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Characteristics of Metal Electroplating to Plasma Sprayed Ceramic Coatings†

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Abstract

The characteristics of metal electroplating to Al_2O_3 and ZrO_2 coatings sprayed by plasma onto mild steel were investigated. It was recognized that copper plating along the porosities connected to the substrate started from the interface between ceramic coating and substrate. The microphotographs show that nonbonded area between flattened ceramic particles in the coating can be filled up with copper. The plating character of copper into coatings depends greatly on the shape and the size of the porosities in the coating which are determined by ceramic type and spraying conditions. Moreover, it is affected greatly by electroplating conditions such as a current density. It is possible to obtain composite coatings of metals and ceramics by composite processing of both thermal spraying and electroplating, which can improve the coating properties and suppress completely corrosion of the substrate.

KEY WORDS (thermal spraying) (ceramic coating) (copper) (electroplating) (composite coating) (plating characteristics)

1. Introduction

Plasma sprayed ceramic coatings are formed by deposition of flattened, rapidly solidified ceramic particles. In the coatings the porosity inevitably appears. Especially, due to the porosity which is connected from the coating surface to the interface between ceramic coating and substrate, an electrolyte penetrates easily through the coating and reaches to the interface and then causes the corrosion of the substrate. Subsequently, the ceramic coating separates from the substrate and can not be used as an effective protection.[1)] This also occurs heavily even if stainless steel is used as a substrate which is only put in the humid environment. Furthermore, less real contact area exists between ceramic particles.[2)] When ceramic coatings are stressed, fracture occurs easily because cracks initiate and propagate as microcracks along the interface between flattened ceramic particles where not real contact area exists.[3,4)] Conventionally, heat treatments, pore-sealing, etc. are carried out to improve coating properties. Utilizing the porosities in ceramic coating it is possible to produce a composite coating by plating metal into a ceramic coating, so that, an improvement in the mechanical properties of ceramic coatings can be also achieved besides the corrosion behaviour. A few phenomena had been reported about the electroplating of metal in ceramic coating,[5)] but the process and the character of metal plating in ceramic coatings is not clear.

In this report, the process of copper segregation in electroplating in ceramic coating and effect of current density of electroplating on copper segregation were investigated. The characteristics of metal electroplating in ceramic coating are discussed.

2. Materials and Experimental Procedures

Al_2O_3 and ZrO_2 (stablized by Y_2O_3) powders were used to obtain ceramic coatings with different porosity. They were chosen because the connected porosity of ZrO_2 coating is much higher than that of Al_2O_3 coating.[6)] Ceramic coatings were sprayed onto blasted mild steel substrate by spraying conditions shown in **Table 1**. The thickness of the coatings varied from about 40μm to 100μm by changing scanning pass number of the spraying gun.

Copper plating was selected to investigate the plating characteristics of metal in ceramic coating. The electro-

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Table 1 Plasma spraying conditions.

Spraying apparatus	Plasmadyne (Mach 1)
Plasma gas (Ar)	4.2 kg/cm^2
Auxiliary gas (He)	4.2 kg/cm^2
Powder carrier gas (Ar)	5.6 kg/cm^2
Hopper setting	1.5 rpm
Spraying current	800 A
Spraying voltage	35 V
Spraying distance	100 mm
Cooling air pressure	2 kg/cm^2

Table 2 Concentration of the plating solution used.

Reagents	Concentration (g/l)
CuCN	70
NaCN	90
KOH	30

plating was carried out in an alkaline cyanide aqueous solution which was composed of CuCN, NaCN and KOH. The compositions of the solution are shown in **Table 2.** A copper rod was used as the anode. Ceramic sprayed sample was used as the cathode, in which all of the sample surfaces were covered by liquid TRV gum except the coating surface to be plated. During plating, cathode current density was kept constant using potentiostat as a regulated DC current source, and the temperature of the solution was maintained at 40°C.

The microstructures of the plated ceramic coatings were examined by optical microscope and scanning electron microscope (SEM).

The corrosion behaviour of the plated ceramic coatings was determined by measuring their dynamic polarization behavious using potentiostat.

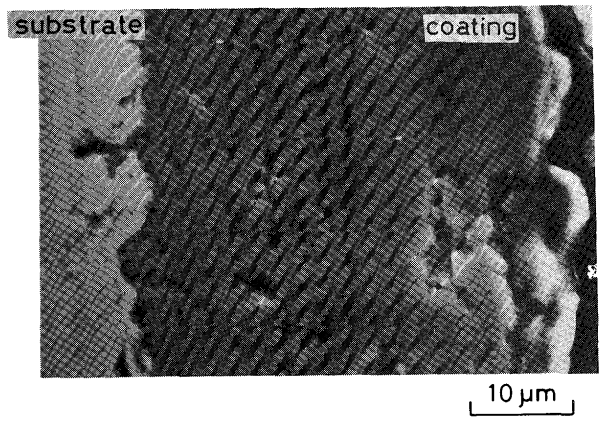

Fig. 1 Typical microstructure of cross-section of Al_2O_3 coating used for electroplating.

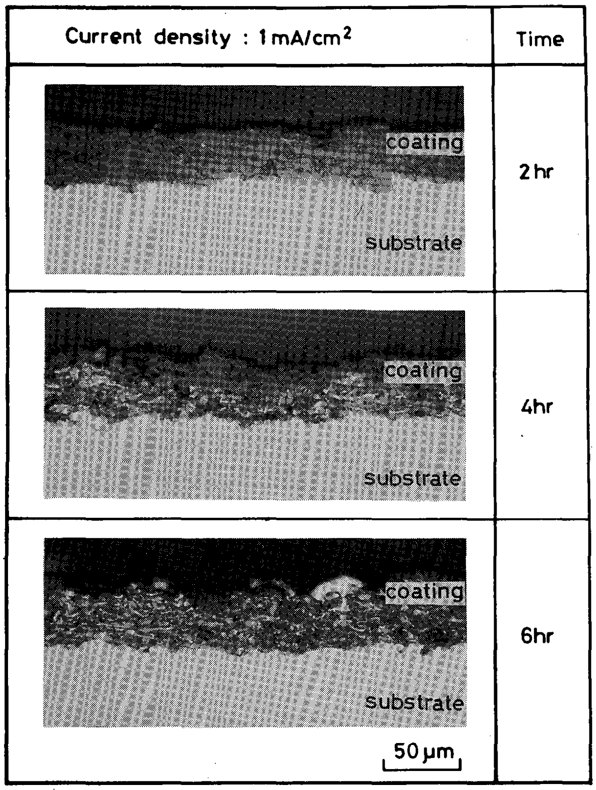

Fig. 2 The change of the microstructures of the Al_2O_3 coatings with plating time at cathode current density of $1mA/cm^2$.

3. Results and Discussion

3.1 Build-up of copper in ceramic coatings

Ceramic coatings consist of flattened, rapidly solidified ceramic particles, which have an layer structure with small real contact between layers. **Figure 1** shows typical structure of cross-section of an Al_2O_3 coating before electroplating. The layer structure and porosity in the coating can be recognized. In electroplating, because of insulating properties of ceramic coatings, plating solution must penetrate the coating to build a conducting bridge through the connected porosity in order to achieve the plating. **Figure 2** shows the change of the microstructures of the Al_2O_3 coatings with plating time for cathode current density of $1mA/cm^2$. Clearly, the copper plating layer was built up from ceramic coating substrate interface and became thicker with an increase in plating time towards the surface of the coating. **Figure 3** shows typical EDX analysis results of copper in a plated Al_2O_3 coating. It is evident from Fig. 3 (b) that copper segregated at the interface. From distribution of copper in the coating shown in Fig. 3(a), it is clear that copper only filled up porosities and apparent contact area between ceramic layers. From typical SEM microstructure of the Al_2O_3 coating plated with copper shown in **Fig. 4**, it is clear that copper ion in the solution is strong enough to penetrate

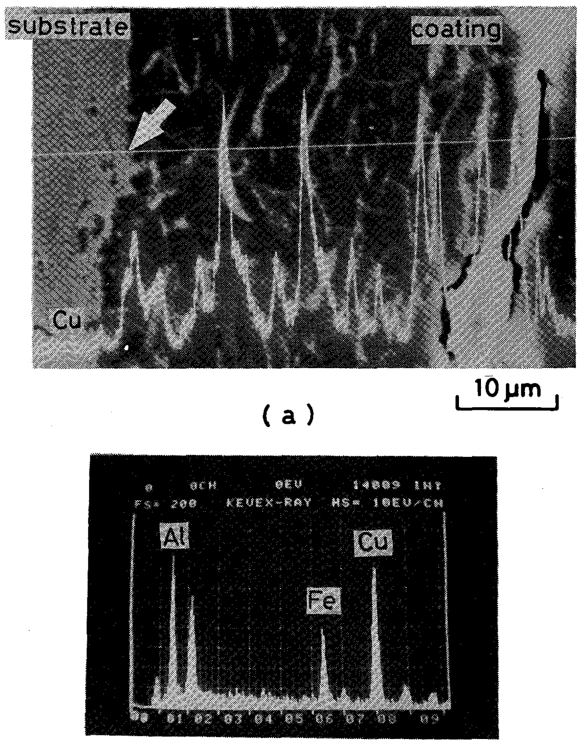

Fig. 3 Typical EDX analysis results for Al_2O_3 coating, (a) distribution of copper in plated Al_2O_3 coating, (b) spot analysis result at the ceramic coating substrate interface.

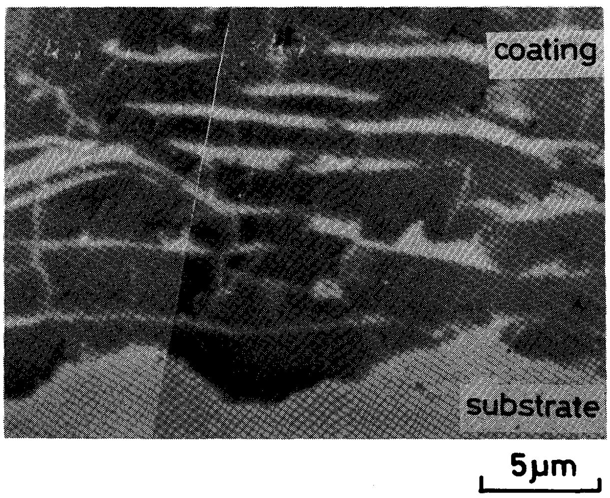

Fig. 4 Typical SEM microstructure of the copper plated Al_2O_3 coating. White strings show copper electroplated in Al_2O_3 coating.

not only porosities and microcracks but also a great amount of nonbonded area which can not be observed by metallographic examination. From the above results, it is possible that the micro-gaps in ceramic coatings including porosities and nonbonded area between flattened ceramic layers can be filled up with metals by electroplating. Further, because of filling up with copper, the detail microstructure of the coating becomes much clear and shows that there exists a lot of nonbonded area between ceramic layers, which would be the source of microcracks to cause easily failure of ceramic coating.

3.2 Effect of cathode current density on plating characteristics

In the process of copper electroplating, it was observed that gas bubbles arised in the vicinity of the surface of the coating being plated. It is considered that this is because the other reduction reaction occurs simutaneously besides the segregation of the copper. This will cause a decrease in the efficiency of cathode current density. Because the efficiency of cathode current density decreases with an increase in current density,[7)] cathode current density would greatly affect the characteristics of metal plating in ceramic coatings.

Figure 5 shows the microstructures of Al_2O_3 coatings electroplated at current density of $0.5mA/cm^2$ and $5mA/cm^2$ respectively. Together with the microstructure shown in Fig. 2, it was recognized that the copper segregated homogeneously in the coating at a lower current density level. But when current density became large gradually, plating front changed to grow at different velocity in a wavy pattern along the coating and segregation of copper in the coating become nonhomogeneous. It grew very fast partially to reach the surface of the coating as shown in Fig. 5. It became clearer when the thickness of ceramic coating becomes thicker as shown in **Fig. 6** where the thickness of Al_2O_3 coatings was dubled comparing with

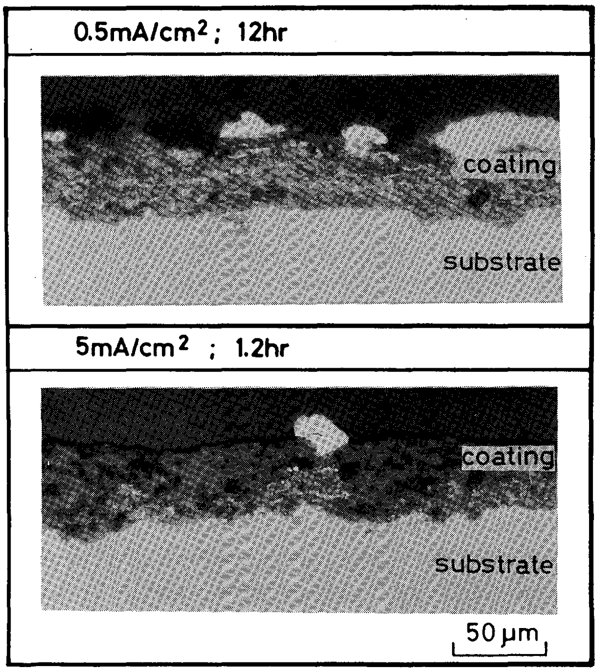

Fig. 5 The microstructure of Al_2O_3 coatings electroplated at cathode current density of $0.5mA/cm^2$ and $5mA/cm^2$.

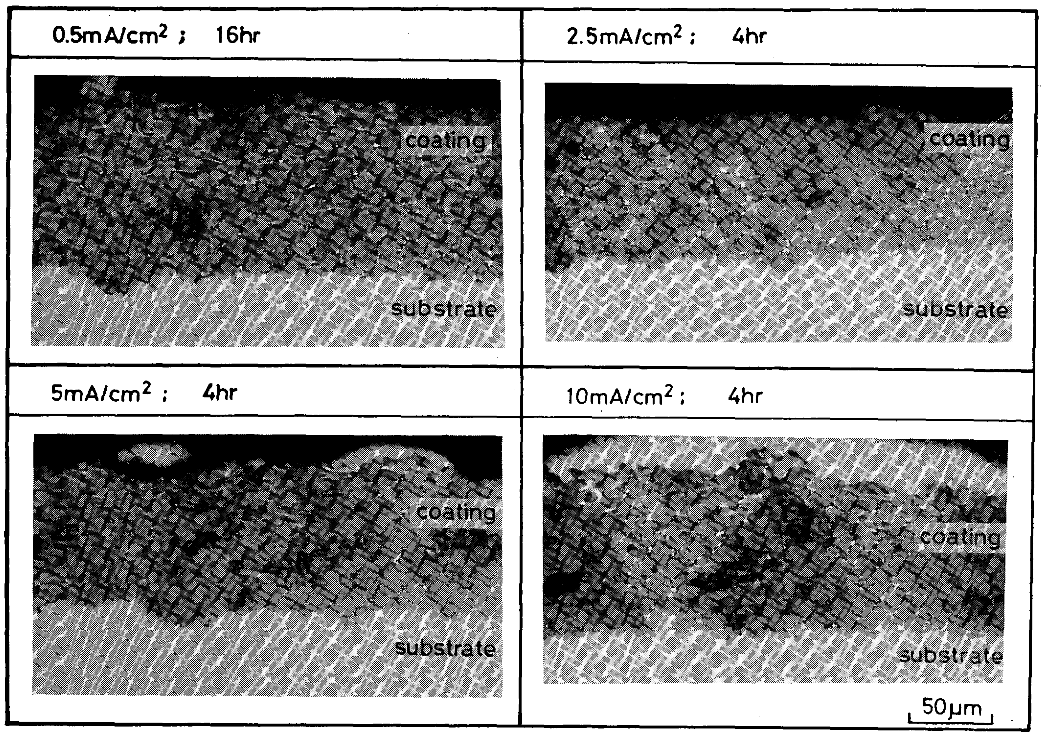

Fig. 6 Effect of cathode current density on the segregation of copper in Al_2O_3 coatings.

that shown in Fig. 5. It is evident that with an increase in current density, plating pattern of copper in the coating changed from wavy form to tree-like and finally to anti-triangle form. Besides, by comparing the microstructures shown in Fig. 2 and Fig. 3, although the applied electric quantity is the same, almost all of the porosities were filled up by copper under conditions of 0.5 and 1mA/cm^2, while in the case of 5mA/cm^2 only a little amount of porosity near the interface was filled up. This is because the efficiency of cathode current density decreased with the increase of current density and it became easy for copper ion to reach to the plating front moving towards the coating surface.

For ZrO_2 coatings, it was recognized that the plating pattern is the same as that for Al_2O_3 coatings. But the cathode current density necessary to obtain homogeneous composite coating was higher for ZrO_2 coating than that for Al_2O_3 coating as shown in **Fig. 7**.

The effect of current density on the segregation of the copper in ceramic coating is schematically shown in **Fig. 8**. The plating front expressed with dotted line grows from the interface between the ceramic coating and the substrate towards the coating surface with time. The pattern of the plating front changes from wavy form to tree-like one and further anti-triangle form with the increase in current density. At a lower current density, although the plating front grows in a wavy form, it is not evident that there is a great difference in its growing velocity between the peak and the valley with time. So that, finally homogeneous segregation of copper in the coating can be obtained. But with the increase of current density as shown in Fig. 8, the difference in growing velocity between the peak and the valley becomes larger even if the plating front in the valley stops growing. Subsequently, non-uniform composite of ceramic-metal is achieved.

3.3 Electrochemical behaviour of electroplated ceramic coating

Due to the connected porosity, the electrochemical behaviours of ceramic sprayed samples are mainly dominated by that of the substrate used.[6] Whether the porosity is filled completely up or not by copper through the electroplating can be detected by electrochemical method. **Figure 9** and **Figure 10** show typical anodic polarization curves for plated Al_2O_3 and ZrO_2 coatings measured with a 3.5%NaCl aqueous solution at a scanning speed of 30mV/min, respectively. The plating was carried out at current density of 1mA/cm^2, and the plating time was adjusted so that the plating front just reached the surface of the ceramic coating. For comparison, the anodic polarization curves of mild steel, as-sprayed mild steel and copper plates are also shown in the same figure. It is evident from the results shown in Fig. 10 that the connected porosity can be completely filled up by electroplating. For Al_2O_3 coating, it is recognized from Fig. 9

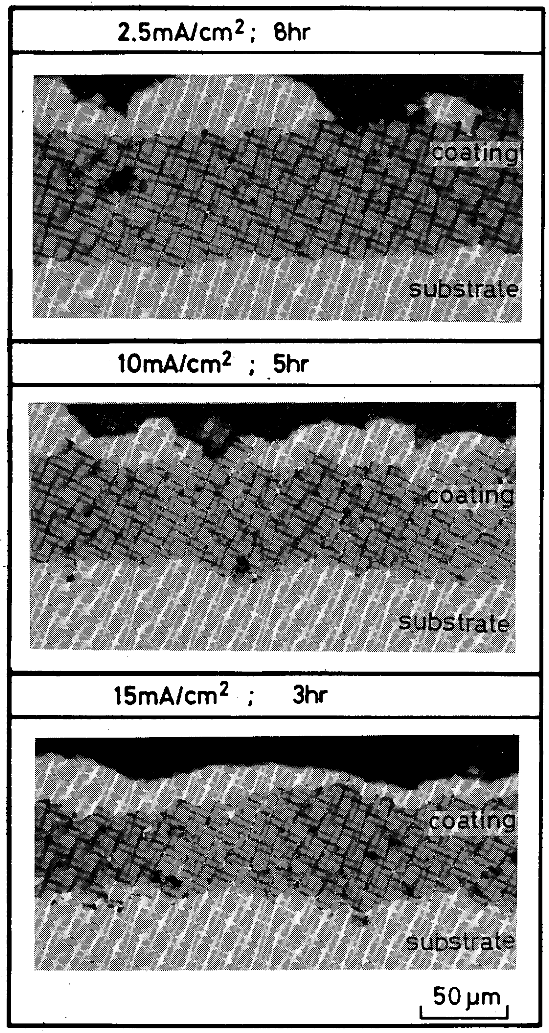

Fig. 7 Effect of cathode current density on the segregation of copper in ZrO_2 coatings.

that there is still a little amount of connected porosity left after electroplating. It is considered that such a difference occurs because of the difference in the flattened state of two kinds of coatings during spraying, which determine the porosity and tortuosity of ceramic coating, and greatly affect the conductance of coating to the ions in the plating solution.

For an as-sprayed sample, it is observed that when polarization potential exceeds about –200mV during anodic polarizing, ceramic coating separates from the substrate because of the corrosion of the substrate at the interface.[6)] **Figure 11** shows the microstrctures of plated two kinds of ceramic coatings after electrochemical measurement. In the coatings, copper is recognized to be left. There is not evidence of separation of the coating from the substrate. Therefore, by producing the composite coatings of ceramics and metal through electroplating, the corrosion of the substrate can be suppressed.

From the results obtained above it can be seen that the characteristics of segregation of copper in ceramic coating are greatly affected by cathode current density. They are also affected by the porosity and tortuosity of ceramic coatings which are determined by the properties of coating materials and spraying conditions. It is easy to obtain homogeneous plating and subsequently uniform composite coating of ceramics and metals for the ceramic coatings with large porosity and less tortuosity, while for the ceramic coatings consisting of well flattened ceramic layers it is necessary to carry out plating at a lower current density in order to obtain the uniform plating coatings.

Although only the characteristics of copper plating

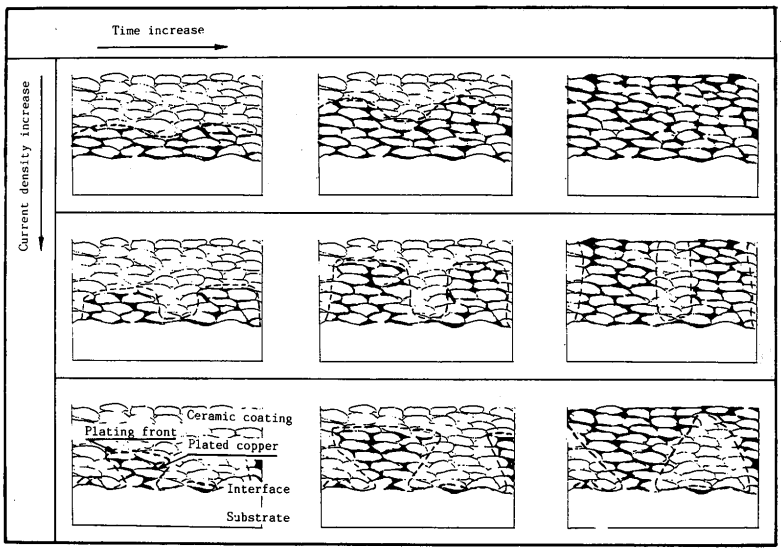

Fig. 8 Schematic diagram of the process of copper segregation in ceramic coatings and the effect of cathode current density.

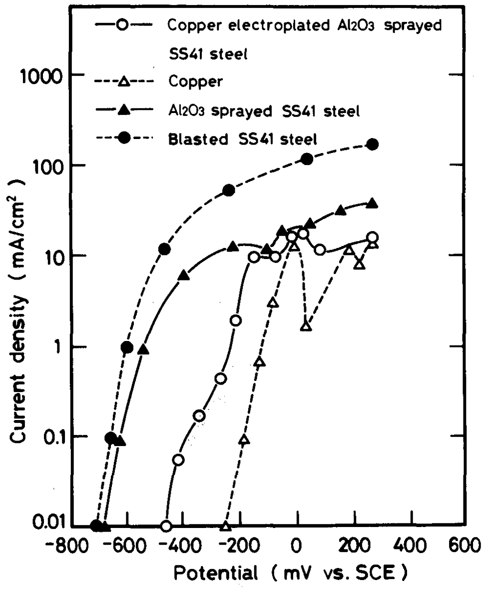

Fig. 9 Typical anodic polarization curves of the copper electroplated Al_2O_3 coating, as sprayed coating, surface blasted mild steel, and copper plates.

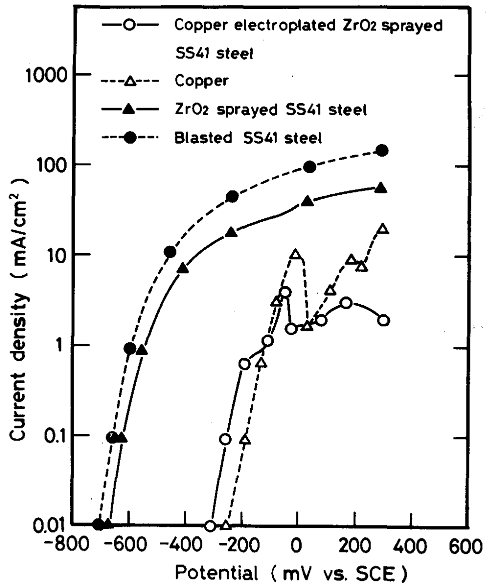

Fig. 10 Typical anodic polarization curves of the copper electroplated ZrO_2 coating, as sprayed coating, surface blasted mild steel and copper plates.

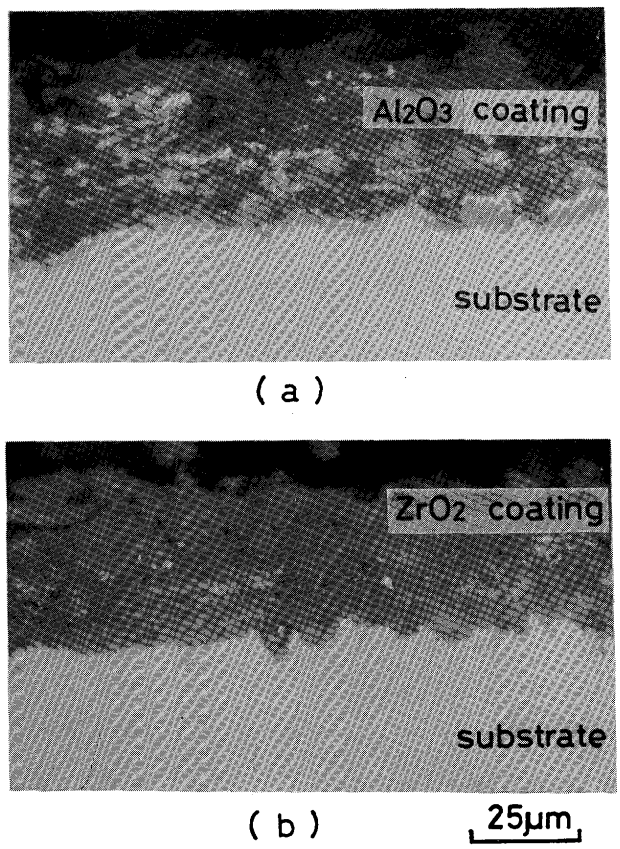

Fig. 11 The microstructures of copper plated ceramic coatings after electrochemical measurement shown in Fig. 9 and Fig. 10, (a) Al_2O_3 coating, (b) ZrO_2 coating.

were illustrated, the other metals can also be plated into ceramic coating with the same characteristics as that of the copper.

4. Conclusion

The characteristics of copper electroplating in ceramic coating were studied using alkaline cyanide aqueous solution. It was recognized that the copper segregated on base of metal substrate from interface between the ceramic coating and the substrate towards the surface of the coating. The cathode current density affects greatly the plating pattern of copper in the ceramic coating. At a lower current density, it is possible to obtain a dense composite coating of ceramics and metals. The current density necessary to obtain uniform composite coatings of ceramics and metals becomes lower when size of porosity become less and ceramic particles flatten better in spraying. The corrosion of the substrate can be suppressed by ceramic-metal composite coatings through electroplating. By copper plated in ceramic coating, it becomes clear that there exists much nonbonded area between flattened ceramic layers, which can not be observed by conventional methods. It could also be utilized to study the microstructure of ceramic coatings.

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