HARDNESS OF NICKEL ELECTRODEPOSITION ON ALUMINIUM ALLOYS: INFLUENCE OF TEMPERATURE AND DURATION OF HEAT TREATMENT

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ABSTRACT. Aluminium and its alloys have a great potential for application in aerospace and automotive industries because of low cost, lightweight and good strength. Depositing hard coatings on Al alloys substrate is often used to improve the poor Al wear resistance.

In this study, the way to improve the mechanical behaviour of Al alloys is to deposit a nickel layer followed by a heat treatment. Al-5%Mg alloy samples were electroplated using pure nickel. The deposition was carried out in a stirred standard nickel-plating Watts bath, with a current density of 2 $A.dm^{-2}$, a pH of 4.2 and a bath temperature of 45°C with different durations: 10, 15 and 20 min. A heat treatment was then performed to improve coating adhesion and surface mechanical properties at different temperatures and durations (450°C / 24h, 450°C / 40h, 500°C / 5h, 500°C / 10h and 550°C / 1h). To determine the hardness of the samples, Berkovich microindentation tests were performed and the Loubet's method was used to take into account the sink-in behaviour. The data processing allowed to find values of elastic modulus E_{IT} = 69.6 ± 6.1 GPa and hardness H_{IT} = 0.76 ± 0.03 GPa for the aluminium substrate closed to the theoretical values.

Microhardness results of the non-treated Ni coatings deposited on Al alloy substrate confirm that their hardness is greater than that of substrate alone. For samples with Ni deposition time of 10 minutes, the highest hardness is obtained after annealing at 450°C during 40h and 500°C during 5h because of the formation of intermetallic phases between substrate and coating determined by X-ray diffraction (XRD). For annealing at 450°C during 24h, Energy Dispersive X-ray emission spectroscopy and XRD show that the time of the heat treatment is not sufficient to diffuse the nickel into the aluminium substrate. The hardness is related to the various phase of (Al,Ni) formed during annealing which depend on one hand of the Ni deposition time in the Watts bath and on the other hand of the pair temperature / time of heat treatment. Finally, a discussion is conducted on the intermetallic phases Al_3Ni_2 and Al_3Ni obtained during heat treatments.

KEYWORDS: Aluminium alloy, Ni electrodeposition coating, hardness, intermetallic phases.

1 INTRODUCTION

Aluminium is an interesting material for industrial applications due to their lightweight, high corrosion resistance, good weldability, and good thermal conductivity properties. However, the applications of aluminium alloys are limited due to their low stiffness, low strength and poor tribological properties [1].

To increase aluminium surface properties in terms of hardness and wear resistance, different techniques of deposition, like plasma sputtering, electrolytic bath etc, have been used to deposit a protective coating [2]. Among these methods, electrodeposition offers several advantages compared with other techniques: low energy requirement, high production rate and waste reduction, uniform

deposition, good reproducibility, precise control and low cost production of large area samples and capability to coat complex component geometries [2, 3]. Nickel is one of the most important and widely used materials for coating aluminium alloys due to its high density, minimum porosity, excellent corrosion and wear resistance and good hardness [4].

In this work, nickel coatings were developed with different deposition times on an Al-5%Mg alloy substrate by electrochemical deposition. Adhesion of the coatings have been improved by several heat treatments, which have promoted the formation of Ni-Al intermetallic phases with superior mechanical properties. The nickel coatings were characterized by microhardness tests and the intermetallic phases formed after annealing were identified by X-Ray Diffraction (XRD) and Energy Dispersive X-ray emission spectroscopy (EDX)**.**

2 METHODS

Al-5% Mg alloy discs (table 1) with 14 mm diameter were mechanically polished using various abrasive papers up to paper grade 4000, degreased in an ultrasonic bath and rinsed with distilled water. The DRX pattern (not show in this paper) confirm the substrate composition, as the most important peaks are ascribed to $Al_{0.95}Mg_{0.05}$. Then, the substrate were chemical pickled in a zincate solution during 30 s and neutralized in an acid solution (97 vol. % methanol + 3 vol. % nitric acid). After a last immersion in the zincate solution, thus prepared substrates were introduced into the electrolytic bath. The nickel layers were deposited using a DC Watts bath (Figure 1) with a pure nickel electrode used as anode. The optimal Ni plating conditions were 4.2 pH, 2 $A.dm^{-2}$ cathode current density, 45°C bath temperature and an agitation of 80 rpm. Three different deposition times were used 10, 15, 20 min leading to Ni layer thicknesses between 5 and 15 µm. After nickel plating, several heat treatments with different temperatures (450°C, 500°C, 550°C) and different times (40h, 24h, 5h, 1h) were used to diffuse the nickel into the Al alloys substrate. The sample names used in this paper are given in the form XX/YYY_ZZ where XX is the time of Ni deposition and YYY and ZZ respectively the temperature and time of the heat treatment.

TABLE 1. Al-5% Mg substrate composition

Elements	Na	**Mg**	Si	S	Mn	Fe	Cu	Zn	Ga	Ag	**Al**
Mass (%)	0.062	**5.22**	0.39	0.054	0.29	0.29	0.032	0.028	0.011	0.024	bal

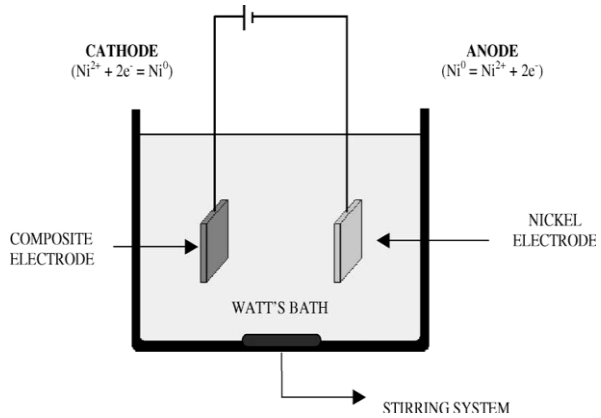

FIGURE 1. Watts nickel-plating scheme [5]

To characterize the hardness of nickel coatings before and after heat treatment, Berkovich indentation tests were performed using a Micro-Combi-Tester (CSM-instruments) with a 100 mN maximum applied load with loading and unloading rate set to 200 $mN.min^{-1}$ and a holding time of 15 s. The tip defects was calibrated using a BK7 sample. Then hardness H_{IT} was calculated as follow:

$$H_{IT} = \frac{P_{max}}{A_c} \quad (1)$$

$$A_c = 24.5 * {h_c}^2 \quad (2)$$

where P_{max} is the maximum applied load, A_c is the contact area and h_c is the contact depth.

In the case of pile up behaviour, the Loubet's model [6] was used to determine h_c:

$$h_c = \alpha_{loub}\left(h_{max} - \frac{P_{max}}{S}\right) \quad (3)$$

where h_{max} is the maximum depth during loading, S is the contact stiffness and α_{loub} = 1.2.

The intermetallic phases of the samples were investigated by using a PANalytical's X'Pert PRO diffractometer. The X-ray source was a Cu tube equipped with a monochromator selecting the $K\alpha_1$ radiation, $\lambda = 0.15406$ nm. The XRD patterns were recorded in the $\theta/2\theta$ Bragg-Brentano geometry at room temperature. EDX was performed on the cross section of the samples to determine the thickness of the Ni diffusion in the substrate using scanning electron microscopy (Jeol JSM-IT100).

3 RESULTS AND DISCUSSION

The hardness and elastic modulus of the Al-5%Mg substrate were measured and the results obtained (table 2 and E_{IT} = 69.6 ± 6.1) are in good agreement with those in the literature [7, 8]. As expected after Ni-plating, the hardness increases and is more than twice that the one of the substrate.

TABLE 2. H_{IT} of the Al-5%Mg substrate and nickel coatings before and after different annealing heat treatments

Sample	Ni deposition time (min)	Temp. (°C)	Time (min)	H_{IT} (GPa)
Al-5%Mg substrate	-	-	-	0,77 ± 0,02
Ni-plating	10	-	-	1.88 ± 0.09
10/450_24	10	450	24	1,62 ± 0.11
10/450_40	10	450	40	4.82 ± 0.16
10/500_5	10	500	5	4.84 ± 0.15
15/500_5	15	500	5	2.94 ±1.39
10/500_10	10	500	10	3.84 ± 0.15
10/550_1	10	550	1	3.64 ± 0.94
15/550_1	15	550	1	4.79 ± 0.30

When the sample is annealed at 450°C for 24h and 40h, the hardness increases considerably with the time of the heat treatment. Annealing involves the diffusion of Ni elements into the substrate and modifies the microstructure. When the time is insufficient, as for 10/450_24, the hardness is in the range of that obtained for the Ni-plating substrate. The increase in the hardness is attributed to the formation of the two intermetallic phases Al_3Ni and Al_3Ni_2, as show in Figure 2.

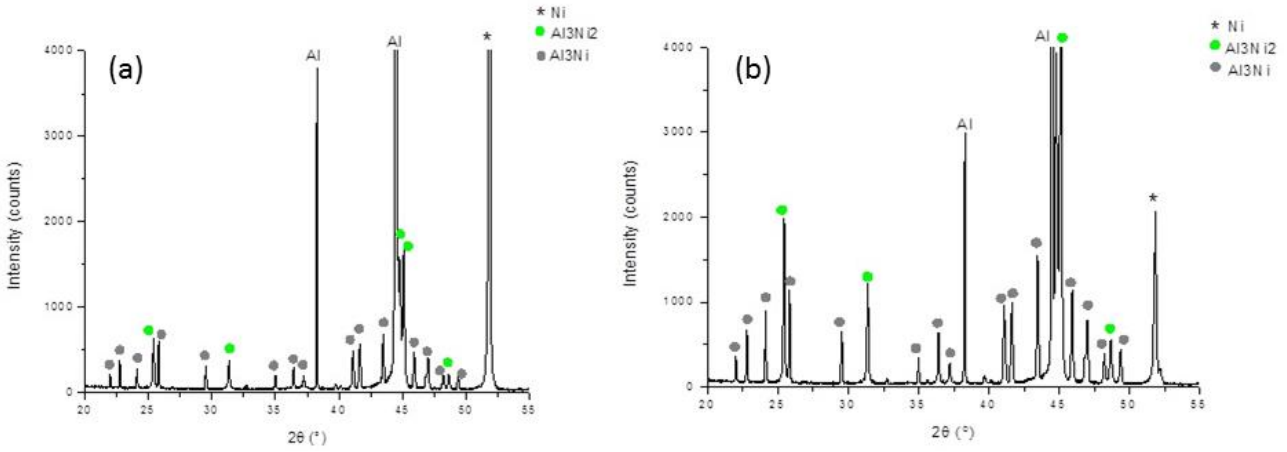

FIGURE 2. XRD patterns recorded for a) 10/450_24 and b) 10/450 _40

The SEM cross-sectional images show (Figure 3) that the Ni diffusion depth is about 15 µm for both samples, but the EDX analyses indicate that for 10/450_24, the surface is composed of 100% Ni whereas for 10/450_40, 95% of Ni and 5% of Al are on the top of the sample (table 3), that confirms the formation of the intermetallic phases.

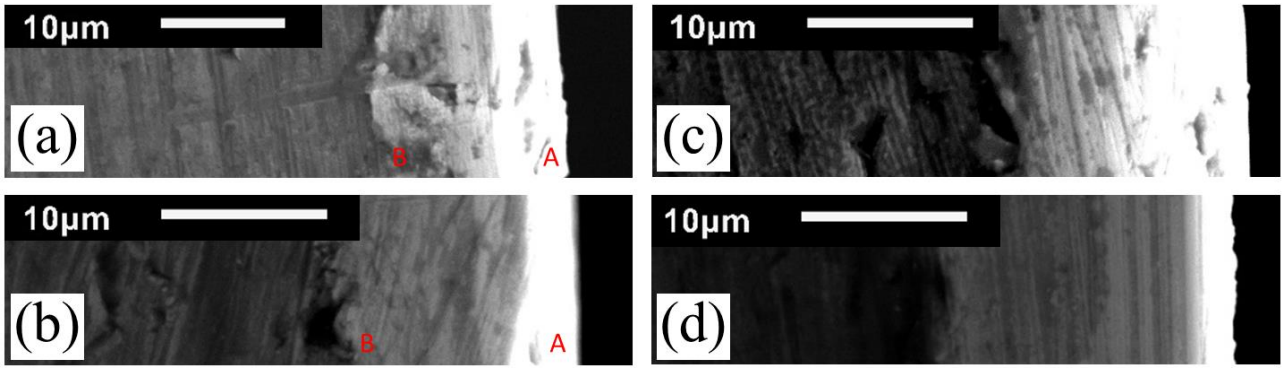

FIGURE 3. SEM cross-section image for a) 10/450_24, b) 10/450 _40, c)10/500_5 and d)15/550_1

TABLE 3. EDX analyses in area A and B reported in Figure 2

Sample	Area A		Area B	
	Ni	Al	Ni	Al
10/450_24	100	0	50	50
10/450_40	95	5	47	53

The samples 10/450_40, 10/500_5 and 15/550_1 show the greatest hardness around 4.8 GPa. However, for samples 10/500_5 and 15/550_1, the intensity of the diffraction peaks ($2\theta = 52°C$ and $2\theta = 76°C$, not show here) corresponding to Ni are higher (Figure 4) than for 10/450_40, which indicates a non-complete reaction of Ni with Al. The SEM cross section images highlight (Figure 3 b,c,d) the same depth magnitude of Ni diffusion for the three samples.

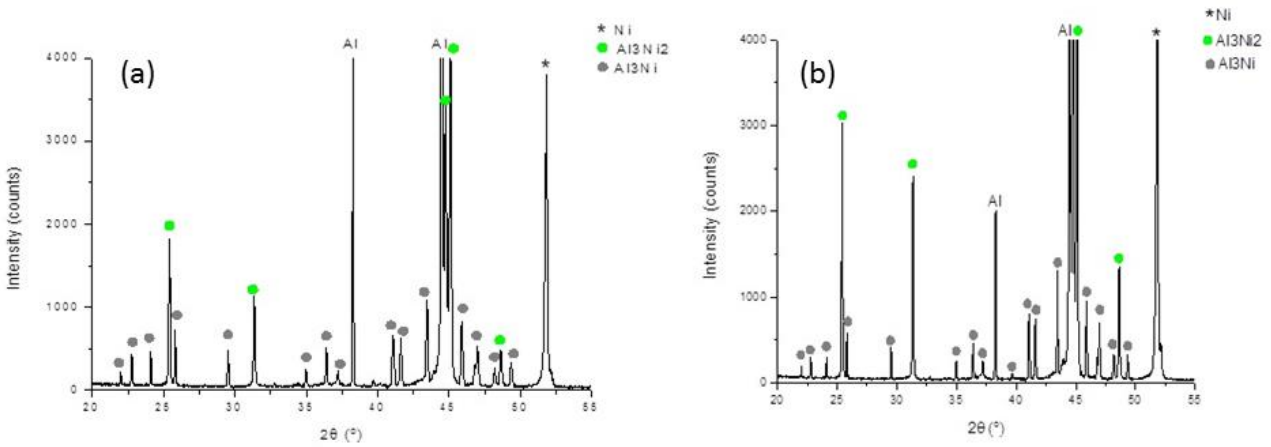

FIGURE 4. XRD patterns recorded for a) 10/500_5 and b) 15/550_1

Now, if we compare 10/500_5 (Figure 4a) and 10/500_10 (Figure 5a), as DRX patterns show, the Al_3Ni phases are larger in the sample 10/500_10. The hardness of this later is weaker than the one of 10/500_5, therefore the intermetallic Al_3Ni are less hard than the Al_3Ni_2 one. According to Rezaei et al., A_3Ni_2 is harder than Al_3Ni thanks to its ordered microstructure which makes movement of dislocations more difficult [9]. Another result to be compared is that when the annealing time increases, the diffusion depth of the Ni increases (Figure 5b and Figure 3c). Therefore, for a given temperature, a too long annealing time is not good because more Al_3Ni is formed to the detriment of Al_3Ni_2.

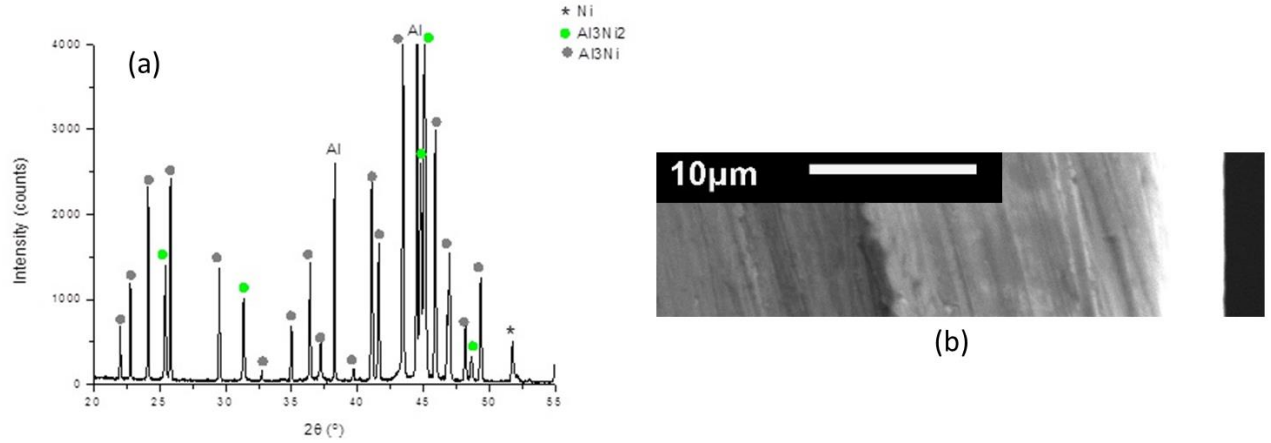

FIGURE 5. a) XRD pattern and b) SEM cross-section image recorded for 10/500_10

A decrease phenomenon of the hardness is also observed if the time of deposit is too long for a same temperature and time of annealing (10/500_5 and 15/500_5, table 2). It seems that if too Ni has been deposited, it does not react correctly with Al for the same annealing conditions.

4 CONCLUSION

In this study, the hardness of Ni electroplated aluminium alloys was studied. The influence of the Ni layer deposition time and the temperature and time of heat treatments are analysed. For 10 minutes of deposition time of Ni layer, the highest hardness is obtained after annealing at 450°C during 40h and 500°C during 5h because of the formation of intermetallic phases. The same hardness is measured for sample obtained after 15 minutes of Ni deposition time and a heat treatment at 550°C during 1 hour. The XRD combined with SEM images and EDX analyses have highlighted the Al_3Ni_2 intermetallic phase further increases the hardness compared to Al_3Ni intermetallic phase. However, the hardness decreases if the deposition time is too long. So, the results obtained in this work highlighted that it is necessary to combine the appropriate deposition time with the temperature and duration of the heat treatment in order to improve the mechanical properties.

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REFERENCES
[1] A. S. Anasyida, A. R. Daud, et M. J. Ghazali, Dry sliding wear behaviour of Al-4Si-4Mg alloys by addition of cerium. *International Journal of Mechanical and Materials Engineering* **4**:127‑130, 2009.
[2] Y. H. Ahmad et A. M. A. Mohamed, Electrodeposition of Nanostructured Nickel-Ceramic Composite Coatings: A review. *Int. J. Electrochem. Sci.* **9**:22, 2014.
[3] D. K. Singh et V. B. Singh, Electrodeposition and characterization of Ni–TiC composite using N-methylformamide bath. *Materials Science and Engineering: A* **532**:493‑499, 2012. doi:10.1016/j.msea.2011.10.115.
[4] T. Lampke, B. Wielage, D. Dietrich, et A. Leopold, Details of crystalline growth in co-deposited electroplated nickel films with hard (nano)particles. *Applied Surface Science* **253**:2399‑2408, 2006. doi:10.1016/j.apsusc.2006.04.060.
[5] J. M. Molina, R. A. Saravanan, J. Narciso, et E. Louis, Surface modification of 2014 aluminium alloy–Al2O3 particles composites by nickel electrochemical deposition. *Materials Science and Engineering: A* **383**:299‑306, 2004. doi:10.1016/j.msea.2004.03.016.
[6] J. L. Loubet, M. Bauer, A. Tonck, S. Bec, et B. Gauthier-Manuel, Nanoindentation with a Surface Force Apparatus, in *Mechanical Properties and Deformation Behavior of Materials Having Ultra-Fine Microstructures*, M. Nastasi, D. M. Parkin, et H. Gleiter, Éd. Dordrecht: Springer Netherlands, p. 429‑447, 1993.
[7] W. C. Oliver et G. M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research* **7**:1564‑1583, 1992. doi:10.1557/JMR.1992.1564.
[8] M. Y. N'jock *et al.*, A criterion to identify sinking-in and piling-up in indentation of materials. *International Journal of Mechanical Sciences* **90**:145‑150, 2015. doi:10.1016/j.ijmecsci.2014.11.008.
[9] M. Rezaei, R. Arabi Jeshvaghani, H. R. Shahverdi, R. Mojaver, et M. J. Torkamany, Formation of Ni-rich aluminide layers on an A356 aluminum alloy by a combined electroplating/laser alloying treatment: Microstructure and tribological characteristics. *Journal of Manufacturing Processes* **29**:310‑319, 2017. doi:10.1016/j.jmapro.2017.07.028.