Enhanced Microhardness of Mild Steel due to Electrodeposition of Copper Controlled by Temperature and pH

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Abstract—The microhardness of the mild steel might be enhanced by the electrodeposition of copper onto it. This work investigates the electrodeposition of Cu on the mild steel substrate controlled by different parameters such as temperature, pH, and current density of bath composition. Therefore, the microhardness and morphological properties of the deposited copper layer have been investigated. It is observed that the microhardness of the studied substrate increases for both the pH and temperature of the electrolytic solution while long-time deposition degrades the hardness of the sample. The microstructure of the deposited copper has been analyzed from the micrographs obtained by scanning electron microscopy (SEM). The surface morphology of Cu-deposited mild steel reveals that the Cu particle is uniformly deposited and somewhere clusters are found. This research aims to establish optimal deposition parameters for achieving the desired properties of electrodeposited copper on mild steel substrates and the microhardness of this material could be enhanced.

Keywords: Electrolytic Solution, Electro-deposition, Microstructure, Current Efficiency, Micro Hardness,

I. INTRODUCTION

Electrodeposition is a common method by which materials are deposited onto a surface through the application of an electric field. Copper (Cu) electrodeposition on mild steel has garnered interest because of its uses in decorative finishes, electronics, and anti-corrosion coatings [1-4]. The range of materials that can be electrodeposited include various metals, metal alloys, semiconductors, metal oxides, nanomaterials, and even conductive polymers. However, Copper (Cu) electrodeposition is a well-known and cost-effective method for applying a thin layer of Cu coating on any metallic substrate. This process is a well-established method due to the precise control over the thickness of the coating, uniform coverage, and the ability to create complex shapes. Moreover, Cu coatings are excellent for enhanced electrical conductivity with less corrosion, and favorable soldering. Generally speaking, mild steel is a commonly used substrate material for Cu deposition. Consequently, the combined effect of coating improves the mechanical properties at a cost that is reasonable for use in industrial settings. However, occasionally material corrosion occurs during coating, which restricts the usefulness.

M. E. Haque and his group investigated chromium electroplating under various operating conditions, including the concentration of $CrCl_3$, and how factors such as pH, temperature, and current density influenced the plating thickness, optical reflectivity, and current efficiency. Their findings revealed that after 90 minutes of deposition with a pH of 3 and bath temperature of 40°C with current density of 20 A/dm² produced the optimal current efficiency. These parameters were crucial in improving performance and quality control in the plating industry, leading to better-developed products [5]. In addition, M. E. Haque et al. studied the effects of polyethylene glycol (PEG) on copper electrodeposition, particularly focusing on the quality of the copper plating. They found that as the PEG concentration increased, the thickness of the Cu^{2+} deposit and current efficiency decreased. However, their investigation revealed that a PEG concentration of 0.01 g/L produced the highest quality electrodeposition [6]. In a related study, N. V. Phuong et al. conducted a mechanistic investigation to understand the role of PEG molecules in the copper electrodeposition process, providing deeper insights into how PEG influences

deposition characteristics [7]. However, they observed that during electroplating, PEG molecules reduced the reductive current of hydrogen compared to PEG-free solutions. They also noted that pH levels influenced the electrode surface [7]. Y. Ivshin et al. studied the electrodeposition of copper coatings on mild steel substrates, focusing on the effects of deposition time, electrolyte composition, and current density on copper coating characteristics. Their research explores the connections between these parameters and properties such as surface roughness, thickness, and homogeneity [8]. Further publications exploring these relationships are essential to advancing electrodeposition technologies. These properties can be improved by electrodeposition, according to research by Priyadarshi et al. A direct current power source is used to deposit pure copper and copper composites containing graphene, graphite, and carbon nanotubes on mild steel [9]. There are two types of baths under investigation: acidic and non-cyanide alkaline glycerol. By altering variables like temperature, duration, and current density, researchers were able to optimize the coating process. To guarantee that the carbonaceous materials in the electrolyte were distributed evenly, they additionally employed a wetting agent. Cube-shaped copper crystals and plate-like structures were visible in the composites according to SEM. The elemental composition was verified by EDSX [9].

However, the nature of the electro-deposited copper and its quality are completely controlled by experimental parameters such as temperature, pH of the electrolytic solution along deposition time. Therefore, the enhancement of the microhardness of coated material is expected to become inconsistent. Therefore, the primary objective of our project is to improve the quality of the electrochemical deposition of copper onto a mild steel substrate. Throughout the investigation, a systematic adjustment of the controlling parameters such as temperature, pH of the solution, current density, and time of deposition is to be achieved to enhance the microhardness of the final product. The outcomes of this study will contribute to the advancement of electrodeposition for applying copper coatings on mild steel and overcome functional limitations.

II. MATERIALS AND METHODS

A. Method of Coating

In this research, the coating process was followed by the electrodeposition method. The coating was performed on a mild steel plate and Copper (Cu) material was deposited on this. The following block diagram shows the overall process of the copper electrodeposition.
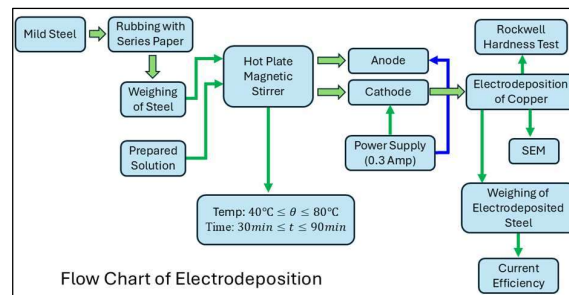

Fig. 1. Block Diagram of Copper Electrodeposition

In this study, the electrodeposition was performed by the Copper (Cu) material coating onto a mild steel plate. The whole procedure of the copper electrodeposition has been depicted in the block diagram in Fig. 1. Moreover, the experimental setup is included in Fig. 2. In this apparatus the electroplating cell consists of a cathode and an anode connected to a direct current power source. Here, the metal substrate is identified as the cathode which is directly connected to the negative terminal of the power supply while the anode is connected to the positive terminal.
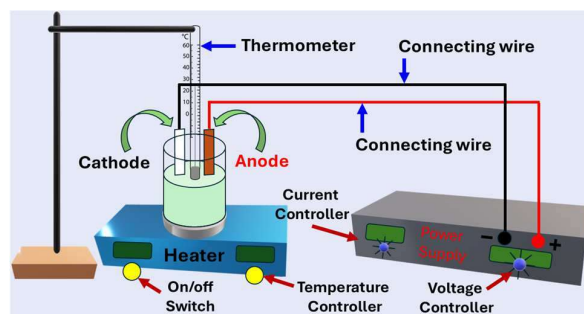

Fig. 2. Schematic cell diagram of copper plating bath

A mild steel substrate served as the cathode for copper deposition. Before plating, the cathode was weighed using an analytical electrical balance. The anode was connected to the positive terminal of the power supply. Both the anode and cathode were placed in a 250 ml Pyrex beaker filled with 200 ml electrolyte, with the option of heating the beaker on a hot plate if necessary. To stir up the solution, an electromagnetic rod was employed. The D.C. power supply's galvanization mode was controlled using the current and voltage adjustment knobs, and the applied current was monitored with a high-impedance digital multimeter. Fig. 2 illustrates the setup. Careful steps were taken to fully submerge the exposed section of the cathode in the electrolyte while preventing the crocodile clips attached to the anode and cathode connected with the solution. The anode and cathode were positioned parallel to each other, about 2 cm apart, throughout the experiment. The plating duration for each trial was timed with a stopwatch. Once the plating was complete, the coupon was removed from the solution, and any excess electrolyte was gently wiped away with tissue paper. The coupon was then

allowed to air dry, and afterward, it was re-weighed using an electronic scale. The difference in weight indicated the amount of metal deposited under the experimental conditions.

B. Experimental measurements

The whole procedure of electrodeposition was followed for 5 different temperatures (θ) ranging from 40°C to 80°C. Parallelly, the electrodeposition was performed for different pH levels ($-\log[H^+]$) of the electrolytic solution ranging from 2.0 to 6.0. Moreover, Cu coating was performed for different times (t) interval of $30min \leq t \leq 90min$. Apart from these, the microstructures of the copper-coated mild steel samples were examined using a Field Emission Scanning Electron Microscope (FESEM), specifically the JEOL JSM 7600F model, with an energy range of 0.2 keV to 40 keV and an operational accelerating voltage between 200V and 30kV. Hardness tests were also conducted on samples using the nano-indentation method with a Digital Micro Vickers Hardness Tester (Vexus MHV-1000Z Series). The hardness values were determined based on the stiffness derived from the unloading curve at a final indentation depth of 1000 nm. To ensure accuracy and reliability, the experiment was performed at three distinct locations on each sample, with 10 indents at each site. Additionally, the current flow as a function of copper sulfate concentration through the coated samples was measured using the two-probe method. Therefore, the current efficiency (C_E) was obtained from the ratio between the actual current (C_A) and theoretical maximum current (C_T) as connected by the equation:

$$C_E = \left(\frac{C_A}{C_T} \right) \times 100\%$$

III. RESULTS AND DISCUSSIONS

To evaluate the optimum enhanced Cu coating on mild steel the experimental parameters such as temperature, pH of electrolyte solution and current density are varied, and the deposition process has been observed for different time intervals. Therefore, the microstructure of the coated steel for the lower temperature (40°C) and higher temperature (80°C) have been obtained. In addition, the following sections discuss the microstructures, hardness, and current efficiency of the samples studied.

A. Microstructural analysis

In the Cu coating process, the temperature and pH play a key role in controlling the microstructural growth onto mild steel substrate during electrodeposition. At first, the coating has been performed at 40°C and the plating bath contains 60 g/L CuSO$_4$, 60 g/L H$_2$SO$_4$, and 0.01 g/L PEG. In this case, the electrodeposition has been operated for 30 minutes for 0.4 Amp/cm^2 current density and the pH level of the solution is 3. The microstructure of the Cu-coated mild steel samples at 40°C sample is presented in Fig.3 (a). The electrodeposition

process offers variation in morphology from semicircular to quasi-spherical shaped microparticles with a size distribution of ~ 0.1 to 1.3 μm. To determine the average size (X_A) of the particles has been estimated by the scaling and calibration of the line profile of different sizes of particles using the ImageJ 1.50i software. Therefore, the Gaussian fitting of the size distributions gives the value of X_A. Fig. 3(b) represents the particle size distribution due to Cu electrodeposition at 40°C on mild steel and the value of X_A is 0.35 μm.

Secondly, the coating was performed at 80°C and the plating bath contained a similar quantity of ingredients as discussed above (60 g/L CuSO$_4$, 60 g/L H$_2$SO$_4$, and 0.01 g/L PEG). In this case, the electrodeposition has also been operated for 30 minutes for 0.4 Amp/cm^2 current density and the pH level of the solution is 3.
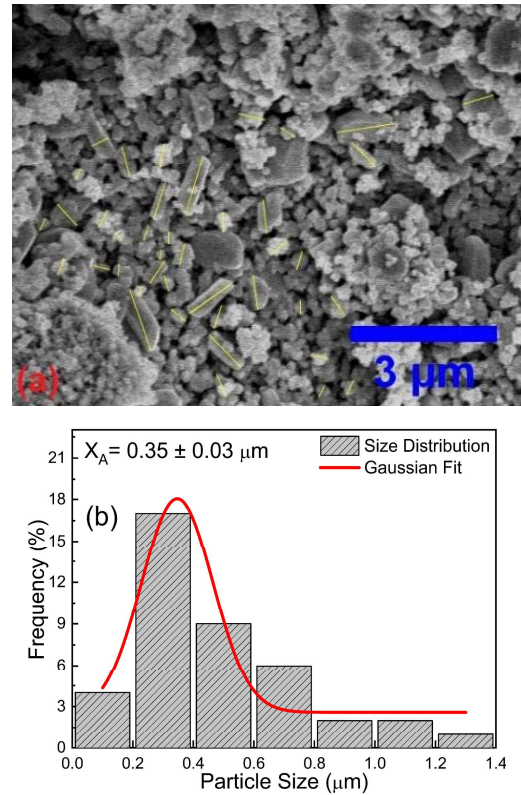

Fig. 3. Microstructure of copper-plated mild steel surface at 40°C represented by **(a)** various sizes of several particles and **(b)** particle size distribution.

Therefore, the microstructure of the Cu-coated mild steel samples at 80°C sample is presented in Fig.4 (a). For this case, the particles are more vivid to observe, and the particles are of long-range ordering with semicircular to quasi-spherical shaped morphology. The size of particles is ranging from ~ 0.7 to 1.5 μm. Therefore, identical clusters are formed during the deposition and larger grains are formed.

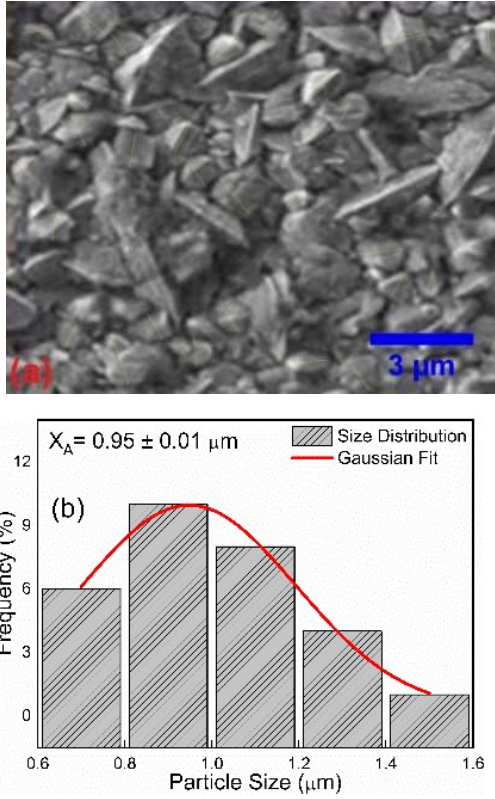**Fig. 4.** Microstructure of copper-plated mild steel surface at 80°C represented by **(a)** various sizes of several particles and **(b)** particle size distribution.

For the electrodeposition at this temperature (80°C), the average size (X_A) of the particles has been estimated as before using the ImageJ 1.50i software. Fig. 3(b) represents the particle size distribution due to Cu electrodeposition at 40°C on mild steel and the value of X_A is 0.95 μm which is larger than the particles formed for electrodeposition at 40°C. Therefore, it is expected that this microstructural evolution will cause the variation in hardness as well as current efficiency which are discussed in the following sections.

B. Microhardness

Fig. 5 includes the variations of microhardness of the Cu-coated mild steel samples due to variations of four different parameters as represented by the current density, time, temperature, and pH of the solution respectively. Here the quantity of ingredients in the electrolytic solution has been kept constant and the solution is composed of 60 g/L $CuSO_4$, 60 g/L H_2SO_4, and 0.01 g/L PEG. Therefore, the values of microhardness are influenced by the electro-deposition process and enhanced products could easily be obtained from this study. At first, the microhardness for samples prepared with different pH values and observed to increase with pH as depicted in Fig. 5(a). In addition, Fig. 5(b) represents the increase in microhardness due to the increase in the temperature of the solution. Furthermore, the current density

(J) was varied from 0.4 A/cm^2 to 0.8 A/cm^2, and it is observed from Fig 5(c) that the microhardness is inversely proportional to the current density. A similar tendency is observed for the electrodeposition time (t) where microhardness linearly decreases with time (Fig. 5(b)).
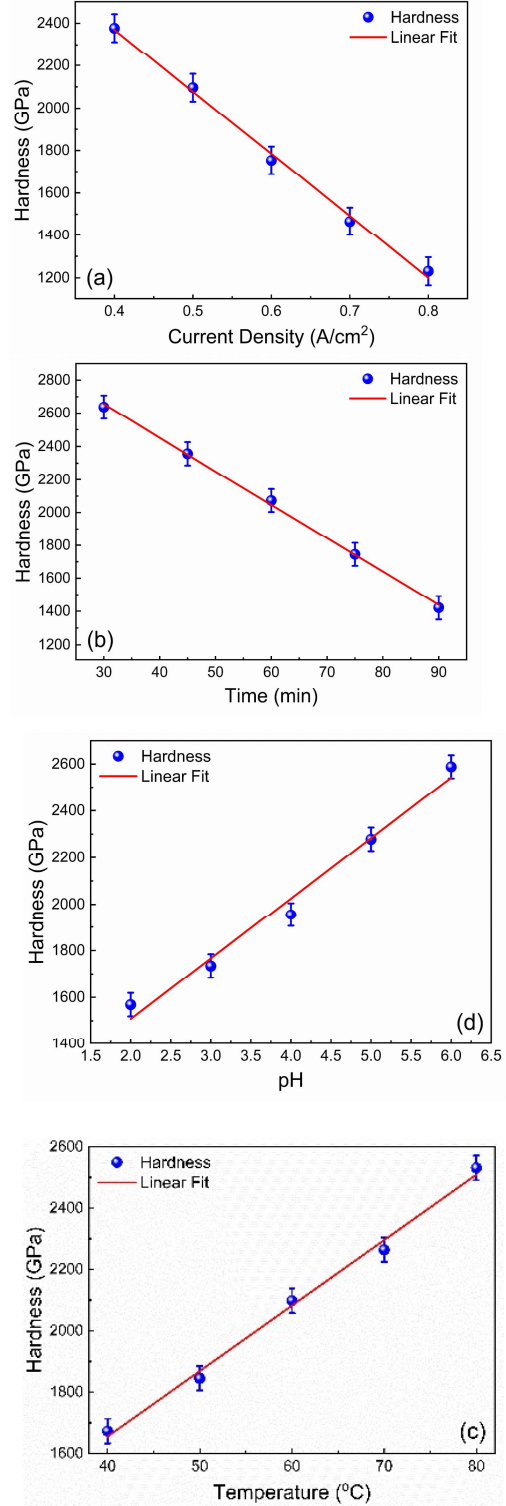
However, for both cases, the temperature and pH are 40°C and 3 respectively. In this circumstance, the maximum value of microhardness is obtained for J =0.4 Amp/cm^2, pH =3, and t = 30 min. Therefore, in the third step, the temperature has been varied from 40°C to 80°C keeping the other parameters the same. Fig. 5(c) represents the increase in microhardness due to the increase in the temperature of the solution. According to the Hall-Petch relationship, the hardness of any material is directly proportional to the grain sizes [10]. Therefore, the samples studied might establish a linear relationship between these factors. Here, the hardness for the sample is the lowest (1673GPa) for electrodeposition performed at 40°C. Smaller particles/grains are responsible for producing short-range ordering that might enhance the ductility of the Cu-coated mild steel. This result is concomitant to the obtained microstructure in Fig.3(a). However, a higher value of microhardness is obtained as the temperature during the electrodeposition is increased and a value of 2531 GPa is observed for 80°C. Therefore, as the temperature is increased, larger grains or clusters are formed which is confirmed for the microstructure of Cu coating at 80°C (Fig. 4(a)). Therefore, a long-range ordering of microparticles is obtained which is responsible for enhancing the microhardness. Apart from these, the microhardness of the Cu-coated mild steel has been observed with the variation of pH of the solution. In that case, each deposition was performed for 30 minutes, and the values of J =0.4 Amp/cm^2, and θ = 40°C. Fig. 5(d) illustrates the increase in microhardness of the coated sample due to an increase in pH level and the maximum value (2588 GPa) is observed for pH = 6.

C. Current efficiency

Typically, higher current efficiency (C_E) corresponds to a faster deposition rate, which can result in finer grain sizes and a more uniform deposit. However, in certain cases, this can also reduce the material's hardness due to insufficient formation of defects like grain boundaries. Moreover, increased deposition rates may restrict the time for atoms to rearrange into more stable, harder configurations, potentially yielding a softer material despite the higher current efficiency. Consequently, alongside hardness measurements, current efficiency has also been evaluated for the Cu-coated samples. Fig. 6 includes the variations of C_E due to variations of four different parameters as represented by the current density, time, temperature, and pH of the solution respectively.
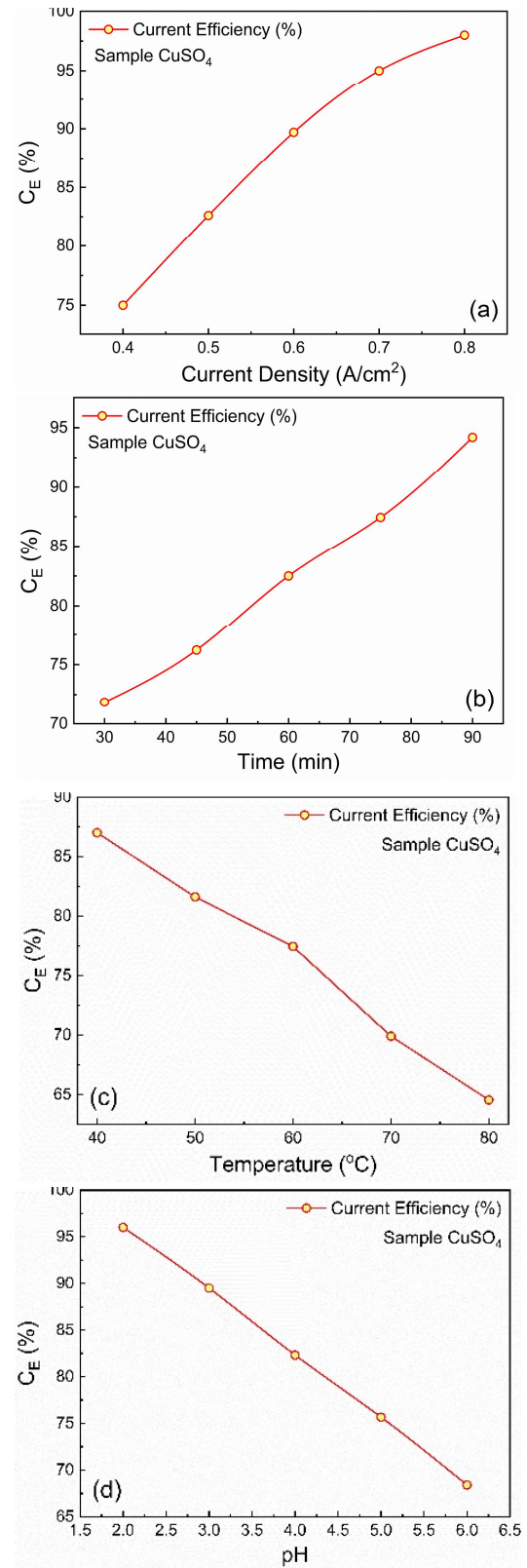

Fig. 6. Current efficiency (%) as a function of **(a)** current density **(b)** Time **(c)** Temperature and **(d)** pH

Here the quantity of ingredients in the electrolytic solution has been kept constant and the solution is composed of 60 g/L $CuSO_4$, 60 g/L H_2SO_4, and 0.01 g/L PEG. At first, the current density (J) is varied from 0.4 A/cm^2 to 0.8 A/cm^2 and it is observed from Fig 6(a) that C_E is proportional to the current density (J). A similar tendency is observed for the electrodeposition time (t) where C_E linearly increases with time (Fig. 6(b)). However, for both cases, the temperature and pH are 40°C and 3 respectively. In these circumstances, the increase in C_E indicates the faster deposition rate which is responsible for the reduction of microhardness observed in Fig. 5(a, b). Therefore, smaller grains are formed due to electrodeposition at higher current density for a long time and the sample becomes more ductile.

However, the third step of increase in temperature from 40°C to 80°C decreases the current efficiency while the other parameters are constant. Fig. 6(c) depicts the decrease in C_E due to the increase in the temperature of the solution. The lowest value of C_E (64.5%) is obtained for the electrodeposition at 80°C. A similar trend of C_E reduction is observed in Fig. 6(d) while the pH level of the 60 g/L $CuSO_4$, 60 g/L H_2SO_4, and 0.01 g/L PEG solution is increased. From these discussions, current efficiency directly affects the quality of the deposited layer. When current efficiency is lower, the deposition process is more controlled, which often leads to larger grains enhancing the microhardness.

IV. CONCLUSION

In this investigation, Cu coating on mild steel has been successfully performed with the variation of current density, time, temperature, and pH level of the solution. The microstructures of the studied deposition confirm that smaller grains are formed at lower temperatures which may enhance the ductility of the material. On the other hand, the electrodeposition at 80°C successfully enhanced the hardness of the Cu-coated mild steel materials. However, the low amount of current efficiency (C_E) is needed to enhance the microhardness of Cu-coated mild steel while ductility could be achieved by a high amount of C_E during electrodeposition. Furthermore, the pH level of the electrolytic solution must be optimum for enhancing microhardness/ductility. Therefore, the sample with the electrodeposition performed at 80 °C applying lower current density, J=0.4 Amp/cm^2 for t= 30 min is suitable for the practical application due its enhanced microhardness.

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