

## Sliding wear behaviors of electrodeposited Ni composite coatings containing micrometer and nanometer Cr particles

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Received 21 May 2008; accepted 28 August 2008

**Abstract:** Micrometer and nanometer Cr particles were co-deposited with Ni by electroplating from a nickel sulfate bath containing a certain content of Cr particles. Cr microparticles are in a size range of 1–5  $\mu\text{m}$  and Cr nanoparticles have an average size of 40 nm. The friction and the wear performance of the co-deposited Ni-Cr composite coatings were comparatively evaluated by sliding against  $\text{Si}_3\text{N}_4$  ceramic balls under non-lubricated conditions. It is found that the incorporation of Cr particles enhances the microhardness and wear resistance of Ni coatings. The wear resistance of Ni composite coating containing Cr nanoparticles is higher than that of the Ni composite coating containing Cr microparticles with a comparable Cr particle content. The co-deposition of smaller nanometer Cr particles with Ni effectively reduces the size of Ni crystals and significantly increases the hardness of the composite coatings due to grain-refinement strengthening and dispersion-strengthening, resulting in a significant improvement of wear resistance of the Ni-Cr nanocomposite coatings.

**Key words:** Ni-Cr composite coating; electrodeposition; microhardness; wear

### 1 Introduction

Electrodeposited composite films consisting of a metal matrix with dispersed particles are frequently used as composite coatings for diverse purposes, such as wear resistance, antifriction and antiseizing problems in coal starting, dry lubrication and dispersion hardening. These coatings typically contain oxide particles or carbide particles in micrometer. For example, there are  $\text{Al}_2\text{O}_3$ [1],  $\text{La}_2\text{O}_3$ [2] and  $\text{SiC}$ [3–4] in an electrodeposited matrix such as nickel. Electrodeposited nickel-base composite films have received considerable attention, but interest commonly is focused on their mechanical and wear resistance properties rather than oxidation behavior. In view of the growing interest in the electroforming of materials for high temperature application, the electrodeposited metal Ni matrix/Cr composite coating (termed as EMCCs Ni-Cr) was fabricated by co-deposition of Ni and micrometer-sized Cr particles decades ago[5]. However, its oxidation behavior is less reported. Recently, ZHANG et al[6–10] developed a

novel electrodeposited Ni matrix/Cr composite coating (termed as ENCCs Ni-Cr) by co-deposition of Ni and Cr nanoparticles. Compared with pure metal coatings or composite coatings containing micro-sized particles, the co-deposited Ni-Cr nanocomposite coatings exhibit a superior hot corrosion and oxidation resistance due to the formation of a continuous chromia scale [6–8], which can be used in power plants [8] operating in a wide range of fuels including natural gas, kerosenes, diesel oils, residual oils, and gaseous fuels made from coal, biomass, and waste, etc. In the environments, erosion from solid particles and gas flow is one of the important factors leading to the recession of steel boiler components. Thus, a higher wear resistance is also needed for the co-deposited Ni-Cr composite coating used in those power plants. However, the friction and wear behaviors of the co-deposited Ni-Cr composite coatings reinforced with micro- and nano-sized Cr particles have not received much attention. Meanwhile, the study on the influence of the size of Cr particles on the wear resistance is limited. In this study, the Ni matrix composite coatings containing micro- and nano-sized Cr particles were

**Foundation item:** Project(9951Z012) supported by the Major Programs of the Heilongjiang Provincial Education Department, China; Project(11531319) supported by the Scientific Research Fund of Heilongjiang Provincial Education Department, China; Project(06-13) supported by the Scientific Research Startup Foundation of Heilongjiang Institute of Science and Technology, China

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DOI: 10.1016/S1003-6326(08)60271-X

electrodeposited, and their wear behaviors were evaluated under non-lubricated condition. For comparison, the electrodeposited pure Ni coating was also prepared.

## 2 Experimental

Pure Ni specimens with dimension of 15 mm×10 mm×2 mm were cut from a pure electrolytic nickel plate (99.9%) and then were abraded by 800# grit Cr waterproof paper. After being ultrasonically cleaned in acetone, they were electrodeposited with a 60 μm-thick film of Ni-Cr composite from a nickel sulfate bath containing 150 g/L NiSO<sub>4</sub>·7H<sub>2</sub>O, 15 g/L NH<sub>4</sub>Cl, 15 g/L H<sub>3</sub>BO<sub>3</sub>, 0.1 g/L C<sub>12</sub>H<sub>25</sub>NaSO<sub>4</sub>, and a certain content of pure Cr particles. EMCCs Ni-Cr were prepared from the bath by the addition of Cr microparticles in a range of 1–5 μm with a mean value of 2.3 μm, and ENCCs Ni-Cr were prepared from a bath with Cr nanoparticles with an average size of 40 nm. The addition dosage of Cr particles in the electrolyte was 100 g/L. The suspensions were stirred for 24 h before deposition. Before the electrodeposition, the samples was degreased in alkaline solution, dipped in acid (10%HCl) and finally washed with distilled water. Magnetic stirring was employed at the cell bottom to maintain the uniform particle concentration and prevent sedimentation. Electrodeposition was carried out in 1 000 mL beaker. The current density used was 3 A/dm<sup>2</sup>, the temperature was 35 °C, pH was 5.5–6.0, and the stirring rate was 600 r/min. For comparison, specimen of nickel with 60 μm-thick Ni film was also deposited using the same parameters and the same bath but without adding Cr nanoparticles. After the deposition, the as-deposited samples were rinsed by using distilled water and then ultrasonically cleaned for analysis.

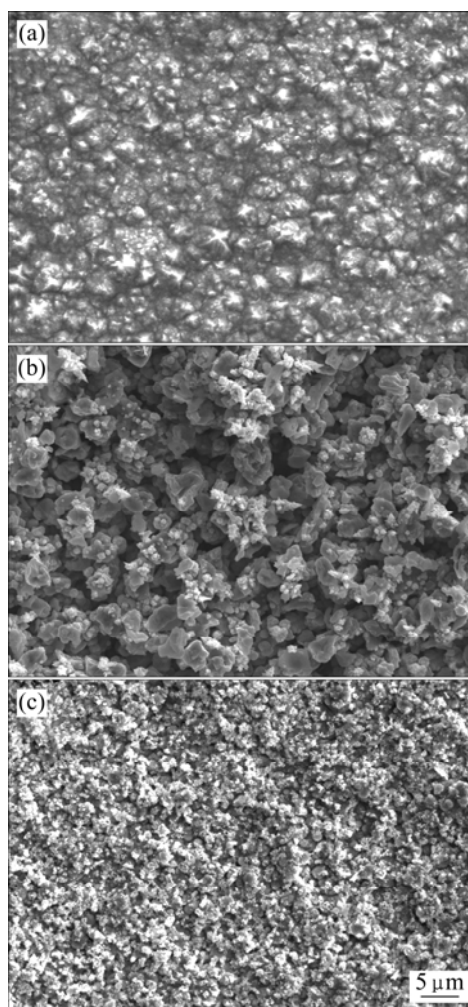
The surface morphology and the composition of the composite coatings were characterized by a scanning electron microscope (SEM, MX2600FE) with energy dispersive analyzer system (EDAX). Measurements of the Vickers microhardness of nickel film and Ni-Cr composites were performed on the surface at a load of 0.49 N for 10 s and the corresponding final values were determined as the average of ten measurements. The friction and wear tests performed at room temperature by a ball-on-disc type tribometer with a constant rotation speed of 200 r/min at a constant radius of 2.5 mm and load of 150 N under non-lubricated conditions. Si<sub>3</sub>N<sub>4</sub> ceramic balls with 2 mm in diameter were used as the counter body. Each wear test lasted for 1 h for a total distance of 188.4 m. The friction coefficients vs cycling number were recorded automatically during the test. All the friction pairs were cleaned by ultrasonically washing in acetone before and after each test. The mass loss of the

samples to an accuracy of 0.1 mg was detected to evaluate the wear resistance of the coatings. Three replicating tests were carried out so as to minimize data scattering, and every value reported was an average of three measurements. After the wear test, the worn surfaces of the coatings were investigated using SEM.

## 3 Results and discussion

### 3.1 Microstructure of coating

The surface morphologies of the as-electrodeposited pure Ni film and Ni-Cr composite coatings containing the micro- and nano-sized Cr particles are shown in Fig.1. It is evident that the incorporation of the Cr particles greatly affects the surface morphology of the coatings. A regular pyramidal structure as shown in Fig.1(a) is observed on the surface of the pure Ni film. Whereas, with the addition of Cr particles, the morphology is changed to nodular, as shown in Figs.1(b) and (c). The embedment of Cr nanoparticles leads to the generation of surface with more uniform and microcrystalline structure



**Fig.1** SEM images of pure Ni film (a), EMCC Ni-12.4Cr (b) and ENCC Ni-11.0Cr (c)

than micron-sized Cr particles. Furthermore, smaller Ni grains could be observed in the ENCC Ni-Cr compared with the EMCC Ni-Cr as well as in the pure Ni coating. In addition, EDAX analysis (Table 1) shows a amount of co-deposited Cr particles in the coatings. It is noticed that the size of Cr particles has a little influence on the degree of co-deposition, which is in agreement with Ref.[11].

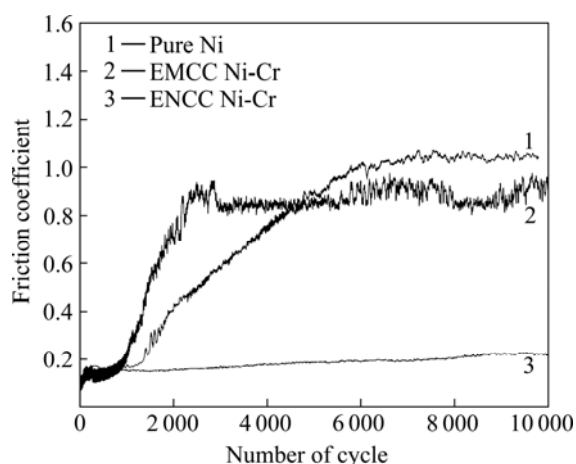
**Table 1** Cr contents in coatings

Coating	Concentration of Cr in electrolyte/(g·L <sup>-1</sup> )	Cr mass fraction in coatings/%
Pure Ni	0	0
EMCC Ni-Cr	100	12.4
ENCC Ni-Cr	100	11.0

### 3.2 Wear resistance

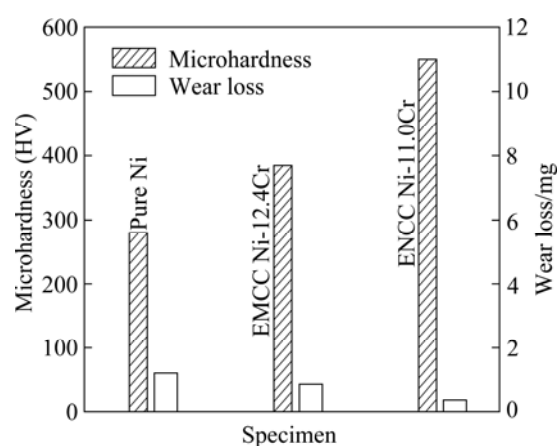
Fig.2 shows the friction coefficient of the as-electrodeposited pure Ni film and Ni-Cr composite coatings containing the micrometer and nanometer Cr particles under non-lubricated conditions at load of 150 N. It is found that, in the first 1 000 cycles, all coatings exhibit a same friction coefficient of about 0.15. For the pure Ni film, it increases dramatically to 1.0 after 6 000 cycles and then maintains at a constant level. With the addition of Cr microparticles, it increases dramatically to 0.9 after 2 500 cycles and then maintains at a constant level. However, for ENCC Ni-Cr, it exhibits little change and keeps stable during the test. From Fig.2, it can be seen that ENCC Ni-Cr exhibits a lower friction coefficient (more than three times lower than that of the pure Ni film or EMCC Ni-Cr) under identical wear test condition. In addition, the friction coefficient of ENCC Ni-Cr is more stable than that of the Ni film or EMCC Ni-Cr.

The microhardness and the wear loss of the as-electrodeposited pure Ni film and Ni-Cr composite



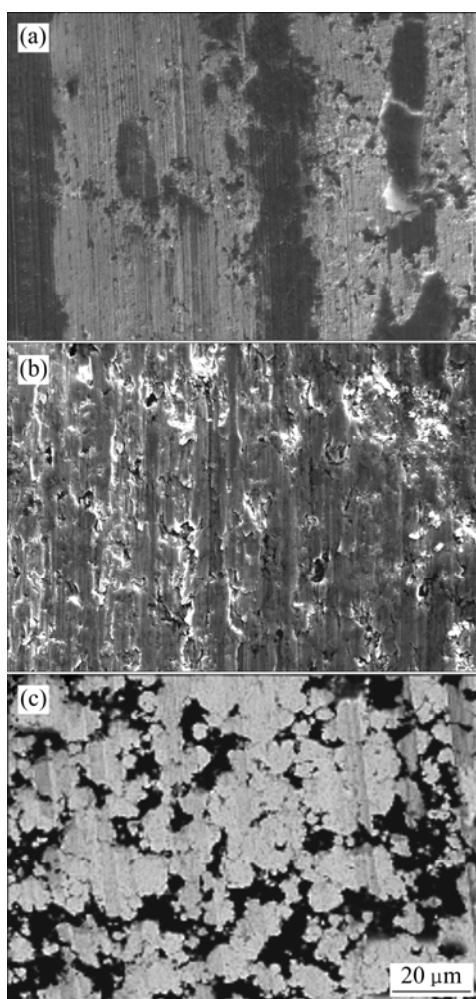
**Fig.2** Typical friction coefficient curve of as-deposited pure Ni film, EMCC Ni-12.4Cr and ENCC Ni-11.0Cr

coatings containing the micrometer and nanometer Cr particles under the same condition are shown in Fig.3. The microhardness of pure Ni is about HV280. With the addition of Cr microparticles, the microhardness of Cr composite coating increases significantly to HV385 and the wear loss decreases to 0.9 mg as compared to 1.2 mg for pure Ni coating. However, with the addition of Cr nanoparticles, the microhardness increases significantly to HV550, while the wear loss is 0.4 mg as compared to 0.9 mg for EMCC Ni-Cr. From Fig.3, it can be found that, under the same condition, the wear resistance of ENCC Ni-Cr is the best, while that of the pure Ni film is the worst. The results suggest that the friction and the wear resistance of the electrodeposited Ni-Cr composite coatings is strongly dependent on particle size at a given particle content.



**Fig.3** Microhardness and wear resistance of as-deposited pure Ni film, EMCC Ni-12.4Cr and ENCC Ni-11.0Cr

The difference in the wear behavior of the as-electrodeposited pure Ni film and Ni-Cr composite coatings containing the micrometer and nanometer Cr particles under the same condition can be further verified by the worn surface morphologies shown in Fig.4. Cracking and spalling can be seen on the worn surface of the pure Ni coating (Fig.4(a)). The presence of the cracking and spalling causes lots of wear loss. Furthermore, a larger tendency for plastic deformation of asperity junctions results in a higher and unstable friction coefficient. The results suggest that the loading-bearing capacity and the wear resistance of the as-deposited Ni film are rather weak. Significant plastic deformation with large grooves is observed on the worn surface of EMCC Ni-Cr (Fig.4(b)). However, there is no obvious plastic deformation and abrasive grooves on the worn surface of ENCC Ni-Cr (Fig.4(c)). This implies that the incorporation of the Cr particles can largely reduce the wear of the coatings, while the wear-reducing effect of the nanometer Cr particles is more effective than that of the Cr microparticles.



**Fig.4** SEM images of worn surface of pure Ni film (a), EMCC Ni-12.4Cr (b) and ENCC Ni-11.0Cr (c)

From above results, the incorporation of Cr nanoparticles instead of Cr microparticles in the matrix can largely improve the tribological performance of the co-deposited Ni-Cr composite coatings. FENG et al[1] reported that embedding of nanoparticles perturbs the crystal growth of Ni, inducing a reduction in the crystal size and giving deposits a significantly increased hardness values. QU et al[12] also reported that the existence of CeO<sub>2</sub> nanoparticles, as the secondary phase, reduces the grain size of Ni-matrix. Accordingly, the higher microhardness value of the Ni-Cr nanocomposites may be due to the decrease of the grain size of Ni-matrix of the composites, which is favored by the Cr nanoparticles, as shown in Fig.1(c). With the grain refinement of Ni-matrix, the load carrying ability and the resistance to plastic deformation[1, 12–15] increase. It is also 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. The amount and size of particles define two kinds of reinforcing

mechanisms in metal matrix composite materials, namely, dispersion-strengthening and particle-strengthening. A dispersion-strengthened composite is characterized by a dispersion of fine particles with a particle size ranging from 0.01 to 1.00 μm, and volume percent ranging from 1 to 15 through a dislocation-particle interaction or Orowan hardening mechanism. In this case, the matrix carries the load and the fine particles impede the motion of dislocations[16]. A particle-reinforced composite contains more than 20% (volume fraction) of particles larger than 1 μm. The load is carried by both the matrix and the particles. Strengthening is achieved because particles restrain deformation of matrix by a mechanical constraint. Accordingly, in this study, the microhardness increase noted in ENCC Ni-Cr is also related to the dispersion-strengthening effect caused by Cr particles in the composite coatings, which impedes the motion of dislocations in metallic matrix [17–19]. During the friction process, the co-deposited Cr nanoparticles gradually protrudes out of the matrix, which carries the load transferred from the matrix, and as a result, the amount of thermal plastic deformation and scuffing wear at high temperature caused by the heat generated in the sliding is reduced. That is also the reasons why the friction coefficient of ENCC Ni-Cr is more stable and more than three times lower than that of the as-deposited Ni film or EMCC Ni-Cr.

## 4 Conclusions

- 1) The as-co-deposited Ni-Cr composite coatings show a lower friction coefficient and a better wear resistance compared with the as-deposited pure Ni film.
- 2) The ENCC Ni-Cr exhibits a lower friction coefficient and a higher wear resistance than the EMCC Ni-Cr under the same condition. The reason is that the incorporation of nanometer Cr particles in the deposit effectively reduces the size of Ni crystals and greatly increases the hardness of the composite coating through grain refinement-strengthening and dispersion-strengthening effect.

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(Edited by YANG Hua)