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Materials

Influence of current density on nano-Al_2O_3/Ni+Co bionic gradient composite coatings by electrodeposition

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Abstract: Metal and nano-ceramic nanocomposite coatings were prepared on the gray cast iron surface by the electrodeposition method. The Ni-Co was used as the metal matrix, and nano-Al_2O_3 was chosen as the second-phase particulates. To avoid poor interface bonding and stress distribution, the gradient structure of biology materials was found as the model and therefore the gradient composite coating was prepared. The morphology of the composite coatings was flatter and the microstructure was denser than that of pure Ni-Co coatings. The composite coatings were prepared by different current densities, and the 2-D and 3-D morphologies of the surface coatings were observed. The result indicated that the 2-D structure became rougher and the 3-D surface density of apices became less when the current density was increased. The content of nanoparticulates reached a maximum value at the current density of 40 $mA\cdot cm^{-2}$, at the same time the properties including microhardness and wear-resistance were analyzed. The microhardness reached a maximum value and the wear volume was also less at the current density of 40 $mA\cdot cm^{-2}$. The reason was that nano-Al_2O_3 particles caused dispersive strengthening and grain refining.

Key words: electrodeposition; composite coating; current density; nano-Al_2O_3; microstructure; mechanical properties

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1. Introduction

The nano-particulate composite electrodeposition is one of the most important surface modification technologies in recent years. The coatings by electrodepositing are of good chemical stability, high microhardness, and good wear resistance. Moreover, the electrodeposition technology has many advantages such as precise control, near room temperature operation, low energy requirement, rapid deposition rate, capability to handle complex geometry, low cost, and simple scale-up with easily maintained equipment [1-5]. The various electrodeposited metal- and alloy-based, especially, Ni-based or nickel alloy-based coatings containing various ceramic nano-particulates including nano-ZrO_2/Ni [6], nano-Al_2O_3/Ni [7-8], CNT/Ni [9-10], nano-TiO_2/Ni [11], nano-diamond/Ni [11], nano-SiC/Ni-Co [12], nano-Si_3N_4/Ni-Co [1, 13], nano-SiC/Zn-Ni [14], nano-Al_2O_3/Co-Ni [15], nano-Si_3N_4 [16], have been prepared. The gray cast iron is a widely used material. Due to the limitation of processing technology, the surface properties of gray cast iron are poor. Therefore, it is essential to improve the surface properties of gray cast iron by electrodeposition.

In this article, Ni-Co was used as the metal matrix and nano-Al_2O_3 was chosen as the second-phase particulate. The morphology of the composite coatings was observed and analyzed. When the current density was changed, the surface morphology and properties changed too. The influences of current density on the composite coating including surface morphology, 2-D and 3-D morphologies, microhardness, and wear resistance were investigated.

2. Experimental

The electrolyte consists of $NiSO_4\cdot 6H_2O$ (300 $g\cdot L^{-1}$),

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$NiCl_2 \cdot 6H_2O$ (40 g·L^{-1}), H_3BO_3 (35 g·L^{-1}), and a little $CoSO_4$. To prevent pinhole, a little wetting agent, such as Na_2SO_4-12CH_2, is usually added.

The average granularity of nano-Al_2O_3 (from Hongsheng, Zhejiang, China) is 60 nm, the purity is more than 99.99%, the specific surface area is 180±10 m^2/g, and the crystal structure of nano-Al_2O_3 is γ-Al_2O_3. The nickel plate of 80 mm×40 mm was used as the anode. Some rectangular gray cast iron specimens with the size of 20 mm×20 mm and the surface roughness less than 0.05 μm were used as the cathode substrate to be plated. The substrates were sequentially wiped with oil and rust by reagents, and then immersed immediately in the plating bath to allow the electrodeposition of the target composite coating.

To make nano-Al_2O_3 suspend in the plating bath, the electrolyte was vibrated by ultrasonic for 120 min before experiments. In the process of electrodeposition, the technology parameters were determined, *i.e.*, the pH value was 3-4, the temperature of the electrolyte was 45°C, the content of nano-Al_2O_3 in the electrolyte was 20 g/L, and the stirring style was mechanical stir together with ultrasonic vibration. First, the gray cast iron specimen was plated for 30 min in the electrolyte without nano-Al_2O_3. Second, the gray cast iron specimen was moved into the nano-composite electrolyte and plated for 40 min. The morphology of the nanocomposite coating surface was observed by means of SEM (JSM-5500LV, Japan electronic), the 3-D morphology was observed by a laser co-focusing microscope, and the content of elements in the coating was measured by means of energy spectrum. The microhardness of the composite coating was measured with a microsclerometer (HXD-1000TM) at an applied load of 0.49 N and a holding time of 5 s. The result was the average of five measure values of each sample. The friction and wear test was conducted on a quick speed wear machine (SKODA-SAVIN). The wear resistance of the coating was determined with the volume loss after wear. The counterpart was made from hard metal, whose size was ϕ30 mm×2.5 mm and the rotating speed was 625 r/min. The test load was 29.4 N, and the revolutions were 600 times. Three measure values of each sample were carried on and the results were the average.

3. Results and discussion

3.1. Morphologies of the nano-composite coating and the pure Ni-Co coating

Compared with the Ni-Co coating, the sizes of crystal grains in the n-Al_2O_3/Ni-Co nanocomposite coating largely decrease due to the dimension effect of nanoparticles (Fig. 1). The high active surface of nanoparticles provides an amount of nucleus for Ni atoms in the process of electrodeposition. The overpotential of metal forming nucleus reaction decreases. The composite coating with fine and compact microstructure is obtained because of the higher nucleation rate [11].

Fig. 2 shows a section of the composite coating. The connection between the coating and the substrate is very compact. The thickness of the composite coating is about 85 μm. The typical microstructure of the gray cast iron substrate, *i.e.*, the large flaky graphite and thin flaky pearlite, can be seen. The morphology of thin flaky pearlite looks like fishbone and arrays very uniformly.

Fig. 3 shows the line scan element curves of the composite coating. The distribution curves of elements Al, Fe, C, and Ni can be seen clearly. Al distributes more at the outer layer of the coating because the content of nano-Al_2O_3 particles in the composite coating is gradient. Since the substrate is gray cast iron, Fe is more in the substrate but exiguous in the coating, and C distributes mainly in the flaky graphite. Contrary Ni is more in the coating but exiguous in the substrate.

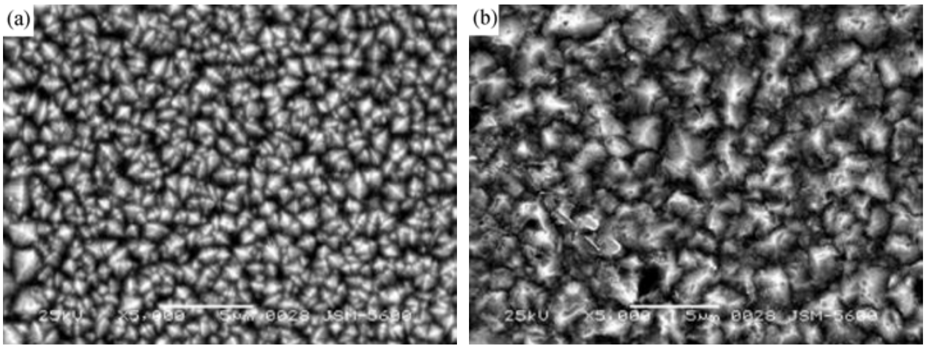

Fig. 1. Surface morphologies by the current density of 20 mA·cm^{-2}: (a) pure Ni-Co coating; (b) composite coating.

3.2. Influence of current density on the electrodeposition course

Fig. 4 shows the relationship between current density and the mass fraction of the co-deposited Al_2O_3 nano-particulates in the coating. It shows that the mass fraction of the Al_2O_3 nano-particulates in the composite coating increases with increasing current density when the current density is less than 40 mA·cm^{-2}. A similar behavior is observed in other cases [12, 15]. Before the maximum value, the tendency that absorbed particles arrive in the cathode surface increases, which is consistent with Guglielmi's two-step adsorption mode [17]. Ni^{2+} of the anode is electrolyzed slowly, and there is not enough time to adsorb Al_2O_3 nano-particles. It is difficult for Al_2O_3 particles to be embedded in the coating when current density is low. With the increase of cathode current density, the cathode absorbs positive ion nano-particles and the co-deposition speed of nano-Al_2O_3 and metal matrix increases. But when the current density reaches a certain value, the deposited speed of the metal matrix is faster than that of nano-particulates, and the content of Al_2O_3 particulates in the coating decreases. Therefore, the metal deposition dominates the co-deposition process [12].

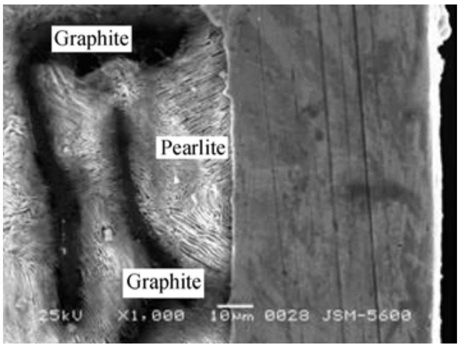

Fig. 2. Cross-section of the composite coating.

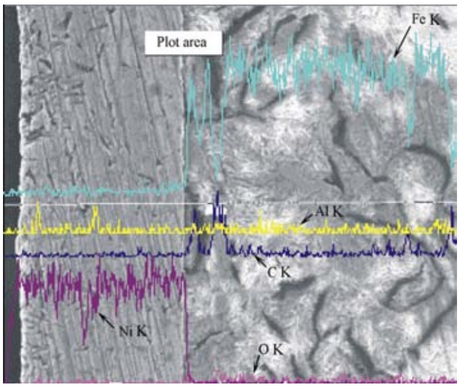

Fig. 3. Line scan element curve of the composite coating.

3.3. Influence of current density on the composite coating

Fig. 5 shows the surface morphologies of the coatings by different current densities. It can be seen that the structures of the composite coating are compact and the grains are fine when the current density is low. With increasing the current density, the structures of the composite coating become rougher. Fig. 6 shows the 3-D morphologies of the composite coatings by a laser co-focusing microscope. It can be seen that the composite coating has a similar rule to 2-D surfaces. The 3-D morphologies become rougher with increasing current density. When the current is low, the deposition speed is slow, and Ni and embedded nano-Al_2O_3 form an amount of nucleus that can not agglomerate too quickly. Thus the microstructure is fine and compact; on the contrary, it is rough and loose.

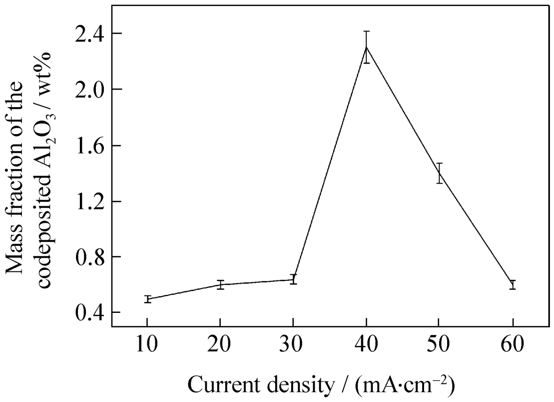

Fig. 4. Mass fraction of the codeposited Al_2O_3 *vs*. current density.

3.4. Wear resistance of the Ni-Co/Al_2O_3 nanocomposite coatings by different current densities

Fig. 7 shows the hardness of the Ni-Co/Al_2O_3 nanocomposite coatings at different current densities from 10 to 6 mA·cm^{-2}. When the current density is 40 mA·cm^{-2}, the microhardness value of the nanocomposite coating reaches a maximum value of Hv 555. The result corresponds to the fact that the mass fraction of nano-particulates in the nanocomposite coating and reaches a maximum value at 40 mA·cm^{-2} (Fig. 3). Fig. 8 shows the relations between the wear volume loss and current density. The wear volume loss reaches a minimum value of 126 mm^{-3} when the current density is 40 mA·cm^{-2}, and the result accords with the transformation trend of microhardness (Fig. 7). The effects of grain refining and dispersive strengthening become stronger with increasing the nano-Al_2O_3 content in the composite coating; thus the microhardness of the composite coating increases and the wear volume loss decreases with increasing the nano-Al_2O_3 content [1, 11].

4. Conclusions

(1) The Ni+Co coating and the Ni+Co/nano-Al_2O_3 composite coating were prepared on the gray cast iron

surface. The result indicates that the composite coating is compact and fine. The course of the composite electrodeposition was analyzed, and the metal deposition dominates the co-deposition process.

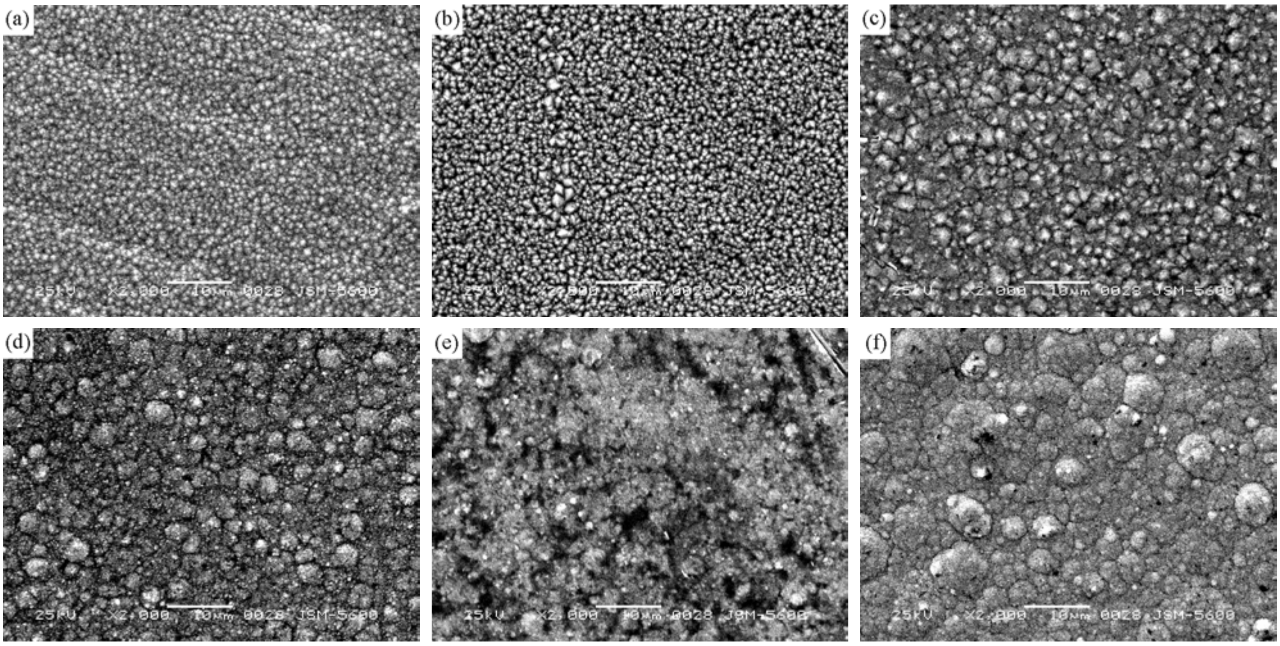

Fig. 5. Surface morphologies of the composite coatings (SEM) by different current densities: (a) 10 mA·cm^{-2}; (b) 20 mA·cm^{-2}; (c) 30 mA·cm^{-2}; (d) 40 mA·cm^{-2}; (e) 50 mA·cm^{-2}; (f) 60 mA·cm^{-2}.

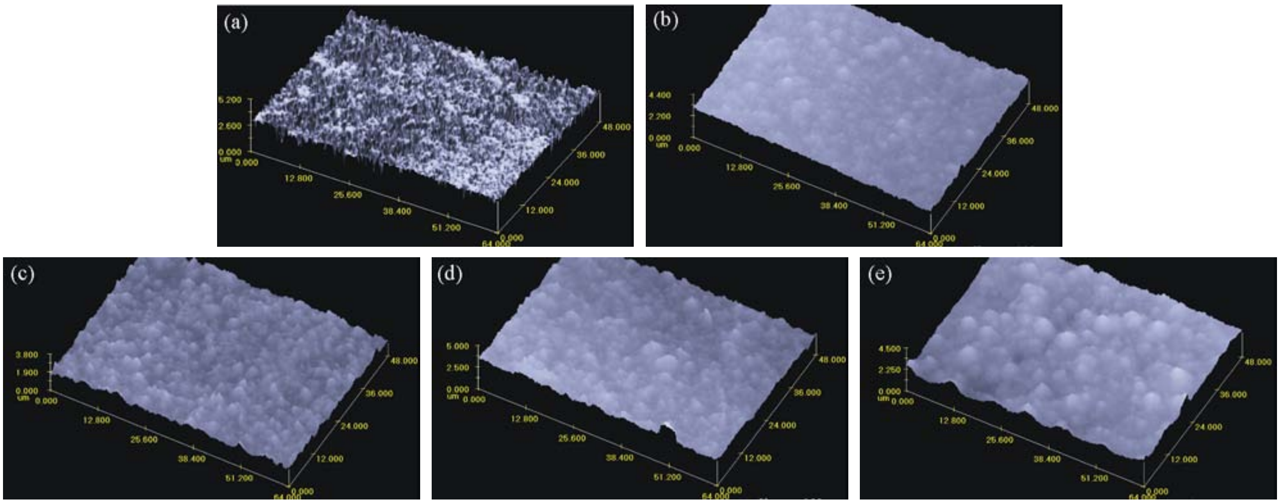

Fig. 6. 3-D surface morghologies of the composite coating by different current densities: (a) 20 mA·cm^{-2}; (b) 30 mA·cm^{-2}; (c) 40 mA·cm^{-2}; (d) 50 mA·cm^{-2}; (e) 60 mA·cm^{-2}.

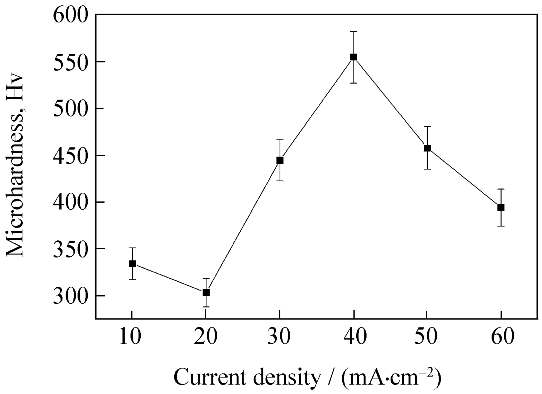

Fig. 7. Current density *vs.* microhardness.

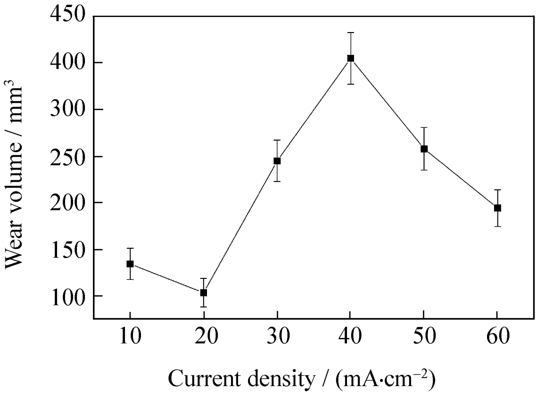

Fig. 8. Wear volume loss *vs.* current density.

(2) The observation of 2-D and 3-D morphologies of the composite coating suggests that the microstructures become rougher with increasing current density.

(3) The nano-Al_2O_3 content reaches a maximum value when the current density is 40 mA·cm^{-2}. At the same time, the microhardness of the composite coating also reaches a maximum value and the wear volume loss reaches a minimum value, which is caused by nanoparticulate grain refining and dispersive strengthening effects.

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