Preparation of ZrO₂-Al₂O₃ micro-laminated coatings on stainless steel and their high temperature oxidation resistance①

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Abstract: Micro-laminated ZrO_2-Al_2O_3 coatings were prepared by electrochemical depositing ZrO_2 film and Al_2O_3 film alternatively in ethanol solutions containing aluminum nitrate and zirconium nitrate, with small amounts of yttrium nitrate added respectively into both solutions. The micro-laminated ZrO_2-Al_2O_3 coating is of nanostructure. FE-SEM analyses show that the cross section of the micro-laminated coatings has alternate six-layer films of ZrO_2 and Al_2O_3, with the thickness of each layer in the range of nanometer or submicron. The surface of the micro-laminated coatings is composed of nano-particles. SEM, XRD and mass gain measurement were adopted to study the oxidation resistance of coatings on stainless steel. It has been found that all the coatings are effective in protecting the substrate from oxidation, and micro-laminated coatings exhibit more excellent protectiveness performance. Mechanisms accounting for such effects have been discussed.

Key words: ZrO_2; Al_2O_3; micro-laminated coatings; electro-deposition; oxidation; stainless steel

CLC number: TG172.82   **Document code:** A

1 INTRODUCTION

In recent years, micro-laminated coatings with a great potential for applications have attracted considerable interest. The micro-laminated coatings can dramatically improve many properties including fracture toughness, fatigue behavior, impact behavior, oxidation resistance, hot corrosion resistance, etc[1]. It is evident that the formability, shape, and the fracture resistance of the coatings during forming and in service depend not only on the properties of the individual layers and their thickness ratio, but also on manufacturing techniques[2].

To date, many techniques have been developed to produce laminated composites, such as chemical vapor deposition(CVD), physical vapor deposition(PVD), electrophoresis, sol-gel and electro-deposition. Among these processes, the electro-deposition is an attractive method for the preparation of micro-laminated coatings since it is simple and inexpensive compared with CVD and PVD, etc. It is well known that electro-deposition methods can produce high quality metallic coatings, but it is rarely used to obtain oxide films. As early as 1993, HE et al[3−11] developed an electro-chemical method to prepare oxide coatings or films. That is, the thin oxide films were prepared by an electrochemical deposition-pyrolysis in an organic solvent containing small amounts of yttrium, aluminum, zirconium or chromium salts. Recently, Marinova et al also used this electrochemical deposition method to prepare ZrO_2[12, 13], La_2O_3[14], Al_2O_3[15] and CeO_2[16], and successfully deposited these oxide films on metal substrate in a non-aqueous electrolyte.

To improve the resistance against high-temperature oxidation and electrochemical corrosion of metals, the surface on which the corrosive agents act may be modified by ceramic films. Among the oxides, ZrO_2 and Al_2O_3 coatings have been extensively studied as barriers against oxidation on metal substrates. This is due to the fact that ZrO_2 has the advantage of a higher mechanical toughness and a thermal expansion coefficient close to those of many metals, and can act as reactive element. While Al_2O_3 has a high melting point, stability at high temperature and a very low solubility particularly in molten salt, and it is expected to show an excellent corrosion resistance. Some

reports have been dedicated to the study of corrosion protection of metals by ZrO_2 or Al_2O_3 coatings respectively, but few of them involved the use of micro-laminated coatings of ZrO_2 and Al_2O_3 on metals.

In the present study, an electrochemical method using a non-aqueous electrolyte was utilized for deposition of ZrO_2 and Al_2O_3 micro-laminated coatings on stainless steel. The oxidation and spallation resistance of the micro-laminated ceramic coatings were investigated, and mechanisms accounting for such effects were also discussed.

2   EXPERIMENTAL

An electrochemical deposition method was used to prepare micro-laminated oxide coatings on the sample surface. The concentrations of $Zr(NO_3)_4 \cdot 5H_2O$ + 8% (mass fraction, the same below if not mentioned) $Y(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ + 1% $Y(NO_3)_3 \cdot 6H_2O$ were both 0.1 mol/L respectively in ethanol solutions. The specimen acted as the cathode, and two platinum sheets(25 mm × 15 mm) were used as the anodes. The distance between the anodes and cathode was 15 mm. The applied current density was about 0.005 A/cm^2 via adjusting voltage, the deposition time was 20 to 90 s, and a post-heat treatment for each run was performed in air at 300 ℃ for 30 min. This process was alternately repeated up to a desired times. In order to compare the oxidation resistance of laminated coatings with that of non-laminated coatings, the deposition conditions of each layer should be the same.

The stainless steel has a composition (mole fraction) of 19.8% Cr, 9.08% Ni, 0.37% Ti, and 70.75% Fe. The specimens were cut to a size of 15 mm × 10 mm × 2 mm. All surfaces of the specimens were ground to 1 500 grit SiC paper, followed by ultrasonic cleaning with alcohol and deionized water.

High temperature oxidation of the specimens was carried out in a horizontal furnace at 900 ℃ in air for 100 h. The specimens were placed in quartz crucibles, which had been heated to a constant mass. After a certain time period of oxidation, mass gains were weighed using an electronic balance with an accuracy of 10^{-5} g. Oxidation kinetic curves were plotted separately by using the mass gains and spallation mass of the specimens vs time.

The cross sections and surfaces of the micro-laminated oxide coatings were characterized with a high-resolution FE-SEM (Phillips XL-30). The composition and phases of the oxide scales formed by oxidation at 900 ℃ for 100 h were analyzed by EDS and XRD. The surface morphology of the oxide scales after oxidation at 900 ℃ for 100 h was observed using SEM.

3   RESULTS

Fig. 1(a) shows the FE-SEM cross section micrograph of ZrO_2 and Al_2O_3 micro-laminated coatings on substrates heated at 600 ℃ in air for 1 h. The alternate six-layer coatings of ZrO_2 and Al_2O_3 are observed clearly and the thickness of each layer is in the range of nanometer or submicron. Fig. 1(b) shows the FE-SEM surface micrograph of ZrO_2 and Al_2O_3 micro-laminated coatings on substrates heated at 600 ℃ in air for 1 h. The coatings are composed of nano-particles, in which a few micro-holes are observed. The sizes of particles by electro-deposition method are almost the same as that of particles obtained by sol gel technique[17], but electro-deposition coatings are denser than sol gel coatings.
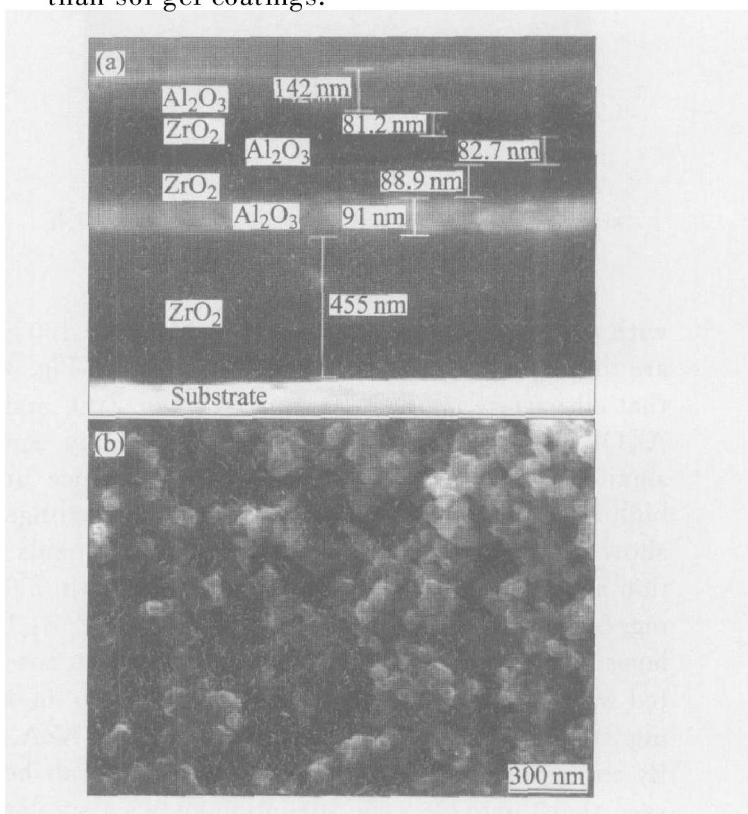

Fig. 1   FE-SEM micrographs of ZrO_2 and Al_2O_3 micro-laminated films on substrates heated at 600 ℃ in air for 1 h
(a) —Cross section; (b) —Surface

Fig. 2 shows the morphologies of the outer surface of the stainless steels with coated two-layer and six-layer ZrO_2 and Al_2O_3 micro-laminated coatings heated at 600 ℃ in air for 1 h. The coatings of two layers present cracks on the surface, while the coatings by six depositions are homogeneous and continuous. Therefore, six-layer coatings are chosen as the criterion of oxidation resistance experiment.

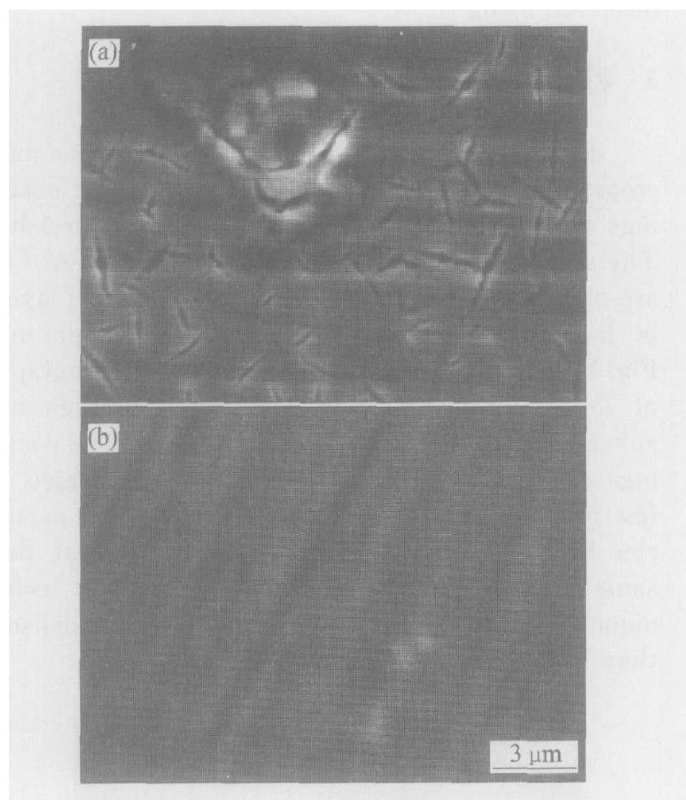Oxidation kinetics of stainless steel substrates

Fig. 2 SEM micrographs of ZrO_2 and Al_2O_3 micro-laminated coatings on stainless steel heated at 600 ℃ in air for 1 h
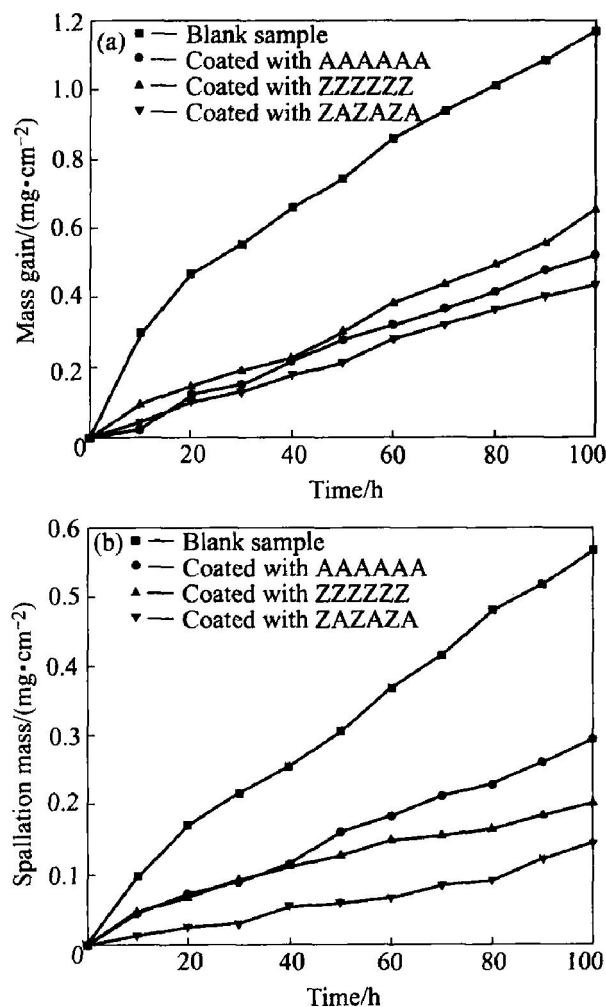
(a) —Two layers; (b) —Six layers

Fig. 3 Oxidation kinetics of stainless steel substrates with and without coatings at 900 ℃ in air for 100 h

(Z: 1 ZrO_2 layer; A: 1 Al_2O_3 layer)

(a) —Mass gain vs time;

(b) —Oxide spallation vs time

with and without coatings at 900 ℃ in air for 100 h are illustrated in Fig. 3. It can be seen from Fig. 3 that all surface-applied ZrO_2, Al_2O_3, or ZrO_2 and Al_2O_3 micro-laminated coatings on the alloy can significantly improve the oxidation resistance at high temperature. The specimen without coatings show a mass gain of about 1. 2 mg/ cm² after oxidation at 900 ℃ in air for 100 h, compared with 0. 6 mg/ cm² for the specimen coated with ZZZZZZ(Z: 1 layer of ZrO_2), 0. 5 mg/ cm² for the specimen coated with AAAAAA (A: 1 layer of Al_2O_3), 0. 4 mg/ cm² for the specimen coated with ZAZAZA. By comparing Fig. 3(a) with Fig. 3(b), it can be seen that the oxide scale spallation shows a similar trend as the mass gain, that is, the large mass gains correspond to the large-scale spallation.

SEM surface morphologies of the oxide scale after oxidation at 900 ℃ in air for 100 h are shown in Fig. 4. The alloy without coatings shows a rough surface with two different areas, the bright area and dark area as shown in Fig. 4(a). In the bright area, the oxide scale is mainly composed of Cr and Fe oxides, the dark areas are holes and pores, indicating that the scale has broken away. The specimen with ZrO_2 and Al_2O_3 micro-laminated coatings shows uniform scale morphology with no obvious spallation, as observed in Fig. 4(b). The specimens with ZrO_2 (Fig. 4(c)) or Al_2O_3 (Fig. 4(d)) coatings also show scales spallation to a cer-

tain degree. The leaf-like areas in Fig. 4(c) are Zr rich oxide.

Fig. 5 shows the XRD spectra of the four specimens with and without coatings after oxidation at 900 ℃ in air for 100 h. It is shown that the oxide scales formed on the uncoated alloy are mixed Fe and Cr oxides. EDS analysis shows that the mass ratio of Cr to Fe for the specimens uncoated is 1. 1, the mass ratio of Zr to Al and Fe for the specimens coated with ZrO_2 and Al_2O_3 micro-laminated coatings is about 4∶2∶1, the mass ratio for the specimens coated with ZrO_2 is about 3∶3∶1, and the mass ratio of Al to Cr and Fe for the specimens coated with Al_2O_3 is about 3∶2∶1, respectively. These results can be explained as that the sample coated with ZAZAZA six-layer coatings has no oxide spallation during oxidation at 900 ℃, so it still maintains the compositions of the original coatings. Since the diffusion velocity of Fe in alloy is faster than that of Cr in the alloy, there is a small
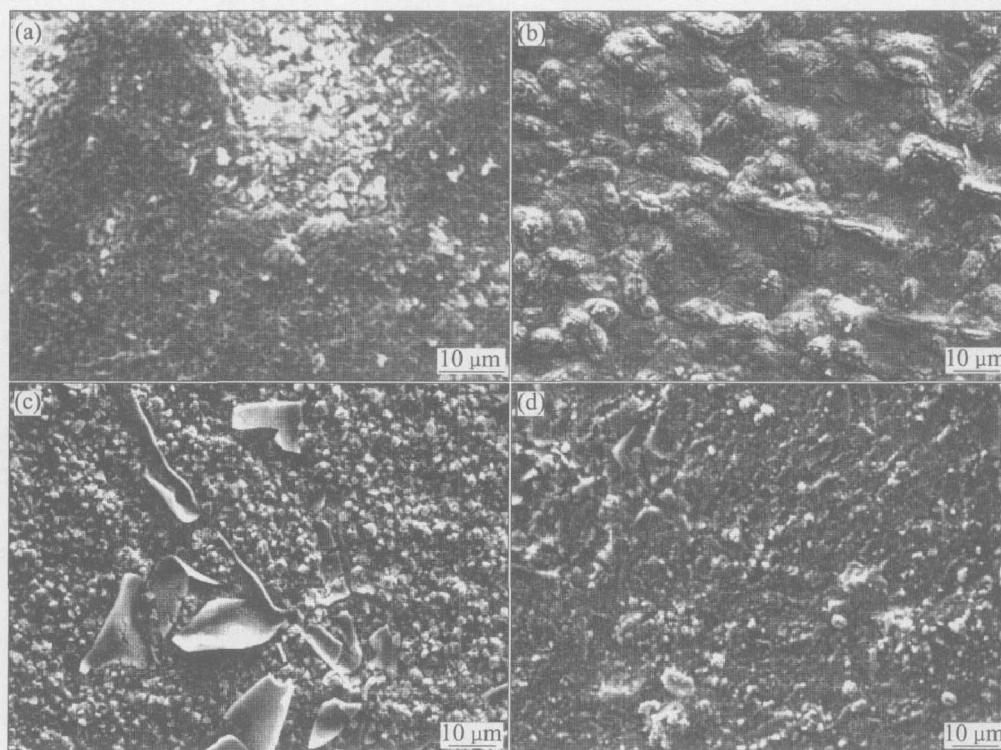
Fig. 4 SEM surface morphologies after oxidation at 900 ℃ in air for 100 h
(a) —Blank sample; (b) —Coated with ZAZAZA; (c) —Coated with ZZZZZZ; (d) —Coated with AAAAAA
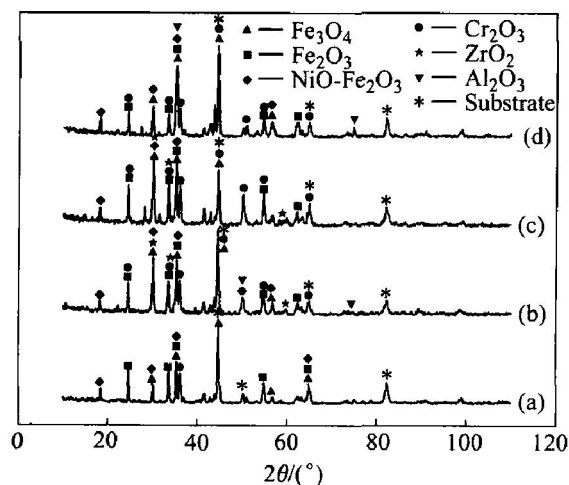

Fig. 5 XRD spectra of specimens after oxidation at 900 ℃ in air for 100 h
(a) —Blank sample; (b) —Coated with ZAZAZ;
(c) —Coated with ZZZZZZ; (d) —Coated with AAAAAA

quantity of Fe diffusing into surface. As to the samples coated with ZZZZZZ or AAAAAA, because they partially have oxide spallation, subjacent oxide films containing a large amount of Cr are exposed to surface; consequently, a lot of Cr can be detected by EDS spectrum. However, the Fe content of the surface of samples coated with ceramic coatings is very low, compared with the blank sample.

4   DISCUSSION

Micro-laminated coatings on stainless steel exhibit most excellent protection effect. Mechanisms accounting for such effects are discussed as follows.

4. 1   Synergic effects of ZrO₂ and Al₂O₃

The micro-laminated coatings can make use of the characteristics of ZrO₂ and Al₂O₃, respectively. Al₂O₃ (containing trace yttrium) layer on the alloy surface have a positive influence on the oxidation and spallation resistance[6]. This layer can decrease the inward transport of oxygen to a certain degree, thereby reduce the oxidation rate. However, Al₂O₃ layer may still spall at high temperature for a long time, because of thermal stress between the layer and alloy substrate, which is corresponding to the sample coated with AAAAAA as shown in Figs. 4 and 5. As to ZrO₂ (containing trace yttrium) layer, owing to both Zr and Y are reactive elements, applied ZrO₂ thin films on alloys containing Cr can promote the selective oxidation of Cr in alloys and enhance the adhesion between the oxide scale and the alloy. These properties are beneficial to enhancing the oxidation resistance of the alloy. But in another aspect, ZrO₂ is a good oxygen ion conductor, which should restrict the ability for ZrO₂ films to resist the oxidation of alloy imperfectly. This result is corresponding to the sample coated with ZZZZZZ as shown in Figs. 4 and 5.

When a combination of Al₂O₃ layers with ZrO₂ layers is in micro-laminated coatings on speci-

mens, the oxidation resistance of the specimens can be improved greatly. From Figs. 4 and 5, compared with samples coated with AAAAAA or ZZZZZZ, the mass gain and oxide spallation mass of the sample coated with ZAZAZA are less, and no evidence of spallation is observed. This is probably due to the fact that the thermal expansion coefficient of ZrO_2 is very close to those of many metals or alloys, and suitable to act as intermediate layer, while Al_2O_3 is a very good diffusion barrier material, and suitable to act as top layer in micro-laminates. When micro-laminates are designed as a form of ZAZAZA ···, advantages of ZrO_2 and Al_2O_3 can complement, that is, ZrO_2 can make the best of enhancing the adherence between coatings and substrates and preventing crack initiation, while Al_2O_3 can make the best of preventing diffusion of substrate species into coatings or vice versa during annealing and enhancing corrosion protection of coating and substrate, so the micro-laminated coatings of ZrO_2 and Al_2O_3 can significantly improve the oxidation resistance of the alloys.

4. 2　Effects of micro-laminated coatings

Micro-laminated ceramic coatings with a great potential for applications in the near future may be one of the most effective ways to toughen ceramics. From Fig. 2, we can see that the thickness of each layer is in the range of nanometer or submicron in the laminated ceramic coatings. The layer spacing is so small that the defects size and dislocation movement can be effectively suppressed by a large number of interfaces in micro-laminated ceramic coatings. Consequently, the properties of the micro-laminated ceramic material are superior to those of appropriate single material. In deed, the micro-laminated ceramic coatings are more effective in resisting oxidation of stainless steel substrates at high temperature.

Two dominant ceramic toughening mechanisms, crack deflection and crack blunting, are shown schematically in Fig. 6[18]. In many laminated systems, layer de-lamination can occur ahead of an advancing crack or as the result of a crack encountering an interface. These local de-laminations can result in crack deflection, which can significantly reduce the local stress intensity because of the large deviation in crack path. Crack blunting can be a result of propagating crack encountering a ruptured region or a large and hard particle. Further crack growth requires re-nucleation of the crack in the micro-laminated ceramic layer. This arresting and re-nucleation process results in a significant increase in the amount of energy required for crack growth. Consequently, micro-laminated ceramic materials can dramatically improve many

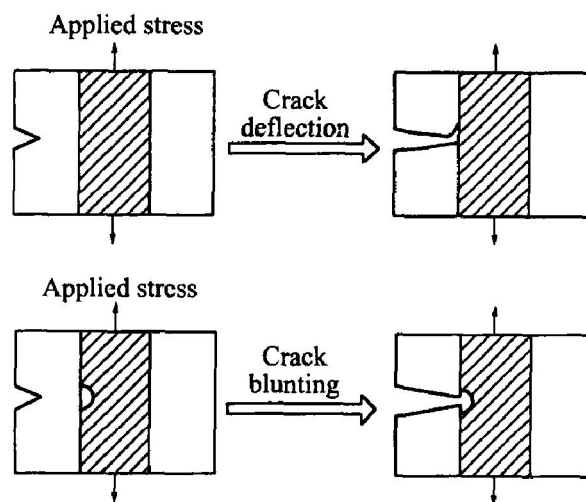properties including fracture toughness, corrosion resistance, etc.

Fig. 6　Schematic diagram of toughening mechanisms for micro-laminated composites

4. 3　Effects of nano-composites

From Fig. 2, the micro-laminated coating surfaces are composed of nano-particles, so the effects of nano-composites cannot be ignored, either. According to Refs. [19, 20], nano-phase can enhance the adherence between ceramic coatings and alloy substrates, more effectively peg cracks and prevent crack initiation, resist high flux of heat into substrates, promote the outwards diffusion of the solute element in the alloy and reduce the critical content required to form a selective oxide scale. Therefore, nano-composite coatings are effective in resisting the oxidation of the alloys at high temperature.

5　CONCLUSIONS

1) The micro-laminated ceramic coatings are prepared using electrochemical deposition. FE-SEM analyses show that the cross section of the micro-laminated coatings is composed of alternate six-layer coatings of ZrO_2 or Al_2O_3, and the thickness of each layer is in the range of nanometer or submicron. The surface of the micro-laminated coatings is composed of nano-particles.

2) The micro-laminated coatings of ZrO_2 and Al_2O_3 show excellent protectiveness to stainless steel at high temperature, which is superior to that of coatings of only single ZrO_2 or Al_2O_3.

3) The relevant mechanisms of the excellent performance of the micro-laminated ceramic coating may be that the layer spacing is so small that the defects size and dislocation movement can be effectively suppressed by a large number of interfaces in micro-laminated ceramic coatings. Consequently, the properties of the micro-laminated ceramic ma-

terial are superior to those of single material.

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(Edited by LONG Huai-zhong)