

Advanced Surface Improvement of Al-Alloys Using Hard Chromium-Nano Ceramic Composite Electroplating

Sattar Hantosh A. Alfatlawi¹, Talib Abdulameer Jasim², Wafa Mahdi Jodia²

¹Department of Ceramic Engineering and Building Materials, College of Material's Engineering, University of Babylon, Iraq.

²Lecturers, Department of Metallurgicals Engineering, College of Material's Engineering, University of Babylon, Iraq .

*Corresponding Author email: Sattaralfatlawi@gmail.com; mat.sattar.h@uobabylon.edu.iq

ABSTRACT: There are many methods to improve the surface of aluminum or aluminum alloys according to the applications, including electroplating techniques. In this study, Composite of hard chromium-Nanoceramic Co-deposit was achieved. Nanozirconia (Nano-ZrO₂), Nanotitanium oxide (Nano-TiO₂), and Nano-aluminum oxide (α -Nano-Al₂O₃) were used in the bath of hard chromium electroplating on 1050 Al-alloy. Light optical microscope with digital camera (LOM) was used for microstructure examination. Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS or EDX) were employed for co-deposit analyses and thickness characterization. Micro hardness tester for hardness was evaluated. The hardness increased with increasing the content of Nanoceramic particles in the electroplating path, ZrO₂, α -Al₂O₃ and TiO₂ respectively. Moreover, the thickness was increased with increasing ZrO₂, α -Al₂O₃ and TiO₂ content. The results showed that, the maximum hardness and maximum thickness at the samples with Nanotitanium particles were 1227MPa, 17.2 μ m respectively.

KEYWORDS: Al-alloys, Electroplating, Hard chromium electroplating, Co-deposit electroplating, Nano ceramic particles.

INTRODUCTION

Aluminum and aluminum alloys are used since many centuries because of low density, high strength/weight ratio, high thermal conductivity, high electrical conductivity, high ductility, magnetic neutrality, high reflectivity and high scrap value. There are many techniques that have been used to improve the aluminum surface such as wear and corrosion resistance, those used in specific applications that required in many industries. That led to detect of many methods such as anodic oxidation, plasma electrolytic oxidation, micro-arc oxidation etc., to create an anti-corrosion layer and hard with various additives of materials prepared for that purpose [1-3].

Plasma electrolytic oxidation was used to improve the surface of aluminum alloys by increase the wear resistance and coefficient of friction, that using slurry electrolyte from a silicate-alkaline solution with basalt mineral powder [4]. The composite chromium-Nano ceramics electroplating is used because the many of advantages can be achieved such as; uniform distribution of the reinforcing particles, the using with any shape and size, can be deposition with low temperatures, industrial equipment is not required, low energy losses, more coating rates [5,6].

The aluminizing method was used to deposited the Al₂O₃ on electrochemical responses to produce the copper and alumina as single layer coatings and Cu/Al₂O₃ double layers that by reverse pulsed current electroplating [7]. With composite coatings by the electroplating process, the ceramic or organic particles are used on the substrate because of the high corrosion resistance, that are used at same time with the reduced metal ions are precipitated [8, 9].

Physical properties of chromium were making electrical deposit of chromium useful for decorative and engineering applications [10]. Generally, chrome plating was optimal due to its high corrosion resistance, high wear resistance and hardness as well as cheap process [11]. Jasim studied the effect of hard chromium electroplating reinforced by Nano zirconium oxide particles on St.37, and it concluded that the wear resistance and hardness increased with increasing the zirconium oxide in composite deposit chromium-Nano zirconium oxide [12]. The effects of current density, stirring rate and concentration of Nano aluminum oxide on hard

chromium electroplating were investigated. The concluded results were that, the wear rate decreases with increasing the stirring velocity and increasing of Nano ceramic concentration in electroplating path [13]. Sancarokalu, et al, studied the effect of Nano silicon carbide on the properties of chromium co-deposit, the silicon carbide particles were adsorbed on the substrate (cathode surface) [14].

In addition to electroplating and anodizing, there are other common ways were used to improve the surface of aluminum and its alloys, such as; coating, polishing, sanding, laser ablation, ion implantation and nanoparticle composite deposition [15]. The last years Nanoceramic particles were used with the leaser and the electroplating to produce hard composite layer to improve corrosion resistance. Jiru et al studied the influence of manganese, and magnesium on the corrosion behavior of aluminum samples in acidic ambience [16]. Jain et al studied the microstructure and wear by using the friction stir process to introduce titanium oxide to reinforce the surface of aluminum [17]. There are many similar studies for this work that we cannot mention in this paper in order to avoid lengthening.

RESEARCH OBJECTIVE

The main objective of this study was improved the aluminum alloy surface in a method of hard chromium-nano ceramic co-deposit composite. Previous studies focused on the problem of low hardness of aluminum and their alloys, which considered a major obstacle in many industrial applications, almost repeated same materials for electroplating in these studies, this paper was used a composite of Nano ceramic materials were precipitating co-deposit of chromium-nanoceramic particles (Zirconium oxide, Titanium oxide and Aluminium oxide). The aim was try to get the best results in improving the surface of the aluminum alloys, especially the hardness increased with increasing the deposit thickness that lead to increase the wear and corrosion resistance. That achieved by the electroplating process. These were done using a technique the hard chromium electroplating with Nano ceramic particles, expected to achieve the best results.

METHODOLOGY

The procedures of work was prepare the samples of (1050 Al-alloy) by lathe machine with selected cutting conditions such as cutting speed, depth of cut, feed and dry cutting. Then, grinding, polishing, zincate and electroplating processes were prepared. So have been conducted the tests of hardness by micro-hardness machine. Light optical microscope with digital camera was used for microstructure examination. Scanning electron microscope and Energy-dispersive X-ray spectroscopy were using to evaluate the type of deposit layers and elements.

Experimental work

The samples were machined by lathe machine at finishing cutting conditions; cutting speed 450 m/min, depth of cut 0.5 mm, feed 0.1 mm/rev and dry cutting, with diameter 25 mm and 3 mm thickness. Then, involving grinding, polishing, zincate and electroplating processes were prepared. Electroplating was hard chromium according to ASTM B177 / B177M - 11(2017) standard [18]. The bath consists of (300g/l of Cr₂O₃, 3g/l of concentrated H₂SO₄), the anodes were from lead-7Sn. The samples were cathode in the electroplating cell. The Nano zirconium oxide (ZrO₂), Nano aluminium oxide (Al₂ZO₃), and Nano Titanium oxide (TiO₂) with particle size (20-30 nm) were used in the unit cell each individually. Magnetic stirrer with hot plate was used for mixing and heating the electroplating bath, the used temperature for all experiments was 45°C. Table 1 showed the chromium plating parameters that used for the electroplating processes. The samples were prepared for microstructure and hardness by cutting, grinding, and polishing according to ASTM E3—11(2017) samples preparation standards. Micro Vickers hardness was carried out using Vickers hardness test with (0.4N) testing load and 15 sec. testing time as in table 2. The microstructure carried out using light optical microscope equipped with digital camera. Scanning electron microscope was tested by using SEM. The composition of deposit and co-deposit layers was evaluated using SEM and EDS.

Table 1. Parameters of hard chromium electroplating.

Sample No.	S0	S1	S2	S3	S4
CrO3	0	300 g/L	300 g/L	300 g/L	300 g/L
H2SO4	0	3 g/L	3 g/L	3 g/L	3 g/L

Voltage(V)	0	6	6	6	6
DC current (A)	0	20	20	20	20
Time (Min.)	0	30	30	30	30
Temperature (C °)	0	50	50	50	50
Mixing Velocity (rpm)	0	800	800	800	800
Nano ZrO ₂	0	0	0	6 g/l	0
Nano TiO ₂	0	0	6 g/l	0	0
α -Nano Al ₂ O ₃	0	0	0	0	6 g/l

Table 2. Micro-hardness results.

Sample No.	Test 1 (Hv MPa)	Test 2(Hv MPa)	Test 3(Hv MPa)	Mean value
S0 (Without electroplating)	33	37	36	35.5
S1(Hard chromium deposit)	890	880	920	897
S2 (Chromium with TiO ₂)	1220	1240	1250	1237
S3 (Chromium with ZrO ₂)	1089	1100	1040	1076
S4(Chromium with α -Al ₂ O ₃)	1090	1080	1098	1086

RESULTS DISCUSSION

Microstructure

The samples were prepared for microstructure according to ASTM E3 standard [19]. These samples were cut and mounted by epoxy resin. The cross section examined as polished without etching to show the layers of electrodeposits. As appear in fig.1 the microstructure was free from chromium deposit in sample (S0) because the sample was not electroplated. As shown in fig.1, there is only base metal (pure aluminum) at the cross section of the sample. Fig.2 (A, B) showed the microstructure and composition of sample (S1). Fig.2 (A) showed three layers appear in this micrograph, the dark brown at the left represents the mounting layer. The base metal was the light brown layer at the right and a thin layer of chromium deposit between them. Fig.2 (B) showed the EDS map of sample S1. There are copper layer (blue layer) precipitated on the base metal at bottom of image, chromium layer (green) precipitate on copper layer. The carbon appears as a pink color may be from carbonized cyanide. The cyanide was change to cyanide carbonate when exposed to air for a long time. Fig.3 (A,B) displays the micrograph at the cross section of sample S2 which electroplated by hard chromium bath with Nano TiO₂ as a reinforcing agent. Fig.3A shows four layers, base metal at the right, mounting material at the left of image and copper layer, co-deposit of hard chromium and TiO₂ between them, as shown in micrograph in fig.3A, the co-deposit layer appears as wavy layer as a result of Nanoceramic particles. Fig.3B displays the EDS analysis of the co-deposit.

Fig.4, four layers appeared in micrograph at cross section of sample S3. These layers consist of base metal the light brown at right of image, copper layer, the brown layer precipitated at Cu-layer, mounting layer, the dark brown at the left of image, and co-deposit layer of chromium with Nano-ZrO₂ between them. The co-deposit layer appeared less thick compared with co-deposit layer in fig.3. That means the ability of Nano ZrO₂ to precipitate with chromium deposit is less than Nano-TiO₂ may be because the low density of TiO₂ (Bulk density of TiO₂ Nanoparticles 0.24 g/cm³ and the true density is 3.9g/cm³, and the true density of Nan-ZrO₂ is 6.03g/cm³) [20]. Fig. 5(A,B) displayed the Micrograph and EDS analysis at sample (S4). Fig.5 (A) showed that the deposit at sample S4. The deposit consists of Cu- layer and co-deposit of chromium with Nanoaluminum oxide (Al₂O₃). The co-deposit layer at micrograph of sample S₄ was more uniform and wide wavy structure. That means, the Nano-

Al₂O₃ precipitates with chromium deposit to form smooth layer. Fig.5 (B) appeared there is Al₂O₃ precipitated with hard chromium.

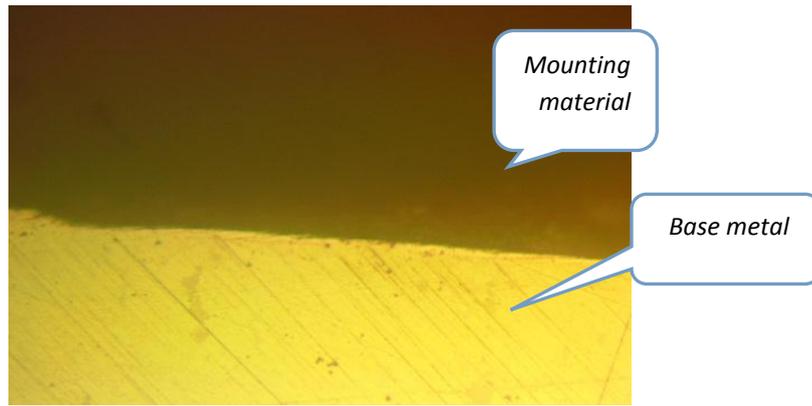


Figure 1. Base metal without electrodeposit (S₀)

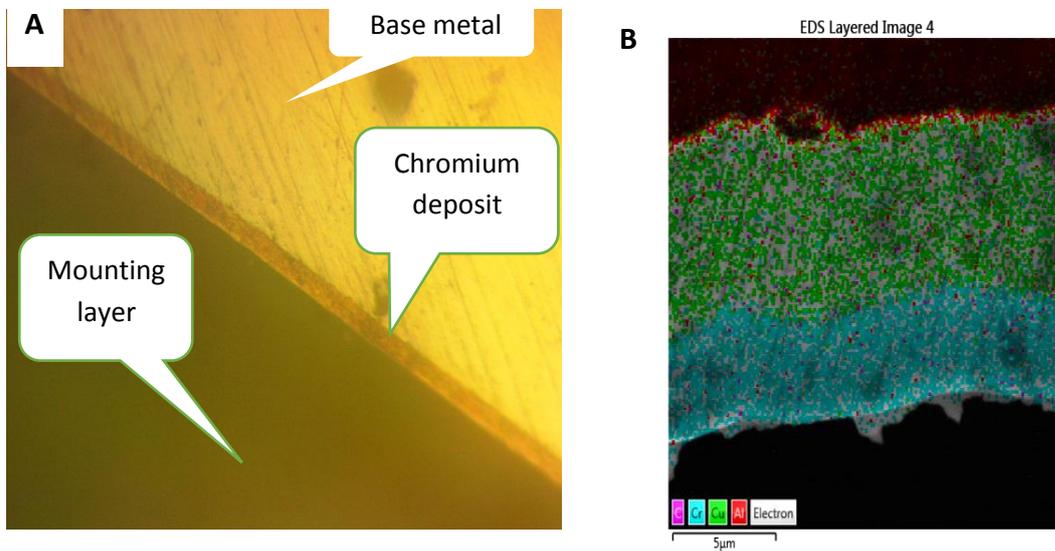


Figure 2. The chromium deposit.

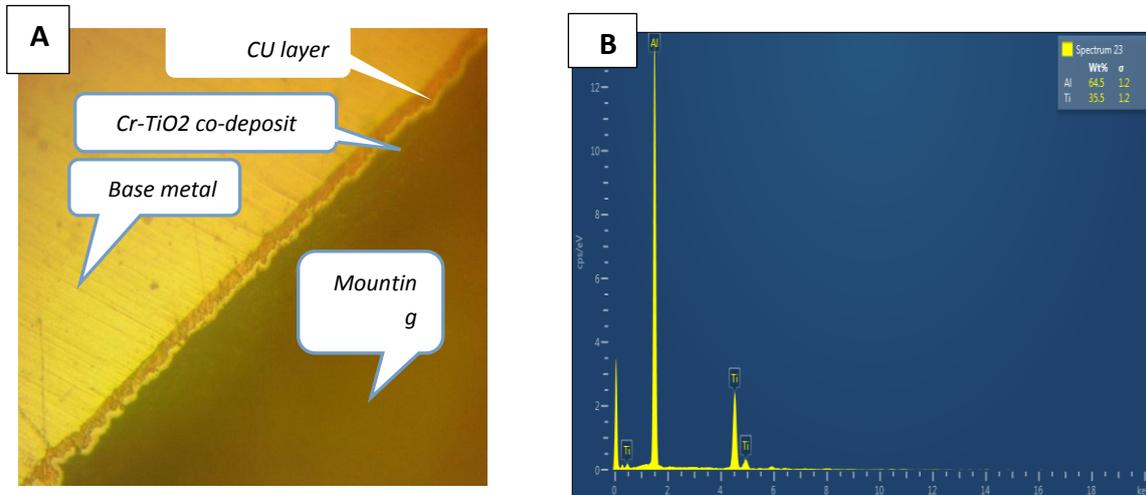


Figure 3. (A, B) The chromium co-deposit at sample (S₂).

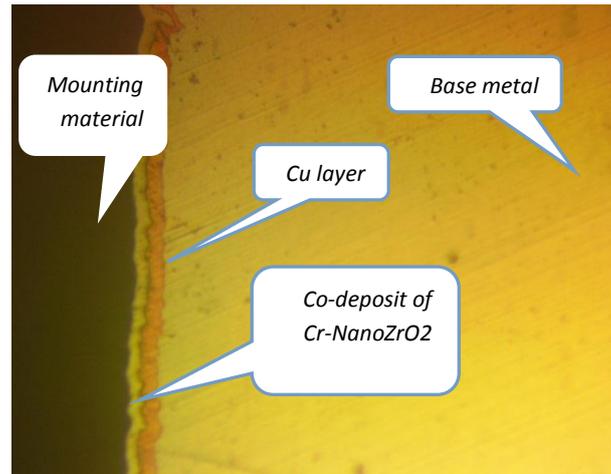


Figure 4. Co-deposit of chromium and ZrO_2 at sample (S3)

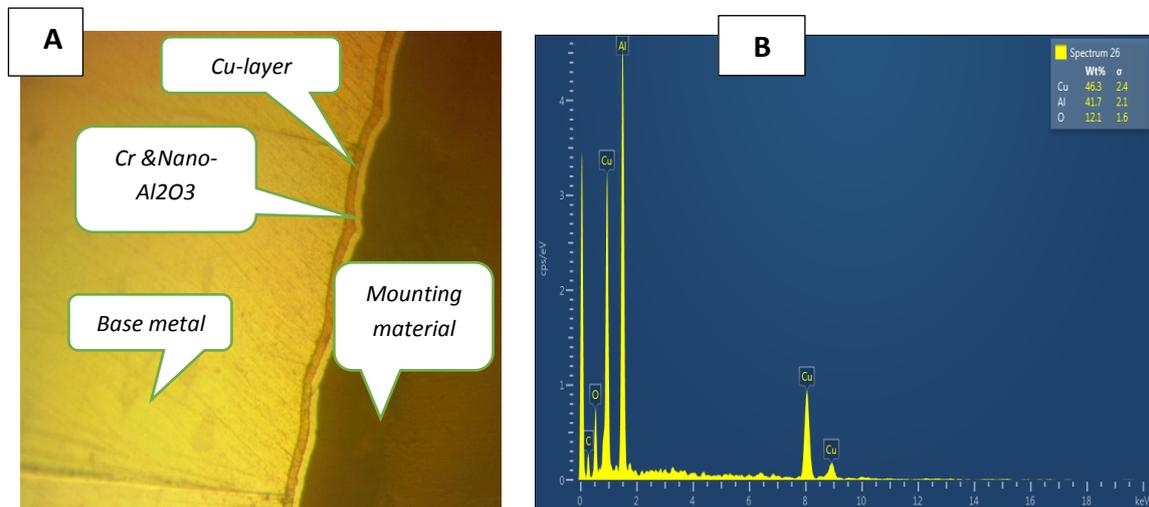


Figure 5. (A,B) The chromium co- deposit at sample S4.

Hardness

The hardness test was done using micro-hardness machine. Three tests for each sample, were done, the testing load and testing time was (30 gr., and 30 sec. respectively) displayed in table 2. Fig.6 the hardness of samples increased after hard chromium electroplating. The hardness of sample S0 was 35.5 MPa, but in hard chromium deposit at the sample S1 the hardness increased to 879MPa. The effect of Nano ceramic particles increased the hardness of co-deposit, to the maximum hardness about 1237 MPa at the Cr-TiO₂ composite layer at the sample S2. The hardness of Cr-ZrO₂, and Cr-Al₂O₃ were 1076, 1186MPa respectively. The hardness of co-deposit increased about 44% compared with only hard chromium deposit. The reason for that, were the effect of Nano-ceramic particles as a hard particles and its effects as dispersion hardening particles which act as barrier to block dislocation motion [21].

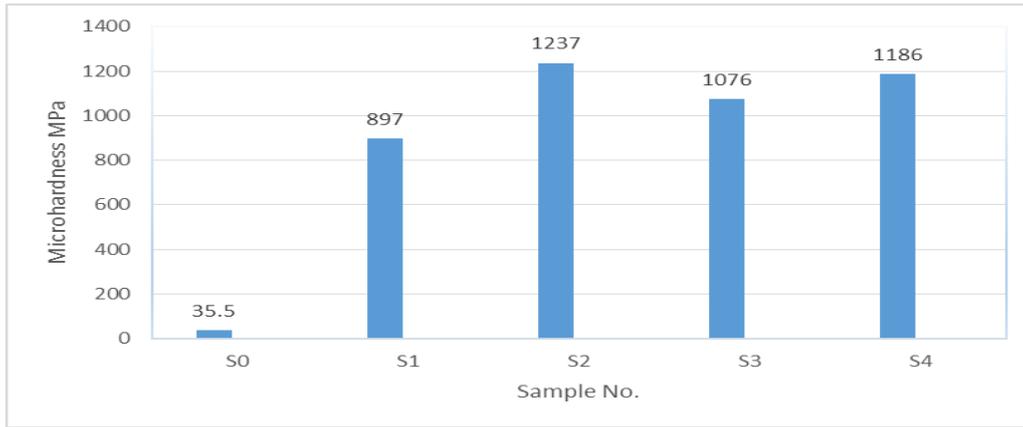


Figure 6. Micro hardness of samples before and after electroplating with and without Nanoparticles

SEM & EDS Tests

Scanning electron microscope (SEM) and (EDS) were used for evaluation of the type of deposit layers, as shown in fig. 7, 8, 9, and 10, the elements consists the deposit layer were determined. Fig.7 showed the SEM image and EDS at first layer of deposit, fig 7A, represented the SEM image at the first layer between the base metal and chromium layer, fig7B showed the EDS diagram at copper layer. The construction of this layer consists of Al the base metal and the copper deposit. Fig.8A showed the image of the position of spectrum 4 at the boundaries of spectrum3 which represent the copper layer. Fig.8B appeared the EDS diagram of Al₂O₃ layer which consists of Al and O₂ and cu the copper deposit. Mean that, Some of Al₂O₃ Nano particles immersed in copper layer. Fig. 9A appeared the position of Nano Ti particles in co-deposit Cr-Ti layer. Fig.9B showed the EDS diagram of spectrum 23. As appear from fig.9B the composition of the layer which consist from Al and Ti particles.

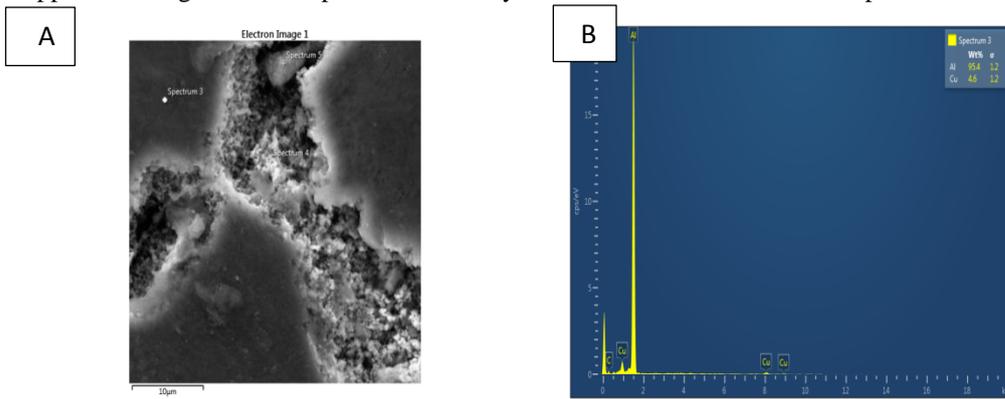


Figure 7. The SEM image and EDS at the first layer which represents the copper layer.

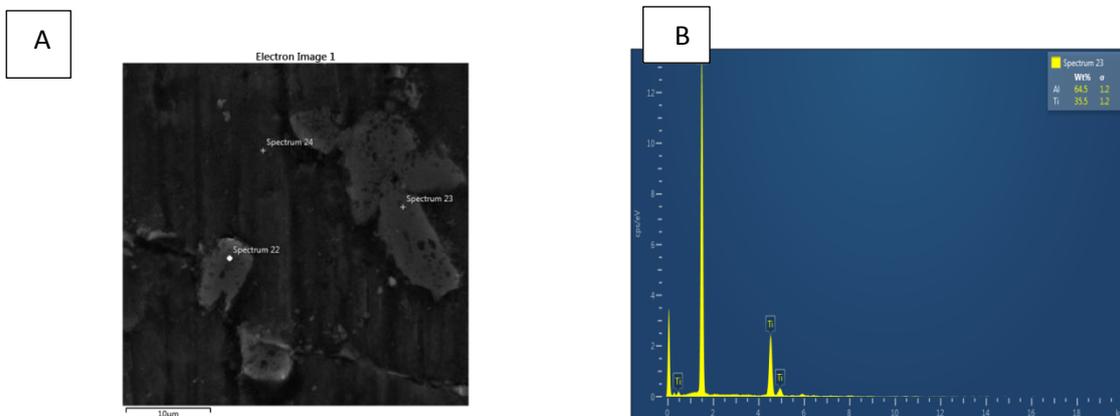


Figure 8. The SEM image at spectrum 23 which shows the Nano Ti particles at the deposit.

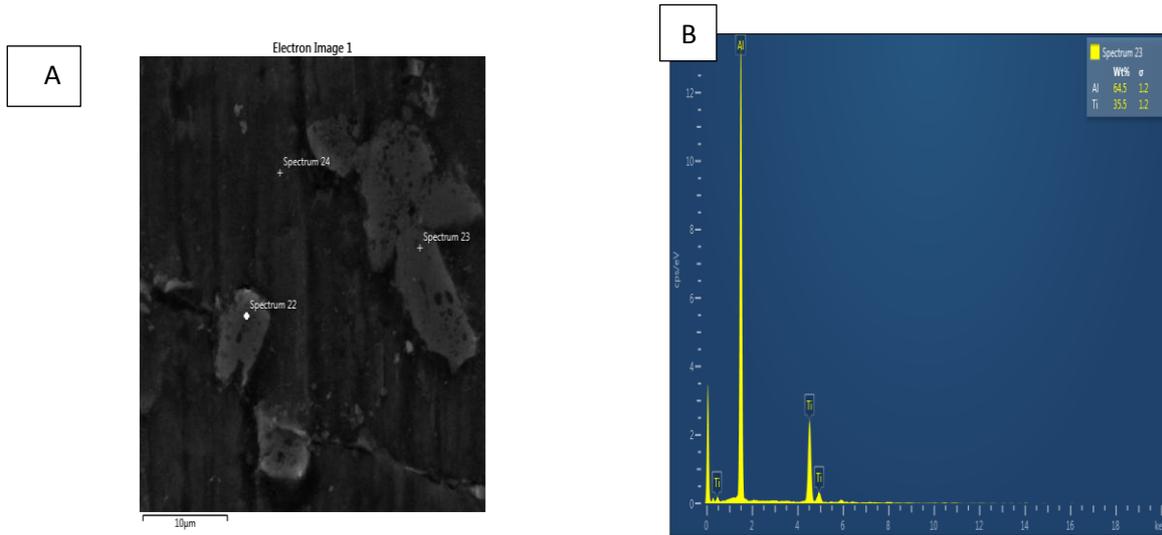
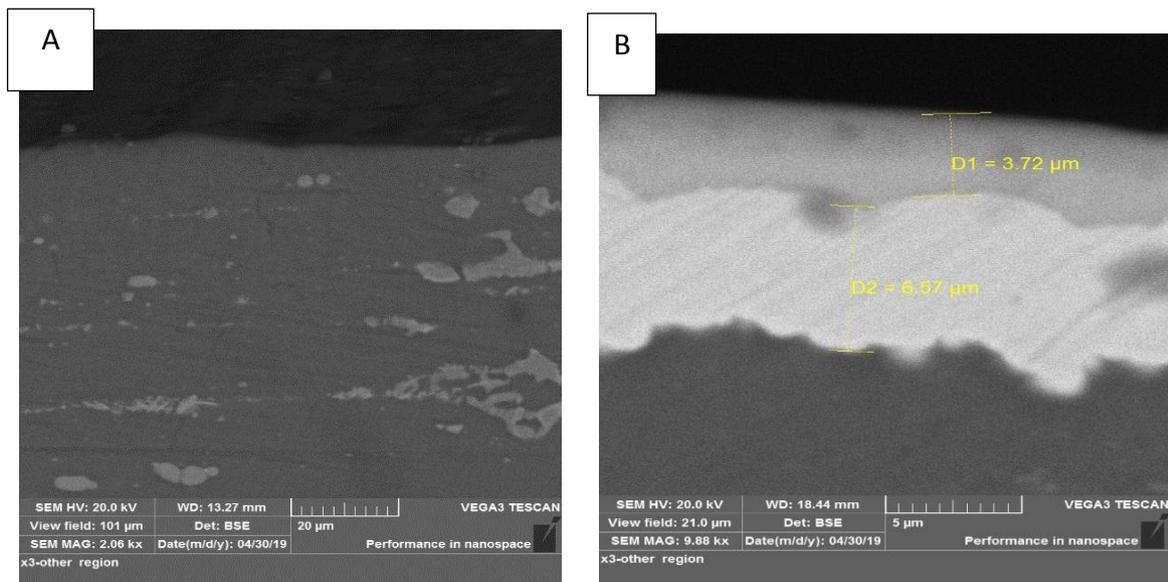


Figure 9. SEM image at spectrum 23 which shows the Nano Ti particles at the deposit.

Thickness of Co-Deposit Layers

Fig. 10 displayed the thickness of co-deposit of samples. Fig. 10 A showed the SEM image for sample S0, in this image, the thickness was Zero. The thickness of deposit in sample S1, in fig. 10B was 9.3 µm. There are two layers, the first was Cu layer and the other was chromium without ceramic particles. The thickness of co-deposit in sample S2 in fig. 10 C was 17.2 µm. There are two layers consist of Cu for the first layer and co-deposit of Cr-TiO₂. The thickness of co-deposit in sample S3 in fig. 10 D was 11 µm. There are two layers consist of Cu for the first layer and co-deposit of Cr-ZrO₂. The thickness of co-deposit in sample S4 in fig. 10D, was 16.6 µm, there are two layers consist of Cu at the first layer and co-deposit of Cr-Al₂O₃. The higher thickness was the co-deposit of Cr-NanoZrO₂. A; without electroplating, B; hard chromium electroplating deposit without Nanoceramic particles, the thickness was 9.3 µm , C; Electrodeposit with Nano-TiO₂ particles, the thickness was 17.2 µm, D; Electrodeposit with nano-ZrO₂ particles the thickness was 11 µm, E; Electrodeposit with nano-Al₂O₃ particles, the thickness is 16.6 µm.



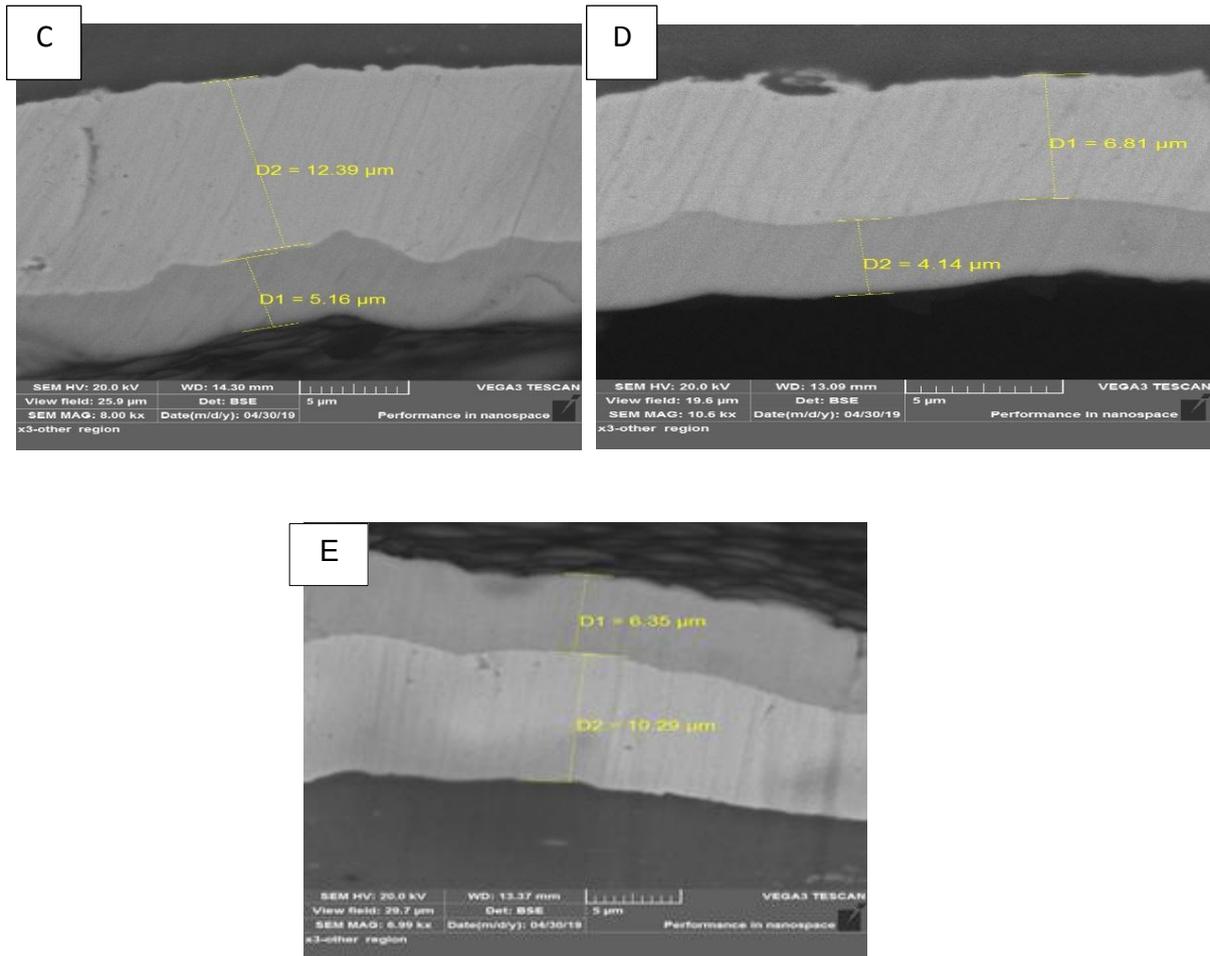


Figure 10. (A,B,C,D and E): The SEM images showed the thickness of deposit layers.

CONCLUSION

The results obtained from this study can lead to the following conclusions;

- The surface of Al-alloy can be improved by hard chromium-nanoceramic composite electroplating.
- The thickness of co-deposit depends on true density of Nano-ceramic particles, in other word, high true density lead to low deposit thickness.
- The increasing deposit thickness of nanoceramic composite electroplating lead to increase the hardness.
- The highest thickness was in sample electroplated by co-deposit of Cr-TiO₂
- The layers of coating were compact and uniform, as this was evident in all the previous figures.

REFERENCES

- [1] L. Famiyeh and X. Huang, "Plasma Electrolytic Oxidation Coatings on Aluminum Alloys Microstructures, Properties, and Applications, Modern Concepts", *Material Science*, Vol. 2, Issue 1, Pp. 2-13, 2019. MCMS.MS.ID.000526, china.
- [2] S.H. Awaad, 2019, "Study on Al₂O₃ Duplex coatings Deposited By New Micro-Arc Oxidation Processes Using Natural Addition of Rice Hushes Ash and Porcelanite Rocks of Pre-Anodized 6061 Al-Alloys", *International journal of mechanical engineering and technology*, Vol.10, issue 2, Pp. 1640-1654, 2019.
- [3] S.H. Awaad, "Double Layer Coatings For Surface Improvement of 6061 Al- Alloys By Anodized And Micro plasma Oxidation Process Using New Hydroxyapatite and rock Additives Modified Electrolytes", *Journal of engineering and applied science*, Vol.14, No.22, Pp.1-14, 2019.
- [4] O.P. Terleeva, A.I. Slonova, A.B. Rogov, A. Matthews and A. Yerokhin, "Wear Resistant Coatings with a High Friction Coefficient Produced by Plasma Electrolytic Oxidation of Al Alloys in Electrolytes with Basalt Mineral Powder Additions", *Materials (MDPI)*, Vol. 12, 2738, Pp. 1-15, 2019.

- [5] M. Sabzi, A. Obeydavi, and S.H. Mousavi Anijdan, "The effect of joint shape geometry on the microstructural evolution, fracture toughness, and corrosion behavior of the welded joints of a hadfield steel", *Mech Adv Mater Struc.* Pp. 1–11, 2018. Accepted, <https://doi.org/10.1080/15376494.2018.1430268>.
- [6] S.H. Mousavi Anijdan, M. Sabzi, M. Ghobeiti-Hasab, and A. Roshan- Ghiyas, "Optimization of spot welding process parameters in dissimilar joint of dual phase steel DP600 and AISI 304 stainless steel to achieve the highest level of shear-tensile strength", *Mater Sci Eng A*, 2018.
- [7] M. Sabzi and S.M. Dezfuli, "Deposition of Al₂O₃ ceramic film on copper-based heterostructured coatings by aluminizing process: Study of the electrochemical responses and corrosion mechanism of the coating", *Applied ceramic technology, The American Ceramic Society*, 2019. DOI: 10.1111/ijac.13072, Iran.
- [8] H. Liu, and Z. Liu, "Evaluation of microstructures and properties of laser-annealed electroless Ni-P/Ni-Mo-P duplex coatings", *Surf Coat Technol.*, Vol. 330, 270–276, 2017.
- [9] S. Li, Y. Zuo, and P. Ju, "Erosion-corrosion resistance of electroplated Co-Pd film on 316L stainless steel in a hot sulfuric acid slurry environment", *Appl Surf Sci.*, Vol. 331, 200–209, 2015.
- [10] G.A. Lausmann, "Chromium electroplating", *Series of electroplating and surface treatment*, Pp. 2, 2007.
- [11] D.Y. Zhuk, "Use of hard coatings for valves", *Valve Magazine*, 2000.
- [12] T.A. Jasim, "Hard chromium electroplating reinforced by Nano zirconium oxide particles", *International Journal of Scientific & Engineering Research*, Vol. 6, no. 7, Pp. 2071-2078, 2015.
- [13] T.A. Jasim, "Enhancement of chromium plating by Nano ceramic particles", *International Journal of Scientific & Engineering Research*, Vol. 6, no. 3, Pp. 877-882, 2015.
- [14] O. Sancakođlu, M. Erol, B. Agaday, and E. Çelik, "Electrodeposited C-SiC Composite Coating: Effect of the Pulse-Current Current Frequency on Morphology and Hardness", *Materials science, Engineering and Chemistry*, Vol. 47, no. 5, Pp. 601, 2013.
- [15] L. Torrisi and C. Scolaro, "Treatment Techniques on Aluminum to Modify the Surface Wetting Properties", *Acta Physica Polonica A*, No. 1, Vol. 128, 2015.
- [16] W.G. Jiru, M.R. Sankar, and U.S. Dixit, Improving Acid Corrosion Resistance of Pure Aluminum by Laser Surface Alloying with Magnesium and Manganese; Conference Paper, J. Jones. (1991, May 10). Networks (2nd ed.) [Online], 2017. Available: <http://www.atm.com>.
- [17] V.K.S. Jain, J. Varghese, and S. Muthukumar, "Effect of First and Second Pass on Microstructure and Wear Properties of Titanium Dioxide Reinforced Aluminum Surface Composite via Friction Stir Processing", *Arabian Journal for Science and Engineering*, 17, 2018.
- [18] Standard Guide for Engineering Chromium Electroplating; ASTM B177 / B177M – 11, 2017.
- [19] Standard Guide for Preparation of Metallographic Specimens, ASTM E3 – 11, 2017.
- [20] US Research Nanomaterials, Inc.; 3302 Twig Leaf Lane, Houston, TX 77084, USA; <https://www.us-nano.com/inc/sdetail/269>.
- [21] U. Lagerpusch, V. Mohles, and E. Nembach, "On the additivity of solid solution and dispersion strengthening", *Materials Science and Engineering A*, 319–321, Pp. 176–178, 2001.