ZrO_2 and ZrO_2-Y_2O_3 coatings deposited by double pulsed plasma arc

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Abstract **A novel surface technique has been developed to produce ZrO_2 and ZrO_2-Y_2O_3 coatings on the surface of alloys by using double pulsed plasma arc to react with a solution film containing nano-oxide particles. These coatings exhibit smooth surface and excellent adhesion with substrate. The morphologies of the ceramic coatings and phases were analyzed. It was shown that the oxidation resistance of l8-8 stainless steel was markedly improved by applying ZrO_2 and ZrO_2-Y_2O_3 coatings.**

Keywords: double pulsed plasma arc, ceramic coatings, high temperature oxidation.

Ceramic coatings have the advantages of high melting point, high hardness, good insulation, good chemical stability. There are two types of techniques that are generally used to produce ceramic coatings: physical methods and chemical methods. People are interested in their combinations to develop new and more efficient coating techniques including, for example, EPVD, LICVD or micro-arc oxidation deposition[1,2].

In the present study, a novel technique has been developed to produce ZrO_2 and ZrO_2-Y_2O_3 coatings on the surface of metals by using double pulsed plasma arc to react with a solution film containing nano-oxide particles. The characteristics of the coatings and behavior of high temperature oxidation of stainless steel deposited by such coatings will be studied.

1 Experimental methods

Fig. 1 is a schematic drawing which shows the ceramic coating deposited by double pulsed plasma arc to react with a solution film containing nano-oxide particles. The system to deposit ceramic coating consists of a pulse power source, two Zr electrodes which are located over the surface of solution film and moved into two dimensions controlled by a computer. When the distance between the tips of two electrodes and the surface of solution film is close enough, a serial discharge happens at the two gaps between the tips of Zr electrode 1 and 2, and the solution surface respectively. By this way, double pulsed plasma arc can be produced on the solution surface. High energy produced in these double pulsed plasma arc can make the nano ceramic particle in solution deposit on the surface of alloys and sinter together to form ceramic coatings.

The material was 1Cr18Ni9Ti with a size of 10 mm × 25 mm × 2.5 mm. The surface of sample was ground to 600 grit SiC finish, cleared in acetone. The electrode was an industrial pure Zr wire with a diameter of l mm. Sample 1 was covered with 0.003 mol/L ZrO_2 nano-particle solution, and sample 2 was covered with 0.003 mol/L ZrO_2 nano-particles + 0.003 mol/L $Y(NO_3)_3$ solution, in which $[Zr^{4+}]:[Y^{3+}]=9:1$.

Cycling oxidation was carried out in air at 1000℃ and room temperature to assess the high temperature oxidation resistance. The samples were weighted after intervals by an electron analysis balance whose accuracy was 0.1 mg.

X-ray diffraction (XRD) was used to identify the crystal structures of the ceramic coatings. Scanning electron microscopy (SEM) was used to observe the morphologies of the ceramic coatings and the oxide scales. Energy dispersive spectroscopy (EDS) was used to determine the chemical compositions of the sample surface after oxidation.

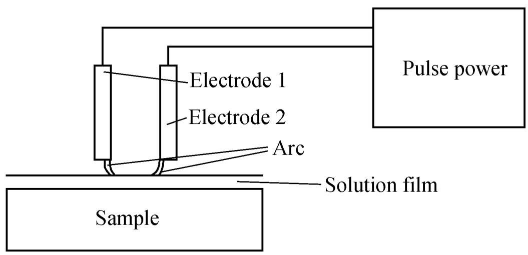

Fig. 1. Schematic drawing of the system producing ceramic coating.

2 Experimental results

Fig. 2(a) and (b) show the surface morphologies of ceramic coatings deposited on samples 1 and 2 respectively. It can be seen that the ceramic coatings deposited on sample 1 is pretty uniform and its grain size is about 200 nm. But there are many micro-cracks in the ceramic coatings deposited on sample 2. These experimental results, perhaps, can be attributed to the difference of solutions in both cases. It is reasonable to assume that ceramic coating could be produced by double pulsed plasma arc to react with a solution film containing nano oxide particles more easily than that containing ions.

Fig. 3 shows the oxidation kinetic curves for 1Cr18-Ni9Ti samples coated with ZrO_2 and ZrO_2+Y_2O_3. 1Cr18Ni9Ti sample was also oxidized for comparison. The oxidation tests were performed at 1000℃ in air. It can be seen that the oxidation resistance of 1Cr18Ni9Ti alloy is effectively improved by depositing ZrO_2 and ZrO_2+Y_2O_3 coatings. The mass gains of samples 1 and 2 were reduced by factors of 3.6 and 3, and the amounts of scale spallation were decreased by factors of 26 and 20 respectively.

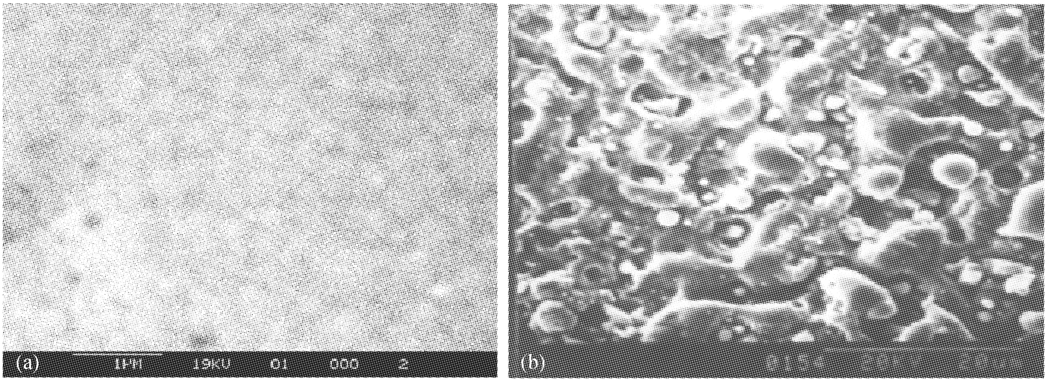

Fig. 2. SEM images of ceramic coatings on sample 1 (a) and sample 2 (b).

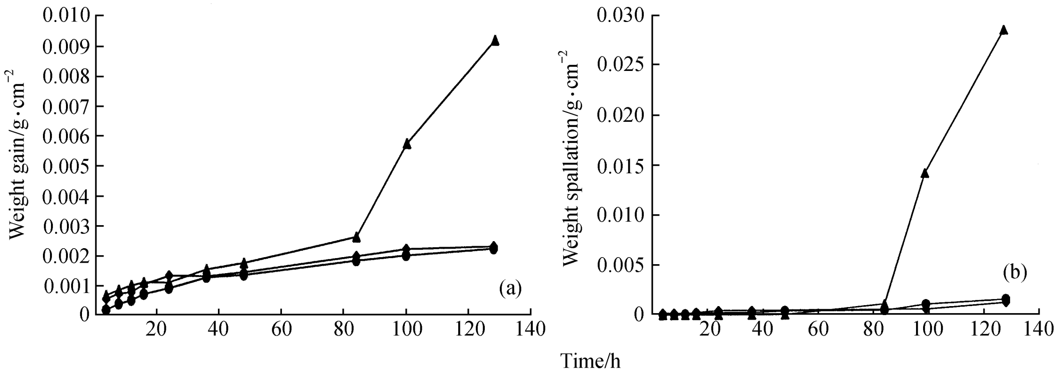

Fig. 3. The weight gain curves (a) and weight spallation curves (b) for three samples. ●, Sample 1; ◆, sample 2; ▲, 1Cr18Ni9Ti sample.

Table 1 EDS analysis on the surface of samples 1 and 2 after oxidation at l000℃

Sample	Fe (at.%)	Cr (at.%)	Ni (at.%)	Ti (at.%)
1Cr18Ni9Ti	55.36	29.94	14.71	—
1	3.45	5.87	0.28	—
2	3.63	10.50	0.38	0.28

The EDS analyses on the sample surfaces after oxidation are listed in table 1. Compared with the stainless steel sample, the ratio of Cr to (Cr + Fe + Ni) on the surfaces of samples 1 and 2 increased from 30% to 61% and 71%, indicating that the selective oxidation of Cr in the stainless steel was promoted by depositing ZrO_2 and $ZrO_2+Y_2O_3$ coatings.

The result of X-ray diffraction for the coating proves that the phase structure of coating on sample 1 is monoclinic and has cubic ZrO_2, the coating on sample 2 has not only cubic ZrO_2, but also cubic ZrO_2-8%Y_2O_3 and monoclinic ZrO_2, which, due to the expansion of the volume, decreased the combining force of coating with substrate[3].

3 Discussion

A technique to prepare ceramic coatings by use of the pulsed plasma arc has been invented in 1998[4]. However, the explosive role produced by pulsed plasma arc may blow away the solution film on the alloy surface and even the deposited layer, which is not beneficial to obtaining a uniform and thick coating. In the present research, it was proved that double pulsed plasma arc has a tendency to avoid the solution to be blown away in the middle of the double pulsed plasma arc. Therefore, the rate to deposit ceramic coating can increase effectively. Another reason can attribute to the characteristics of the solution film containing nano oxide particles, which is easy to adhere to the surface of alloy and improve the adhesion of coating with alloy.

The improvements of the oxidation resistance were caused by the promotion of selective oxidation of Cr in the steel. Zr and Y in ceramic coatings played the reactive element role in the oxidation process, which changes the mechanisms of the diffusion of metal ions in the oxide scales, and improves the adhesion of the oxide scales with the substrates.

4 Conclusion

A novel surface technique has been developed to produce ZrO_2 and ZrO_2-Y_2O_3 coatings on the surface of alloys by using double pulsed plasma arc to react with a solution film containing nano-oxide particles. These coatings exhibit smooth surface and excellent adhesion with substrate. These results can attribute to the characteristics of double pulsed plasma arc and solution film containing nano oxide particles. It was shown that the oxidation resistance of l8-8 stainless steel was markedly improved by applying ZrO_2 and ZrO_2-Y_2O_3 coatings. This result can attribute to the reactive element effect in the oxidation process.

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