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Corrosion resistance of Al_2O_3 coating on a steel substrate

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An Al_2O_3 coating on a A3 steel substrate was prepared by sol-gel method with Al powder, $Al(NO_3)_3$, and $NH_3{\cdot}H_2O$ as raw materials. To understand the influence of the Al powder, the sintering temperature and the sol viscosity on the corrosion resistance of Al_2O_3 coatings, the corrosion behaviors were investigated in HCl, NaOH and NaCl aqueous solutions. The results indicate that the corrosion resistance of the coating, made by adding Al powder during the process, is better, and Al_2O_3 coatings corroded in NaOH solution more than in HCl. The corrosion-resistance of the coating enhances with the increase of the sintering temperature and the sol viscosity.

Key words: Sol-gel method, Al_2O_3 coating, Al powder, Corrosion resistance.

Introduction

Corrosion is a widespread phenomenon in the use of metals. In the world annual production of metal about 10% of the metal product has to be scrapped due to corrosion. The loss caused by corrosion of industrial machines is far more than the cost of the metal. A thin coating of $A1_2O_3$ has excellent optical properties, high mechanical strength and hardness, good transparency and insulation, wear resistance, corrosion resistance and is chemically inert. So in the last several decades, α-Al_2O_3 coatings [1-4] and doped-Al_2O_3 coatings, such as electrolytic Al_2O_3/ZrO_2 two layer coatings [5-6], Ni/Al_2O_3 composite coating [7] and Fe/Al_2O_3 coatings [8], have been under investigation for their possible use as protective coatings against high-temperature oxidation, corrosion. For example, Hawthorne *et al.* [9] made an Al_2O_3 coating by adding Al_2O_3 powder into an Al_2O_3-sol, which had superior anti-corrosion properties.

The sol-gel process has become one of the most successful techniques for preparing nano-crystalline metallic oxide materials, which has many advantages, such as easy control of composition and fabrication of large area coatings, coating homogeneity, low processing temperature, low cost, and a simple fabrication cycle. In the present study, Al_2O_3 coatings were produced from a boehmite sol, to which was added Al powder in the preparation process. To understand the influence of the Al powder, sintering temperature and sol viscosity on the corrosion resistance of Al_2O_3 coatings, the corrosion of samples was investigated in 2 M HCl, 2 M NaOH, and 2 M NaCl aqueous solutions.

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Experimental

Preparation

The preparation procedure was as follows: First, $Al(NO_3)_3$ (1.0 M, 50 ml) was prehydrolyzed with 0.15 molar $NH_3{\cdot}H_2O$ at 85 °C. Then HNO_3 (0.01 mol) and PVA (20 ml, 3 wt%) were added. After 0.5 hour, Al powder was added and dispersed in the solution, then continuously stirred for another 12 hours to obtain a transparent sol. Second, the A3 steel was prepared though polishing and cleaning. The coating layer was prepared with the sol on the A3 steel substrates. Lastly, the samples were dried at room temperature and sintered at 400 °C, 500 °C and 600 °C for 2 hours.

Experimental measurement and characterization

The corrosion resistance of coated substrates was investigated at room temperature in 2 M HCl, 2 M NaOH, and 2 M NaCl aqueous solution. The corrosion rate of the coatings, which is the rate of weight loss, was calculated by comparing its mass with an electronic balance (sensitivity 0.1 mg) before and after immersion. Thus the corrosion rate of the coatings could be calculated.

The Al_2O_3 obtained was characterized by X- ray powder diffraction, using a D8 DISCOVER X- ray diffractometer with Cu K_α radiation ($\lambda = 0.154184$ nm) from 20° to 63° in 2θ, operating at 40 kV and 100 mA. Also the sol viscosity was determined by a NDJ-8S digital viscometer. A QUANTA200 FEI scanning electron microscope was used to observe the surface morphology of the corroded samples.

Results and Discussion

The influence of doping Al powder

Fig. 1 shows X-ray diffraction pattern of the powder prepared from the xerogel. Unlike a conventional boehmite sol, Al powder was added in the sol preparation process. It is

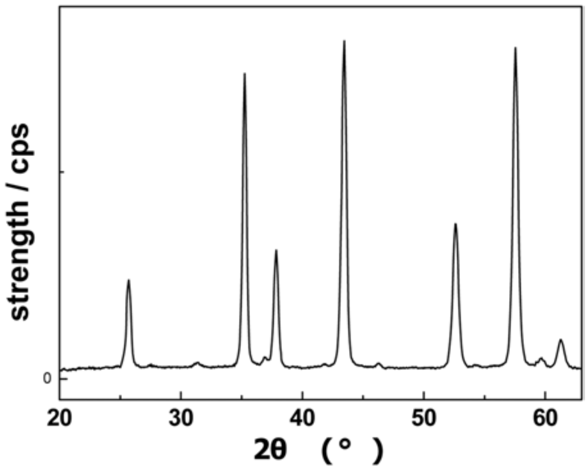


Fig. 1. XRD pattern of Al_2O_3 power.

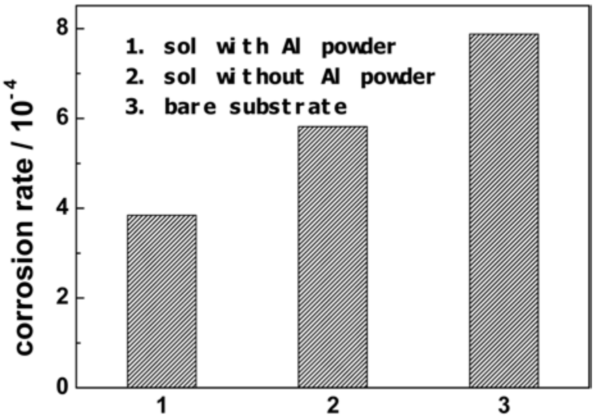


Fig. 2. The corrosion rate of samples.

clear that all the diffraction peaks in the pattern can be identified as from the Al_2O_3 phase, which is consistent with the literature [10].

Fig. 2 shows the corrosion rate of three samples immersed completely into boiling 2M HCl for 10 minutes. Sample 1 is the A3 steel substrate coated with the sol with Al powder, sample 2 is without the Al powder, and sample 3 is the bare substrate. This clearly indicates that the Al_2O_3 coating can enhance the corrosion resistance of the A3 steel substrate, and the coating with Al powder performs better.

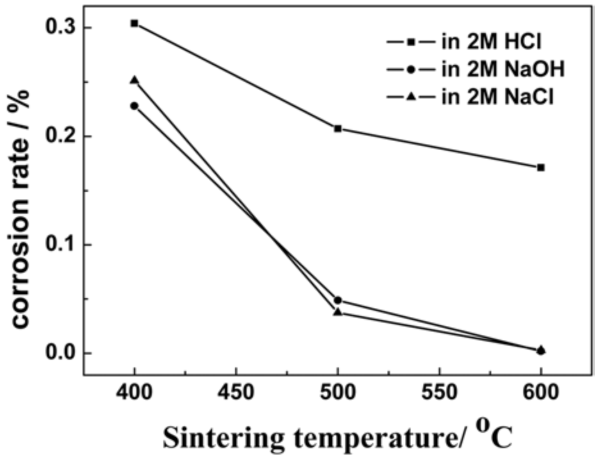


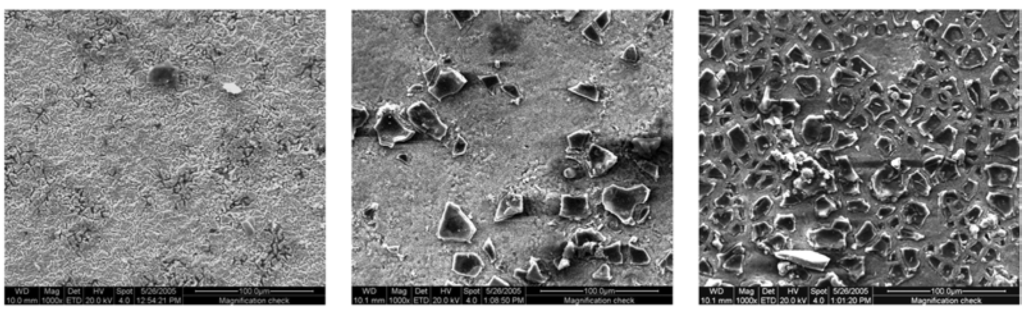
Fig. 3. The corrosion rate of the coatings.

The influence of the sintering temperature

As discussed above, the corrosion resistance of Al_2O_3 with the Al powder is better, so all the following coatings were produced with the sol with added Al powder. Fig. 3 shows the corrosion rate of the samples in 2 M HCl, 2 M NaOH and 2 M NaCl, which were sintered at various temperatures. The evidence is that the coating performed better in an alkaline solution than in an acid. Also the corrosion resistance of the coating improved with an increase of the sintering temperature. In 2 M NaOH, the weight loss of the samples, sintered at 400 °C, 500 °C and 600 °C, was 0.228%, 0.0489% and 0.002%, respectively. The same trends were achieved in 2 M HCl, and 2 M NaCl.

Ceramic calcination is a material densification process. A moderate sintering temperature and holding time can increase the grain size and bulk density, decrease the porosity, which is helpful in improving the strength of the coatings and the corrosion resistance of the metal substrate. This is the reason that the Al_2O_3 coating sintered at a higher temperature gives superior anti-corrosion properties.

Fig. 4 shows the corrosion of Al_2O_3 coatings sintered at 600 °C in the corrosive media of HCl, NaOH, and NaCl. The corrosion resistance of the surface corroded in NaOH is better than that in HCl. In particular in HCl,



a. corroded in HCl   b. corroded in NaCl   c. corroded in NaOH

Fig. 4. SEM of the corrosion of Al_2O_3 coatings sintered at 600 °C.

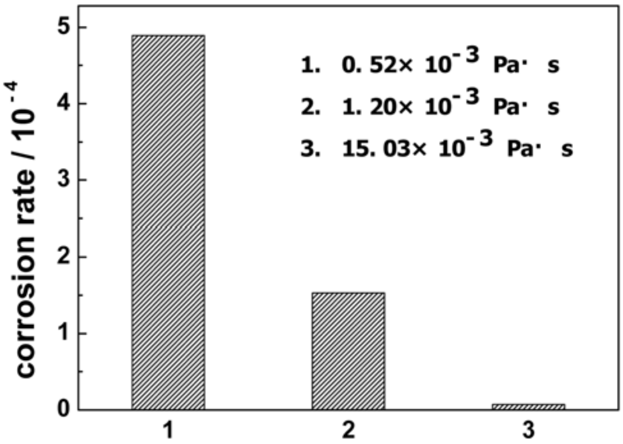
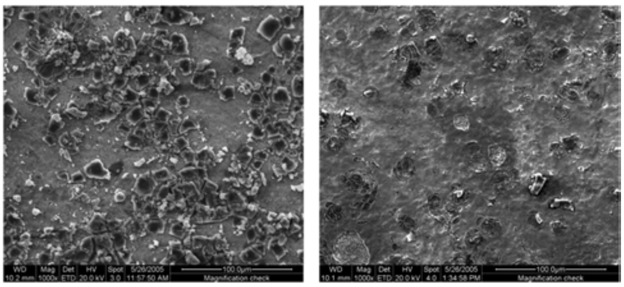


Fig. 5. The corrosion rate of the coatings coated by sol with different viscosity.



a. sol viscosity: 0.52×10^{-3}Pa·s b. sol viscosity:15.03×10^{-3}Pa·s

Fig. 6. SEM of the coatings corroded in NaOH.

all of the coating dissolved into the corrosive solution and the substrate was seriously corroded.

The influence of the sol viscosity

To clarify the influence of sol viscosity on corrosion, coatings coated by sols with different viscosities were evaluated. From Fig. 5, it can be seen that the weight loss decreases with an increase in the sol viscosity.

Fig. 6 shows the surface morphologies corroded in NaOH. For the Al_2O_3 coating formed from a low glutinous sol, corrosion cracks and dissolution were apparent. Comparatively, the coating, shown in Fig. 6 (b), is nearly intact except for a few pits, and it exhibits excellent protection for steel against corrosion. It is commonly concluded that the corrosion resistance improves with an increase in the viscosity of the sol. But if the sol viscosity is too high, it will tend to flake off, and even not form a continuous Al_2O_3 coating, as pointed out by Zhang [11], which will be investigated in another project.

Conclusions

The following conclusions may be drawn from the present study:

(1) Using the sol-gel method, a boehmite sol and Al_2O_3 coating can be obtained with $Al(NO_3)_3$, Al powder, and $NH_3{\cdot}H_2O$ as raw materials.

(2) By adding Al powder, the Al_2O_3 coating was more corrosion resistant.

(3) The corrosion resistance of the coating improved with a increase of the sintering temperature and the sol viscosity, and the coating performs better in an alkaline medium and a neutral medium than in an acidic medium.

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