

Thermal treatment effect on the mechanical, tribological and corrosion properties of Ni-W alloy obtained by direct and pulse plating electrodeposition

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Abstract

Ni-W electrodeposits have emerged as one of the most suitable alternatives to hard chromium mainly due to their remarkable mechanical and tribological properties. Additionally, advanced technologies that require materials resistant to high temperatures could benefit from the use of Ni-W coatings. In this work, the effect of thermal treatment at different temperatures (300°C, 500°C, 700°C) on the characteristics of Ni-W coatings obtained by direct and pulse plating was studied. The morphology, composition, crystalline structure, hardness, wear rate, friction coefficient and corrosion resistance of the thermally treated coatings were analyzed and compared with the performance of hard chromium coatings. Results indicate that the pulse plated Ni-W coatings show better mechanical and tribological properties than the ones obtained by direct current. A significant improvement of hardness in Ni-W layers was achieved by thermal treatment, mainly in the films grown by pulse plating, with minor changes in wear resistance and corrosion performance.

Keywords: nickel-tungsten, pulse plating, thermal treatment, microstructure, hardness, wear

1. Introduction

The high level of interest in Ni-W alloys during the last years can be explained by their remarkable physical properties and their numerous possible applications. Namely, Ni-W alloys exhibit good mechanical (tensile strength, hardness) and tribological (wear resistance) properties, oxidation resistance and high melting temperature that make them very attractive for engineering applications.¹⁻³ One of the most claimed applications of Ni-W electroplating is as a more environmentally friendly alternative to hard chromium process in demanding industries like aviation and automotive.⁴⁻⁶ In addition, advanced technologies such as micro- and nano-electromechanical systems, sliding contacts or high-temperature superconductors, that require materials resistant to relatively high temperatures, while maintaining their mechanical properties, could benefit from the use of Ni-W alloys.^{7,8}

It has been demonstrated that pulse plating can lead to an enhancement of the functional characteristics of Ni-W coatings by means of a selective alteration of mass transport conditions and the consequent modification of the alloy composition and microstructure.⁹⁻¹³ In a previous work¹⁴ an acid Ni-W electrolyte based on sodium citrate was proposed and pulse plating and chemometric techniques were combined to obtain Ni-W coatings with improved uniformity, efficiency and hardness in comparison to those obtained by direct current.

On the other hand, several researchers have proposed the application of a thermal treatment to improve the mechanical properties of Ni-W coatings.¹⁵⁻¹⁹ In this work the effect of thermal treatment at different temperatures (300°C, 500°C, 700°C) on the characteristics of Ni-W coatings obtained from an acid citrate bath by direct and pulse plating have been studied and their structural and functional properties are compared to those of hard chromium coatings under the same experimental conditions. Most of the

published studies have focused on the characteristics and performance of Ni-W coatings obtained from ammoniacal citrate baths, which lead to higher faradaic efficiency but lower the tungsten content in the alloy.¹ Furthermore, there are only a few researches that have analyzed the effect of temperature on Ni-W deposits obtained by pulse plating.^{15,18,20,21} In order to prepare advanced coatings that could meet the increasingly rigorous requests from leading industrial sectors, a deeper understanding of the properties of Ni-W electrodeposits is essential.

2. Experimental Procedure

Electroplating

Ni-W coatings were electrodeposited on polished carbon steel substrates (UNE-EN 10130, $R_a \sim 1.574 \mu\text{m}$, 9 cm^2) from a sodium citrate solution. The electrodeposition was carried out under galvanostatic conditions by a multi-potentiostat VMP3 (Biologic Science Instruments, Grenoble, France) using a two-electrode configuration (separated by a distance of 3.5 cm), with a cell volume of 800 mL.

Prior to the electrodeposition process, substrates were degreased in a commercial solution (45 g L⁻¹ Uniclean 251, Atotech) at 60°C and pickled and activated with hydrochloric acid (50% vol.) during 60 s. The electrolyte composition and plating parameters selected for this study were optimized in a previous work¹⁴ and are given in **¡Error! No se encuentra el origen de la referencia..** Direct current (DC) (-0.04 A m^{-2}) and a previously studied¹⁴ pulse current (PC) sequence ($i_c = -0.04 \text{ A m}^{-2}$, $t_c = 31 \text{ ms}$, $t_{\text{off}} = 20 \text{ ms}$) were applied to obtain the Ni-W coatings. A constant charge of 216 C m^{-2} was applied for both direct and pulse plated deposits, which was estimated to yield a thickness of $20 \pm 1 \mu\text{m}$.

For comparison purposes, chromium coatings were obtained on substrates of the same characteristics. The plating bath and conditions used are shown in **¡Error! No se encuentra el origen de la referencia..** After the pretreatment described for Ni-W plating, the substrates were activated in a chromium electrolyte by applying an anodic current of 0.3 A m^{-2} during 90 s. Chromium electrodeposition was carried out in a two-electrode electrochemical cell (electrodes were separated by a distance of 3.5 cm) with a volume of 800 mL by direct current (-0.3 A m^{-2}). A charge of 1620 C m^{-2} was applied in order to have the same thickness than Ni-W layers.

Thermal treatment

The electroplated coatings were subjected to thermal treatment at various temperatures (300°C , 500°C , 700°C) in a CWF 11/23 chamber furnace (Carbolite, Derbyshire, UK) under a controlled argon atmosphere. Samples were heated from room temperature to the selected temperature at a rate of $10^\circ\text{C min}^{-1}$. Once the target temperature was reached, it was maintained for 1h. Cooling processes were also carried out inside the furnace under a controlled atmosphere until the samples reached room temperature.

Characterization of the coatings

The appearance of Ni-W surfaces was initially evaluated by visual inspection. The Ni-W thickness was determined by X-ray fluorescence spectroscopy, with a Fischerscope XDAL-FD (Helmut Fischer, Hünenberg, Switzerland). A Talysurf Intra 50mm surface profilometer (Taylor Hobson, Leicester, UK) was employed to assess the surface roughness. Morphological observations of Ni-W surfaces were undertaken by means of a Carl Zeiss Ultra Plus field emission scanning electron microscope (Zeiss, Jena, Germany). Chemical composition of the coatings was determined by an Apollo X energy dispersive spectrometer (Ametek EDAX, New Jersey, U.S.A.). X-ray diffraction (XRD) measurements were performed with a X'Pert PRO MRD diffractometer (Cu

radiation, $\lambda_{\text{Cu}} = 1.5418 \text{ \AA}$; PANalytical, Almelo, The Netherlands) from $2\theta = 5^\circ$ to $2\theta = 145^\circ$, with a step size of 0.04° and a counting time of 1 s per step. The grain size was estimated applying the Scherrer equation on the (111) XRD peak.

Microhardness was evaluated on polished cross-sectional areas of Ni-W deposits, by using a Vicker's microindenter Fischerscope HM2000 (Helmut Fischer, Hünenberg, Switzerland) with a load of 50 mN. Wear tests were conducted using a THT ball-on-disk tribometer (CSM Instruments, Peseux, Switzerland) under unlubricated conditions, at room temperature. An alumina ball of 6 mm diameter was used as counter body and the tests were conducted using a 10 N load for Ni-W coatings and 5 N load for chromium coatings. The rotation speed was kept at 0.1 m s^{-1} and the sliding distance was 7000 m for Ni-W and 500 m for Cr. After some preliminary tests, different experimental conditions (e.g. applied load) were selected to study the tribological performance of Ni-W and Cr coatings due to the significantly superior wear performance of Ni-W deposits. The average friction coefficient, μ , was evaluated during the tests and the profilometer was employed to determine the width of the wear track for the studied samples, from which volume loss of the worn deposits was analyzed. The wear rate of the coatings was calculated by means of their volumetric wear factor, K , using equation (1),²²

$$K = \frac{V}{Nd} \quad (1)$$

where V is the wear volume, N is the normal load and d is the sliding distance.

The corrosion performance of the electrodeposited samples was investigated in a 250 mL three electrode Flat Cell (Princeton Applied Research, Oak Ridge, USA) placed inside a Faraday's cage, by means of a 1287 potentiostat-galvanostat with a 1255B impedance interface (Solartron Analytical, Leicester, UK). All measurements were

conducted in an aerated 5 wt.% NaCl solution at room temperature with a geometrical working area of 1 cm^2 . A Ti-Pt mesh and Ag/AgCl/NaCl (3M) electrode (Princeton Applied Research, Oak Ridge, USA) were used as counter and reference electrodes respectively. First, the corrosion potential, E_{corr} , was measured at open circuit and recorded during 30 min. Afterwards, a linear potentiodynamic sweep between $E_{\text{corr}} \pm 15 \text{ mV}$ was performed at 0.1667 mV s^{-1} and the polarization resistance, R_p , was calculated. In order to obtain the anodic and cathodic Tafel slopes (b_a , b_c), partial potentiodynamic scans (0.1667 mV s^{-1}) on different samples obtained at the same experimental conditions were performed, scanning from the open circuit potential (OCP) towards the anodic or cathodic direction. The cathodic and anodic potentiodynamic scans were never carried out consecutively as it was observed that the cathodic scan modified the anodic response to some extent. The corrosion current density (i_{corr}) was calculated by means of the Stern-Geary relation²³. Corrosion data (R_p and i_{corr}) are referred to the exposed geometric area of the sample. The reproducibility of the presented data was generally checked by using 6 to 10 replicates, and typical results are reported.

3. Results and discussion

Physical properties

Appearance and thickness

The obtained Ni-W coatings were grey, featuring a more whitish tonality than Ni deposits, presumably due to the presence of W. Visual inspection did not revealed differences in surface finish in coatings obtained by direct current (DC) and pulse plating (PP). Similarly, no significant changes in their colour and brightness after the thermal treatment were detected.

As expected, the Ni-W layers had a thickness of $20.0 \pm 1.1 \mu\text{m}$ in both direct current and pulse plating conditions, which means a current efficiency of 40.2 %. Although current efficiency was quite low, presumably due to the hydrogen evolution reaction that accompanies alloy electrodeposition,²⁴ it was still considerably higher than the one reported for hard chromium plating (10-20%).^{25,26} Moreover, layer thickness was uniform across the Ni-W surfaces, unlike the typical inhomogeneous and poor throwing power of hard chromium.²⁷

Hardness

Some of the most demanded attributes for Ni-W coatings are related to their mechanical and tribological characteristics, in order to ensure that they can satisfactorily replace hard chromium in several industrial applications. The hardness of the as-deposited coatings was $757 \pm 24 \text{ HV}$ in the case of DC Ni-W coatings and $909 \pm 30 \text{ HV}$ for PP Ni-W coatings. Pulse plating led to Ni-W layers with superior hardness, closer to the one obtained in as-deposited hard chromium layers ($1152 \pm 24 \text{ HV}$).

Fig. 1 shows the effect of thermal treatment temperature on hardness for the studied electrodeposits. The hardness of Ni-W coatings obtained by direct current increases considerably with the thermal treatment temperature up to 500°C , reaching a maximum of $1151 \pm 82 \text{ HV}$. At 700°C , the hardness of the DC Ni-W deposits drops slightly ($1099 \pm 64 \text{ HV}$). On the other hand, the hardness of Ni-W layers obtained by pulse plating increased with the thermal treatment temperature, reaching a value of $1793 \pm 179 \text{ HV}$ at 700°C , which is significantly higher than the hardness reported by other authors for Ni-W coatings.^{15-18,21}

The evolution of the hardness of hard chromium coatings upon thermal treatment is also included in Fig. 1. As the temperature of the thermal treatment increased, the

performance of hard chromium layers deteriorates, i.e., the hardness is reduced by half its initial value (503 ± 124 HV) at 700°C .

Tribological properties

The effect of the annealing temperature on the wear resistance and the friction coefficient of the studied coatings is also shown in Fig. 1. The wear rate and the friction coefficient of as-deposited Ni-W coatings were lower than those of hard chromium coating. In spite of having applied considerably longer sliding distance for the Ni-W samples (Ni-W: 7000 m vs. Cr: 500 m), the depth of wear track after the ball-on-disk measurements was 4.8 ± 1.2 μm for DC Ni-W, 4.4 ± 1.1 μm for PP Ni-W layers and 7.4 ± 1.1 μm for Cr coatings. Furthermore, the friction coefficient of DC Ni-W surfaces was 0.53 ± 0.04 , of PP Ni-W was 0.50 ± 0.02 and of Cr was 0.64 ± 0.02 .

On the other hand, the values of the volumetric wear factor and friction coefficient remained low for the Ni-W coatings treated at different temperatures. DC Ni-W surfaces showed K values that ranged from $7.1 \times 10^{-7} \pm 1.7 \times 10^{-7}$ to $8.4 \times 10^{-7} \pm 1.0 \times 10^{-7}$ $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$ and μ values of 0.50-0.54. In turn, PP Ni-W layers had lower K values, varying from $6.1 \times 10^{-7} \pm 1.6 \times 10^{-7}$ to $7.3 \times 10^{-7} \pm 1.7 \times 10^{-7}$ $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$, and lower μ , ranging from 0.47 to 0.50 depending on the applied temperature. In the case of Cr coatings, thermal treatment had an important effect on their wear characteristics, causing an increase in K from $1.1 \times 10^{-6} \pm 2.0 \times 10^{-7}$ $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$ for the as-deposited coatings to the completely wear out of the layer after the thermal treatment at 700°C . Thermal treatment also led to an increase in friction coefficient, which varied from 0.64 up to 0.87. The sensitivity of conventional hard chromium to temperature and the worsening of its wear properties at elevated service temperatures has been reported previously.^{28,29}

The outstanding wear properties, even after a thermal treatment, exhibited by the developed Ni-W coatings in this research and their preeminence over hard chromium are superior than those previously reported.^{20,30} Particularly remarkably are the improved wear and friction characteristics of Ni-W deposits obtained by the proposed pulse plating sequence.

Corrosion

Fig. 2 shows the overall potentiodynamic behaviour of the studied coatings in 5 wt.% NaCl aerated media. The electrochemical corrosion parameters determined from the Tafel polarization data are listed in Table 2. The corrosion potential of the as-deposited coatings was ~ -520 mV vs. $E_{\text{Ag}/\text{AgCl}/\text{Cl}^- (3\text{M})}$, which agrees the values reported by other authors for Ni-W^{31,32} and hard Cr³³ deposits in chloride media. E_{corr} values of Ni-W coatings tended to increase slightly with thermal treatment, reaching values of ~ -430 mV vs. $E_{\text{Ag}/\text{AgCl}/\text{Cl}^- (3\text{M})}$. The E_{corr} values corresponding to chromium surfaces remained more stable after thermal treatment at different temperatures. On the other hand, the as-deposited and annealed DC Ni-W and PP Ni-W samples did not show significant changes on polarization resistance, which remained in values nearby ~ 1.5 kohm cm². The registered R_p values are of the same order of magnitude as the results reported by other authors for Ni-W coatings with high W content in chloride media^{31,34} and they are similar to the R_p obtained for conventional hard chrome coatings at the same conditions (Table 2).

According to the polarization curves corresponding to Ni-W coatings, the electrochemical corrosion performance was analogous in deposits obtained by direct current and pulse plating. The anodic polarization branches showed a monotonic increase of current with potential, with a slope in the anodic Tafel region, b_a , of 54 ± 3 mV dec⁻¹ in DC Ni-W and 81 ± 3 mV dec⁻¹ in PP Ni-W. The described anodic

polarization curves were similar to the one of as-deposited hard chromium ($b_a = 78 \pm 7$ mV dec⁻¹) and correspond to a uniform corrosion mechanism, ascribable to metal dissolution. In case of the cathodic polarization branches, the studied Ni-W coatings exhibited values of cathodic slopes, b_c (DC Ni-W: $- 528 \pm 30$ mV dec⁻¹, PP Ni-W: $- 620 \pm 25$ mV dec⁻¹), characteristic of mass transport controlled processes. The diffusion process was more pronounced in chromium surface ($b_c = - 918 \pm 31$ mV dec⁻¹). Considering that the corrosion tests were carried out in neutral chloride solution, the mass transport control process could be related to the oxygen reduction reaction (ORR). At more negative potentials, a slope change was registered for all the as-deposited coatings, related to the water reduction reaction. After the thermal treatment, as the temperature increased, steeper cathodic slopes were obtained for all the studied coatings and higher mass transport controlled limiting current density was registered. The observed changes in E_{corr} and in the cathodic Tafel slope of Ni-W deposits after the thermal treatment at different temperatures might be related to the formation of superficial oxides.³⁵

The estimated corrosion current density (i_{corr}) by Stern-Geary approach was $\sim 15 \mu\text{A cm}^{-2}$ for Ni-W coatings obtained by direct current and pulse plating. The value of this parameter is slightly higher than other results found in bibliography^{31,34} and higher than the value registered for chromium surfaces ($\sim 5 \mu\text{A cm}^{-2}$). There was a slight increase of the corrosion current density of the studied Ni-W surfaces with the thermal treatment temperature, though it was of the same order of magnitude as the as-plated coatings. The i_{corr} of Cr coatings experienced an increment after thermal treatment, getting values comparables to Ni-W layers.

Microstructural properties

In order to understand the functional properties of developed Ni-W coatings and the effect of the applied thermal treatment on their characteristics, a morphological and microstructural analysis of the surfaces was performed.

Morphology

The as-deposited and thermal treated Ni-W coatings were analyzed by means of field emission scanning electron microscope. A nodular structure was obtained both by direct current and pulse plating, with globular nodules of different sizes and gaps among them, indicating that they were composed of domains with different sizes.³⁶ All the samples showed a cracked morphology visible both on the surface and across the section of the layers in Fig. 3. The formation of cracks can be mainly related to the significant hydrogen embrittlement and tensile stress formation that occurs during Ni-W electrodeposition.²⁴ The residual stress of the coatings and its release by crack formation can also be caused by the free volume (voids) trapped in the grain boundaries deposition and its subsequent shrinkage. The amount of free volume created and stored is affected by the atomic radius difference between Ni and W, the grain size, the thickness and the deposition parameters.^{37,38} The applied thermal treatment did not seemingly affect the morphology of the Ni-W coatings, so that the nodular microstructure, the density and the width of the cracks were comparable irrespective of the annealing temperature (Fig. 4).

The roughness of the Ni-W electrodeposits obtained by direct and pulse current was similar ($\sim 1.10 \pm 0.05 \mu\text{m}$), showing a smoother surface finishing than the substrate. The surface roughness was not significantly affected by the applied temperature either.

Contradictory results can be found in the literature^{2,16,31} regarding the corrosion performance of Ni-W coatings due to differences in the testing procedures and to the combined effect of different characteristics of the coatings, such as their composition,

structure, grain size and morphology. Taking into account the size and the density of cracks on the studied Ni-W coatings in this work, it is assumed that cracking is the dominant factor affecting their corrosion performance in a chloride medium. Thus, the limited corrosion resistance of Ni-W coating obtained by DC and PP can be ascribed to their cracked morphology, being their behaviour comparable to that of hard chromium. This assumption was corroborated by the inspection of the coatings after the corrosion tests by FE-SEM. In Fig. 5 the micrographs of Ni-W coatings treated at 700°C after the potentiodynamic test are showed. Ni-W surfaces presented some protruding formations on the cracked regions constituted by blade-like crystals that fill the cracks and spread to the surrounding area. EDX analysis allowed confirming that the observed protrusions were iron oxides, presumably coming from the dissolution of the steel substrate.

Microstructure

The X-ray diffractograms of the Ni-W coatings are plotted in Fig. 6 and the estimated grain sizes by Scherrer's equation are listed in Table 3. The peaks of the diffraction patterns for as-deposited and thermal treated Ni-W deposits correspond to pure fcc nickel and the (111) texture stands out, which is attributed to the preferred crystalline growth along this orientation due to the lower strain in that direction.³⁹ A shift of this peak to lower angles with respect to pure fcc Ni was observed, which can be attributed to the tungsten atoms' incorporation into the nickel lattice. According to Schuh et al.⁴⁰, possibly a coexistence of a non-equilibrium solid solution with a metastable solid solution exists, even exceeding the solubility limits of W in the Ni-W alloy. Therefore, although the studied Ni-W layers have W content of 20.7 at. %, it is not surprising that they are constituted of a solid solution of W with Ni matrix.^{16,39}

Pulse plated Ni-W coatings exhibit narrower XRD peaks than Ni-W layers obtained by direct current. Accordingly, the grain size is higher for as-deposited and thermal treated

PP Ni-W films (Table 3). From the XRD patterns, the existence of a small fraction of amorphous Ni-W in DC films cannot be ruled out. Actually, the lower hardness of DC Ni-W coatings might be ascribed to the formation of this fraction of amorphous phase during electrodeposition and the transition from the conventional Hall–Petch relation to breakdown behaviour (inverse Hall–Petch).^{6,39,41} The grain size of the Ni-W coatings did not show big changes with thermal treatment, which according to Marvel et al. can be explained by grain growth limitation factors,⁴² and demonstrates the thermal stability of the developed nanocrystalline films, compared to nanocrystalline nickel.^{15,43} On the other hand, hard chromium showed an increase of the grain size from 9 nm for as-deposited coating to 58 nm for the one treated at 700°C. The increase of grain size in chromium coatings can explain the decrease in hardness caused by thermal treatment.^{44, 45}

According to XRD data, the applied thermal treatments does not induce remarkable changes neither in the width nor in the intensity of XRD peaks, both for DC and PP Ni-W layers. Interestingly, a slight shift of the (111) peak to higher angles is observed as the annealing temperature increases, which can be associated with a shrinkage of the unit cell size. This phenomenon could be related to the W segregation at the grain boundaries during thermal treatment and the concomitant stabilization of the microstructure of Ni-W alloys. A similar behaviour has been observed in annealed Cu-Ni alloys.⁴⁶ Such effect probably hinders dislocation motion, contributing to the high hardness of the annealed films. The eventual presence of a second phase oxide particles also limiting grain growth could also contribute to improve hardness of Ni-W coatings.^{42,47}

The low wear rate and friction coefficient values for the developed Ni-W coatings compared to hard chromium can be understood on the basis of their high W content,

low grain size and cracked morphology.^{15,39,48} Both parameters did not undergo significant changes after thermal treatment, which indicates the thermal stability of the tribological characteristics of the developed Ni-W layers. Archard's law predicts an inverse linear relation between wear rate and hardness, but Rupert and Schuh⁴⁹ reported that wear resistance of Ni-W coatings can deviate from Archard scaling due to the nanocrystallinity and microstructural stability of the alloy. Furthermore, Sunwang et al.¹⁸ reported an improved hardness in Ni-W coatings obtained by reverse pulse plating after thermal treatment at 700°C with a minimal decrease of wear resistance, which was attributed to minimal grain growth, grain boundary relaxation and the presence of an adhesive wear mechanism. Additionally, Wasekar et al.²⁰ obtained Ni-W coatings with friction coefficient independent of applied load and hardness.

The reduction of wear resistance in chromium layers with thermal treatment can be explained by the observed increase in grain size. Furthermore, thermal treatment may presumably cause an increase in stress relief, which can contribute to the deterioration of mechanical and wear characteristics of hard chromium.⁴⁴

4. Conclusions

The effect of thermal treatment at different temperatures on the properties of Ni-W coatings obtained by direct current and pulse plating was studied. Pulse plating allowed obtaining Ni-W layers with better mechanical and tribological properties than by direct current, using the same electrolyte. This might be ascribed to the formation of a small fraction of amorphous phase during electrodeposition of Ni-W by direct current and to an inverse Hall–Petch behaviour.

Thermal treatment caused a significant improvement of hardness, mainly in those samples obtained by pulse plating, rendering even higher hardness than the values reported in literature for this alloy after annealing at 700°C. The observed increase in

hardness might be related to W segregation at the grain boundaries during thermal treatment and the concomitant stabilization of the microstructure of Ni-W alloys. On the other hand, the performance of hard chromium layers deteriorated with thermal treatment, reducing by half its initial hardness value at 700 °C.

The wear resistance of the developed Ni-W coatings outperformed the tribological characteristics of hard chromium. Moreover, unlike chromium surfaces, the wear rate and friction coefficient of the deposited Ni-W layers showed minimal changes after the applied thermal treatment presumably due to their nanocrystallinity and microstructural stability.

The corrosion performance of the studied Ni-W coatings in chloride medium was affected by their cracked morphology but it was still comparable to that of hard chromium.

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