ZrO_2-Y_2O_3 Ceramic Coatings Prepared by Cathodic Plasma Electrolytic Deposition

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ABSTRACT

A cathodic plasma electrolytic deposition process (CPED) was developed to prepare ZrO_2-Y_2O_3 ceramic coatings. The coacervate materials deposited on the cathode surface can be directly sintered to form ceramic coatings by the plasma energy produced from the micro-discharge in the aqueous electrolytic solution. The CPED mechanism has been investigated by measuring the current vs. time and potential distribution between the electrodes during the cathodic gaseous discharging process. SEM, EDS and XRD analysis showed that the as-deposited coating contains Y_2O_3 partially stabilized ZrO_2. The coatings show smooth surfaces, uniform microstructure and excellent bonding to the metal substrate.

Keywords: Cathodic plasma electrolytic deposition (CPED), Micro-discharging of cathodic gaseous envelope, ZrO_2-Y_2O_3 ceramic coating

1. INTRODUCTION

Plasma electrolytic deposition (PED) is a new surface modification technique which is developed from the traditional electrolysis routine. This process generally includes plasma electrolytic oxidation technique (or micro-spark oxidation) and plasma electrolytic cementation technique /1/.

The micro-spark oxidation technique was invented by Schulz and Betz /2/. It has been successfully applied to surface modification of Al, Mg, Ti, Ta metals and their alloys. The metals or alloys were used as the anode in an aqueous electrolytic solution. When a high voltage is applied, the micro-spark discharge on the surface of the anode can sinter the coacervate to form ceramic coatings. The metal source in forming the ceramic coating comes from the base material. Due to the discharge characteristics of the anode micro-spark oxidation (AMSO), this method is limited to valve metals and alloys. He *et al.* have proposed a cathodic micro-spark electrolytic deposition (CMED) routine that overcomes the weakness of AMSO technique by applying a pre-deposited oxide film barrier on the cathode surface /3-6/. Under certain voltage, micro-spark discharge is generated through the oxide layer. The plasma energy of micro-spark decomposes the coacervate, and sintered a layer of ceramic coating onto the cathode surface, similar to a pyrolysis process. The contents of the coating mainly come from the solution.

An important advantage of CMED is the applications of this technique are not limited to valve metals and alloys. However, the request of a pre-deposited oxide layer is a shortcoming to industrial applications. So far no investigation has been reported on the direct deposition of thick ceramic coatings on cathode surface.

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This paper reports the investigation on the direct deposition of ZrO_2-Y_2O_3 thick ceramic coatings from aqueous solution by CPED technique. The coating formation mechanisms and the effects of processing parameters have been discussed.

2. EXPERIMENTAL

The schematic diagram of the apparatus used in this research is illustrated in Fig. 1. This system includes a power source, an electrolysis cell, a cooling system, and the voltage, current recording units. The electrolytic solution is made of 0.1M $Zr(NO_3)_4$ + 0.04M $Y(NO_3)_3$ aqueous solution. Platinum plate of 20 × 17 mm and Fe-25Cr-5Al alloy bars of $\Phi 4 \times 40$ mm were used as the anode and cathode, respectively. The distance between the electrodes is 10 mm. The surface of the samples was ground to 800# SiC paper. The top of the samples close to the air/solution interface was wrapped with a polymer (PTFE) tape in order to avoid the occurrence of micro-spark around that position. SEM, EDS and XRD were used to study the surface morphology, composition and phases of the ZrO_2-Y_2O_3 thick ceramic coatings.

The current through the circuit and the potential between the electrodes were monitored as a function of time in order to analyze the process of the cathodic gaseous discharge. The collected current and voltage signals were automatically recorded by a computer via an isolating module and A/D transfer. In the potential distribution investigation experiment, a 0.2 M NaCl aqueous solution, a Pt anode and a cathode of Fe-25Cr-5Al plate were used to eliminate the influence of the deposited layer. The distance between the electrodes is 10 mm, and the applied voltage is 150 V above the critical voltage. A capillary tube was mounted in a readable displacement instrument. It could move and position between the electrodes with the precision of 10 μm. The potential distribution was studied by continuous measurement of the potentials using a calomel electrode, which is connected to the capillary tube.

3. EXPERIMENTAL RESULTS

3.1 The discharge process

The current density vs. time curve during the cathodic micro-spark electrolytic deposition was illustrated in Fig. 2. The aqueous solution consisted of 0.1M $Zr(NO_3)_4$ + 0.04M $Y(NO_3)_3$. The current density curve showed that the current first increased with the voltage between the electrodes, accompanied by a large amount of hydrogen bubbles. As the voltage reached a critical value, a peak current density of ~9 A/cm^2 was reached, followed by a sharp drop to ~1 A/cm^2. At this moment the whole cathode surface was covered by a white gas film with randomly moving micro-sparks. We named this as the cathodic gaseous envelope micro-spark discharge (CGEMD). After a long time discharge, the current dropped down to almost zero and the micro-spark discharge disappeared, leaving a layer of ZrO_2-Y_2O_3 ceramic with a certain thickness formed on the sample surface. The coating thickness depends on the applied voltage. A higher discharge voltage produces a thicker coating. This method of preparing ceramic coatings is named as the cathodic plasma electrolytic deposition (CPED) or cathodic gaseous envelope micro-spark electro-deposition.

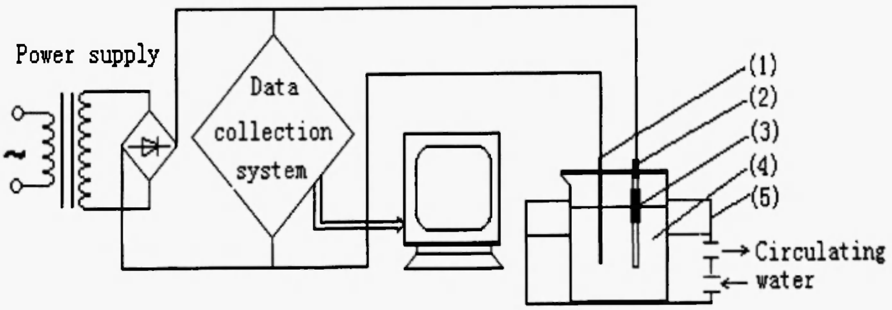

Fig. 1: Schematic diagram of the Cathodic Plasma Electrolytic Deposition System: 1. platinum anode, 2. specimen cathode, 3. a polymer tape, 4. electrolytic aqueous solution, and 5. cooling bath.

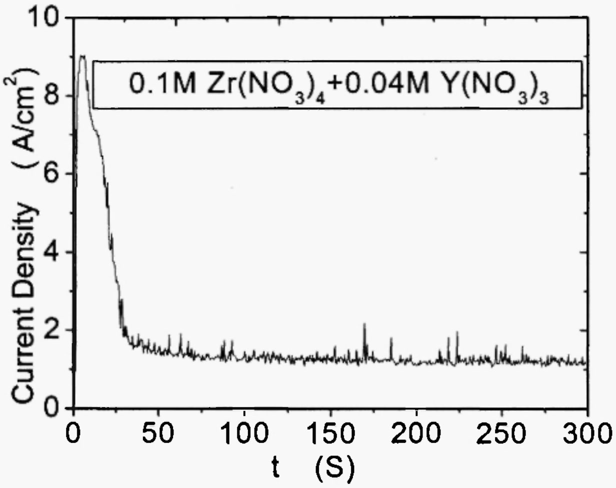

Fig. 2: Current as a function of time during cathodic gaseous envelope micro-spark discharge.

3.2 Effect of discharge voltage on ZrO_2-Y_2O_3 ceramic coating

Fig. 3 exhibits the relation of the deposition mass of ZrO_2-Y_2O_3 and the applied voltage after micro-spark discharge for 1 h in 0.1M $Zr(NO_3)_4$ + 0.04M $Y(NO_3)_3$ aqueous solution. It shows that the deposition increased with increasing voltage. While a high voltage can obtain a thick coating, the coating surface roughness is high as a result of severe bombardment of high energy plasma. In this experiment, a relatively low voltage of 140~160 V was selected as the optimum value in consideration of both coating effectiveness and quality.

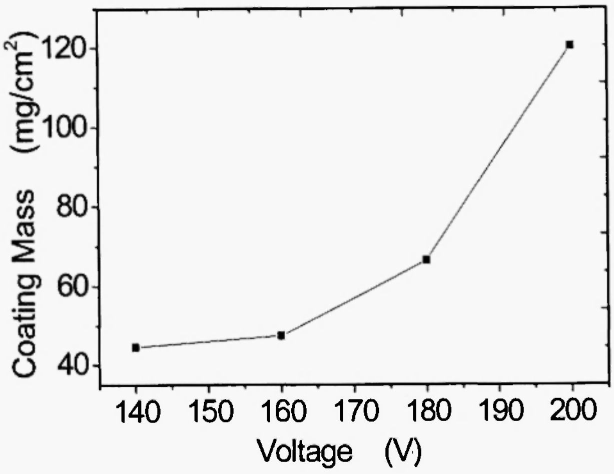

Fig. 3: Relation of coating mass gains and applied voltage.

3.3 Surface morphologies and phase composition

Fig. 4 shows the surface and cross-section morphology of an ZrO_2-Y_2O_3 coating deposited with 140 V for 1 h in the above solution. The coating possesses smooth surface, dense structure, with a thickness of ~60 μm. The cross section micrograph showed no gap and crack between the coating and substrate, evidence of strong bonding to the substrate. The elemental distribution in the ZrO_2-Y_2O_3 coating measured by EDS in Fig. 5 shows that the coating mainly contained ZrO_2 with small amounts of Y, Fe, Cr and Al. The content of Y is lower than it was in the solution. Fe, Cr and Al came from the Fe-25Cr-5Al substrate.

The X-ray diffraction spectra of the as-deposited ceramic coating are plotted in Fig. 6, showing the possible existence of m-, c-, t- and t'- ZrO_2 phases. Using the calculation method suggested in reference /5/, the computed percentage of m-ZrO_2 phase in ZrO_2-Y_2O_3 ceramic was ~17%. It is believed that the addition of Y_2O_3 stabilized c-, t- and t'-ZrO_2 phases at ambient temperature.

4. DISCUSSION

4.1 The distribution of electric potential

The distribution of electric potential between the electrodes during deposition in 0.2M NaCl aqueous solution is demonstrated in Fig. 7. It can be seen that during the period of gaseous envelope discharge, the potential on the anode surface was relatively high. However, the voltage drop in this area and in the electrolytic solution was quite small, less than 10% of the total voltage. On the other hand, 80% of the applied voltage dropped over the cathodic surface region within 1 mm from the cathode, forming a high electric field of 10^5 V/m. The breakdown of the gaseous envelope and the formation of high energy micro-spark plasma were attributed to the high electric field. Therefore, the cathode geometry has an insignificant effect on the current distribution because the main voltage difference was concentrated over the cathodic surface, and only a small voltage was ha applied in the electrolytic solution. The high voltage concentration on the cathode surface is

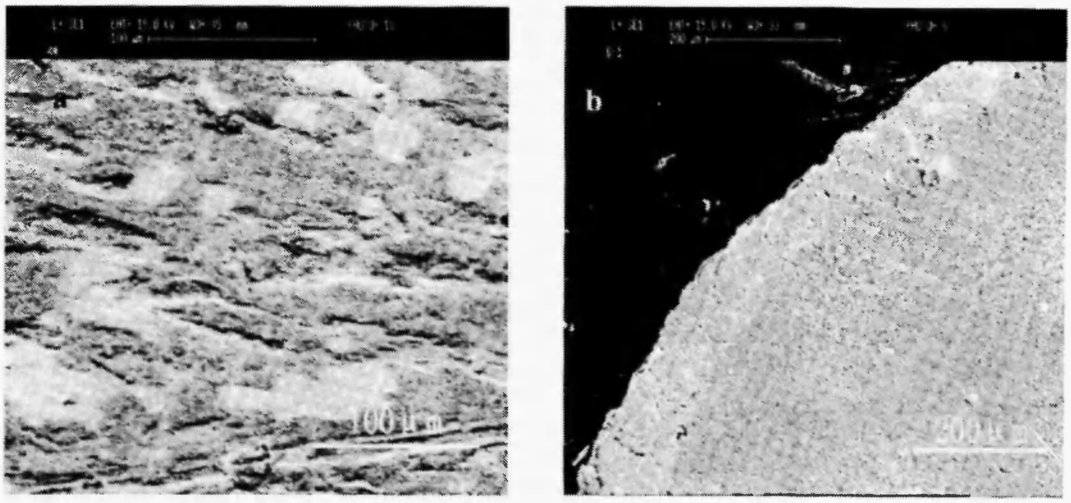

Fig. 4: SEM surface morphology (a) and cross-section microstructure (b) of an as-deposited ZrO_2-Y_2O_3 coating.

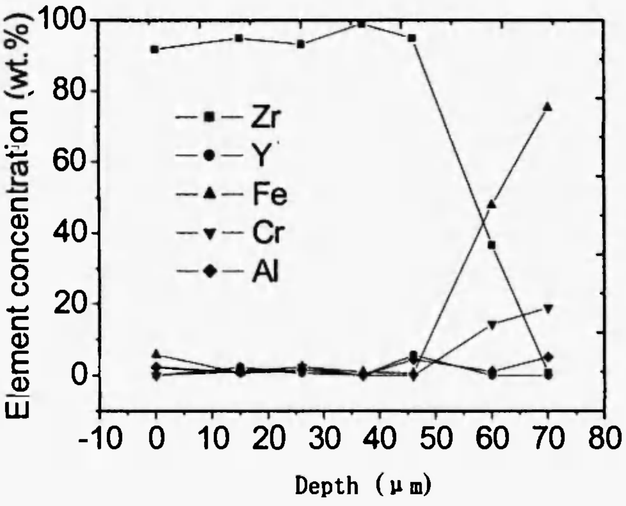

Fig. 5: Cross-section elemental distribution of an as-deposited ZrO_2-Y_2O_3 coating.

beneficial to the uniform deposition of CPED technique.

During the deposition process, the breakdown of the gaseous envelope triggered micro-spark discharge; and the high energy plasma caused physical and chemical reactions, including complex electrochemical processes and high temperature phase transformation. For instance, the formation of hydrogen near the cathode basified the solution close to the cathode, facilitating the gel like hydroxides of Zr and Y, which were further sintered to ZrO_2-Y_2O_3 ceramic layer by the high energy released from the micro-spark plasma.

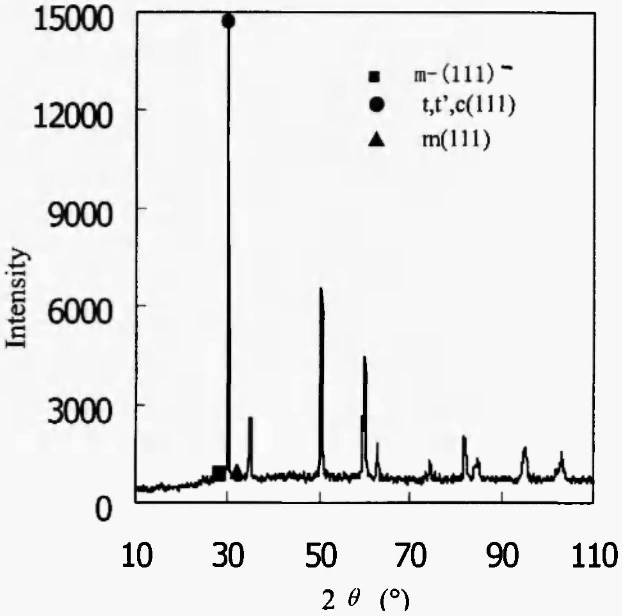

Fig. 6: XRD spectra of the as-deposited ZrO_2-Y_2O_3coating.

4.2 The thermo-chemical reactions and composition of ZrO_2-Y_2O_3 ceramics

In as-deposited ZrO_2-Y_2O_3 coating, the concentration of Y_2O_3 was below the content in the solution (Fig. 5), probably because the solubility of $Zr(OH)_4$ is smaller than that of $Y(OH)_3$. Thus the

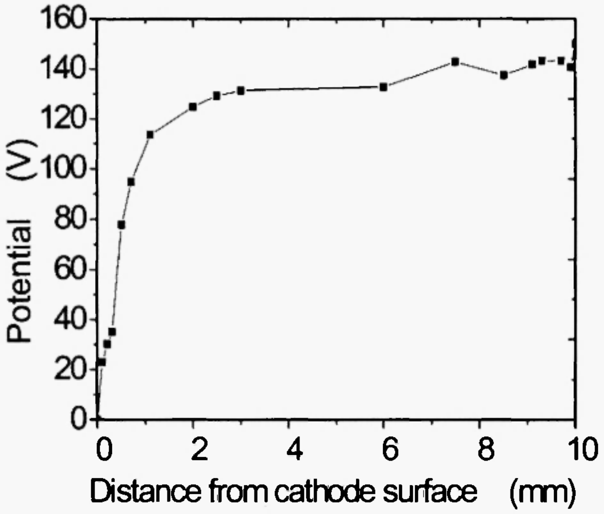

Fig. 7: Potential distribution between electrodes during cathodic micro-spark discharge process.

hydroxide coacervate formed near the cathode does not follow the original composition in the solution. Therefore, adjusting the ratio of [$Zr(NO_3)_4$] : [$Y(NO_3)_3$] in the solution may lead to ZrO_2-Y_2O_3 coatings with designed composition.

It is understood that the thermo-chemical reactions during the deposition and sintering processes are rather complex. Firstly, the high energy released from the spark converted the hydroxide into ZrO_2-Y_2O_3 ceramic coating. Secondly, the micro-spark caused thermo-chemical decomposition of $Zr(NO_3)_4$ and $Y(NO_3)_3$ in the solution, to form ZrO_2-Y_2O_3 directly. Thirdly, some ceramic coating may enter the solution as small particles due to the impact of the spark discharge; then the particles could be driven back to the cathodic surface and re-sintered into the oxide. Finally, the high temperature plasma generated by the micro-spark discharge could melt a part of the metal substrate, forming ZrO_2-Y_2O_3 ceramic coating containing small amounts of substrate elements, with strong metallurgical bonding to the substrate. The rapid cooling of the molten ceramics in the solution resulted in small crystalline microstructure of the coatings.

4.3 The thickness and uniformity of the coatings

The spark deposition mechanisms can be further discussed below. At the initial stage, the cathodic micro-spark was triggered by the discharge through the gaseous envelope. Once a layer of ceramic coating formed on the cathodic surface, the discharge mechanism would change from the gaseous envelope discharge to the breakdown discharge of the thin ceramic layer. The micro-spark usually occurred on the weak areas of the ceramic coatings and deposited more oxide on these areas, therefore increasing resistance at these positions. Then the micro-spark would move to other weak spots. This effect automatically moves the deposition to the thin coating areas, resulting in relatively thick and uniform ceramic coatings.

The above analysis showed that the CPED process does not restricted by the substrate metals. A variety of electrolytes may be deposited onto metal substrates to form ceramic coatings. Compared with the previous deposition techniques, CPED has the advantages of simple equipment, easy operation, and tailored coating composition and phase structure. These advantages make CPED process a potential technique for direct ceramic coatings on metal substrates. This technique deserves further investigation.

5. CONCLUSIONS

1. A novel coating technique, cathodic plasma electrolytic deposition (CPED), has been developed to produce ceramic coatings. ZrO_2-Y_2O_3 ceramic coatings with a thickness of ~60 μm were successfully produced on metal substrates.
2. The formation of ZrO_2-Y_2O_3 ceramic coating is the result of a series of complex physical and chemical reactions during the high energy plasma discharge processes. XRD analysis indicated that the ceramic coating is an yttria partially stabilized zirconia.
3. During the CPED processes, electric discharge under a voltage above the critical voltage generated cathodic micro-spark and plasma on the electrode surface. The high energy plasma decomposed the components in the solution to form a hydroxide coacervate, and sintered the coacervate into ZrO_2-Y_2O_3 coating.
4. This novel CPED technique can deposit various ceramic coatings on a wide range of metal substrates. Compared with other coating techniques,

CPED has the advantages of simple equipment, easy operation, tailored coating composition, and strong coating-substrate bonding. These advantages make CPED a promising technique for industrial applications.

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