

Research Article

Preparation and Mechanical Properties of Ni-TiN Composite Layers by Ultrasonic Electrode Position

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Abstract: Ultrasonic electrodeposition was used to prepare nanocermet Ni-TiN composite layers on steel substrates. The action of mechanical disturbance by ultrasonic waves on electrolyte mass transfer, the inhibition of nanoparticle aggregation by ultrasonic cavitation and the effect of electric pulse parameters on the nucleation and growth of grains were investigated. The nanocermet Ni-TiN composite layer consisted of nanocrystalline nickel (30~60 nm). The micro-hardness of the composite layers increases a little when TiN content increases from 0% to 2%. However, micro-hardness increases greatly when V is increased from 2% to 9%. The maximal micro-hardness for Ni-TiN composite layers is 860 HV, 908 HV and 950 HV, respectively.

Keywords: Composite layer, mechanical property, preparation

INTRODUCTION

Nanocomposite electrodeposition is a method used to co-deposit insoluble solid nanoparticles (usually ceramic particles) and a metal matrix as a plating layer by adding particles to the electrolyte before electrode position (Liu *et al.*, 2012; Clark *et al.*, 1997; Robertson *et al.*, 1999; Zhang *et al.*, 2011; Kim and Woo, 1998). Nanocomposite layers possess many special properties and have been used in industrial applications. To obtain a series of layers with different properties, several strengthening and toughening mechanisms must act together to produce a cooperative effect (Tan and Xu, 2004; Benea *et al.*, 2011; Podlaha, 2010; Vidrine and Podlaha, 2011; Steinbach and Ferkel, 2011). Owing to its great significance in industrial applications, nanocomposite electrodeposition has been the focus of much research (Koch *et al.*, 2001; Lee *et al.*, 1999; Gan *et al.*, 2001; Dai and Zhang, 2010; Li and Wang, 2009; Xiao *et al.*, 2001).

Factors influencing the preparation of nanocomposite layer include electrolyte pH, electric pulse parameters and additive type and content. The grain size of the co-deposited metal matrix and the distribution and content of nanoparticles are the main factors determining the properties of the composite layer. Ultrasonication is an efficient method for dispersing suspended microparticles in solution (Wu *et al.*, 2008; Morgan *et al.*, 2001; Yang *et al.*, 2008; Qiao *et al.*, 2009; Muller and Ferkel, 1999; Huang *et al.*, 1999; Chen *et al.*, 2001). Here we report the preparation of nanocermet Ni-TiN composite layers on steel substrates by ultrasonic electrodeposition.

Experimental observations and analysis were used to identify the optimum ultrasonic and electrodeposition conditions. This treatment yielded Ni-TiN nanocomposite layers with excellent properties. The results provide a technical basis for modification of the surface properties of metal hardware in the future.

EXPERIMENTAL PROCEDURE

Nickel plates of 50 mm 40 mm 3 mm were used as the anode and 20# steel plates of 30 mm 20 mm 1 mm as the cathode. The space between the anode and cathode was 50~70 mm. TiN nanoparticles with an average size of ~30 nm and purity greater than 99.99% were employed. The composition of the electrolyte is shown in Table 1.

Ultrasonic pulsing during electrode position was carried out with power of 0~300 W and a frequency of 20~50 kHz. The frequency of the rectangular-pulse electricity was 400~800 Hz, with an occupational proportion of 10~90% and pulse current density of 20~60 A/dm².

Cold-rolled steel plates were polished with emery paper, chemically cleaned and etched and then electroplated by ultrasonic electrodeposition. After plating, they were rinsed with distilled water, dried with ethyl alcohol and prepared for examination. The surface morphology and microstructure of Ni-TiN nanocomposite layers were observed by scanning electron microscopy (SEM; Oxford Microanalysis Group JSM-5600LV) and high-resolution transmission electron microscopy (HRTEM; Philips Tecnai-G2-10-S-Twin). A conventional scratch tester (WS-92

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Table 1: Electrolyte composition and plating conditions

Parameter	Value
NiSO ₄ content (g/L)	300
NiCl ₂ content (g/L)	60
H ₃ BO ₃ content (g/L)	40
Wetting agent	Trace
Shining agent	Trace
Surface activating agent	Trace
TiN nanoparticle content (g/L)	4~10
Temperature (°C)	30
pH	5.5

equipped with an acoustic emission detector) was used to evaluate the adhesion of layers to the substrate. The radius of the diamond pin was 0.2 mm. All tests were performed using a continuous increase in normal load from 0 to 100 N at a loading rate of 100 N·min⁻¹. Surface hardness was determined on an ultrasonic micro hardness instrument (SH-75) using a load of 0.1 N. The TiN particles content in composite layers (denoted by V) was surveyed by gravimetric analysis (HIDEN, IGA-003).

RESULTS AND ANALYSIS

Effect of ultrasonic power: During the preparation of Ni-TiN nanocomposite layers, variation of the ultrasonic power led to different cavitation and mass transfer effects. The content and dispersion of TiN nanoparticles in the layers for different ultrasonic power are shown in Table 2.

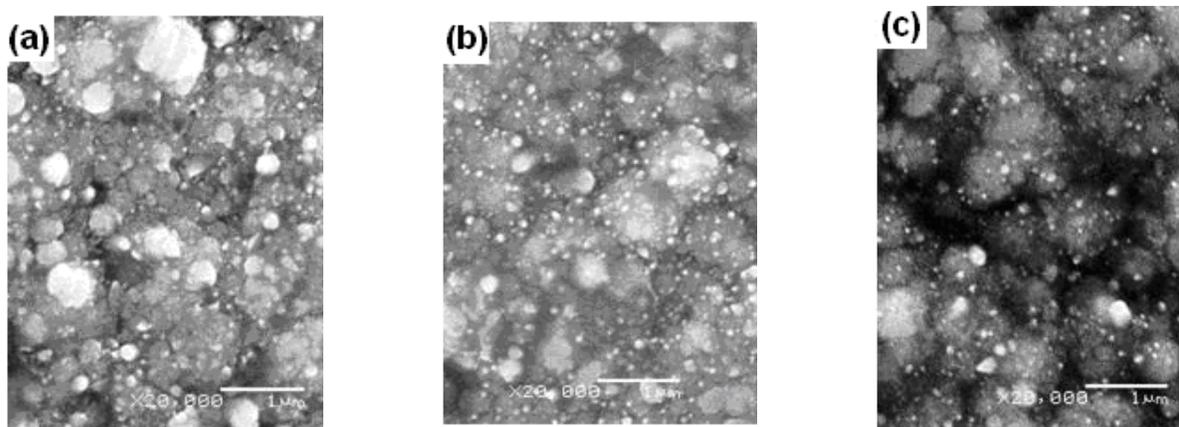
For a given TiN nanoparticle content in the electrolyte, the greater the ultrasonic power, the stronger were the mechanical disturbance and cavitation effects, which accelerated the mass transfer process and inhibited TiN nanoparticle aggregation in the electrolyte, leading to homogeneous dispersion of the nanoparticles in the plating layer. However, high

Table 2: Content and dispersion of TiN nanoparticles in the layers

Ultrasonication time (min)	0	40	40	40
Ultrasonic power (W)	0	100	200	300
Nanoparticle content (vol/%)	7	8	10	6
Nanoparticle aggregation	Yes	Slight	None	Slight

ultrasonic power affected the oriented deposition and content of TiN nanoparticles in the layers. SEM images of the dispersion and aggregation of TiN nanoparticles in the Ni-TiN nanocomposite layers are shown in Fig. 1.

Figure 1a shows that TiN particles in the composite layer were few in quantity and appeared to aggregate to a certain extent when electrodeposited with powerful mechanical stirring instead of ultrasonication. Figure 1b shows that electrode position of TiN particles using appropriate ultrasonic parameters led to homogeneous dispersion in the plating layer, with hardly any evidence of aggregation. For electrodeposition at greater ultrasonic power, TiN particles in the composite layer were rather few in quantity and exhibited slight aggregation (Fig. 1c). Traditional mechanical dispersion depends on agitation for particle suspension in the electrolyte and is less effective once all the particles are suspended. In comparison, ultrasonic waves are more efficient in dispersing nanoparticles in the electrolyte. Acoustic streams produced by ultrasonic waves led to the homogeneous dispersion of suspended particles at a macroscopic level. High-pressure waves and strong vibrations disrupted groups of aggregated particles and further homogenized the particles at a microscopic level. According to Guglielmi's model of composite electrodeposition, particle adsorption on the electrode surface may be divided into weak and strong adsorption, in which the former process is reversible.



(a) Mechanical stirring, no ultrasonication (b) Moderate ultrasonication (200 W) (c) Strong ultrasonication (300 W)

Fig. 1: Distribution of TiN nanoparticles in composite layers deposited under different ultrasonic power

At high ultrasonic power, the increased cavitation effects led to collision of TiN nanoparticles and subsequent aggregation. Moreover, the greater stirring effect dislodged TiN nanoparticles that were not firmly adsorbed on the cathode surface, affecting the oriented deposition of particles and thus decreasing the TiN nanoparticle content in the composite layer.

EFFECT OF PULSE CURRENT

In experiments, Ni ions and TiN nanoparticles were directionally deposited on the surface of the cathode using a single-directional pulse current. For ultrasonic power of 200 W for 40 min, the TiN nanoparticle content and the size of nickel grains in composite layers obtained using different pulse parameters (current density i_D , on-duty ratio t_p/t_i) are shown in Table 3.

Nickel grains and TiN nanoparticle dispersion in composite layers obtained with different pulse parameters were observed by HRTEM, as shown in Fig. 2. When the average current density was relatively low and the pulse interval was short, the nickel grains were large and were not on a nanometer scale (Fig. 2a). An increase in average current density led to increased deposition of metal ions and TiN nanoparticles, as well as the nucleation and growth of Ni grains. High-amplitude and narrow-pulse electricity accelerated the nucleation and inhibited the growth of crystalline grains, resulting in nano-sized nickel grains homogenous in size, as shown in Fig. 2b.

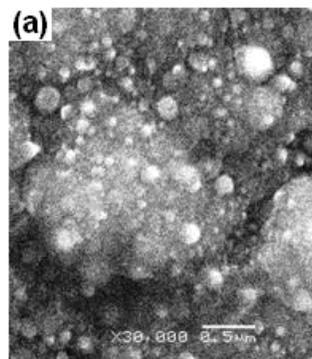
This behavior can be explained as follows. When pulsed electricity was employed, the pulse interval hindered the growth of crystalline grains and changed the growth direction, thus preventing grains from increasing in size. The size of grains in the deposited layer depends on the velocity of nucleation and growth.

An increase in nucleation velocity and decrease in growth velocity led to the formation of nano-sized crystalline grains. The co-deposited nanoparticles also restrained grain growth, enhanced the nucleation of nickel grains, accelerated the nucleation velocity and consequently increased the probability of obtaining nano-sized grains at relatively low current density. The cathode overpotential increased with the average current density and the electric field intensified. As a result, electrostatic gravitation between the cathode and Ni^{2+} and positively charged TiN nanoparticles increased and expedited Ni^{2+} deposition, which enhanced the capability of Ni^{2+} to surround TiN nanoparticles and increased the content of TiN particles in the plated layer.

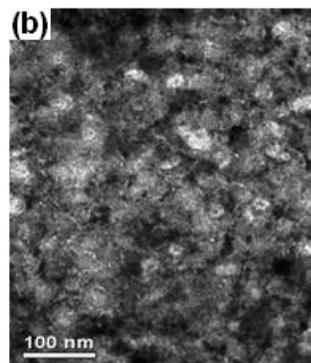
Pulsed electricity of high amplitude with a short pulse time and low occupancy could help to maintain a

Table 3: TiN nanoparticle content and nickel grain size in the composite layers

TiN content (vol%)	i_D (A/dm ²)	Ni grain size (nm)	t_p/t_i
4	20	300~500	1/2
5	40	200~300	1/2
8	40	100~200	1/4
11	60	50~80	1/6
9	80	30~50	1/6



(a) Short pulse interval and low current density



(b) Higher pulse amplitude, short pulse time and low on-duty ratio for the pulse current

Fig. 2: Surface morphology of Ni-TiN nanocomposite layers obtained under different pulse current parameters

higher average current density and longer pulse interval, leading to better experimental result. However, when the cathode current density was too high, Ni^{2+} ions were deposited at a much higher velocity than TiN nanoparticles. Moreover, H^+ ions on the surface of the cathode separated out largely in the form of hydrogen gas, which hindered the deposition of nanoparticles and thus decreased the TiN nanoparticle content in the plated layer.

Compound effect of ultrasonic electrode position:

The electrodeposition process involves mass transfer of the electrolyte and oxidation–reduction reactions on the electrodes. Both the cavitation effect of ultrasonic waves and the tiny jets produced by the waves when

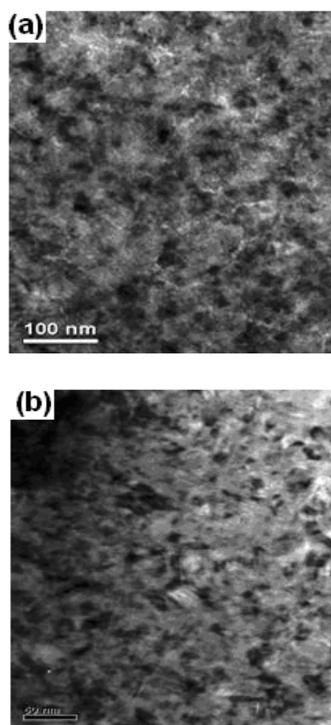


Fig. 3: Surface morphology of Ni-TiN nanocomposite layer obtained by ultrasonic electrode position at a scale of: (a) 100; and (b) 50 nm

spreading in the electrolyte improve the efficiency of mass transfer during electrodeposition, keeping the surface of the electrodes clean so that they are continuously activated. This results in acceleration of the oxidation–reduction reactions and plating deposition. Moreover, inhibition of cathode polarization has been observed.

During ultrasonic electrodeposition, the ultrasonic field promotes the co-deposition of TiN nanoparticles and nickel. Usually a surface activating agent is added to the electrolyte, which ionizes the TiN particles, facilitating their adsorption and deposition on the cathode. The cavitation effects and tiny jets produced by ultrasonic wave clean gas and impurities from the surface of TiN particles, improve the wetting of TiN nanoparticles by the electrolyte and make it easier for TiN particles to absorb activating agents and deposit onto the cathode. This is another major reason why the plated layer was rich in TiN nanoparticles.

Other characteristics of ultrasonic electrodeposition are that matrix metal grains tend to be fine and the growth direction changes to a random direction. Nanoparticles that enter and disperse homogeneously in the composite layer increase the amount of nuclei for nucleation of nickel grains and also hinder their growth, thus causing the grains to be fine. Application of

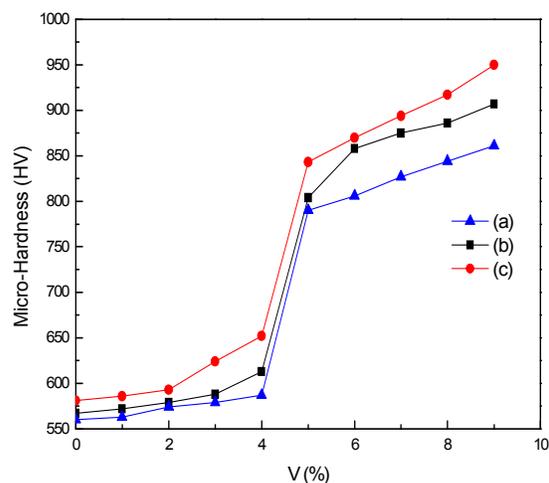


Fig. 4: The effect of V on micro-hardness of Ni-TiN composite layers deposited under different ultrasonic power (a) Mechanical stirring, no ultrasonication; (b) Moderate ultrasonication (200 W); (c) Strong ultrasonication (300 W)

ultrasonic waves may cause a further decrease in the size of matrix metal grains. On one hand, the mechanical force produced by acoustic streams and ultrasonic cavitation may break the normal growth of grains and disrupt larger grains to produce smaller nuclei, leading to “nucleus multiplication”. On the other hand, the high pressure induced by cavitation may cause instantaneous local super-cooling, thus decreasing the critical radius of nuclei and promoting nucleation. An increase in nucleation and decrease in growth lead to small nickel grains.

By combining ultrasonic treatment with electrodeposition, nano-sized Ni-TiN composite layers consisting of TiN nanoparticles and nickel grains of 30~60 nm could be obtained. The surface morphology observed by HRTEM is shown in Fig. 3.

Mechanical properties of Ni-TiN composite layers:

The micro-hardness of the three types of Ni-TiN composite layers as a function of V is shown in Fig. 4. The micro-hardness of the composite layers increases a little when V increases from 0% to 2%. However, micro-hardness increases greatly when V is increased from 2% to 9%. The maximal micro-hardness for Ni-TiN composite layers prepared by DC, PC and UPC deposition are 861 HV, 907 HV and 950 HV, respectively. The micro-hardness improvement in composite layer is related to the dispersion hardening effect caused by TiN particles, which has higher micro-hardness and enhances the properties of Ni-TiN composite layers.

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CONCLUSION

- Proper utilization of the mechanical disturbance and cavitation effects of ultrasonic waves could improve the mass transfer of the electrolyte and inhibit the aggregation of TiN nanoparticles, leading to homogeneous dispersion of the particles in the plated layer.
- Electricity pulses of high amplitude, narrow width and low occupancy accelerated the nucleation and inhibited the growth of metal grains, resulting in nano-sized nickel grains of homogeneous size.
- By appropriately controlling the electric pulse and ultrasonic parameters and choosing suitable types and quantity of agents, Ni-TiN nanocomposite layers consisting of TiN nanoparticles and nickel grains (30-60 nm) can be obtained.
- The micro-hardness of the composite layers increases a little when TiN content increases from 0% to 2%. However, micro-hardness increases greatly when V is increased from 2% to 9%. The maximal micro-hardness for Ni-TiN composite layers is 860 HV, 908 HV and 950 HV, respectively.

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