Electrodeposition and characterization of Ni–W/ZrO₂ nanocomposite coatings

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Abstract. Ni–W/ZrO₂ nanocomposite coatings were prepared by electrodeposition in Ni–W plating bath containing ZrO₂ nanoparticles. The influences of preparation parameter, such as ZrO₂ nanoparticles concentration, current density and stirring rate, on weight percentage of codeposited ZrO₂ nanoparticles in the nanocomposite coatings were investigated. The surface morphology of Ni–W/ZrO₂ nanocomposite coating was characterized by scanning electron microscopy (SEM). The microhardness, wear resistance and corrosion resistance properties of Ni–W/ZrO₂ nanocomposite coatings were studied. The results indicated that the addition of ZrO₂ nanoparticles leads to an increase in microhardness and wear resistance of the nanocomposite coatings and a reduction in the wear weight loss. The corrosion behaviour of Ni–W/ZrO₂ nanocomposite coatings was evaluated by the anodic polarization curves and weight loss measurements. The results revealed that Ni–W/ZrO₂ nanocomposite coating has better corrosion resistance than the Ni–W alloy coating.

Keywords. Electrodeposition; Ni–W/ZrO₂ nanocomposite coatings; microhardness; wear resistance; corrosion resistance.

1. Introduction

The composite coatings of metal and alloy have been developed for improved material properties with regard to corrosion resistance, wear resistance, high temperature stability and high microhardness (Aal *et al* 2006; Krishnaveni *et al* 2008; Robin *et al* 2011). Electrodeposition is one method to produce metal and alloy matrix composite coatings. Nanocomposite coatings can be formed by the addition of nanoparticles into the metal and alloy matrix. The nanoparticles used, as reported in the literature, include SiC, Al₂O₃, TiO₂ and CNTs (Sharma *et al* 2006; Chen and Gao 2010; Hu *et al* 2010; Saha and Khan 2010; Allahkaram *et al* 2011; Hou and Chen 2011). The co-deposition of the nanoparticles with metal and alloy phases to form nanocomposites can bring a remarkable improvement on physical and chemical properties of the coatings.

The electro-codeposited Ni–W alloy coating has been of considerable interest for its excellent microhardness, wear and corrosion resistance even at high temperature, and the preparation process is in accordance with the consideration of environmental protection. It can therefore become a good substitute for hard chromium, so that there are many reports on the procedures, structures and properties of Ni–W alloy in recent years (Chianpairot

et al 2011; Panagopoulos *et al* 2011; Arunsunai Kumar *et al* 2012; Beltowska-Lehman *et al* 2012; Wang *et al* 2012).

In this study, Ni–W/ZrO₂ nanocomposite coatings were prepared by the electrodeposition in a nickel–tungsten plating bath containing ZrO₂ nanoparticles. The effect of preparation parameters, such as the concentration of ZrO₂ particles in the plating bath, current density and stirring rate, on the weight percentage of ZrO₂ nanoparticles codeposited in the composite coatings, were evaluated. The surface morphologies, microhardness, wear resistance and corrosion resistance properties of Ni–W/ZrO₂ nanocomposite coatings also were investigated.

2. Experimental

The plating bath is composed of 20 g L^{−1} NiSO₄·6H₂O, 30 g L^{−1} Na₂WO₄·2H₂O, 60 g L^{−1} citric acid and ZrO₂ nanoparticles from 2.5 to 10 g L^{−1} at pH 6 adjusted by the addition of ammonia. The insoluble Ir–Ta oxide electrode was used as an anode. The cathode was the copper sheet of 50 mm × 40 mm × 5 mm. The substrates were sequentially ultrasonically cleaned in acetone for 10 min, rinsed with 5% H₂SO₄, washed in distilled water, and then immersed immediately in the plating bath. Prior to plating, the ZrO₂ nanoparticles of a mean diameter 50 nm were dispersed in the electrolyte in the presence of sodium dodecyl sulfonate. The operating conditions for plating

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were current density ranging from 6 to 18 A dm⁻², stirring rate from 60 to 240 rpm and a bath temperature of 60 °C.

The surface morphology and the components of Ni–W/ZrO₂ nanocomposite coatings were studied by using a scanning electron microscope (SEM, TS5136) with energy dispersive analyser system (EDX). Vickers microhardness tests were conducted on a DUH-W201 microhardness tester using a load of 50 g, applied for 10 s. The wear resistance test was carried out with a P-200 abrasion device under a load of 50 N and a rotating speed of 400 rpm for 2.5 h. Each microhardness value was the average of five measurements.

A conventional three-electrode cell was used to conduct the electrochemical experiments. The counter electrode was platinum electrode and the reference electrode was a saturated calomel electrode (SCE). The working electrode was Ni–W alloy and Ni–W/ZrO₂ nanocomposite coating with an expressed area of 1 cm². Electrolyte solutions were prepared with analytical grade reagents and distilled water. Electrochemical measurements were conducted at 25 °C using CHI 660D electrochemical workstation. The anodic polarization curves in 30 wt% NaOH solution were measured through linear potential scan by scanning the potential at 1 mV s⁻¹. All of the measurements were carried out at room temperature. Each electrochemical experiment was repeated three times to verify the reproducibility of experimental results.

The Ni–W alloy and Ni–W/ZrO₂ nanocomposite coating were used in weight loss measurement. The corrosive velocity of the samples in 30 wt% NaOH solution at room temperature was determined by measuring weight changes. Before each experiment, the sample area was measured and the sample mass was weighed. After salt immersion and before weighing at the selective time, the samples were extracted and their surfaces were scrubbed, cleaned with alcohol, dried with hot air, and then weighed again. In this way, the mass loss per unit surface area was calculated. The samples were reused to obtain another weight loss value for a longer immersion. The weight loss value is the mean value of three specimens for every kind of sample.

3. Results and discussion

3.1 Polarization behaviour of Ni–W/ZrO₂ electrolyte

Figure 1 shows the cathodic polarization behaviour of Ni–W/ZrO₂ electrolyte with different concentrations of ZrO₂ nanoparticles. It is seen that the addition of ZrO₂ nanoparticles into the electrolyte causes the reduction potential of Ni–W to shift towards larger negatives, but the slope of reduction curve remains unchanged. The shift to more negative reduction potential can be attributed to the decrease in the active surface area of the cathode for the adsorption of ZrO₂ nanoparticles on the cathode surface,

and the decrease in the ionic transportation by ZrO₂ nanoparticles, which does not significantly affect the electrochemical reaction mechanism (Wu *et al* 2003).

3.2 Influence of preparation parameters on weight percentage of ZrO₂ nanoparticles in composite coating

Figure 2 shows the relationship between the weight percentage of the codeposited ZrO₂ nanoparticles in the nanocomposite coatings and the concentration of the same nanoparticles in the plating bath, at current density of 12 A dm⁻² and stirring rate of 180 rpm. It can be noted that the weight percentage of ZrO₂ nanoparticles in the nanocomposite coatings increases sharply with the increase of ZrO₂ nanoparticles concentration in the plating bath. The codeposition of ZrO₂ nanoparticles by the electrodeposition technique may be attributed to the adsorption of ZrO₂ particles on the cathode surface

Figure 1. Cathodic polarization curves for the codeposition of Ni–W/ZrO₂ at different concentrations of ZrO₂ nanoparticles in the plating bath at 60 °C.

Figure 2. Effect of ZrO₂ nanoparticles content in the plating bath on the weight percentage of ZrO₂ in the composite coatings.

(Guglielmi 1972). In other words, a higher concentration of ZrO₂ nanoparticles in the plating bath enhances the adsorption rate, thus, resulting in a higher weight percentage of ZrO₂ nanoparticles.

Figure 3 shows the effect of current density on weight percentage of the codeposited ZrO₂ from plating bath containing 10 g L⁻¹ ZrO₂ nanoparticles with stirring rate at 180 rpm. It is observed that the weight percentage of the codeposited ZrO₂ nanoparticles increases initially with the current density and reaches a maximum at 12 A dm⁻². When current density is higher than 12 A dm⁻², the weight percentage of the codeposited ZrO₂ nanoparticles decreases. At low current density, the increase of ZrO₂ particles content can be attributed to the increase of adsorbed nanoparticles to arrive in the cathode surface. The process is controlled by the adsorption of nanoparticles. As the current density is greater than 12 A dm⁻², the movement of metal ions from electrolyte to the cathode surface was faster than that of ZrO₂ nanoparticles by mechanical agitation. In this case, the rapider the electrodeposition of the metal matrix, the fewer are the nanoparticles embedded in the composite coatings (Guglielmi 1972).

The stirring rate strongly affects the weight percentage of ZrO₂ nanoparticles in Ni–W matrix, since ZrO₂ should be transported to the cathode surface for the codeposition. The influence of stirring rate on the weight percentage of the codeposited ZrO₂ nanoparticles is shown in figure 4. The weight percentage increases with stirring rate and reaches a maximum value at 180 rpm. Then, it decreases with increase in the stirring rate. When the stirring rate is lower than 180 rpm, the fluid flow is not capable of transporting all the particles to the cathode surface and the codeposition behaviour of ZrO₂ nanoparticles is apparently controlled by nanoparticles transfer. When the stirring rate is too high, the increasing streaming velocity of the suspension may also sweep away the loosely adsorbed ZrO₂ particles on the cathode surface, and make

the rate of particles removal higher than that of attachment, resulting in a decrease in the weight percentage of ZrO₂ nanoparticles in the composite coating (Yeh and Wan 1997).

3.3 Surface morphology of the nanocomposite coating

Figure 5 shows surface morphologies of Ni–W alloy coating and Ni–W/ZrO₂ nanocomposite coating electrodeposited from the nickel–tungsten plating bath containing 4.8 wt% ZrO₂ nanoparticles. It can be observed that the Ni–W/ZrO₂ nanocomposite coating is smoother than the Ni–W alloy coating. It is evident that the codeposited ZrO₂ nanoparticles are uniformly distributed in the Ni–W matrix by electrodeposition. As long as the ZrO₂ nanoparticles in the coatings are uniformly distributed, Ni–W/ZrO₂ nanocomposite coatings could possess excellent mechanical and corrosion resistance properties.

3.4 Microhardness of Ni–W/ZrO₂ nanocomposite coatings

Figure 6 shows the relationship between the microhardness and weight percentage of codeposited ZrO₂ particles in the Ni–W/ZrO₂ nanocomposite coatings. It is seen that Ni–W/ZrO₂ nanocomposite coating (720 Hv for 4.8 wt% ZrO₂) has a much larger microhardness than that of Ni–W alloy coating (506 Hv) and the microhardness of nanocomposite coatings increases with the increase in weight percentage of ZrO₂ nanoparticles in the coatings. The reason is that ZrO₂ nanoparticles uniformly distributed in the Ni–W matrix could restrain the growth of Ni–W alloy grains and the plastic deformation of the matrix under loading (Shi *et al* 2006). The grain fining and dispersive strengthening effects become stronger with increasing weight percentage of ZrO₂ nanoparticles in composite coatings. Thus, the microhardness of Ni–W/ZrO₂ nano-

Figure 3. Effect of the current density on the weight percentage of ZrO₂ nanoparticles in the composite coatings.

Figure 4. Effect of stirring rate on the weight percentage of ZrO₂ nanoparticles in composite coatings.

Figure 5. SEM images of surface morphology of (a) Ni-W alloy coating, (b) Ni-W/ZrO₂ nanocomposite coating (containing 4.8 wt% ZrO₂).

Figure 6. Variation of microhardness with the weight percentage of codeposited ZrO₂ nanoparticles in nanocomposite coatings.

Figure 7. Wear weight loss of ZrO₂ nanoparticles in Ni-W/ZrO₂ nanocomposite coatings.

composite coatings increases with the increase of ZrO₂ nanoparticles content.

3.5 Wear resistance of Ni-W/ZrO₂ nanocomposite coatings

The wear weight loss of Ni-W/ZrO₂ nanocomposite coatings is shown in figure 7. It can be seen that the wear weight loss of Ni-W/ZrO₂ nanocomposite coatings is smaller than that of Ni-W alloy coating, and decreases gradually with the increasing content of ZrO₂ nanoparticles in the coatings. It is indicated that the wear resistance of Ni-W/ZrO₂ nanocomposite coatings is closely related with ZrO₂ nanoparticles content, and the nanocomposite coating has much better wear resistance than Ni-W alloy coating.

The morphology of worn surface of the Ni-W alloy coating and Ni-W/ZrO₂ nanocomposite coatings (4.8 wt%)

is shown in figure 8. There are some obvious abrasive grooves on the worn surface of Ni-W alloy coating in figure 8(a). This reveals that, without the incorporation of ZrO₂ nanoparticles in Ni-W matrix, wear resistance of the Ni-W alloy coating is weak. For Ni-W/ZrO₂ nanocomposite coating, the abrasive grooves on the worn surface are significantly decreased and the feature shows less abrasive width and depth, as seen in figure 8(b).

The wear resistance of Ni-W/ZrO₂ nanocomposite coatings is enhanced with increase in the weight percentage of ZrO₂ nanoparticles in the coatings because of dispersion strengthening and particle strengthening provided by ZrO₂ nanoparticles. During the wear process, the ZrO₂ nanoparticles gradually protruded out and transferred the loads from the matrix, accordingly, the wear resistance of Ni-W/ZrO₂ nanocomposite coatings was enhanced (Hou *et al* 2002). ZrO₂ nanoparticles may also serve as a solid lubricant between contact surfaces, abating the wear of composite coatings.

Figure 8. Morphology of worn surface of Ni–W alloy (a) and Ni–W/ZrO₂ nanocomposite coatings (b).

Figure 9. Anode polarization curves for Ni–W alloy and Ni–W/ZrO₂ nanocomposite coatings in 30 wt% NaOH solution.

Figure 10. Weight loss with immersion time for Ni–W alloy and Ni–W/ZrO₂ nanocomposite coatings in 30 wt% NaOH solution.

3.6 Corrosion resistance property of nanocomposite coating

3.6a Anodic polarization curves: Figure 9 shows the anodic polarization curves for Ni–W alloy and Ni–W/ZrO₂ nanocomposite coating (4.8 wt%) in 30 wt% NaOH solution. Both of these show an active–passive transition by anodic polarization. It can be seen that E_{corr} of the Ni–W/ZrO₂ nanocomposite coating is approximately 215 mV positives more than that of the Ni–W coating. For Ni–W/ZrO₂ nanocomposite coating, the polarization curve shows a relatively wide passive region and a smaller passive current density than that of Ni–W alloy coating. This indicates that Ni–W/ZrO₂ nanocomposite coating has better corrosion resistance than Ni–W alloy coating.

3.6b Weight loss measurements: Figure 10 shows the weight loss data resulting from immersion for 30 days in 30 wt% NaOH solution for Ni–W alloy and Ni–W/ZrO₂ nanocomposite coating. It is observed that the corrosive velocity of Ni–W alloy is approximately 10 times that of Ni–W/ZrO₂ nanocomposite coating. The result indicates that the corrosive velocity of Ni–W/ZrO₂ nanocomposite coating significantly decreases in contrast to the Ni–W alloy and that ZrO₂ nanoparticles could, therefore, provide excellent anti-corrosion performance for Ni–W matrix. The weight loss measurement results also confirm that the addition of ZrO₂ nanoparticles elevates the anticorrosion performance of Ni–W matrix remarkably, which is in accordance with the results of electrochemical measurements.

In the present work, ZrO₂ nanoparticles were uniformly distributed in Ni–W matrix, and filled in crevices, gaps and micron holes. The ZrO₂ nanoparticles act as inert physical barriers to the initiation and development of defect corrosion. This modifies the microstructure of Ni–W matrix and, hence, improves the corrosion

resistance of nanocomposite coating (Chen *et al* 2005; Praveen *et al* 2007).

4. Conclusions

(I) The codeposition of ZrO₂ nanoparticles with Ni–W matrix depends on the ZrO₂ nanoparticles concentration in the bath, current density and stirring rate. The maximum weight percentage of ZrO₂ particles in the nanocomposite coatings was obtained at 10 g L⁻¹ ZrO₂ nanoparticles in the plating bath, current densities 12 A dm⁻², and stirring rate at 180 rpm.

(II) The addition of ZrO₂ nanoparticles lead to an increase in microhardness and wear resistance of Ni–W/ZrO₂ nanocomposite coatings. Moreover, the microhardness and wear resistance of Ni–W/ZrO₂ nanocomposite coatings increases with the weight percentage of ZrO₂ nanoparticles in the coatings.

(III) The electrochemical methods and weight loss measurements show that Ni–W/ZrO₂ nanocomposite coating has better corrosion resistance than Ni–W alloy coating.

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