Influences of Bath Stirring Rate on Synetics of Nano Composite Ni-SiC-Gr Coatings on St37 via Electrodeposition Process

M. Rostami [a]*, R. Ebrahimi-Kahrizsangi [a], A. Saatchi [b]

[a]*Najafabad Branch, Islamic Azad University, Najafabad, Iran*
[b] *Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran*

ARTICLE INFO

ABSTRACT

In this study, electrochemical deposition of Ni-SiC-Gr nano composites was studied. The Watts bath was used for electrodeposition. The SiC and graphite powders were suspended in the electrolyte and stirred. The effects of changes in bath stirring rate on the composite coating were investigated. The X-Ray diffraction (XRD), scanning electron microscopy (SEM) and field emission scanning electron microscopy (FE-SEM) methods were used to characterize the micro structure of deposited layer. The results showed that the micro-hardness at the first stage increases with increases in stirring rate value. The coating that precipitated at 500 rpm showed maximum hardness. Analysis of microstructure with SEM showed a homogeneous and uniform distribution of elements in the coated layer. The optimum condition for electrodeposition were as: pH=4.2, current density= 4A/dm^2, stirring rate =500 rpm and 45°C.

1. Introduction

The effects of different parameters on Ni-based coatings can vary to a great extent. In recent years, the effect of many parameters on nickel-based composite coatings has been investigated by researchers. In this study, in order to produce nano composite Ni-SiC-Gr coatings, the effects of bath stirring rate variations on micro-hardness and surface morphology of the coatings have been studied. In most reports for electroplating two important factors, namely, the temperature and solution pHhave been reported 45-55°C and 4-4.5, respectively [1,2,5]. Their optimum limit, 45°C as temperature, pH=4.2 as constant parameters were used for coating in this project.

One of the most important reasons for developing nano composite Ni-SiC-Gr coatings is the extensive applications of Ni-based coatings in military industries. The essential feature of such composite coatings is high surface hardness and resistance to thermal wear. Also, due to the presence of graphite with a lamellared structure, they are self-lubricant, too. General characteristics, morphology and topography, weight percent of elements in coatings, phase analysis and micro-hardness of nano composite Ni-SiC-Gr coatings have been investigated in the present study.

*Corresponding author. Tel.: +989195040709.
E-mail address:*mohsen.ross62@yahoo.com(M. Rostami).

2. Materials and methodology

The importance of knowing the tools and instruments which are necessary for doing the research regarding a specific subject cannot be ignored. Prior to categorization of the instruments, the principles of their updating and calibration is another essential factor. The experiments will be accomplished in accordance with the devised plan and the instruments, materials and the tools for measurements and analysis will be introduced.In the present study the coating has been applied on St37 steel substrates. Generally, the preparation of the substrate includes three stages: degreasing, acid pickling and polishing. In order to make nano composite Ni-SiC-Gr coatings, $0.1 \times 1 \times l$ mm^3 steelsubstrates were used. The coated samples were then studied with respect to the phases, morphology, surface micro-hardness and microstructure. In this study, 250cc Pyrex beaker was used for Watts bath. The Watts bath volume was 100cc.A digital scale (Sarturius) with 0.1g precision was used for weighing the samples and materials. At first, Watts solution with 100cc total volume in a 250cc beaker was prepared by using 200g/l nickel sulfate, 20g/l nickel chloride, 40g/l boric acid, 12g/l nanosize powder of SiC, 5g/l CTAB powder, 5g/l SDS, 1g/l saccharine and 1g/l graphite powder. For adjusting pH=4.2, soda and 5% sulfuric acid were used. After the preparatory stages, Watts bath cycle was initiated by using rectifier DC, so that the graphite anode was connected to the positive pole and the steel cathode to the negative one. The duration of each experiment was assigned 20 min [16].By changing stirring rate of Watts bath from 0 rounds per minute (rpm) to 1250rpm, nano composite Ni-SiC-Gr coatings were produced. The stirring rates for developing such coatings were 0, 250, 500, 750, 1000 and 1250rpm.

In the present study the most important instruments were a planetary ball mill, X-ray diffractometer (XRD), rectifier, magnetic stirrer, Mercury thermometer, digital scale, pH tester, scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), pulsed DC electrical source and micro-hardness tester.To study the phases in the coatings X-Ray diffraction (XRD) was used and the resulted peaks were analyzed and compared by using *Xpert High Score*. Also, in order to observe the morphology, topography and SiC and Gr distribution in nickel matrix, scanning electron microscopy (SEM) was employed. Maximum magnification was 100kX, maximum voltage was 30kV and maximum filament current was 3A. For elemental analysis of the coating, SEM analyzer (EDAX) was used. It turned out to be practically impossible to study the images resulted from EDAX in magnifications higher than 20kX. Therefore, FE-SEM was used for solving this problem. Micro-hardness tester (Micromet3) was used for investigating micro-hardness of Ni-SiC-Gr composite coatings. Prior to these tests, the coatings were cold mounted and after soft abrasion, micro-hardness tests were taken from three different points of the samples. A kind of resin along with a hardener was used for cold mounting of the samples. Finally, the average of micro-hardness values was recorded as the hardness value of the coating. The applied force and the duration of each test for taking micro-hardness were 50g and 3 sec, respectively. Hardness testing was done on three different points, near the substrate, middle point and far from the substrate; the average of these three hardness values was reported as the final hardness.

3. Results and Discussion

For electrochemical deposition, the stirring rates of 0, 250, 500, 750, 100 and 1250rpm were used. This study aims at investigating the influence of stirring rate of Watts bath with the presence or absence of the coating elements (in the bath), morphology and particles distribution, weight percent and micro-hardness of the coatings. To study the effect of the stirring rate on the hardness and simultaneous precipitation of SiC and Gr particles in nanocomposite Ni-SiC-Gr coatings, micro-hardness of the coatings were

Table1. Micro-hardness, elements weight percentand Ni-SiC-Grnano composite coatings fixed terms with bath stirring rate shifts

Current type	$T(°C)$	Time (min)	Current density(A/dm²)	Volt (V)	PH	Stirring rate (rpm)	Gr (wt%)	Si (wt%)	Micro-hardness (HV)	sample
DC	45	20	4	2.5	4.2	0	0.25	0.15	372	N_1
DC	45	20	4	2.5	4.2	250	0.22	0.48	426	N_2
DC	45	20	4	2.5	4.2	500	0.33	0.89	584	N_3
DC	45	20	4	2.5	4.2	750	0.28	0.72	521	N_4
DC	45	20	4	2.5	4.2	1000	0.22	0.69	438	N_5
DC	45	20	4	2.5	4.2	1250	0.17	0.61	412	N_6
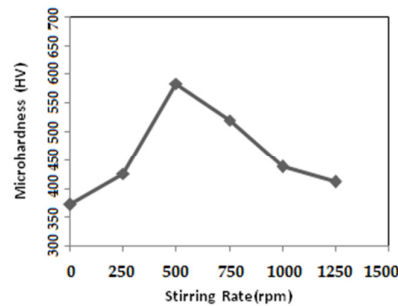
Fig.1. Micro-hardness changes diagram of Ni-SiC-Grnano composite coatings versus bath stirring rate.

examined; the results are shown in Table 1. The diagram in Fig. 1 shows the value of micro-hardness for pure nickel and Ni-SiC-Gr coatings versus different stirring rates.

As can be seen in Table 1 and Fig. 1, the hardness of pure nickel coating in electroplating bath (stirring rate=500rpm) is 332HV. Also, it was observed that in the electrolyte bath with increase of turbulence due to increase of stirring rate, micro-hardness of nano composite Ni-SiC-Gr coating increases in the beginning, reaches a peak in higher speeds and then tends to decrease.

In a bath containing 12g/l of SiC nanoparticles and 1g/l Gr nanoparticles, under fixed and optimum conditions, with stirring rate of 500rpm, micro-hardness value reaches 584HV. In fact, with increase of bath stirring rate, the amount of simultaneous precipitation of particles in the coating first increases and then starts to decrease. This can be explained by the fact that the particles have caused the increase of micro-hardness in the coating after

entering it [6,7]. The reason for decrease of micro-hardness of the coatings in stirring rates higher than 500rpm can be the intense turbulences in the solution. In the mentioned mechanism, the collision of particles in the coating results in their being plucked from the surface, hence causing the decrease of simultaneous precipitation of SiC particles in nano composite Ni-SiC-Gr coatings [6,22] and consequently, the decrease of hardness.

It is observed that with decrease of electrolyte turbulence or even with its absence, most of the particles tend to agglomerate at the bottomof Watts bath, thus producing electrolyte sludge, which results in lowering the amount of suspending particles in the suspension [6]. This, in turn, causes the decrease of hard SiC nanoparticles in the produced coating and decrease of average micro-hardness of the coatings. When the particles have been deposited in the form of electrolyte sludge, only a small amount of the particles with sufficient synetic energy are capable of suspension in the bath and rarely

enter the nanocomposite coating [6,8]. On the whole, it can be concluded that with increase of stirring rate, the particles have been suspended and due to surface ionization (as a result of high current), the situation for reaching of the particles to the surface has been facilitated [9]. Another explanation for increase of micro-hardness in nanocomposite coatings up to optimum speed is that with increase of stirring rate up to optimum limit, the hydraulic force applied to the solution causes the disintegration of many agglomerates and reinforcement particles have easily contributed to the production of charged suspension [11]. Based on this, it can be said that the contribution of the particles to production of nanocomposite Ni-SiC-Gr coating has increased, thus ending in increase of the coating hardness.

Decrease of hardness in stirring rates higher than the optimum limit can be explained by throwing speed of the particles. Since the particles hit the substrate surface with high speeds while they are charged, because of high collision force and inadequacy of the surface charge for attraction of the particles to the surface, hard SiC particles are plucked from the coating and enter the electrolyte cycle. In such a state, only those particles can be attracted to the substrate surface which have high electromagnetic force [12,13]. This causes the decrease of hard particles in the coating, hence the decrease of micro-hardness. In other words, in turbulences higher than optimum limit, the intensity of stirring in the electrolyte reaches to an extent that remaining of the particles in the surface becomes impossible and the particles will have to leave the coating before being stabilized in it [2,6]. Therefore, the weight percent of the particles decreases, too. This decrease for stirring rates higher than 500 rpm is shown in Figs. 2 and 3. To put it another way, increase of stirring rate to lower

optimum limit results in the increase of soft absorption, while increasing up to higher than optimum limit results in decrease of duration of remaining of the particles in nanocomposite Ni-SiC-Gr coatings as an outcome of collision factor and scanning of particles from the surface [13,18,19]. This decrease in the duration of particles stability on the surface is followed by lowering the level of their contribution to the surface [21]. X-ray diffraction patterns for nanocomposite coatings produced by 500 and 1000 rpm are shown in Fig. 4.
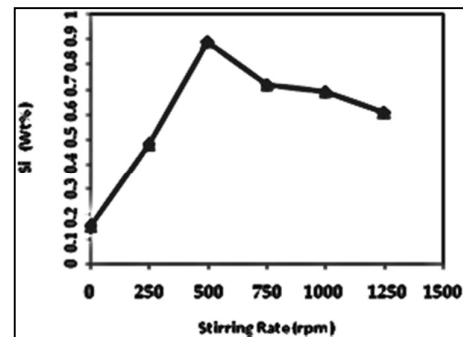

Fig.2. Si weight percent changes diagram of Ni-SiC-Gr nanocomposite coatings versus increase of bath stirring rate.
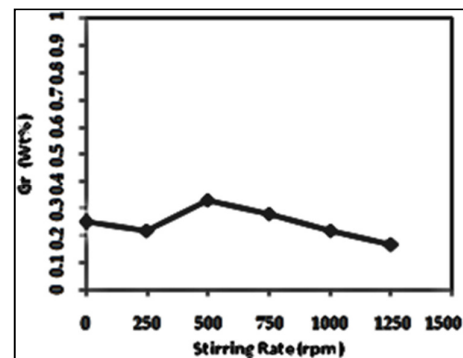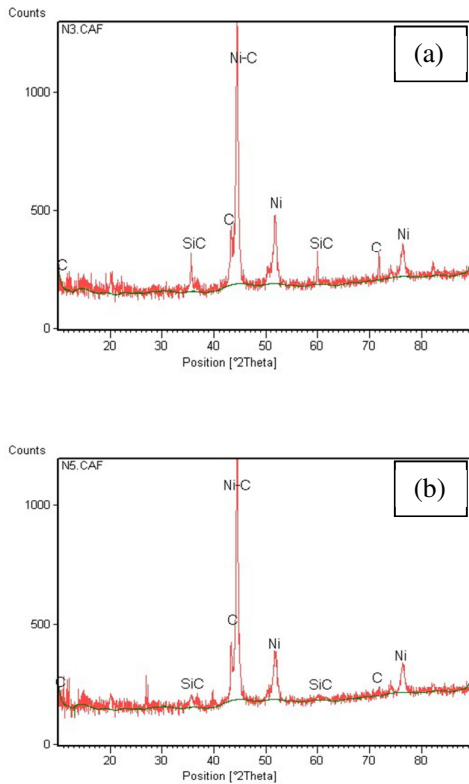

Fig.3. Gr weight percent changes diagram of Ni-SiC-Grnanocomposite coatings versus increase of bathstirring rate.
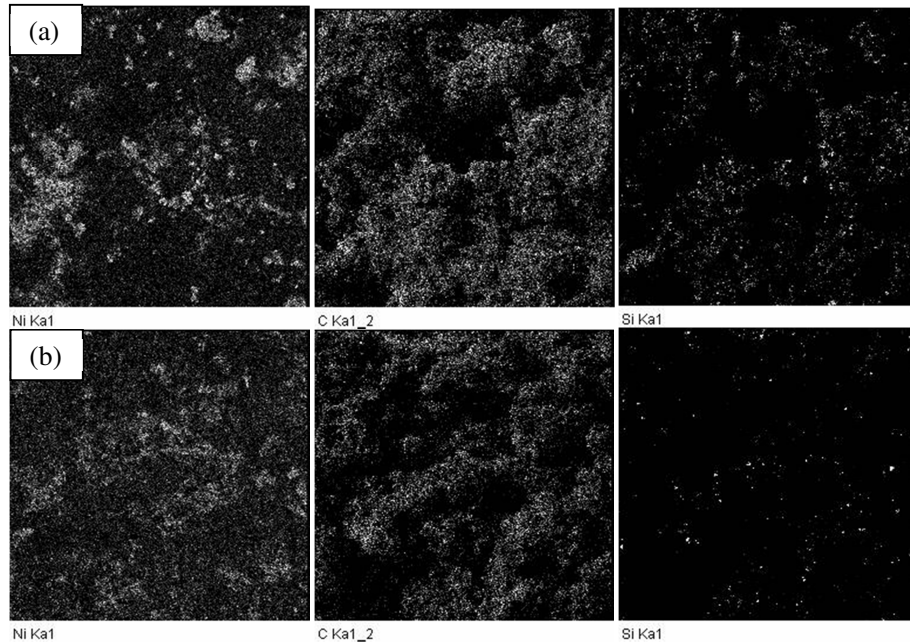
Fig. 4. XRD paterns of nanocomposite coatings (a) nanocomposite coating with 500 rpm stirring rate (b) nano composite coating with 1000 rpm stirring rate.

Moreover, based on SEM images in Fig. 5, it can be seen that the amount of secondary and hard SiC particles in N_3 sample is more than N_5 sample, which confirms the above claims. As can be seen in SEM images in Fig. 5a, N_3 coating is more condense than N_5 coating and SiC nanoparticles and Gr micro-particles have adequately precipitated in Ni matrix; but as can be observed in Fig. 5b, N_5 coating shows lower density than N_3, and its density has decreased. Higher density in N_3 coating can be related to the presence of more SiC nanoparticles in that coating which can also be witnessed in X-ray diffraction pattern shown in Fig. 4.

This is also confirmed in Fig. 6 by the distribution and presence of the three principal elements of the coating.
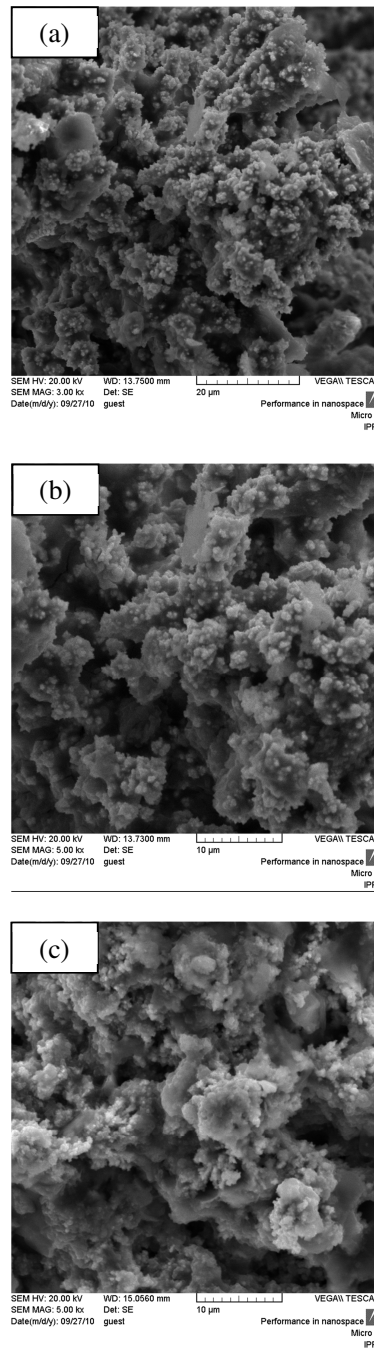
Fig.5. SEM surface micrograph of nano composite coatings with 3000 and 5000 magnification (a,b) nano composite coating with 500 rpm stirring rate (c) nano composite coating with 1000 rpm stirring rate.

Fig.6. SEM (MAP) surface micrograph of nanocomposite coatings with 500 magnification (a) nano composite coating with 500 rpm stirring rate (b) nano composite coating with 1000 rpm stirring rate.

In SEM studies, after observing that in the second group the images with 3000 and 5000 magnifications cannot account for morphological and topographic investigations of nanocoatings, it was decided to take images of the next nano composite samples with maximum possible magnification via FE-SEM. Therefore, FE-SEM images with 60kX and 150kX magnifications were also used in the present study for a better and more precise study of presence and distribution of SiC nanoparticles in the coatings, as shown in Figs. 7 and 8.

Fig. 7 shows FE-SEM images of nano composite coatings with 60kX and Fig. 8 shows FE-SEM images taken from N_3 and N_5 samples with 150kX magnification. As can be seen inFig. 7a, SiC nanoparticles along with Gr micro-particles have precipitated in Ni matrix (sample N_2). Also, in Fig. 7b, SiC nano particles and Gr micro-particles can be found in N_3. Observing N_4 and N_5 images reveals that in N_4 coating (Fig. 7c) the density of reinforcement particles has decreased a little compared to N_3 and following that, the

density of reinforcement particles in N_5 shows more decrease compared to N_4.

FE-SEM images with 150 kX magnification were used for studying the topography of N_3 and N_5 samples. As can be seen in Fig. 8, SiC nanoparticles as well as Gr micro-particles have precipitated in Ni matrix. Considering the above mentioned results and discussions, the presence of all three nano composite elements in Ni-SiC-Gr coating was proved. Moreover, the greatest percent of silicone and graphite and nickel was observed in the sample produced by 500 rpm.

4. Conclusions

1) It was observed that nano composite Ni-SiC-Gr coatings could be adequately produced on (St37) steel substrate under different conditions of application.

2) Since the greatest weight percent of Si and C are observed in 5000 rpm stirring rate, this can be explained by the manner of attraction of the suspension particles to the substrate surface. Therefore, with increase of stirring
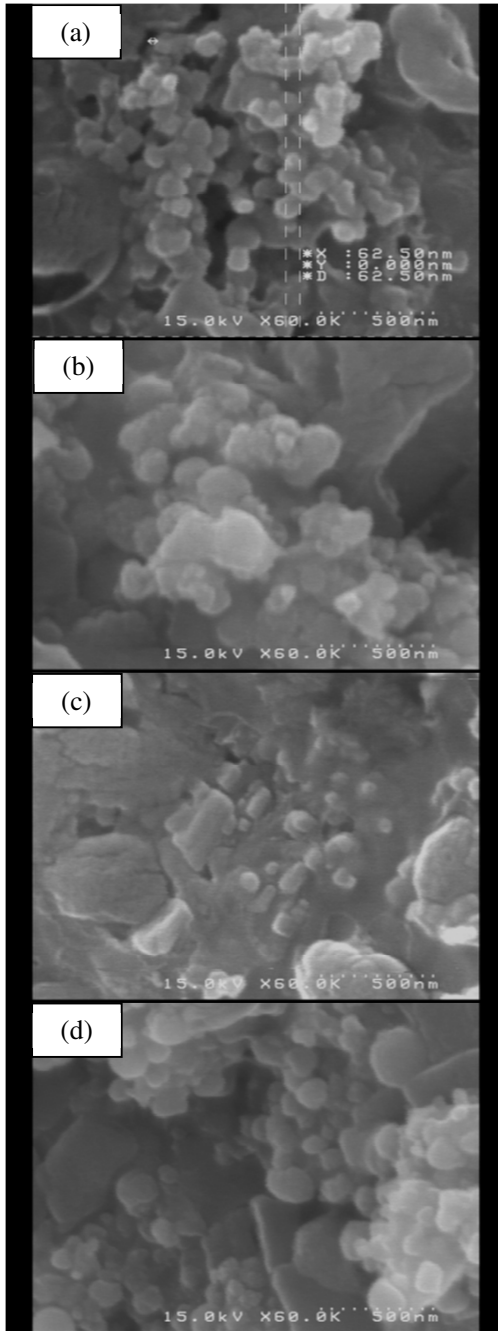
Fig.7. FE-SEM surface micrograph of nano composite coatings with 60kXmagnification (a) nano composite coating with 250 rpm (b) 500 rpm (c) 750 rpm (d) 1000 rpm stirring rate.
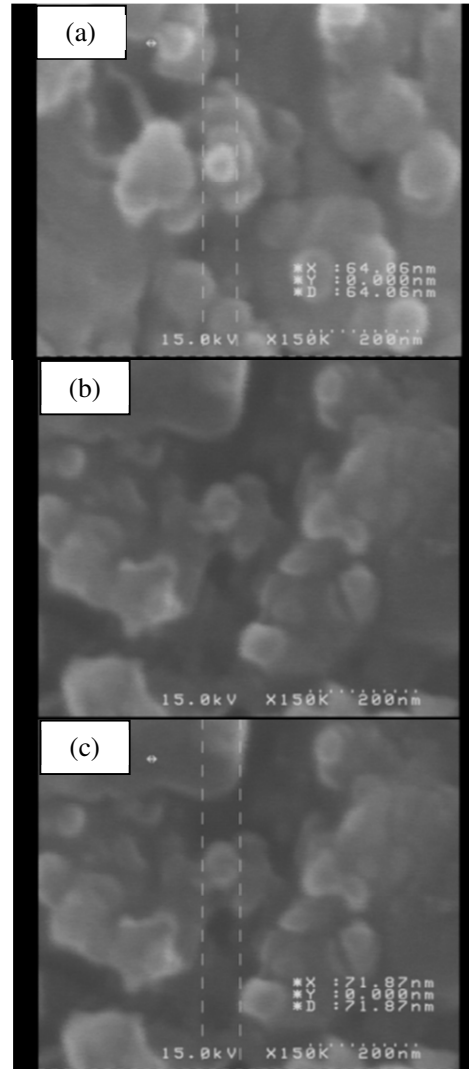
Fig.8. FE-SEM surface micrograph of nano composite coatings with 150kXmagnification (a,b) nano composite coating with 500 rpm stirring rate (c) nano composite coating with 1000 rpm stirring rate.

rate up to 5000rpm, since surface attraction of suspension particles dominates the repellent force of the surface (due to collision), weight percent of the particles and hence micro-hardness will increase. In speeds higher than 5000rpm since the repellent force of the surface dominates the surface attraction of suspension particles, weight percent of particles and hence micro-hardness will decrease.

References

[1] A. shokohfar, K. momeni, "Introduction of the Nanotechnology", Nashrgostar cultural center, Tehran, 2005, p.15-44,.

[2] E. Besharat, "Metals Plating Engineering", Tarrah publication, 2003, Tehran.

[3] M. Okamoto, F. Hussain, R.E. Gorja, "Polymer–matrix nanocomposites", *Journal of Composite Materials*, Vol. 40, 2006, pp. 1511-1519.

[4] T. Lampke, B. Wielage, D. Dietrich, A. Leopold, "Details of crystalline growth in codeposition electroplated niekle films with hard (nano)particles",*Applied Surface Science*, Vol. 253, 2007, pp. 2399-2408.

[5] M. Lekka, N. Kouloumbi, M. Gajo, P. Luigi Bonora, "Corrosion and wear resistant electrodeposited composite coatings", *ElectrochimicaActa*, , Vol. 50, 2005, pp. 4551-4556.

[6] M. Ghorbani, "Metals Plating", *Sharif . T .U scientific publication*, vol. 1, Tehran, 2007.

[7] L.Barchi, U.Bardi, S. Caporali, M. Fantini, A. Scrivani, A. Scrivani, "Electroplated bright aluminium coatings for anticorrosion and decorative purposes", *Progress in Organic Coatings*, Vol. 67, 2010, pp. 146-151.

[8] A. Ghasemi, V.S. Raja, C. Blawert, W. Dietzel, K. U.Kainer, "The role of anions in the formation and corrosion resistance of the plasma electrolytic oxidation coatings", *Surface and Coatings Technology*, In Press, Accepted Manuscript, 2011.

[9] A.A. Zuleta, O.A. Galvis, J.G. Castaño, F. Echeverría, F.J. Bolivar, M.P. Hierro, F.J. Pérez-Trujillo, "Preparation and characterization of electroless Ni–P–Fe_3O_4 composite coatings and evaluation of its high temperature oxidation behavior", *Surface and Coatings Technology*, Vol. 203, 2009, pp. 3569-3578.

[10] J. Alexis, B. Etcheverry, J.D. Beguin, J.P. Bonino, "Structure, morphology and mechanical properties of electrodeposited composite coatings Ni–P/SiC", *Materials Chemistry and Physics*, Vol. 120, 2011, pp. 244-250.

[11] Y.T. Wu, L. Lei, B. Shen, W.B. Hu," Investigation in electroless Ni–P–Cg(graphite)–SiC composite coating", Surface & Coatings Technology, Vol. 201, 2006, pp. 441–445.

[12] Y. Wu, H. Liu, B. Shen, L. Liu, W. Hu, "The friction and wear of electroless Ni–P matrix with PTFE and/or SiC particles composite", *Tribology International*, Vol. 39, 2006, pp. 553–559.

[13] Y. Wu, B. Shen, L. Liu, W. Hu, "The Tribological behaviour of electroless Ni–P–Gr–SiC composite", *Wear*, Vol. 261, 2006, 201–207.

[14] A. Abdel Aal, S.M. El-Sheikh, Y.M.Z. Ahmed, "Electrodeposited composite coating of Ni–W–P with nano-sized rod- and spherical-shaped SiC particles", *Materials Research Bulletin*, Vol. 44, 2009, pp. 151–159.

[15] Y. Tang, L. Liu, W. Li, B. Shen, "Interface characteristics and mechanical properties of short carbon fibers/Al composites with different coatings", *Applied Surface Science*, Vol. 255, 2009, pp. 4393-4400.

[16] L. Benea, P. Luigi Bonora, A. Borello, S. Martelli, "Wear corrosion properties of nano-structured SiC–nickel composite coatings obtained by electroplating", *Wear*,Vol. 249, 2002, pp. 995–1003.

[17] L. Orlovskaja, N. Periene, M. Kurtinaitiene, S. Surviliene, "Ni–SiC composite plated under a modulated current", *Surface and Coatings Technology*, Vol. 111, 1998, pp. 234–239.

[18] I. Garcia, J. Fransaer, J.-P. Celis, "Electrodeposition and sliding wear resistance of nickel composite coatings containing micron and submicron SiCparticles", *Surface and Coatings Technology*, Vol. 148, 2008, pp. 171-178.

[19] X. Liu, X. Li, A. Yu, W. Huang, "Preparation and tribological performance of electrodeposited Ni-TiB_2-Dy_2O_3 composite coatings", *Journal of Rare Earths*, Vol. 27, 2009, pp. 480-485.

[20] F. Hu, K.C. Chan , "Equivalent circuit modelling of Ni–SiCelectrodeposition

under ramp-up and ramp-down waveforms", *Materials Chemistry and Physics*, Vol. 99, 2008, pp. 424-430.

[21] N. Bala, H. Singh, S. Prakash, "Accelerated hot corrosion studies of cold spray Ni–50Cr coating on boiler steels", *Materials & Design*, Vol. 31, 2010, pp. 244-253.

[22] L. Shi, C. Sun, P. Gao , F. Zhou, W. Liu, "Mechanical properties and wear and corrosion resistance of electrodeposited Ni–Co/SiCnanocomposite coating", *Applied Surface Science*, Vol. 252, 2005, pp. 3591-3599.

[23] W. Chen, Y. He, W. Gao, "Electrodeposition of sol-enhanced nanostructured Ni-TiO$_2$ composite coatings", *Surface and Coatings Technology*, Vol. 204, 2010, pp. 2487-2492.

[24] M. Srivastava, V.K. William Grips, K.S. Rajam, "Electrochemical deposition and tribologicalbehaviour of Ni and Ni–Co metal matrix composites with SiCnano-particles, *Journal of Alloys and Compounds*, Vol. 475, 2009, pp. 664-671.

[25] X.B. Liu, S.H. Shi, J. Guo, G.Y. Fu, "Microstructure and wear behavior of γ/Al$_4$C$_3$/TiC/CaF$_2$ composite coating on γ-TiAl intermetallic alloy prepared by Nd:YAG laser cladding", *Applied Surface Science*, Vol. 255, 2009, pp. 5662-5668.

[26] Y. Hattori, E. Matijević, "Gelatin induced reduction of uniform nano-platelets of Ni(OH)$_2$ to Ni metal", *Journal of Colloid and Interface Science*, Vol. 335, 2009, pp. 50-53.