

Research Article

Nickel Based Coatings Containing TiN Nanoparticles Prepared by Ultrasonic-Electrodeposition Technology

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Abstract: In order to enhance the surface properties of steel substrates, nano Ni-TiN composite coatings were prepared using ultrasonic-electrodeposition technology in this study. The effects of ultrasonic on composite coatings were studied. The X-Ray Diffraction (XRD) study had been utilized to detect the crystalline and amorphous characteristics of Ni-TiN composite coatings. The surface morphology and metallurgical structure of composite coatings were observed with Scanning Electron Microscope (SEM) and High Respective Transmission Electron Microscope (HRTEM). Finally the corrosion resistance was tested. The results show that the ultrasonic has greatly effects on TiN nanoparticles in composite coatings. And the introduction of ultrasonic and TiN particles cause the nickel grains to become fine. The average grain diameter of TiN particles is 30 nm. The Ni grain is measured approximately 60 nm. The test of corrosion resistance shows the nano Ni-TiN composite coating is proved with good corrosion resistance. The corrosion rate of 45 steel is about 5 times than that of Ni-TiN composite coating and the corrosion rate of Ni coating is above thrice than that of Ni-TiN composite coating.

Keywords: Nickel, Coating, TiN, Ultrasonic-electrodeposition

INTRODUCTION

Nano composite coatings are coatings which are formed by components with characteristic dimensionality as nano-size (1~100nm) setting in different matrixes and own better mechanical performances such like higher hardness, wear resistance and corrosion resistance, etc. Xia, *et al.* (2012), Zhou *et al.* (2004), Baumann *et al.* (2011) and Jitputti *et al.* (1995). Composite electrodeposition technology is a method to obtain composite coatings by adding insoluble micrometer or nanometer sized solid particles (such as TiN, AlN, SiC and Al₂O₃, etc.) into the electrolyte to co-deposit the particles and metal matrix with electrodeposition. The electrodeposition of composite coatings can be traced back to studies which produced a graphite-copper composite coating (Feng *et al.*, 2005; Sen *et al.*, 2010; Heidari *et al.*, 2010; Aruna *et al.*, 2007; Low *et al.*, 2006). Due to superiority of both traditional composite materials and modern nano materials, nano composite coatings have become a highlight for researchers all over the world (Fustes *et al.*, 2008; Bund and Thiemig, 2007; Slimen *et al.*, 2011).

The ultrasonic is a mechanical wave and the frequency is about $2 \times 10^4 \sim 10^9$ Hz. During nano Ni-TiN composite coatings are prepared, conventional mechanical dispersing method depends on agitation to

make the particles suspend in the electrolyte and is less effective once all particles are suspending, while comparatively the effect of ultrasonic on the dispersion of tiny particles in the electrolyte is more helpful acutely in virtue of its stirring and dispersing effect than mechanical dispersing method can achieve. In this essay, nano Ni-TiN composite coatings were synthesized using ultrasonic-electrodeposition method. The effects of the ultrasonic on composite coatings were studied. The morphology and microstructure of composite coatings were studied by XRD, SEM and HRTEM. And the corrosion resistance of samples was tested.

EXPERIMENTAL

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Schematic diagram of the experimental setup used for preparing Ni-TiN composite coatings is shown in

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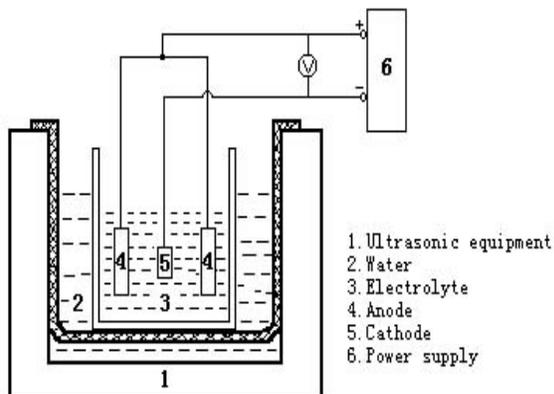


Fig. 1: Schematic diagram of the experimental setup

Fig. 1. Nano Ni-TiN composite coatings were deposited on 45 steel substrates by ultrasonic-electrodeposition process. The anode is a pure Ni plate. The average grain diameters of nano TiN particles (Received from Haitai nano Ltd., PR China) are 20 nm. And the purity is above 99.99%. The basic compositions of the electrolyte are as follows: 250 g/l nickel sulfate, 40 g/l nickel chloride, 30 g/l boric acid and 2-10 g/L TiN particles. The temperature of the plating bath was kept at 50 °C. The pH of the plating bath was 4-5 which adjusted by ammonia water or dilute sulfuric-acid. The current density was 2-5 A/dm². Prior to the deposition, the substrates were mechanically polished to a 0.10-0.15 μm surface finish, then a sequence of cleanings were performed to remove contamination on the substrate surface, the steel substrates were activated for 15 s in a mixed acidic bath, then rinsed with distilled water. The Ni-TiN composite coatings were electrodeposited by gradually changing the ultrasonic wave from 0 to 300 W.

In order to understand the crystal properties of Ni-TiN composite coatings, X-Ray Diffraction measurements (XRD) were performed. The diffraction meter (RIGAKU D/Max-2400) was used with Cu K α radiation. The scan was taken between (20-85°) 2 θ , the operating target voltage was 40 KV, tube current was 100 mA. Using the XRD analysis with the phase identification, we quantified the volume ratio. It is calculated as follows:

$$V_t = \frac{X_t}{C(1-X_t) + X_t} \quad (1)$$

where, C = 1.381 for Cu K α :

$$X_t = \frac{I(101)_t}{I(111)_m + I(111)_m + I(101)_t} \quad (2)$$

Microstructure investigation of cross-sectioned deposits was performed using a JSM-6460Lv Scanning

Electron Microscopy (SEM). The surface morphology and microstructure of composite coatings were observed by SEM and Tecnai-G2-20-S-Twin high respective transmission electron microscope (HRTEM), after being mechanical reducing and ion reducing on Gatan-600 double-ion reducing machine.

Corrosion resistance was tested with entire immersion test. The process was as follow: 45 steel, Ni coating and nano Ni-TiN composite coating specimens were all immersed into 3% NaCl solution for 180 h, with temperature kept at 30°C. Then the loss weight was measured by electronic analytical balance (Sartorius BS210S). The corrosive rate V of each specimen could be calculated by formula:

$$V = \frac{M_c}{T}$$

In which M_c stands for the mass of corrosion and T stands for the corrosion time.

RESULTS AND ANALYSIS

Effects of ultrasonic on nano TiN particles in composite coatings: Given a certain parameters (4 A/dm² current density, 6 g/L TiN particles, 4.5 pH), the effects of ultrasonic on distribution of nano TiN particles in composite coatings is depicted in Fig. 2. Figure 2(a) shows TiN particles in the composite coating which electrodeposited with mechanical stirring instead of the ultrasonic are few in quantity and appear to reunite to some extent. Figure 2(b) shows TiN particles in the composite coating which ultrasonic-electrodeposited with appropriate ultrasonic parameters are dispersed homogenously in deposit. Figure 2(c) shows TiN particles in the composite coating are rather few in quantity and appear to slight reunite when the coating is prepared by ultrasonic-electrodeposited with greater ultrasonic action. The reason is that traditional mechanical dispersing method depends on agitation to make the particles suspend in the electrolyte and is less effective once all the particles are suspending, while the effect of ultrasonic on the dispersion of tiny particles in the electrolyte is more helpful. Acoustic streams produced by ultrasonic make the TiN particles disperse homogenously in electrolyte and high-pressure wave and violent stochastic vibration aroused by cavitation effect of ultrasonic shatter the groups of reunited particles and further homogenize the particles in microscopy. According to the Guglielmi's adsorption mechanism model of composite electrodeposition, the adsorption process of particles on electrode surface may be divided into weak adsorption and strong adsorption and the weak adsorption process is reversible. When super ultrasonic is adopted, the overmuch cavitation effects of ultrasonic will make the nano TiN particles violent collide and reunite again, while the overmuch stirring effect of ultrasonic will wash the nano TiN particles which infirmly absorb to the cathode surface

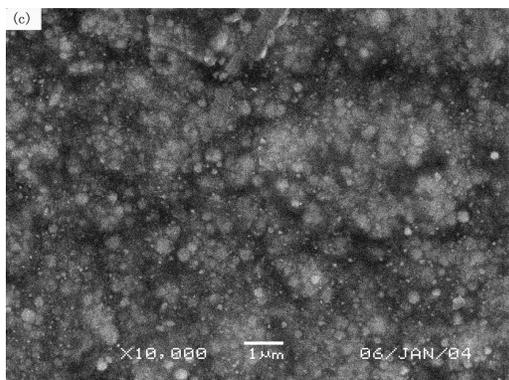
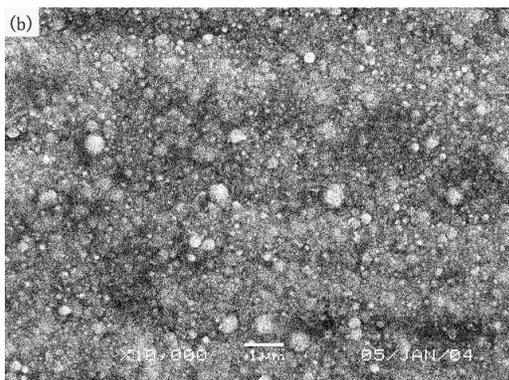
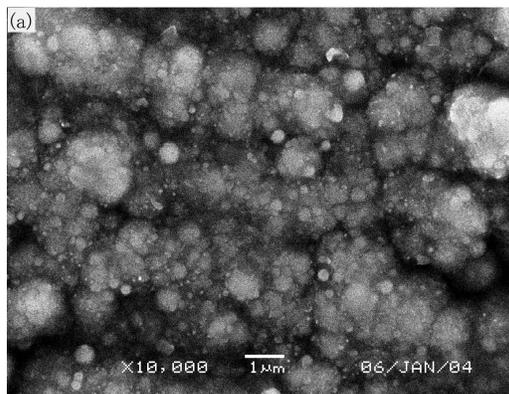


Fig. 2: Distribution of nano TiN particles in composite coating under different action; (a) Mechanical stirring; (b) Moderate ultrasonic action (200 W); (c) Super ultrasonic action (300 W)

into the electrolyte again, affect the oriented deposition of the particles, thus decrease the content of nano TiN particles in the composite coating.

Effects of ultrasonic on X-Ray diffraction of composite coatings: The X-Ray diffraction patterns of nano Ni-TiN composite coatings prepared by ultrasonic-electrodeposition method and electro deposition method are displayed in Fig. 3. XRD analysis of the coatings showed the crystalline peaks of Ni and TiN. There is a tendency of the decrease of Ni peaks as the ultrasonic power increases from 0 W to

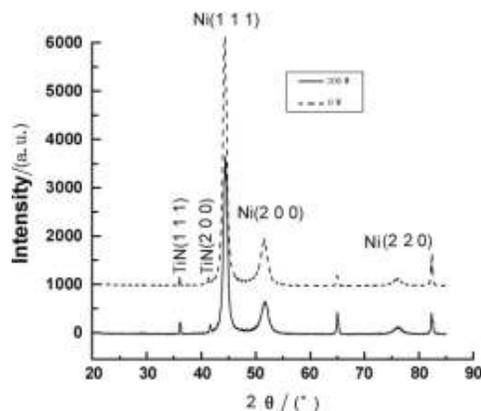


Fig. 3: XRD patterns of nano Ni-TiN composition coatings

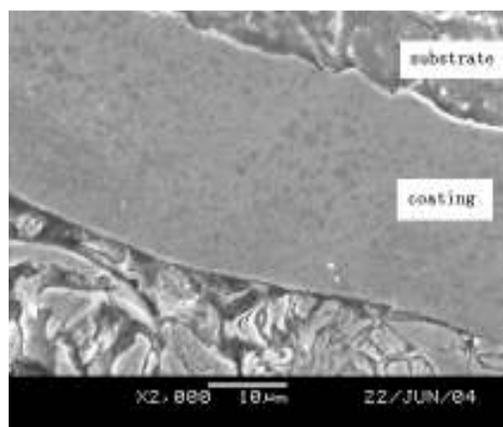


Fig. 4: The cross-sectional SEM morphology of Ni-TiN composite coating

300 W, which agrees with a previous study by Xia *et al.* (2012). During the process of ultrasonic-electrodeposition, the nickel grains are fine and the growing direction change from superior direction to random direction. The reason is that nano particles which enter and disperse homogeneously in the composite coating increase the amount of nuclei for nucleation of nickel grains and also hinder the growth of them. Furthermore, the mechanical force produced by acoustic stream of ultrasonic may break the normal growth of the grains and crash the thicker grains to produce smaller nuclei. And the high pressure arise by cavitation effect may cause instantaneous local super-cooling, thus decrease the critical radius of the nuclei and promote the nucleation. With the increase of nucleation and the decrease of growth, the nickel grains become fine.

Analysis of the microstructure: The cross-sectional micrograph of the Ni-TiN composite coating (Fig. 2b) which had a total thickness of approximately 25 μm is shown in Fig. 4. It can be clearly observed that the Ni-TiN composite coating exhibited a dense structure and

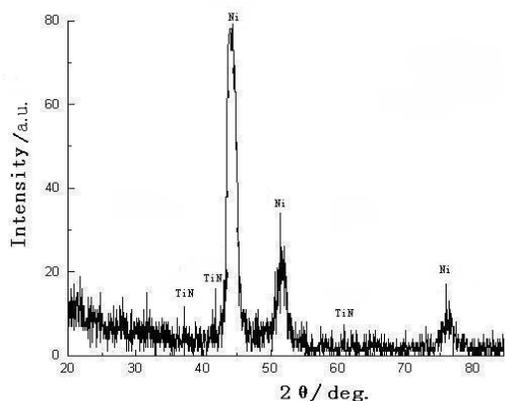


Fig. 5: XRD pattern of nano Ni-TiN composition coating in cross section

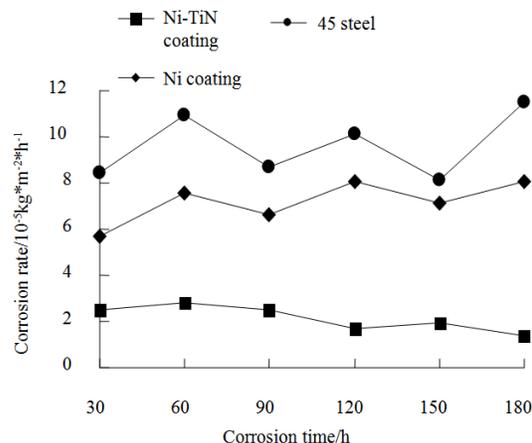


Fig. 7: Curves of corrosion rates of three samples

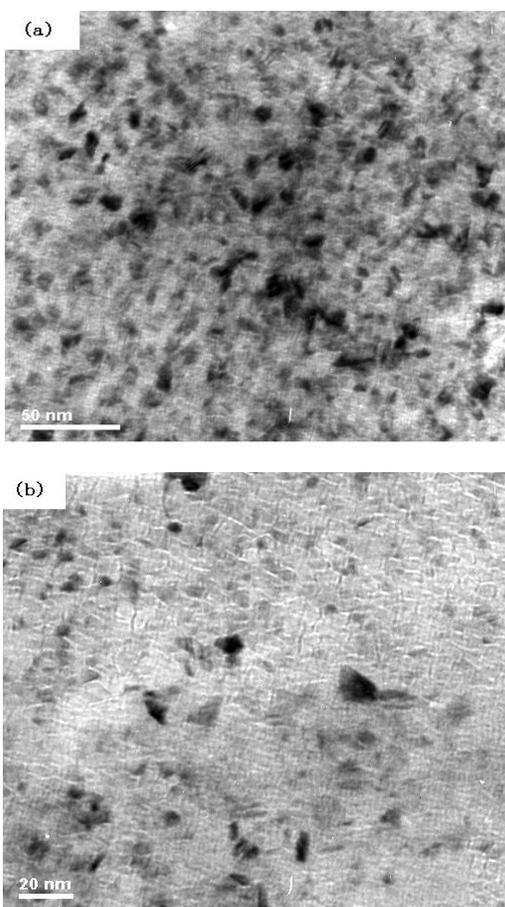


Fig. 6: HRTEM micrographs of nano Ni-TiN composite coatings

better bonding between the deposit and steel substrate was achieved. Figure 5 is the XRD pattern of nano Ni-TiN composition coating in the cross section. The Ni peaks at 44.82, 52.21 and 76.77° are observed. While the TiN peaks are at 36.66, 42.60 and 61.81°.

The ultrasonic-electrodeposited nano Ni-TiN composite coatings were peeled off from the matrix,

polished on 2000 abrasive studs and then reduced on Gatan-600 double-ion reducing machine to thin films. The microstructure inspected on high resolution transmission electron microscope is shown in Fig. 6. The black sections in Fig. 6(a) are nano TiN particles, which diameters are all less than 50 nm and the average grain diameter is 30 nm. It can be seen obviously in Fig. 6(b) that the Ni grains have already reached nanometer size, which are measured approximately 60 nm.

Test of corrosion resistance: Ni-TiN composite coatings and Ni coatings which prepared by ultrasonic-electrodeposition method were tested with 45 steel in Fig. 7. It can be seen that, the Ni-TiN composite coating shows finer corrosion resistance and the corrosion rate of which changes very slowly. And the corrosion rate of Ni coating is faster than Ni-TiN composite coating. While the corrosion rate of 45 steel keeps changing greatly during the whole process. The corrosion rate of 45 steel is about 5 times that of Ni-TiN composite coating and the corrosion rate of Ni coating is above three times that of Ni-TiN composite coating. The better corrosion resistance of Ni-TiN composite coating may be on account of the following factors.

On the one hand, the nickel coating, with the potential of nickel more positive than the carbon steel matrix, belongs to cathode coating, which can only provide mechanical protection for the steel. When there are bigger defects and mechanical damages in the coating, the coating and matrix metal tend to form corroding micro cells in the corroding medium, in which the matrix metal will be accelerated to dissolve as the anode. However, in the nano Ni-TiN composite coatings in which nano TiN particles disperse equally among the grains and grain boundaries, due to its nano size, the TiN particles can minimize the interspaces, improve the compactness of the coating and make it harder for the corroding medium to soak into the micro

holes in the coating, thus enhance the corrosion resistance of the coating.

On the other hand, the strengthening body may form dispersed active phases, therefore, the corroded holes of the nano Ni-TiN composite coatings after corroded in the solution are obviously smaller and equally distributing than those of pure nickel coatings under same conditions. In addition, the existence of stable strengthening body in the metal matrix composites can hinder the enlargement of corroding pits and in the same way the nano TiN particles co-deposited into the coating as strengthening phase hinder the enlargement of corroding pits, thus enhance the corrosion resistance.

CONCLUSION

- The ultrasonic had greatly effects on nano TiN particles in composite coatings. TiN particles were dispersed homogenously in composite coatings which prepared with appropriate parameters (4 A/dm² current density, 6 g/L TiN particles, 200 W ultrasonic, 4.5 pH). XRD analysis of the coatings showed the introduction of ultrasonic and TiN particles caused the nickel grains to become fine
- SEM and XRD analysis showed the coating had a total thickness of approximately 25 μm. The Ni peaks at 44.82, 52.21 and 76.77° were observed. And the TiN peaks were at 36.66, 42.60 and 61.81°
- HRTEM analysis displayed there was hardly any reunion of nano TiN particles in the composite coating and the average grain diameter was 30 nm. The Ni grains had already reached nano size., which were measured approximately 60 nm
- The test of corrosion resistance showed the nano Ni-TiN composite coating was proved with good corrosion resistance. The corrosion rate of 45 steel was about 5 times than that of Ni-TiN composite coating and the corrosion rate of Ni coating was above thrice than that of Ni-TiN composite coating.

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