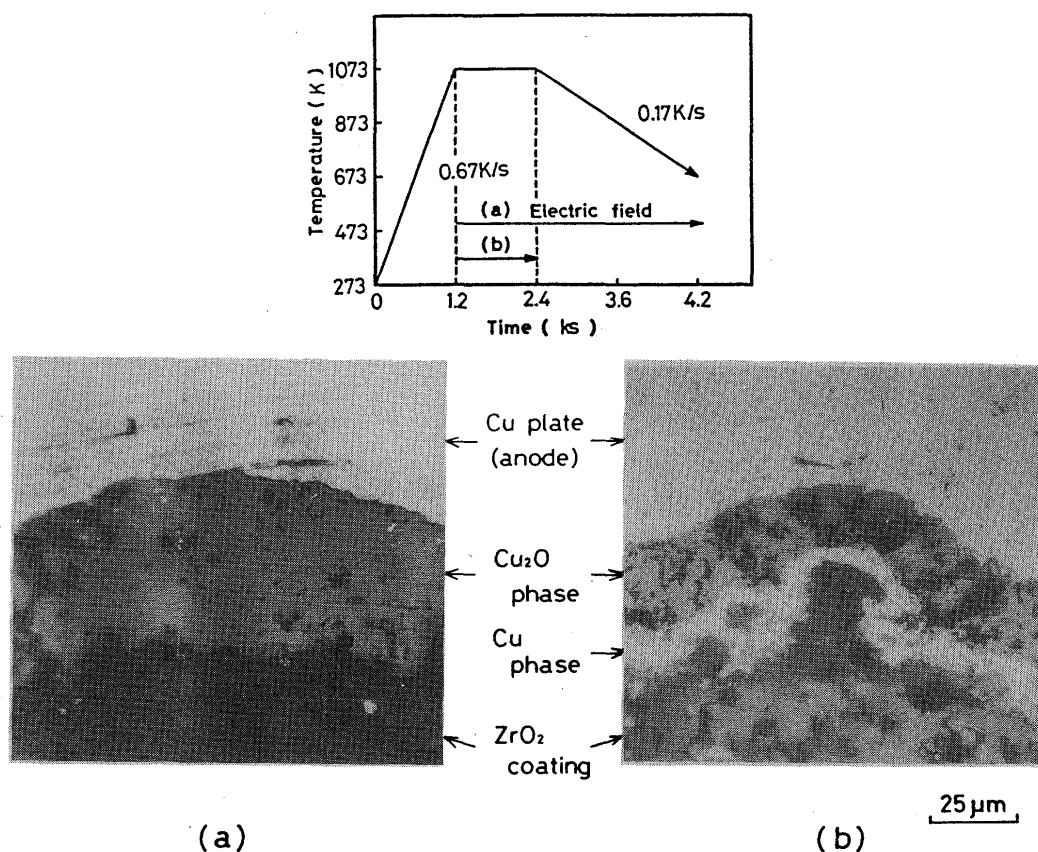


Fig. 6 Microstructures of anode side interface part of electric field treated  $\text{ZrO}_2(8\text{wt}\% \text{Y}_2\text{O}_3)$  coating and Cu plate electrode  
a) With FAT during cooling b) Without FAT during cooling

due to discontinuous current flow at the interface as shown in Fig. 3. Therefore, it is considered that the adhesion between the Cu substrate and  $\text{ZrO}_2$  coating could be improved because of the formation of the Cu-Zr-O phase.

### 3.2 Effect of electric field assisted treatment on adhesive strength of $\text{ZrO}_2$ coatings to Cu substrate

A tensile test was carried out in order to investigate the effect of element behaviour at the interface between the Cu substrate and  $\text{ZrO}_2$  coating on adhesive strength due to FAT. The results of the best for  $\text{ZrO}_2$  (8 wt%  $\text{Y}_2\text{O}_3$ ) are shown in Fig. 7, which presents for a comparison also the measurements for both specimens: as coated and heated, without FAT, at 773 K for 3.6 ks in air. FAT was carried out for 1.2 ks under the conditions shown in Table 3 changing only the electric charge value.

Figure 8 shows the similar results for  $\text{ZrO}_2$  (24 wt% MgO) coatings. As shown in the figures, the heated-only test piece showed about the same tensile strength as the as-coated test piece. The as-coated specimen fractured at the interface of the Cu substrate and  $\text{ZrO}_2$  coating.

The adhesive strength of  $\text{ZrO}_2$  (8 wt%  $\text{Y}_2\text{O}_3$ ) and  $\text{ZrO}_2$  (24 wt% MgO) coatings to the Cu substrate, following FAT remarkably increases as compared to that for the as-

coated specimen. The fracture occurred away from the interface of the Cu substrate and  $\text{ZrO}_2$  coating.

However, the fracture of  $\text{ZrO}_2$  (24 wt% MgO) treated at 920 C occurred at the interface due to formation of a large amount of discontinuous Cu-Zr-O layer. The adhesive strength was not greatly improved by FAT as shown in Fig. 8. These results show that by applying electric field treatment to  $\text{ZrO}_2$  sprayed on Cu, a Cu-Zr-O phase is formed on the cathodic interface between the Cu substrate and the  $\text{ZrO}_2$  coating. This leads to a strengthening of the interface, thereby improving the adhesive strength.

### 3.3 $\text{ZrO}_2$ (8wt% $\text{Y}_2\text{O}_3$ ) coating sprayed on SS41 steel

For the  $\text{ZrO}_2$  sprayed on Cu substrate, Cu-Zr-O phase was formed at the interface by FAT. However, Fe-Zr-O phase was not formed at the interface by FAT, for the  $\text{ZrO}_2$  sprayed on Fe substrate (SS41 steel). Therefore, the effect of temperature of heat-treatment for 3.6 ks in air on the formation of oxides at the interface between the  $\text{ZrO}_2$  coating and SS41 steel was investigated. Oxidation at the interface increased remarkably with the increase of treatment temperature, and the Fe oxide which detected by X-ray diffraction, appeared to be composed of FeO,

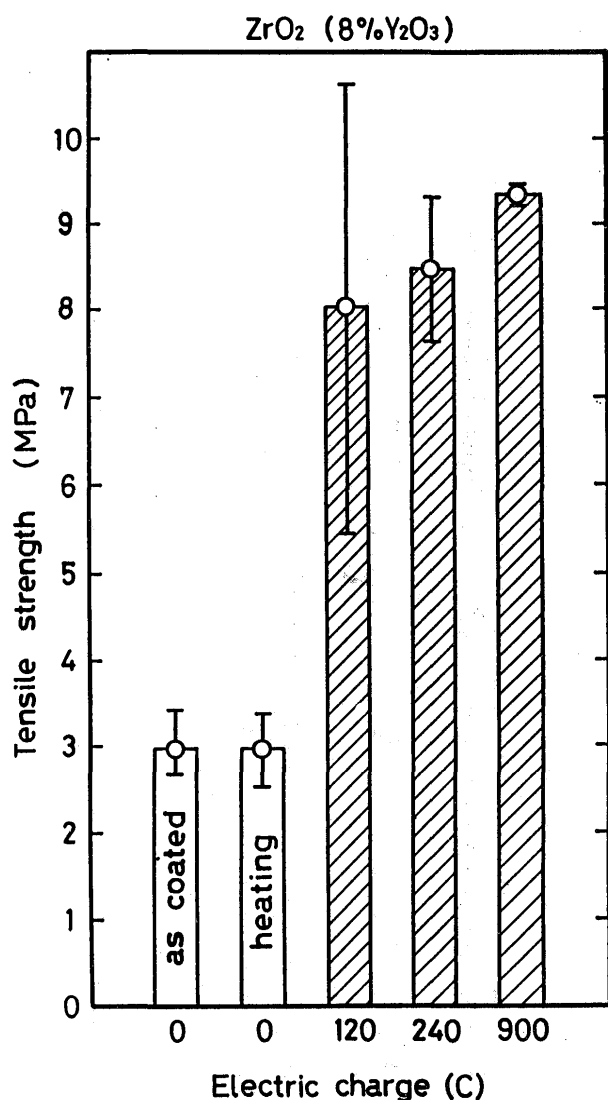


Fig. 7 Effect of FAT on adhesive strength of  $\text{ZrO}_2$  (8 wt%  $\text{Y}_2\text{O}_3$ ) coating sprayed on Cu substrate

$\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . At a temperature of 873 K, an uniform, 4-6  $\mu\text{m}$  thin layer of the Fe oxide was formed. However, when the temperature exceeded 1073 K, a thickness of the oxide layer increased, and  $\text{ZrO}_2$  coating peeled off during heat treatment.

The FAT was carried out for a  $\text{ZrO}_2$  coated piece heated at 873 K for 36ks in air, with the SS41 steel substrate as the cathode and the  $\text{ZrO}_2$  coating as the anode. The FAT conditions employed were those shown in Table 2. Treatment time and current were 300 s and 2000 mA, respectively.

Figure 9 (a) is cross section of a test piece heat-treated in air. Figure 9 (b) shows a cross section of the cathodic side of a similarly heat-treated test piece that was subsequently given FAT. These pictures show the existence of a layer newly formed after FAT. In order to clarify the behaviour of elements at the interface, elemental analysis by EDX was carried out, the results of

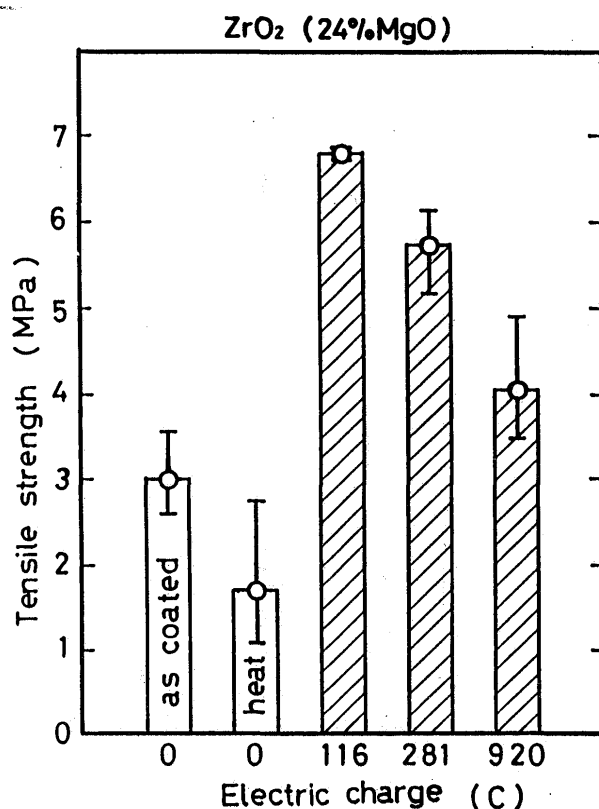


Fig. 8 Effect of FAT on adhesive strength of  $\text{ZrO}_2$  (24 wt% MgO) coating sprayed on Cu substrate

which are shown in Fig 10. For the purposes of comparison, Fig. 10 also shows: (a) analysis of an as-coated specimen, (b) coated and then subjected to FAT, (c) coated and then heat-treated at 873 K for 3.6 ks. in air, and (d), coated, heat-treated as previously, and then subjected to FAT. Figure 10 (d), clearly shows that an Fe-Zr interfacial layer is formed. Figure 10 (c) indicates that a slight mutual diffusion in the heated-only sample occurs, but Fig. 10 (b) -coated plus FAT- and Fig. 10 (a) -as-coated- show no reaction and virtually no diffusion.

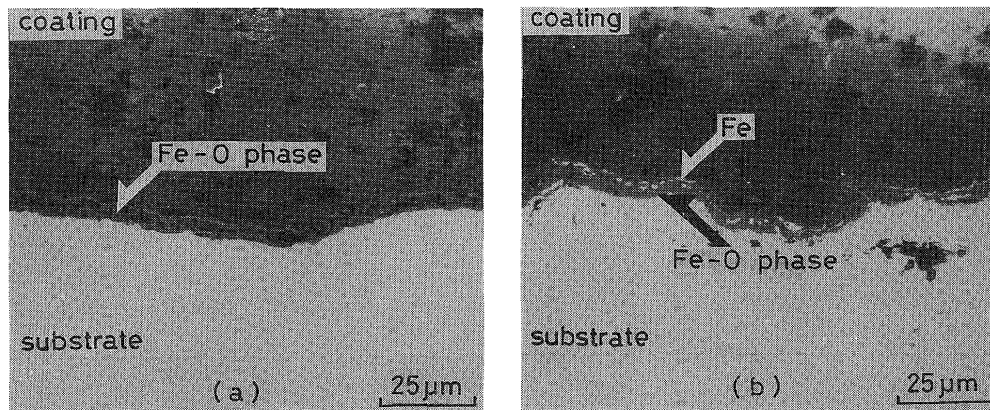
From the results of analysis, it may be considered that the formation of Fe-Zr-O phase indicated in Fig. 10 (d) is due to the activated Fe formed from Fe oxides at the interface by FAT.

### 3.4 Effect of FAT on adhesive strength of $\text{ZrO}_2$ (8 wt% $\text{Y}_2\text{O}_3$ ) coatings to SS41 steel substrate

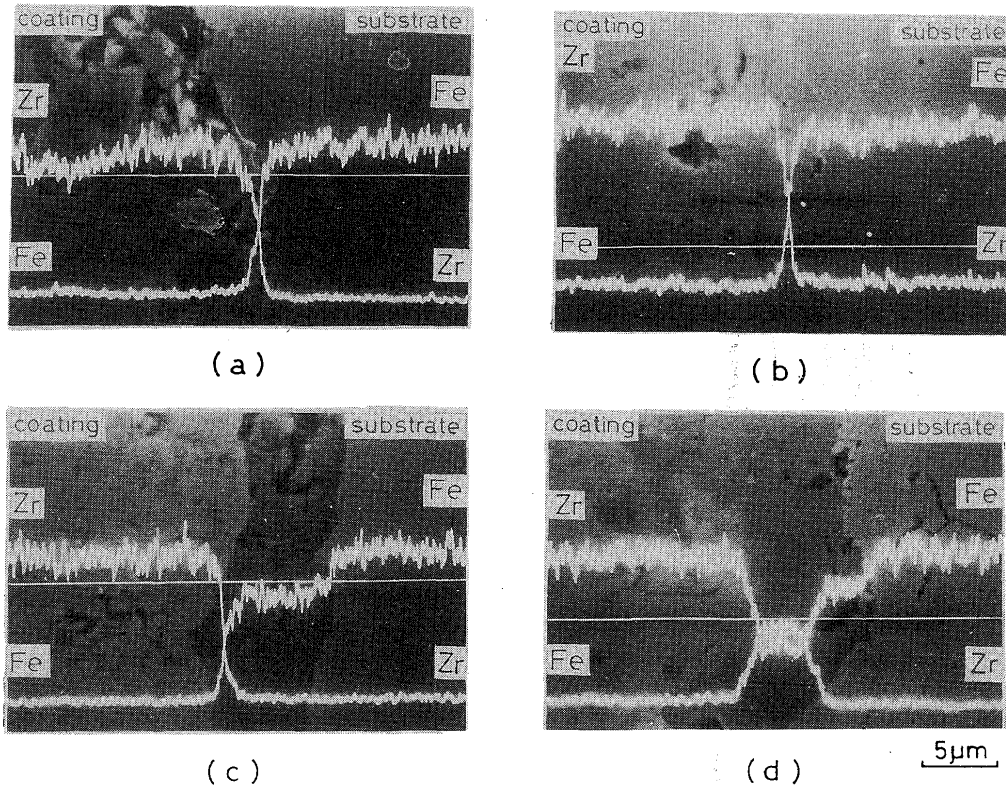
Figure 11 shows the tensile test results for  $\text{ZrO}_2$  coatings sprayed on SS41 steel and then treated in a various ways. The results in this figure are referred to the following specimens (a) as-coated; (b) heat treated in a vacuum (1073 K, 3.6 ks); (c) heat treated in air (1073 K, 3.6 ks); (d) FAT (60 °C) after heat treatment in air.

From these results, it is seen that the test piece heat-treated in a vacuum had about the same tensile strength as the as-coated example; no improvement was seen





**Fig. 9** Microphotographs of  $\text{ZrO}_2(8 \text{ wt\% } \text{Y}_2\text{O}_3)$  coating sprayed on SS41 steel substrate  
 a) Heat treated in air  
 b) Heat treated in air then given FAT: cathode side



**Fig. 10** EDX analysis results of  $\text{ZrO}_2$  coating sprayed on SS41 steel substrate after various treatments  
 a) As coated  
 b) FAT of coated specimen (a)  
 c) Coated specimen (a) after heat treatment in air at 873K for 3.6 ks  
 d) Heat treated specimen (c) after FAT

regarding adhesive strength, and both test pieces fractured at the interface between the  $\text{ZrO}_2$  coating and SS41 steel substrate. The adhesive strength of the test piece heat-treated in air showed some improvement compared to the as-coated specimen; fracture occurred partially inside the  $\text{ZrO}_2$  coating. It may be considered that the interface was strengthened partially by the formation of Fe oxides at the interface.

For the test piece subjected to FAT after heat treatment, the adhesive strength was remarkably improved and fracture occurred inside the  $\text{ZrO}_2$  coating. This is due to the formation of Fe-Zr-O phase at the interface between  $\text{ZrO}_2$  coating and Fe substrate.



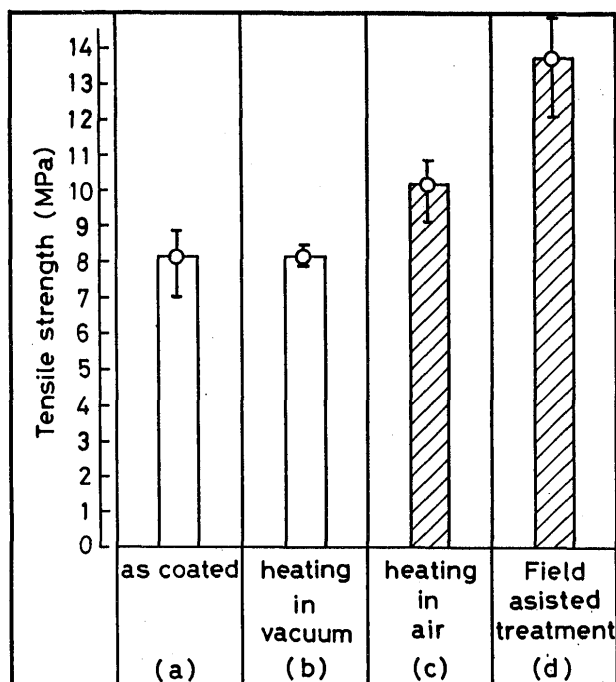


Fig. 11 Effect of various treatments on the adhesive strength of  $\text{ZrO}_2(8 \text{ wt}\% \text{ Y}_2\text{O}_3)$  coatings sprayed on SS41 steel substrate

#### 4. CONCLUSION

This study was done to clarify elemental composition of the interface caused by heat treatment and electric field assisted treatment which was applied to improve the adhesive strength of the interface of ceramic sprayed coatings and metal. The effect of such elemental composition on the adhesive strength of the interface was also examined, using copper and SS41 steel as the substrate and three kinds of 24 wt% MgO, 25 wt%  $\text{CeO}_2$ -3 wt%  $\text{Y}_2\text{O}_3$  and 8 wt%  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  as the ceramic coating. The results are summarized below.

- 1) The electric field assisted treatment applied to three kinds of  $\text{ZrO}_2$  coatings sprayed on Cu substrates involves the formation of a Cu-Cu<sub>2</sub>O phase at the anodic interface and a continuous Cu-Zr-O phase for  $\text{ZrO}_2$  (8 wt%  $\text{Y}_2\text{O}_3$ ) and discontinuous Cu-Zr-O

phase for  $\text{ZrO}_2$  (24 wt% MgO) and  $\text{ZrO}_2$  (25 wt%  $\text{CeO}_2$ -3 wt%  $\text{Y}_2\text{O}_3$ ) at the cathodic interface.

- 2) Adhesive strength of  $\text{ZrO}_2$  coating sprayed on Cu substrate is improved greatly by the Cu-Zr-O phase formed by the electric field assisted treatment, and leads to fracture inside the  $\text{ZrO}_2$  coating during tensile testing.
- 3) When electric field assisted treatment was applied to  $\text{ZrO}_2$  sprayed on SS41, the formation of a reaction phase at the steel substrate was not recognized.
- 4) When the  $\text{ZrO}_2$  sprayed on Fe substrate heat-treated in air was submitted by FAT, an Fe-Zr-O phase is formed at the interface between  $\text{ZrO}_2$  coating and Fe substrate.
- 5) Adhesive strength of  $\text{ZrO}_2$  coating sprayed on SS41 steel is improved by the Fe-Zr-O phase, formed at the interface by heat treatment in air followed by electric field assisted treatment.

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