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Pulse co-electrodeposition and characterization of NiW–WC composite coatings

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ABSTRACT

The present study investigates the influence of pulse current parameters on the structure and hardness of the co-deposited nickel tungsten alloys incorporated by tungsten carbide particles (NiW–WC) for environmentally friendly alternatives to chromium deposits. While a minimum average current density of about 0.04 A/cm^2 is required for sufficient co-deposition kinetics, a decrease of duty cycle from 50% to 10% and a reduction of pulse frequency from 100 Hz to 10 Hz generally result in the increase of the carbide content in the deposits. Furthermore, these pulse parameters also affect the content of tungsten alloyed in the nickel matrix. NiW–WC of high hardness exceeding that of hard chromium coating by about 40% is achieved in the deposits with uniform structure, and with 31 at.% W and 13 wt.% WC particles. The mechanisms controlling the co-electrodeposition process and the corresponding hardness are discussed.

1. Introduction

The co-electrodeposition process, whereby ceramic or organic particles are simultaneously deposited with metal ions on a substrate, has been a subject of interest in the surface coating community, as the obtained composites often show enhanced hardness, wear resistance, and corrosion properties [1]. Examples of the metal/inclusion systems which have been investigated and fabricated successfully include Ni–Al_2O_3 [2,3], Ni–SiO_2 [4], NiW–WC [5], Au-diamond [6], and Cu-carbon nanotube [7]. A recent study on the co-deposition of NiW–WC [5] has demonstrated that, by controlling the applied current density, particle content and particle size, one can produce nickel-based composites of dense structure whose average hardness exceeding those of typical nanocrystalline NiW alloys [8,9].

Pulse plating, which refers to the electrodeposition process where current is imposed in a periodic manner, allows greater control over structures and properties of the deposits through regulations of pulse parameters. Furthermore, the technique usually yields homogeneous coatings with fine grains, uniform morphology and limited amount of defects. Hence, pulse plating has become an important technique for the electrodeposition of metals and alloys [10]. It is however only recently that increasing attention has been given to the use of pulse plating technique for improving the quality of the co-deposits [1,11]. The studies on the co-deposition of some Ni composites, including Ni–Al_2O_3 [3,12] and Ni–SiC [13], for example, have shown that pulse parameters, such as duty cycle and frequency, markedly affect the content of particles incorporated in the base metal. This in turn could influence mechanical properties of the coatings. Currently, the understanding of the effect of pulse parameters on the co-electrodeposition is inconclusive, partly due to a lack of systematic study and also to a complex nature of various pulse plating parameters that may influence both the electrocrystallization of the metal ions and the incorporation of the adsorbed particles.

In the present study, we investigate the co-electrodeposition of NiW and WC, the latter of which is selected as a reinforcing material for the alloy due to its high hardness and superior wear resistance. The enhancement of the hardness of the electrodeposited NiW is important, as it would make the alloy a strong candidate for a replacement of environmentally hazardous hexavalent hard chromium coating [14]. The effects of pulse parameters including peak current density, pulse frequency, and duty cycle on the structure and hardness of the deposits are examined and analyzed. The understanding on possible co-deposition mechanisms and the relationship between processing and properties gained from the study would lead to designs of NiW–WC composites of optimal performance useful for various hard coating applications.

2. Experimental

The co-electrodeposition of NiW and WC was conducted in a plating bath with aqueous bath chemistry: 18 g/l $NiSO_4{\cdot}6H_2O$, 53 g/l $Na_2WO_4{\cdot}2H_2O$, 168 g/l $Na_3C_6H_5O_7{\cdot}2H_2O$, 31 g/l NH_4Cl, 18 g/l NaBr, with the temperature maintained at 75 °C. WC particles with the average particle size of 0.5 μm (ATI Alldyne, Huntsville AL) and solid loading of 1 g/l were used. The pH of the electrolyte was 8.9, and it was unaltered by the WC additions. Copper (1.0 cm × 2.4 cm), polished to a mirror-like finish, and platinum were respectively employed as a cathode and an anode. Prior

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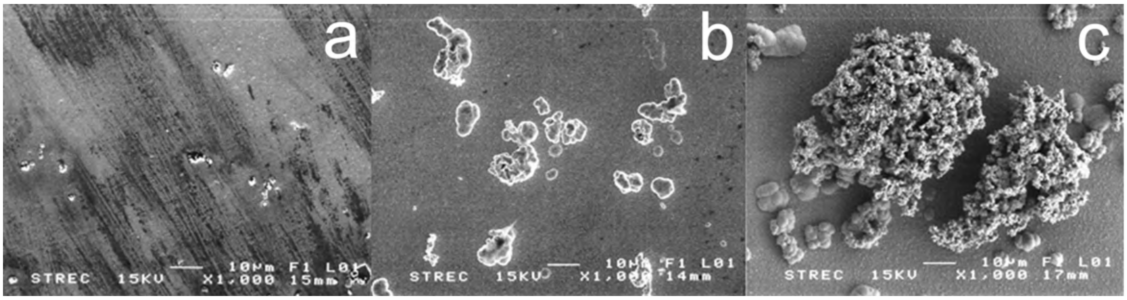

Fig. 1. Surface morphology of pulse electrodeposited NiW–WC composites processed with peak current density of 0.1 A/cm^2, frequency of 100 Hz, and duty cycle of (a) 10%, (b) 30%, and (c) 50%.

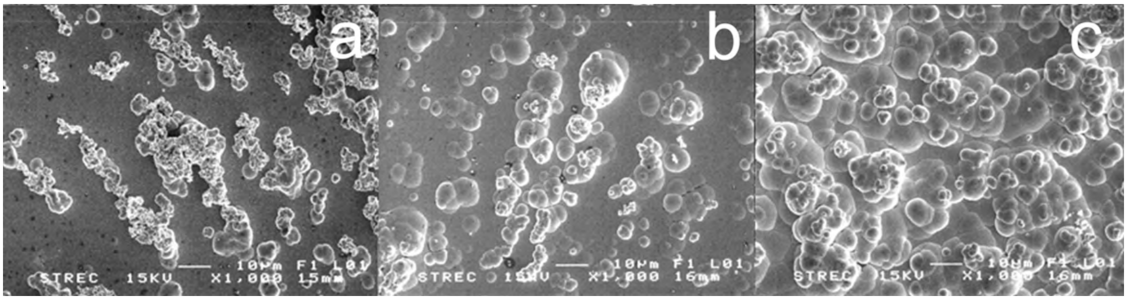

Fig. 2. Surface morphology of pulse electrodeposited NiW–WC composites processed with peak current density of 0.4 A/cm^2, frequency of 100 Hz, and duty cycle of (a) 10%, (b) 30%, and (c) 50%.

to plating, a copper substrate was activated in 10% H_2SO_4, and the WC-filled electrolyte was sonicated in an ultrasonic bath to assist in particle deagglomeration. To suspend WC particles in the solutions, a magnetic bar was continuously rotated at 500 rpm.

The current was applied to the system by a pulse rectifier (Dynatronix, DUPR 10-3-6) in a square-wave periodic pulse condition. Three main pulse parameters are subjects of the investigation and they were varied systematically. These include the peak forward current density (I_p) of 0.1 A/cm^2 and 0.4 A/cm^2, the pulse frequency (ν) of 10 Hz and 100 Hz, and the duty cycle (θ) of 10%, 30% and 50%. Additionally, a set of WC-free NiW control specimens was prepared using the similar procedures but without an addition of particles in the electrolyte. Since WC incorporations as investigated in this study do not significantly affect the cathodic efficiency of the system, the WC content in the coatings in weight percent was estimated by subtracting the weight of the co-deposits by the weight of WC-free specimens processed under the same conditions, and dividing the obtained value with the weight of the co-deposits. Energy-dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) were employed to characterize the composition (Ni and W contents) and surface morphology of the specimens. Hardness of the materials was assessed using a Vickers micro-indenter.

3. Results and discussion

3.1. Co-electrodeposition and structures

Crack-free NiW–WC deposits with fairly uniform appearance were obtained in all cases of processing parameter sets employed. Micrographs, which show surface morphology of the as-deposited specimens, are presented in Figs. 1–3. It appears that the morphology of the deposits under investigation is conformed to two main types. In the first type, which characterizes the structure of most specimens and replicates the structure found in those fabricated using the DC condition [5], an alloy matrix is dispersed by agglomerates of alloy nodules, within which contains WC particles (e.g., condition $I_p = 0.4$ A/cm^2, $\nu = 10$ Hz, $\theta = 30\%$ (Fig. 3b)). The nodules' size appears much larger than the size of WC particles, and the nodules cluster into a network as duty cycle is increased. At $\theta = 50\%$, the highest duty cycle considered, the nodular network becomes visibly porous (Fig. 3c), owing to the generation of hydrogen bubbles upon the deposition [5]. The second type of morphology is characterized by an alloy matrix that is uniformly dispersed by a ball of WC agglomerates with an approximate size of 50 μm. This type of morphology is unique to the pulse co-electrodeposition, and is observed only in the specimens that were fabricated with I_p, ν, and θ of 0.1 A/cm^2, 100 Hz, and 50% (Fig. 1c); and 0.4 A/cm^2, 10 Hz, and 10% (Fig. 3a).

Fig. 4 shows the average WC content in the co-deposited specimens which vary from negligibly small amount to a high content of 67 wt.%. It is observed that all of the pulse parameters, including peak current density, duty cycle and pulse frequency not only

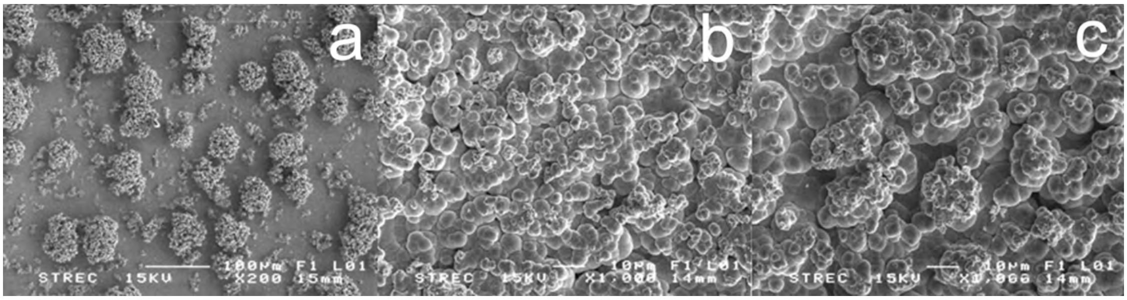

Fig. 3. Surface morphology of pulse electrodeposited NiW–WC composites processed with peak current density of 0.4 A/cm^2, frequency of 10 Hz, and duty cycle of (a) 10%, (b) 30%, and (c) 50%.

exhibit marked impacts on the deposits' morphology, but also on the particles' inclusion rate. We may rationalize the influence of each of the pulse parameters by first considering a proposed co-deposition mechanism of the NiW–WC system in the DC mode.

Boonyongmaneerat et al. [5] demonstrated that the addition of WC particles affects a meso-scale structure of the NiW deposits, while grain structure and chemical composition of the alloys are undisrupted. Furthermore, using the DC condition, the increase of current density was identified to generally improve the particle incorporation rate. The authors argued that WC particles carry negative surface charge that can induce absorption of NiW and H cations on the particles, forming surface complexes that facilitate the simultaneous deposition of the particles onto the cathode's surface [5,15,16]. In addition to such electrochemical effect, the migration and incorporation of the surface-modified WC particles is also induced by convective mass transfer, which is influenced by hydrodynamic condition of the plating bath.

Pulse plating offers the applications of the on- and off-currents to the system, and this subsequently can affect the co-deposition in two levels. Firstly, current pulsing influences the charging and discharging times of the electrolytic double layers at the cathode surface, and may in turn affect the relative content of the alloying components in the deposits [17]. This is indeed evidenced when the W content in the NiW alloys is examined, as will be discussed in the subsequent section. Secondly, current pulsing can affect the rate of particle incorporation, since the mechanisms that control the incorporation during the on- and off-current periods are distinct. Upon an on-current pulsing, the deposition of the particles is both electrochemical and physical in nature. During pulse-off period, however, no electrochemical reaction is present but the particles are allowed to migrate and accumulate at the cathode through convection, ready to be deposited in relatively large portion in the next pulse-on period [18].

Turning now to our results, with the low peak current (I_p) of 0.1 A/cm^2, WC content in the deposit is negligible at low duty cycles of 10% and 30% (Fig. 4). Clearly, for these conditions, the average current density, controlled by I_p and θ, appears too small to propel fast reduction kinetics of the metal ions. At this low I_p, appreciable alloy and particle co-deposition is achieved as the duty cycle is increased to 50%. At higher I_p of 0.4 A/cm^2, relatively fast deposition kinetics is obtained, and the corresponding increase of WC content in the deposits is observed, especially for $\theta = 10\%$ and 30%, underlining the electrochemical co-deposition mechanism stated above.

The general trend that relates the increase of WC content with the decrease of duty cycle (e.g., for $I_p = 0.4$ A/cm^2) parallels to the results of some prior studies on pulse co-electrodeposition [12,18,19]. Considering a profile of current waveform as duty cycle is decreased, there presents shorter pulse-on and longer pulse-off durations. Correspondingly, the adsorption of free ions at the cathode which is favored during pulse-on is suppressed, while the convection of the particles to the double layer during pulse-off is promoted. In effect, this may explain the relatively high contents of the particles incorporated in the metal matrix found at lower duty cycles.

Similar effect, although at lesser degree, is obtained when pulse frequency is altered. For duty cycles of 10% and 50%, a reduction of pulse frequency leads to an increment of WC content. Although the decrease of frequency does not affect the total duration that current is applied per second, it provides longer pulse-off period. This in turn may promote the population of particles that arrive at the cathode and hence facilitate the incorporation of particles at larger amount. The longer pulse-on, which is also induced at lower pulse frequency, however, will counter such effect.

While the exact mechanism of how the pulse parameters influence the arrangement of WC particles within the alloy matrix remains unclear, it can be anticipated here that the pulse current does play a role in controlling the condition of surface charge of the particles during their incorporation stage at the cathode. For the second type of surface morphology with WC agglomerates dispersed in the matrix, for example, pulse current may induce differential loss of the ions on the particles' surface. Consequently, the inter-particle electrostatic repulsive force of the individual surface-modified WC particles may be overcome, and the counter inter-particle Van der Waals attractive force renders agglomeration of the particles as they advance to the double layer at the cathode surface.

3.2. Hardness

The measured hardness of the co-electrodeposited NiW–WC specimens presented as a function of the pulse parameters is shown in Fig. 5. The hardness ranges from 1.7 GPa to a high value of 14.2 GPa. The results also show that the standard of deviation of the hardness of all co-deposited specimens is between 3% and 12%. This is significantly lower than that obtained from the DC condition, which is as high as 40% [5], and hence underscores the influence of pulse current on greater structural uniformity and particle distri-

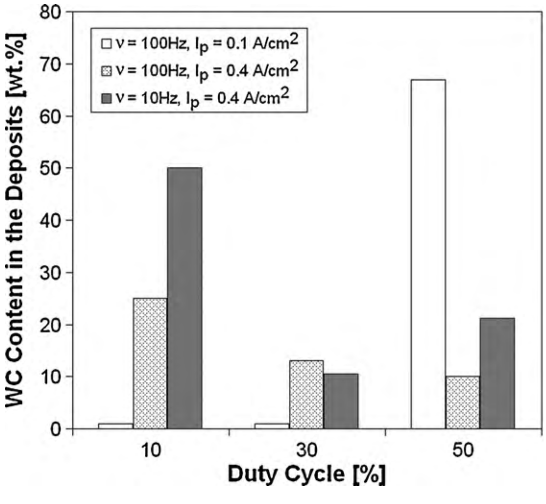

Fig. 4. The average WC content in NiW–WC composite coatings fabricated at various peak current densities, pulse frequencies, and duty cycles.

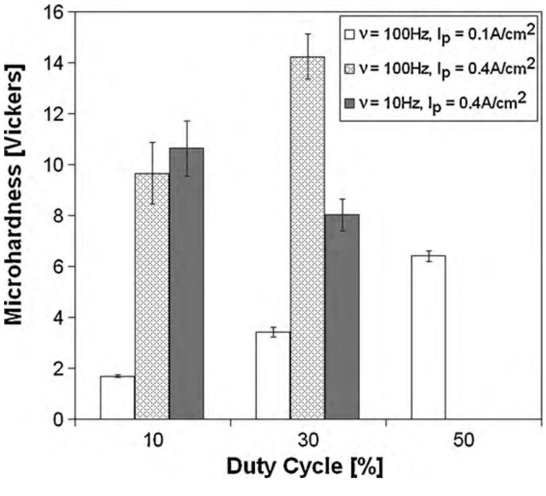

Fig. 5. Microhardness of NiW–WC composite coatings fabricated at various peak current densities, pulse frequencies, and duty cycles.

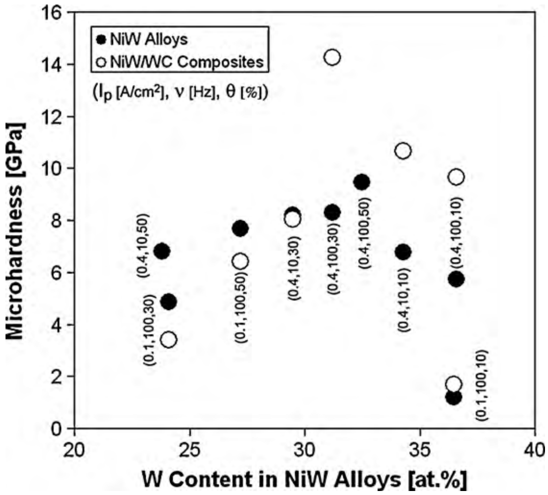

Fig. 6. Microhardness of the NiW alloys (black) and NiW–WC composite coatings (white) presented as a function of the W content in Ni matrix. The data points located along the same vertical line-up share common pulse parameters (peak current density, pulse frequency, and duty cycle) employed upon electrodeposition as denoted in parentheses adjacent to the data.

bution controls for the composite coatings. It is noted that two sets of the specimens fabricated with relatively high I_p of 0.4 A/cm^2 and high θ of 50% (10 Hz and 100 Hz) are porous and their hardness cannot be assessed.

As discussed earlier, the pulse parameters may affect the composition of the base alloys [17], and this can influence the hardness of the co-electrodeposits correspondingly. In order to analyze various contributions of hardness independently of one another, it is therefore useful to represent the hardness of WC-free and WC-incorporated NiW alloys as a function of the W content, which was characterized by the EDS, as shown in Fig. 6. From the figure, it can be observed that the pulse parameters affect the content of W in the NiW alloys as anticipated, leading to a variation of the alloys' hardness. Particularly, in the WC-free deposits, the increments of the W content from 24 at.% to 33 at.% result in the increase of hardness. Such hardness enhancement is attributed to the reduction of grain size, according to the Hall Petch's effect, and it is induced by W atoms which segregate to the grain boundaries of Ni, stabilize the grain structure, and suppress grain growth [7,8]. For the W content above 33 at.%, however, a decrease of hardness is observed, most likely owing to the formation of sub-nano or amorphous grain structure in the deposits.

With the addition of WC in NiW matrix, the improvement of hardness of the deposits may be expected as the carbide particle is intrinsically hard and may help impede dislocations' motion. Indeed, three sets of specimens show significant hardness enhancement, due to WC incorporation, over their WC-free NiW alloy counterparts, as shown in Fig. 6. These specimens are common to one another in that they are fabricated with the average current density ($I_p \cdot \theta$) above 0.04 A/cm^2 and with a relatively high peak frequency of 0.4 A/cm^2. Furthermore, it appears that, regardless of the type of morphology, relatively high hardness of the co-deposits is achieved with moderately high WC content, between ~10% and 50%, and a formation of dense uniform structure with no porosity present. The maximum hardness of 14.2 GPa, observed in the specimen with 13 wt.% WC processed using 0.4 /cm^2 peak current density, 30% duty cycle, and 100 Hz pulse frequency, is about 40% higher than that of the hard chromium deposit [14].

4. Conclusions

Pulse current is shown to facilitate the fabrication of NiW–WC composite coatings through the improvement of particle distribution and providing greater controls of the particle incorporation rate. Employing 0.5 μm-WC with the solid loading of 1 g/l in the NiW electrolytic bath, the minimum average current density of 0.04 A/cm^2 is required to propel the co-electrodeposition process. Furthermore, a decrease of duty cycle and a reduction of pulse frequency generally result in the increase of WC content in the deposits. Hardness of the composites, however, is not solely controlled by the WC content, but largely by the uniformity of the structure, as well as the content of W in the base NiW alloy which is also influenced by the pulse parameters. A NiW–WC coating with considerably high and uniform hardness of about 14 GPa is achieved with the application of pulse current with peak current, pulse frequency, and duty cycle of 0.4 A/cm^2, 100 Hz, and 30%, respectively. Pulse electrodeposition is therefore demonstrated here as an effective technique for a fabrication of NiW–WC co-deposits of high hardness which can be served as environmentally friendly alternatives to chromium coatings.

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