

## Electrodeposition and mechanical properties of Ni–La<sub>2</sub>O<sub>3</sub> nanocomposites

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Electrodeposition is one method to produce metal matrix composite coatings. Metal matrix nanocomposites can be formed by the addition of nano-sized particles to a host matrix such as Ni. The nanoparticles used is reported in the literature [1–7] include SiC, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, PSZ, and YSZ etc. The codeposition of the nanoparticles with metal phases to form nanocomposites can bring a remarkable improvement on mechanical and physical properties of the coatings. Meanwhile, the morphology, structure, and properties of the composite electrodeposits are affected by several interrelated parameters: composition of the electrolytic bath and particles concentration, presence of additives, temperature, pH, agitation, and applied current density [2–5, 8].

Rare earth oxides have been widely used in electronics, materials and chemical engineering, because of their special characteristics [9–11]. It was found that electrodeposited Ni–La<sub>2</sub>O<sub>3</sub> composite films at high temperatures had the slowest rate and the best resistance to thermal cycling compared to those of bare Ni [12]. The reason was that La<sub>2</sub>O<sub>3</sub> particles in the nanometer size play a major role inhibiting grain-boundary diffusion. However, the mechanical properties of the Ni–La<sub>2</sub>O<sub>3</sub> nanocomposites have not received much attention.

In this work, the behaviors of composite electroplating of nanometric La<sub>2</sub>O<sub>3</sub> particles with Ni to form nanocomposites were studied. The effect of the concentration of La<sub>2</sub>O<sub>3</sub> in the plating bath and plating parameters such as current density, temperature, and stirring rate on the amount of La<sub>2</sub>O<sub>3</sub> codeposited in the composites were evaluated. Microhardness of the Ni–La<sub>2</sub>O<sub>3</sub> nanocomposites as a function of the weight fraction of La<sub>2</sub>O<sub>3</sub> particles in the deposits was also investigated.

Electrodeposition of Ni–La<sub>2</sub>O<sub>3</sub> nanocomposites were deposited in a nickel sulfamate bath consisting of [Ni(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O] (400 g/l), NH<sub>4</sub>Cl (15 g/l), H<sub>3</sub>BO<sub>3</sub> (30 g/l), sodium dodecylsulfate [CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub>Na] (0.1 g/l), and La<sub>2</sub>O<sub>3</sub> particles from 5 to 30 g/l. The La<sub>2</sub>O<sub>3</sub> powder (purity >99.99%) has an average 60-nm particle size. Each plating bath was mixed by magnetic stirring for 2 h, and subsequently by ultrasonic agitation for 30 min just before electroplating. Codeposition was carried out in 500-ml

beaker for 2 h; a steel plate as cathode with dimensions of 20 × 50 × 1 mm was used, and a nickel plate was used as anode. The electrolyte was stirred by a magnetic stirrer during electrodeposition. The temperature of the electrolyte was maintained at a predetermined value by an automatic controller. The operating conditions for plating were current density ranging from 2 to 8 A/dm<sup>2</sup>, bath temperature from 35 to 60 °C, and stirring rate from 400 to 1200 rpm. Because of La<sub>2</sub>O<sub>3</sub> particles dissolve in the bath, the pH of the electrolyte increases with the increase of concentration of La<sub>2</sub>O<sub>3</sub> particles in the electrolyte, as listed in Table 1.

The surface morphology and the components of the deposits were studied by using a field emission scanning electron microscope (FESEM, LEO-1530VP) with energy dispersive analyzer system (EDX). The weight fraction of lanthana was determined by using the lanthanaum to oxygen ratio 2:3 determined by the chemical formula La<sub>2</sub>O<sub>3</sub>. Vickers microhardness tests were conducted on an HXS-1000A microhardness tester using a load of 50 g, applied for 10 s. Each hardness value was an average of five measurements.

Fig. 1 represents that the wt% of the La<sub>2</sub>O<sub>3</sub> in the composite varies with different contents (5–30 g/l) of the La<sub>2</sub>O<sub>3</sub> particles in the electrolyte at current densities 2 A/dm<sup>2</sup>, 50 °C, and 800 rpm. It is seen that the wt% of La<sub>2</sub>O<sub>3</sub> in the deposit rapidly increases with the increase of the La<sub>2</sub>O<sub>3</sub> content in the bath. The greatest particle incorporation occurs at the highest La<sub>2</sub>O<sub>3</sub> addition of 30 g/l. If La<sub>2</sub>O<sub>3</sub> content is too low (15 g/l), the number of nickel ions adsorbed on La<sub>2</sub>O<sub>3</sub> particles is small, leading to the small amount of codeposited particles.

The effect of the current density on the wt% of La<sub>2</sub>O<sub>3</sub> in the composite at pH 5.3, 50 °C, and 800 rpm and at 30 g/l La<sub>2</sub>O<sub>3</sub> in the electrolyte is shown in Fig. 2. It is seen that the wt% of La<sub>2</sub>O<sub>3</sub> in the deposit decreases with the increase of the current density. As the current density increases, the movement of nickel ions from bulk solution to the cathode surface was faster than that of La<sub>2</sub>O<sub>3</sub> particles by the mechanical agitation. So, the lower wt% of the codeposited La<sub>2</sub>O<sub>3</sub> was caused at high current densities. As a result, the optimum current density is a relatively low current density, which allowed

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TABLE I The pH value varied with the content of  $\text{La}_2\text{O}_3$  particles in the electrolyte

| $\text{La}_2\text{O}_3$ particles content | pH value |
|---|----------|
| 0   | 4.1      |
| 5   | 4.4      |
| 10  | 4.6      |
| 15  | 4.9      |
| 20  | 5.1      |
| 30  | 5.3      |

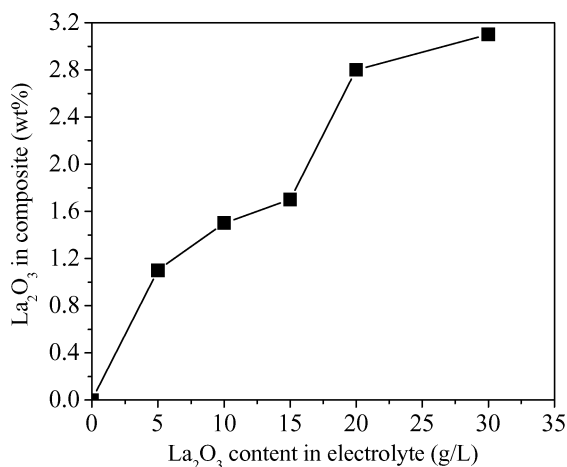


Figure 1 Effect of the  $\text{La}_2\text{O}_3$  content in the electrolyte on the wt% of  $\text{La}_2\text{O}_3$  in the composite.

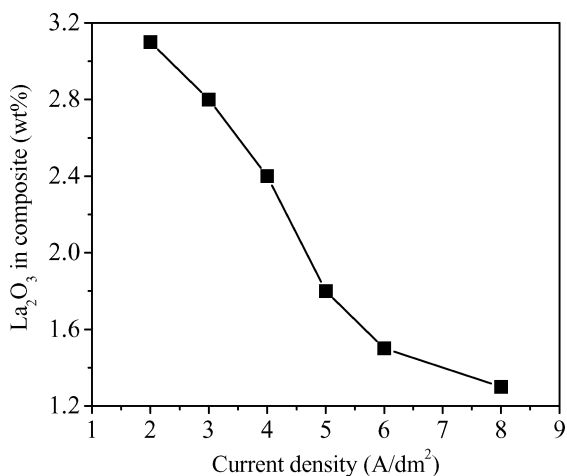


Figure 2 Effect of the current density on the wt% of  $\text{La}_2\text{O}_3$  in the composite.

the maximum wt% of the codeposited  $\text{La}_2\text{O}_3$ . In this investigation, it could be concluded that the optimum current density was  $2 \text{ A}/\text{dm}^2$ .

Fig. 3 represents the effect of temperature on the wt% of  $\text{La}_2\text{O}_3$  in the composite at  $30 \text{ g}/\text{l}$   $\text{La}_2\text{O}_3$ , current densities  $2 \text{ A}/\text{dm}^2$ , pH 5.3, and 800 rpm. It is clear that the temperature of the electrolyte markedly affects the weight fraction of  $\text{La}_2\text{O}_3$  in the composite. The embedded  $\text{La}_2\text{O}_3$  content increases from 2.0 wt% at  $35^\circ\text{C}$  to 3.1 wt% at  $50^\circ\text{C}$ . With the further increase of the temperature value, the wt% of  $\text{La}_2\text{O}_3$  in the composite decreases gradually.

The stirring rate plays an important role in the plating process for the transportation of  $\text{La}_2\text{O}_3$  particles to the

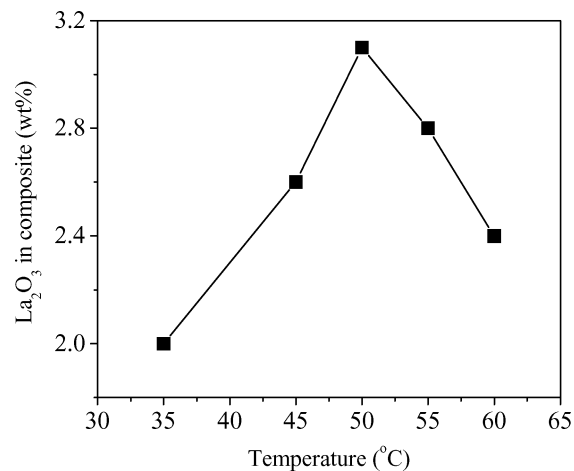


Figure 3 Effect of the temperature on the wt% of  $\text{La}_2\text{O}_3$  in the composite.

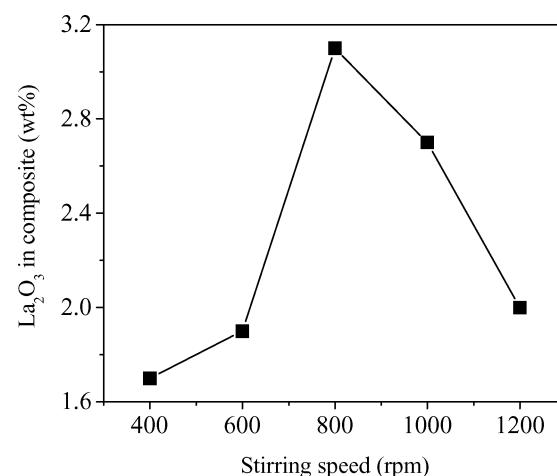


Figure 4 Effect of the stirring rate on the wt% of  $\text{La}_2\text{O}_3$  in the composite.

cathode for the codeposition. Fig. 4 shows the effect of stirring rate on the wt% of  $\text{La}_2\text{O}_3$  in the composite at pH 5.3,  $50^\circ\text{C}$ , current densities  $2 \text{ A}/\text{dm}^2$ , and  $30 \text{ g}/\text{l}$   $\text{La}_2\text{O}_3$  in the electrolyte. It is seen that the amount of  $\text{La}_2\text{O}_3$  in the composite increases with increasing stirring rate up to 800 rpm. The highest wt% of  $\text{La}_2\text{O}_3$  in the composite is obtained at 800 rpm. The wt% of  $\text{La}_2\text{O}_3$  in the composite decreases beyond 800 rpm. It is suggested that, under strong stirring conditions, the  $\text{La}_2\text{O}_3$  particles absorbed on the cathode are partly taken away, which resulted in a decreased amount of the  $\text{La}_2\text{O}_3$  codeposition.

The SEM surface morphologies of electrodeposited pure Ni and Ni- $\text{La}_2\text{O}_3$  nanocomposites is represented in Fig. 5. It shows that the composite deposits register similar nodular surface structure. Compared to pure Ni deposit, the nanocomposite coatings had smaller nodular microstructure. It seems that the increase of the wt%  $\text{La}_2\text{O}_3$  codeposited lead to the generation of surfaces with more smooth and microcrystalline structures. The EDX results show a good uniformity of dispersed phase, confirming the parameters operated in this study is suitable.

The hardness of the electrodeposited composites depends on many factors. Among them, the most important is the composition of the electrolyte. The

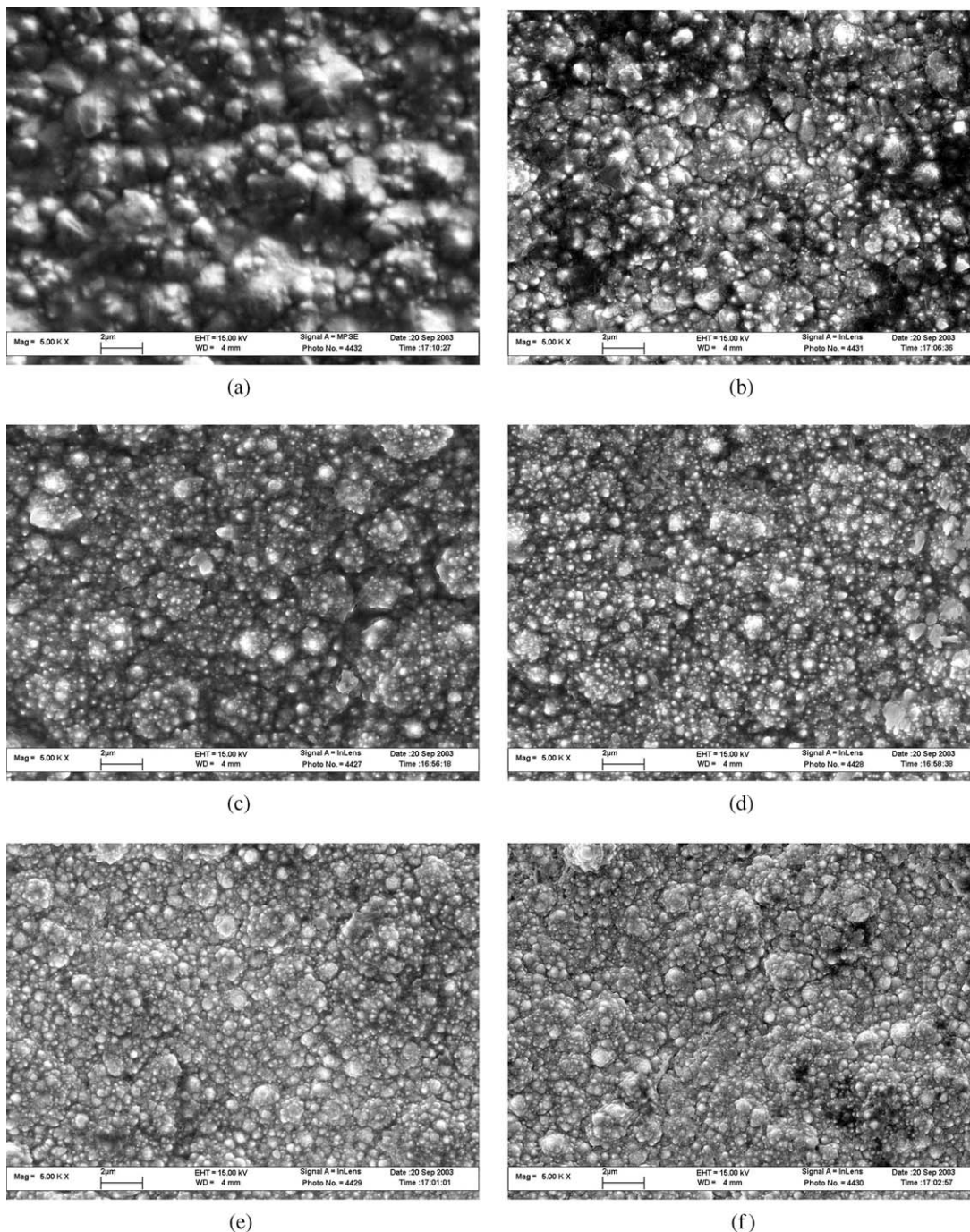


Figure 5 SEM surface micrographs of the electrodeposited pure Ni and Ni-La<sub>2</sub>O<sub>3</sub> nanocomposites obtained at 2 A/dm<sup>2</sup>, 50 °C, and 800 rpm: (a) pure Ni, (b) 1.1 wt% La<sub>2</sub>O<sub>3</sub>, (c) 1.5 wt% La<sub>2</sub>O<sub>3</sub>, (d) 1.7 wt% La<sub>2</sub>O<sub>3</sub>, (e) 2.8 wt% La<sub>2</sub>O<sub>3</sub>, and (f) 3.1 wt% La<sub>2</sub>O<sub>3</sub>.

relationship between the weight fraction of La<sub>2</sub>O<sub>3</sub> in the nanocomposite and microhardness is shown in Fig. 6. It appears that higher weight fraction of codeposited-La<sub>2</sub>O<sub>3</sub> provides better microhardness. Gyftou *et al.* [2] reported that embedding of nanoparticles perturbs the crystal growth of Ni, inducing a reduction in the crystal size, gives deposits with significantly increased hardness values. Wang *et al.* [3] also reported that the existence of nano-sized ceramic particle, as the second-phase, reduces the grain size of Ni-matrix. Accordingly, the higher microhardness value of the Ni-La<sub>2</sub>O<sub>3</sub> nanocomposites may be also due to the decrease of the grain size of Ni-matrix of the composites, which is favored by the nano-sized La<sub>2</sub>O<sub>3</sub> particles. Future studies

are also aimed at establishing the presence of nanometric La<sub>2</sub>O<sub>3</sub> particles in the composites and investigating the microstructure of the coatings by using transmission electron microscopy (TEM) and X-ray diffraction methods.

In summary, Ni-La<sub>2</sub>O<sub>3</sub> nanocomposites were prepared using composite electroplating, which embedded nano-sized La<sub>2</sub>O<sub>3</sub> particles as the reinforcing phase. The maximum wt% of La<sub>2</sub>O<sub>3</sub> in the composites was obtained at 30 g/l La<sub>2</sub>O<sub>3</sub> in the electrolyte, 50 °C, 800 rpm, and current densities 2 A/dm<sup>2</sup>. The microhardness of the Ni-La<sub>2</sub>O<sub>3</sub> nanocomposites increased with the weight fraction of codeposited-La<sub>2</sub>O<sub>3</sub> nanoparticles.

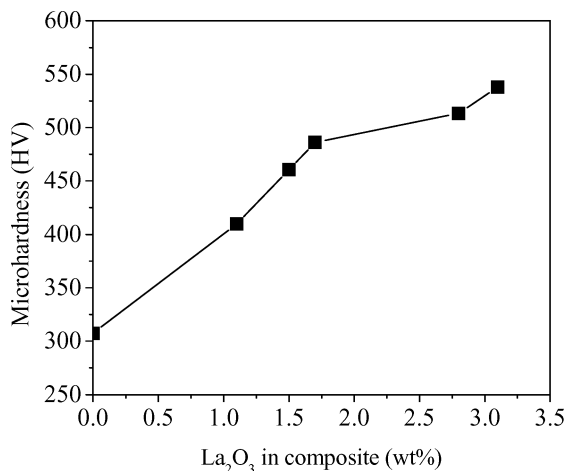


Figure 6 Variation of microhardness with weight fraction of La<sub>2</sub>O<sub>3</sub> particles in the nanocomposite.

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