

Sliding wear behaviors of electrodeposited nickel composite coatings containing micrometer and nanometer La_2O_3 particles

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Micrometer and nanometer La_2O_3 particles were codeposited with nickel by electroplating from a nickel sulfamate bath. The wear behaviors of the composite coatings were evaluated sliding against AISI 1045 steel under non-lubricated conditions. It was found that the incorporation of the La_2O_3 particles enhances the microhardness and wear resistance of Ni coatings. The wear resistance of the Ni composite coating containing nano-sized La_2O_3 particles is higher than that of the Ni composite coating containing micro-sized La_2O_3 particles. The codeposition of the smaller nanometer La_2O_3 particles with Ni effectively reduces the size of Ni crystals and significantly increases the hardness of the composite coatings, resulting in significantly improved wear resistance of the nano-sized $\text{La}_2\text{O}_3/\text{Ni}$ composite coating.

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1. Introduction

Nano-structured composite coatings usually exhibit enhanced mechanical, tribological, anti-corrosion and anti-oxidation properties as compared to pure metal coatings as well as composite coatings containing micro-sized particles. The improvement of these properties can be contributed to the presence of nano-sized particles dispersed in the metallic matrix, and thus depends on the content of the nano-sized particles in the deposits [1, 2]. Electrodeposition offers a cost effective and convenient method of preparing the nano-structured composite coatings onto flat or irregular shaped surfaces [3]. Recently, in order to improve the mechanical, tribological and anti-corrosion properties of the composite coatings by electrodeposition, many kinds of nanometer particles were used such as SiC, Al_2O_3 , Si_3N_4 , PSZ and YSZ etc [4–8]. Nevertheless, few articles have reported on the application of rare earths nanometer particles such as La_2O_3 nanoparticles, which is to enhance the tribological properties of the composite coatings.

Due to the special characteristics of rare earth elements, rare earth oxides have been widely used in electronics, materials and chemical engineering [9–11]. The oxidation of electrodeposited Ni- La_2O_3 composite films at high temperatures showed a significant retardation of oxidation

and the prevention of the scale from cracking compared to oxidation of bare Ni and Ni-plated Ni, because the nano-sized La_2O_3 particles play a major role inhibiting grain-boundary diffusion [12]. In the previous work [13], the higher microhardness was obtained with the Ni- La_2O_3 nanocomposite coatings containing a higher weight fraction of codeposited La_2O_3 nanoparticles. However, the friction and wear behaviors of the Ni matrix composite coatings reinforced with nanometer La_2O_3 particles have not received much attention. In this study, the Ni composite coatings containing micro- and nano-sized La_2O_3 particles were electroplated, and their sliding wear behaviors have been evaluated under non-lubricated conditions. For comparison, the electroplated pure Ni coating was also prepared.

2. Experimental procedure

In order to obtain the electrodeposited nickel composite coatings, a nickel sulfamate bath having the following composition was prepared for plating Ni matrix: 300 g/l $\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, 15 g/l NH_4Cl , 30 g/l H_3BO_3 , 0.1 g/l $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$. The addition of micrometer La_2O_3 (mean diameter 4 μm) and nanometer La_2O_3 particles

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(mean diameter 60 nm) in the electrolyte was 20 g/l, respectively. The plating bath in each experiment was mixed by magnetic stirring for about 8 h, and subsequently by ultrasonic agitation for 30 min prior to electroplating. A steel plate as cathode with dimensions of $30 \times 50 \times 2$ mm was used, and a nickel plate was used as anode. Electrodeposition was conducted in 1000 ml beaker using a current density of 3 A/dm^2 . The bath temperature was maintained at 45°C by an automatic controller. The bath was agitated by a magnetic stirrer with a stirring rate of 800 rpm in the electroplating process.

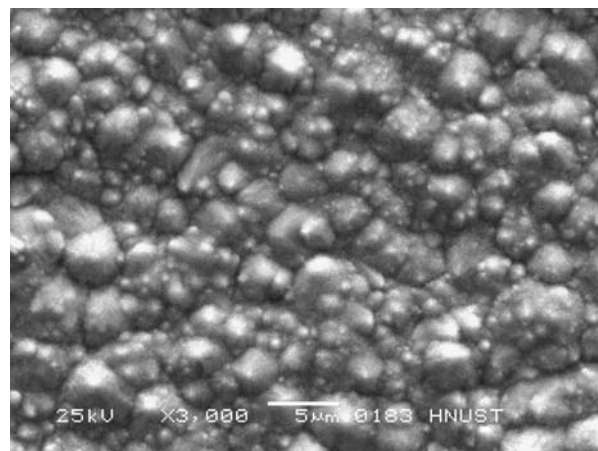
The surface morphology and the composition of the composite coatings were characterized by a scanning electron microscope (SEM, JSM-5610LV) with energy dispersive analyzer system (EDX). The weight fraction of lanthana was determined by using the lanthanum to oxygen ratio of 2:3 determined by the chemical formula La_2O_3 . Vickers hardness tester was employed to examine the microhardness of the coatings using a load of 50 g for 10 s.

The wear behaviors of the coatings were tested on a sliding wear machine, which was similar to the pin-on-disc wear machine. The stationary disc cut from the above steel plate, was 30 mm length and 30 mm width, which was coated with Ni composite deposit with a thickness of $100 \mu\text{m}$ for all the tests. The pin was made of AISI 1045 steel with the chemical composition of C 0.420–0.500, Mn 0.500–0.800, Si 0.170–0.370, $\text{Cr} \leq 0.250$, $\text{P} \leq 0.035$, $\text{S} \leq 0.035$, and thermal treated to achieve average hardness $\text{HRC } 56 \pm 2$. The steel pin was 12.0 mm in length, with an inside diameter of 22.0 mm and an outside diameter of 28.0 mm. The contact surface of the steel pin with disc was polished, so that the average surface roughness value (R_a) was $0.2 \mu\text{m}$ approximately.

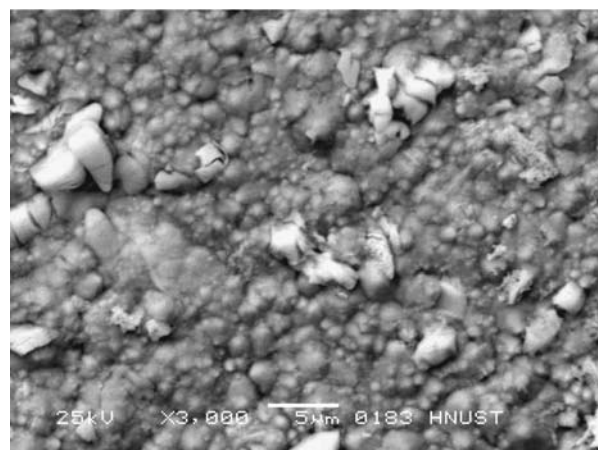
The sliding wear tests were performed at room temperature, with a constant rotation speed of 400 rpm and loads from 5 to 20 N under non-lubricated conditions. Each wear test lasted for 10 min. All the friction pairs were cleaned by ultrasonically washed in acetone before and after each test. The weight loss of the disc, to an accuracy of 0.1 mg, was detected to evaluate the wear resistance of the coatings. The worn surfaces of the coatings on the disc specimens were investigated using scanning electron microscopy.

3. Results and discussion

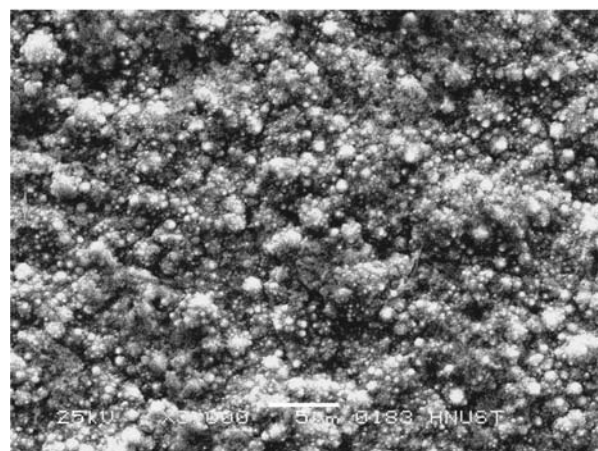
Fig. 1 compares the surface morphology of a pure nickel coating and the Ni composite coatings containing the micron- and nano-sized La_2O_3 particles. It is evident that the incorporation of the La_2O_3 particles greatly affects the surface morphologies of the coatings. An important factor for this alteration is the size of the codeposited particles. The embedment of nano-sized La_2O_3 particles leads to the generation of surfaces with more uniform and microcrystalline structures, than that of micron-sized La_2O_3 particles. Furthermore, smaller Ni grain size could be observed in the nano- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating than



(a)



(b)



(c)

Figure 1 SEM surface morphology of (a) pure Ni coating, (b) micron-sized $\text{La}_2\text{O}_3/\text{Ni}$ composite coating and (c) nano-sized $\text{La}_2\text{O}_3/\text{Ni}$ composite coating.

in the micron- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating as well as in the pure nickel coating. It seems that the codeposition mechanism is different for the nanoparticles and the microparticles and depends considerably on the size of the embedded particles [1].

TABLE I La_2O_3 content in coatings, microhardness of pure Ni and Ni composite coatings

| Coatings | Concentration of La_2O_3 in electrolyte (g L^{-1}) | La_2O_3 content in coatings (wt%) | HV (kg mm^{-2}) |
|---|---|---|----------------------------|
| Pure Ni | 0 | 0 | 295 |
| Micron- $\text{La}_2\text{O}_3/\text{Ni}$ | 20 | 10.6 | 378 |
| Nano- $\text{La}_2\text{O}_3/\text{Ni}$ | 20 | 2.4 | 510 |

In addition, EDX analysis (Table I) shows the amount of codeposited La_2O_3 for the microparticles and nanoparticles reinforced Ni coatings. It is noticed that the La_2O_3 nanoparticles codeposit less than the La_2O_3 microparticles, which is agreement with the similar work of the literature [14]. A possible reason could be the difference in the surface condition of these La_2O_3 particles obtained from different producers. The examination of SEM reveals that the surface structure of the two types of composite coatings is different; as a result, the composite coatings could exhibit different mechanical properties.

The microhardness of the Ni composite coatings is higher than that of the pure Ni deposit prepared under similar plating conditions. A higher hardness values is obtained at a lower weight fraction of nano- La_2O_3 particles in the deposit than in the case of micron- La_2O_3 particles, as depicted in Table I. The greater microhardness value can be mainly attributed to the decrease of the grain size of Ni-matrix of the composite coating, which is favored by the smaller nano- La_2O_3 particles, as shown in Fig. 1c. The embedding of nanometer particles perturbs the crystal growth of Ni, resulting in an increased number of crystalline structural defects and in smaller size of the nickel crystallites, consequently leads to greatly increased hardness values of the composite coatings [1].

It is well known that the hardness and other mechanical properties of metal matrix composites depend in general on the amount and size of the dispersed phase, apart from the mechanical characteristics of the matrix, particles and interfaces. The amount and size of particles define two kinds of reinforcing mechanisms in metal matrix composite materials, namely dispersion-strengthening and particle-strengthening. It was reported in the literature [14] that, a dispersion-strengthened composite is characterized by a dispersion of fine particles with a particle diameter ranging from 0.01 to 1 μm , and volume percent ranging from 1 to 15. Accordingly, in this study, the microhardness increase noted in the nano- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating can be linked to a dispersion-strengthening effect. This implies the importance of achieving a uniform codeposition of non-agglomerated nanometer particles to obtain a dispersion-strengthening effect.

The variation of wear weight loss with load for the pure Ni coating, micron- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating and nano- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating, sliding against AISI 1045 steel under non-lubrication, is shown in Fig. 2. It is seen in Fig. 2 that the wear weight loss of the

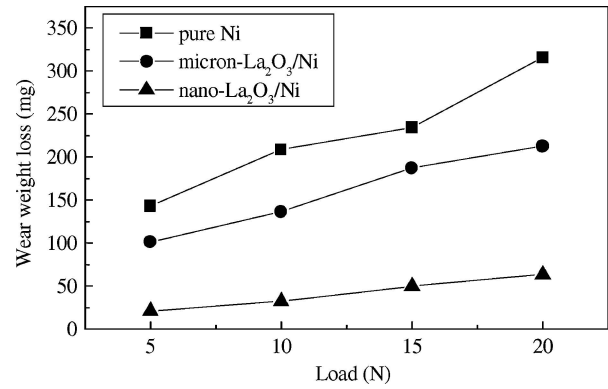
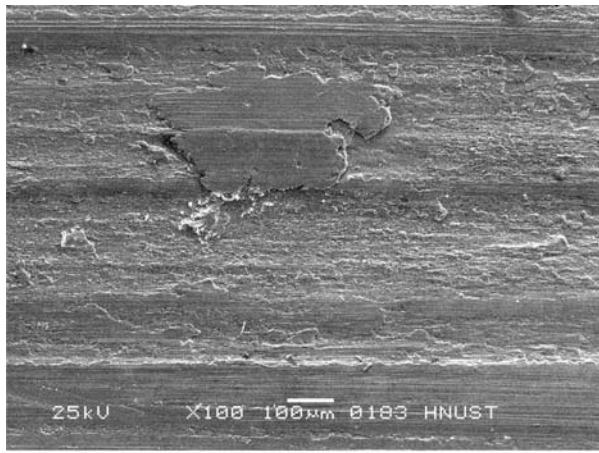


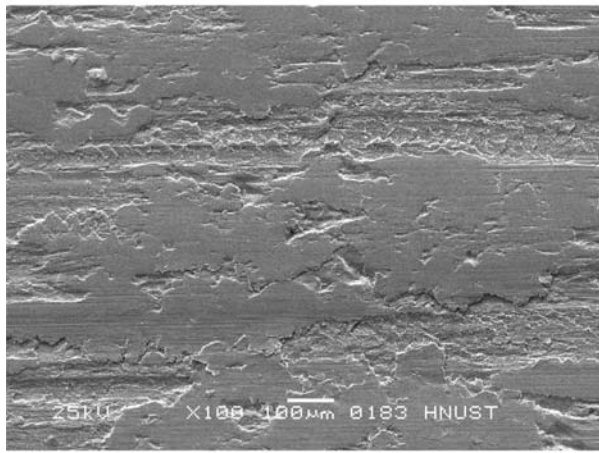
Figure 2 Variation of wear weight loss with load for the pure Ni coating, micron- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating and nano- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating under non-lubrication at a constant rotation speed.

coatings increases with the increase of load from 5 to 20 N under non-lubricated conditions. When the load is higher than 15 N, the wear weight loss of the composite coatings slightly changes with the increase of load, while that of the pure Ni coating greatly increases. It is noticed that, under the same load conditions, the wear resistance of the nano- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating is the best, that of the micron- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating is second, while that of the pure Ni coating is the worst. It reveals that the size of codeposited La_2O_3 particles has a significant effect on the wear behaviors of the composite coatings. The nano- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating exhibits the best wear resistance, which are mainly dependent on the dispersion-strengthening effect caused by the nanometer La_2O_3 particles in the Ni matrix and also as a result of the fine-grained structure of the deposit. It is suggested that the nano- $\text{La}_2\text{O}_3/\text{Ni}$ composite coating can be used in practice as a kind of nano-structured composite coating with an excellent sliding wear behaviors under non-lubricated conditions.

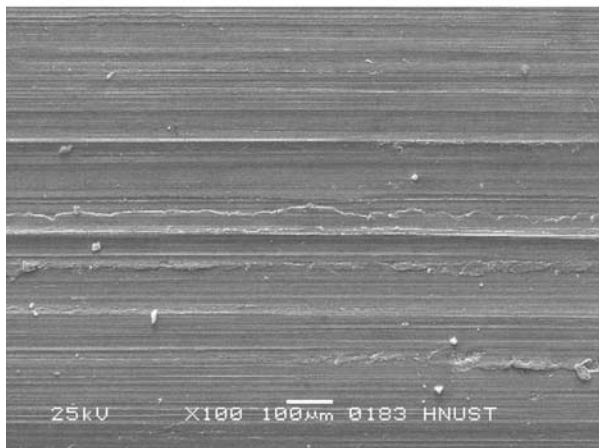
Fig. 3 shows the morphology of worn surface of the pure Ni coating and $\text{La}_2\text{O}_3/\text{Ni}$ composite coatings at a rotation speed of 400 rpm and a load of 20 N. Cracking and spalling can be seen on the worn surface of the pure Ni coating, as shown in Fig. 3(a). The presence of the cracking and spalling causes lots of wear losses. This reveals that, due to without the reinforcement of the particles, the loading-bearing capacity and wear resistance of the pure Ni coating are rather weak. Significant plastic deformation with large grooves is noticed on the worn surface of the Ni composite coating containing the micron- La_2O_3 particles, as seen in Fig. 3(b). However, there is no obvious plastic deformation and abrasive grooves on the worn surface of the Ni composite coating containing the nano- La_2O_3 particles, as shown in Fig. 3(c). It implies that the incorporation of the La_2O_3 particles can largely reduce the wear of the coatings, while the wear-reducing effect of the nano- La_2O_3 particles is more effective than that of the micron- La_2O_3 particles. The incorporation of the nanometer La_2O_3 particles in the deposit reduces the



(a)



(b)



(c)

Figure 3 SEM worn surface of (a) pure Ni coating, (b) micron-La₂O₃/Ni composite coating and (c) nano-La₂O₃/Ni composite coating under non-lubrication at a rotation speed of 400 rpm and a load of 20 N.

size of Ni crystal, increases the hardness of the coatings, which is helpful for the improvement in wear resistance. Besides, the dispersed nanometer La₂O₃ particles in the

matrix significantly enhance the loading-bearing capacity of the nano-La₂O₃/Ni composite coating.

4. Conclusions

In this study, the wear behaviors of the electrodeposited nickel composite coatings containing micrometer and nanometer La₂O₃ particles, sliding against AISI 1045 steel under non-lubricated conditions, were evaluated. The nickel composite coatings show better wear resistance compared with the pure nickel coating. The nano-La₂O₃/Ni composite coating exhibits a higher wear resistance than the micro-La₂O₃/Ni composite coating under the same conditions. The best wear resistance of the nano-La₂O₃/Ni composite coating can be attributed to the incorporation of the nanometer La₂O₃ particles in the deposit, which effectively reduces the size of Ni crystals and greatly increases the hardness of the composite coatings.

Acknowledgments

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