Co-electrodeposition synthesis and characterization of Ni-Al$_2$O$_3$-Cr hybrid nanocomposites

Mehran Masoudi[1], Mansor Hashim[1,2], Halimah Mohamed Kamari[1] and Mohd Sapuan Salit[1,3]

[1]Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

[2]Advanced Materials and Nanotechnology Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

[3]Department of Mechanical and Manufacturing Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.

ABSTRACT

Ni-Al$_2$O$_3$-Cr metal matrix hybrid composite coatings were developed in a conventional Watt electroplating solution, containing suspended nanoparticles of alumina and chromium. The characterization of the composite layer was carried out by scanning electron microscopy (SEM), X-ray diffractometry (XRD) and Energy-dispersive X-ray spectroscopy (EDX) facilities. SEM, XRD and EDX studies showed that a novel hybrid Ni-Al$_2$O$_3$-Cr metal matrix composite (MMC) coating formed successfully on a pure copper substrate with about 11.5 % and 4.4 % vol. Al$_2$O$_3$ and Cr dispersed nanoparticles respectively. A texture modification and grain refinement were found in composite layers. The incorporation of nanoparticles of Al$_2$O$_3$ and Cr changed the preferential nickel growth orientation from (220) to the (200) plane. The SEM studies on the morphology of a Ni- Al$_2$O$_3$-Cr composite surface illustrated that the nickel column growth slowed down in the composite film and the composite coating had a more condensed and smoother surface compared to pure nickel coatings. The mean grain sizes of the pure nickel and composite coats were determined as 103 and 19 nm respectively. The SEM micrographs showed that the nano particles were uniformly dispersed in the electrodeposited nano-structured Ni matrix and the alumina particles agglomerated in sizes of above 100 nm. The micro-hardness and wear resistance test results showed a remarkable improvement in the mechanical properties of the electroplated nickel by creating a nano composite structure of Ni-Al$_2$O$_3$-Cr.

Introduction

Nano composite coating as a result of merging nanotechnology and material science is one of the principal areas to investigate and develop novel thin films. Nowadays, engineers study the positive aspects of employing these new composite layers in the design of industrial parts and components with extended lifetimes and improved properties. In some cases, integrating these new techniques with chemistry and metallurgy has created new materials with previously undiscovered properties. Seeing that the failure of most industrial specimens starts from the surface, it is feasible to use conventional and low alloy metals instead of high value alloys by applying a proper composite coating layer to improve the surface properties.

Dispersed particle metal matrix composite (MMC) coatings reinforced with hard particles generally exhibit superior and attractive mechanical properties such as improved microhardness and wear resistance. Also, MMC coatings based on their matrix and composite elements can have improved oxidation and corrosion resistances. Applying novel wear and corrosion-resistant MMC coatings is a new solution for designing engineering parts which are subject to severe working conditions such as gas turbine blades and slurry pump impellers. It has been shown by several studies that adding a variety of dispersed particle materials to the pure metallic matrices like nickel could improve properties such as hot oxidation, erosion and corrosion resistances, yield strength, hardness and fatigue life [1-10].

Electroplating is known as a rapid and low cost technique for creating composite films on metallic parts. Co-electrodeposition of ceramics, carbides, polymers and metal powders within a metallic matrix like nickel can produce a wide range of MMC coatings. The conventional nickel electroplating method is a matured process with precise controlling parameters and has vast applications in industry for decorative and corrosion protection proposes. A pure nickel layer has moderate mechanical properties and hot oxidation resistance, therefore, besides the desirable properties of nickel, it has a limited function in the fabrication of engineering specimens. In order to improve the nickel layer properties, alloy plating, post heat treatment, diffusion processes like boriding and in the recent past decades, composite coatings have been studied and applied. The variety of dispersed particle composites based on a nickel matrix such as Ni-SiC [11], Ni-Al [4, 12], Ni-Al$_2$O$_3$ [13, 14], Ni –PFTE [15], Ni-CeO$_2$ [16], Ni-Cr [9] and Ni-TiO$_2$ [17] have been already tested and introduced.

In the present work, the co-electrodeposition process has been successfully used to create a hybrid Ni- nano Al$_2$O$_3$ and Cr dispersed particle composite coating from a conventional Watt bath on the pure copper samples. The surface morphology, crystalline structure, wear resistance and the microhardness of the Ni–Al$_2$O$_3$-Cr hybrid nanocomposite have been characterized. The Ni-Al$_2$O$_3$ and Ni-Cr composite coatings have already been

Tele: 0060178487494
E-mail addresses: mehranmasoudi@yahoo.com

studied by other researchers and it has been shown that adding alumina and chromium particles has a positive influence on the mechanical properties, corrosion and hot oxidation resistance of the nickel layer [3, 5, 9, 18-25]. Creating more complicated composites by utilising two or more composite elements is a step further to achieve more advanced properties. Future work on the tabulation and analysis of the reported results in this area and a study of the probable interaction between particles in the electroplating bath and the composite layer will help us to define the main variables in the design and choice of MMC coats based on the properties demanded by industry.

Experimental

The Ni–Al_2O_3-Cr composite coatings were electroplated by applying a constant current in a conventional Watt bath. The bath composition and plating conditions are shown in Table 1. The solution pH was monitored and maintained at 4 using 0.1 mol HCl and 0.05 mol NaOH solutions. Prior to electroplating, a set of 30x10x1 mm size samples were cut from commercial pure copper plates and all samples were polished with emery paper up to grade 2000, cleaned in 0.1 mol NaOH solution, ultrasonically cleaned in acetone for 15 minutes and finally activated in 5 % Hydrochloric acid at room temperature.

The nano-α-Al_2O_3 and Cr particles of 99.8 % purity and with a 50 nm mean particle diameter (produced by the Qinhuangdao TaijiRing Nano-Products Company, China) were added to the nickel Watt electroplating bath. The powders were used as received from the manufacturer without any further treatment. The particles were dispersed and mixed prior to the commencement of the electro-plating process by using a magnetic stirrer at 600 rpm for 2 hours and then an ultrasonic cell (JAC 2010, Kodo TRC, 40 khz, 300 ultrasonic power) was applied for 45 minutes. The reference pure nickel bath and composite solutions were mechanically stirred constantly at 250 rpm using a magnetic stirrer during the electroplating course. The anode was a pure nickel (99.98 %) plate with an area of 25 cm^2. The temperature of the electrolyte was maintained at 45 °C by an automatic temperature controller (PLT, Scientific Company - accuracy±1 °C). The plating was conducted at a current density of 5 A/dm^2 for 1 hour by using a DC power supply with ± 0.05 A current accuracy. After the co-deposition process, the samples were washed with distilled water and then cleaned in a distilled water ultrasonic bath for 15 minutes to remove any loose particles from the surface.

The microstructure and morphology of the surface of the electroplated coatings and the cross section were studied by high resolution scanning electron microscopy (FEI, Nova Nano SEM - 2300). The composite coated samples were cut, ground with 2000 SiC emery paper, polished with diamond paste (1 μm) and etched for 100 s in a solution of acetic acid and nitric acid prior to the SEM studies. The amount of incorporated particles in the nickel matrix was evaluated by using an energy dispersive X-ray spectroscopy (EDX) analyser connected to the SEM. The Cr and Al_2O_3 concentrations were calculated from the aluminium, oxygen and chromium mean content in the composite layer. The crystalline structure and grain size of the nano powders, pure nickel layer and composite coating were determined by X-ray diffractometry (Cu- Kα) at room temperature. The scan rate was 0.15 °min^{-1} over a 2θ range of 10 to 90 degrees. The hardness of the pure nickel and Ni-Al_2O_3-Cr composite layer coatings were determined with a Vickers microhardness measuring device (FischerScope HM2000 S). The test was performed under a 100 g load and the corresponding final values were determined

as the average of a minimum of ten measurements. The wear tests were performed at room temperature by measuring the weight lost during grinding of the samples on 2000# grit SiC waterproof paper. The mass loss of the samples, to an accuracy of 0.1 mg, was monitored to compare the wear loss of the MMC coated samples and the pure nickel electroplated samples. The wear tests were repeated three times on each sample and different sliding distances to minimize the error and data scattering.

Results and Discussion

Figure 1(a and b) shows the Bragg reflection in the XRD pattern of the as-received Al_2O_3 and Cr powders which were matched with rhombohedral alumina oxide and cubic chromium reference peaks. The average particle sizes of the supplied nano Cr and Al_2O_3 powders were calculated to be 58 and 79 nm respectively, by using the X-ray diffraction peak widths in the Scherrer equation, $t = K.\lambda/(\beta.cos\theta)$, by disregarding the effect of microstrains, where t is the average grain size; K is the Scherrer constant (considered as 0.95) and β is the full width half maximum (FWHM) of the selected XRD reflection peaks (in radians 2θ). Considering the expected error and accuracy in applying the Scherrer formula, the results along with the SEM micrographs confirmed that the powders that were used showed no significant deviation from their nominal size (50 nm – as declared by the manufacturer).
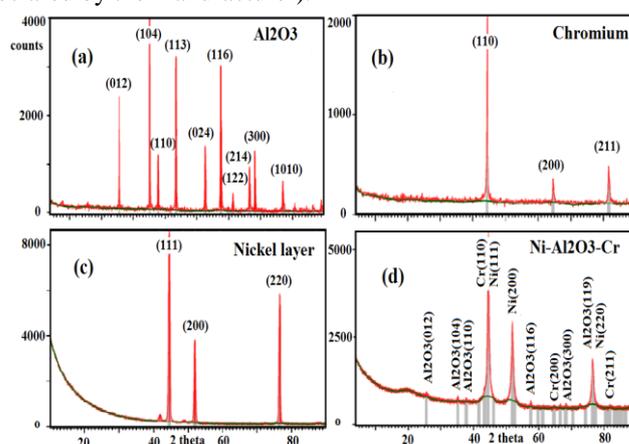
Figure 1. XRD pattern of: (a) Chromium powder, (b) Alumina powder, (c) Pure nickel coating, (d) Ni-Al_2O_3-Cr composite coating.

The SEM top surface and cross section micrographs in Figure 2 show the successful formation of a Ni-Al_2O_3-Cr composite layer with an almost uniform distribution of nano particles. Figure 2(c) shows the uniform particles spreading in the nickel columns section which had been cut by using slight abrasion. EDX analysis in conjunction with SEM high resolution microscopy confirms the presence of about 4.4 vol. % of chromium and 11.5 vol. % of alumina nano particles in the composite layer (Figure 3). The lower deposition rate of chromium compared with that of the alumina particles can be explained in terms of the surface energy of the particles. The adsorption of ions on the surface of the neutral suspended particles creates a driving force to move the particles towards the cathode and it is expected that the adsorption of the ions on the alumina particles with a high surface energy causes a faster deposition rate during electroplating. Further studies are needed to better understanding the deposition mechanisms and the interaction between the different suspended particles in the electrolyte.
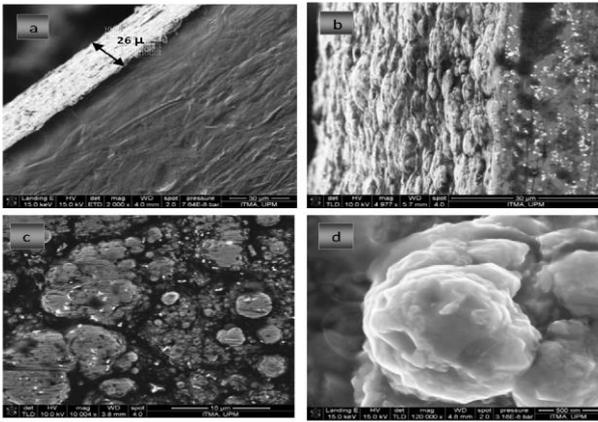
Figure 2. SEM micrographs of Ni-Al2O3-Cr nano composite coating: (a) Cross section, (b) Surface and cross section, (c) Slightly polished top surface view, (d) Ni columns on the surface

The thickness of the composite layer, determined by utilizing the image in Figure 2(a) was found to be 26 microns. However, considering Faraday's law for nickel electroplating, the thickness of the coating layer was calculated to be 23 microns by using the relationship $h = 0.205*C*J*t$, where h is the coating thickness (μm), C is the coefficient of cathode efficiency (~ 0.95), J is the electric current density (A/dm²) and t is the electroplating time in minutes. This difference between the coating thicknesses obtained by experiment and calculation methods observed over several measurements could be attributed to the presence of composite elements which in this case was about 10 % vol. of chromium and alumina content in the nickel matrix.

The characteristic peaks of co-deposited Al_2O_3 and Cr particles were also detected in the composite pattern for which the peaks had a low intensity due to a low concentration of embedded particles in the composite layer. By using Al_2O_3 and Cr peak broadening in the composite layer XRD- pattern, Figure 1 (d), the embedded alumina and chromium mean particle sizes were estimated at about 62 and 112 nm respectively. These results and also the SEM micrographs in Figure 2 show that the deposited alumina particles agglomerate in the composite layer in the shape of white alumina globes with an average size of above 100 nm. The high surface energy of the alumina particles and their tendency to create agglomerated globes has also been reported by other researchers [6, 18, 24].

The surface morphology of the nickel matrix and the composite layer do not show any significant changes, although the nickel crystal columns in the composite coating show a lower level of growth since the dispersed particles enhance the nucleation of the nickel grains and retard the column growth. The XRD pattern of the pure Ni coating in Figure1(c) shows that the Ni layer is orientated in the (220) plane direction, whereas the XRD pattern of the Ni– Al_2O_3-Cr composite layer in Figure 1 (d) shows that the nickel matrix of the composite growth is in the preferred direction of (200).

The average grain size of the pure nickel coatings and the nickel matrix of the Ni- Al_2O_3-Cr composite layer were determined to be 103 and 19 nm respectively by using the Scherrer formula. Clearly, the composite coating had an average grain size much smaller than that of the pure nickel coating electrodeposited under the same conditions. This grain refinement is attributed to the effect of the dispersed particles on the nickel layer nucleation and growth. As reported in other

research studies [26, 27], the added particles increase the nickel nucleation rate and simultaneously hamper the grain growth. The temperature, current density, mixing rate, bath composition and added surfactant chemicals are other parameters which control the grain size of the electrodeposited nickel matrix. The grain refinement along with other hardening mechanisms, such as dispersed hardening, increase the coating hardness and improves the mechanical properties of the composite layer.

The microhardness test result of the annealed nickel plate, the pure Ni coating and the Ni– Al_2O_3-Cr hybrid composite coating in Figure 4 show that the microhardness of the composite coating is almost double that of the pure Ni coating as a result of adding the dispersed nano- Al_2O_3 and Cr particles to the nickel matrix. The hardness of the nickel plating layer is also higher than that of the pure nickel plate because the layer has a smaller grain size and a fine crystalline structure. The grain size of the nickel plate has been estimated to be 5 microns by a metallographic method whereas the mean grain size of the electroplated pure nickel layer is calculated to be 103 nm by applying the Scherer formula.
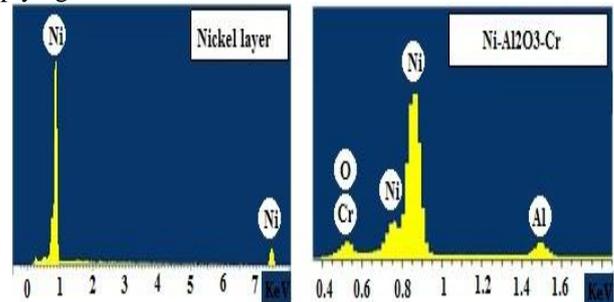
Figure 3. EDX analysis of pure Nickel and composite layer
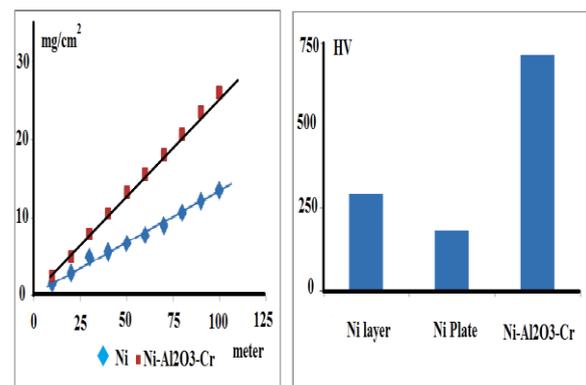
Figure 4. (a). Microhardness test result; (b). Wear test result based on weight lost mg/cm2 versus length of sliding.

The improvement in the hardness of the composite coatings is the result of several hardening mechanisms. The incorporated hard particles in the metal matrix bear the deformation load along with the base metal. This particle strengthening is the dominant hardening mechanism for composites with a rather high volume fraction of dispersed hard particles in the matrix (roughly more than 20 % [24]). In this research, the total incorporated Al_2O_3 and Cr particles in the composite layer are less than 20 % vol., therefore, the dispersion hardening effect has a larger strengthening role. The dispersed nano chromium and incorporated alumina particles act as barriers in front of moving dislocations and create dislocation pile-ups in the nickel matrix and increase the deformation energy and enhance the composite layer hardness. Moreover it has been mentioned that

the grain size of the nickel matrix in the composite layer has been reduced by the presence of the dispersed particles as the result of the effect of the nano particles in the nucleation of the new grains and suppression of grain growth during electroplating. In general, the grain refinement of the metal matrix improves the hardness at room temperature where the nickel grain size is more than about 14 nm [28-31]. This effect can be explained by the Hall-Petch relationship which shows the direct relationship between the hardness and grain refinement.

Figure 4 (b) shows the wear rate of the pure nickel and Ni-Al$_2$O$_3$-Cr composite coated samples. It is seen that the composite coated samples have a lower wear rate than the pure Ni coating which is the result of improving the nickel matrix hardness and having a smoother surface.

Conclusions

In this study, the electro-codeposition of the novel Ni-Al$_2$O$_3$-Cr hybrid nano composite was investigated and a composite layer deposited successfully on pure copper samples in a Watt plating bath. The XRD and EDX spectroscopy tests confirmed the co-deposition of chromium and alumina nano particles in a nano structured nickel matrix with a volume fraction of 4.4 and 11.5 % vol. respectively. The SEM micrographs showed that the nano Al$_2$O$_3$ and Cr particles were dispersed uniformly in the Ni substrate, and the Al$_2$O$_3$ nano particles agglomerated in the shape of spherical globes with an average size of greater than 100 nm. The incorporation of nano particles changed the crystalline growth preferred direction from the (220) to the (200) plane. The nano sized particles slowed down the nickel column growth and caused nickel matrix grain refinement which along with the particle dispersed hardening effect it increased the microhardness of the plating layer by more than twice. The sliding wear resistance of the composite showed considerable improvement as the result of having a smoother surface, a grain refinement of the nickel matrix and an enhanced micro-hardness.

Acknowledgement

References

[1]. Liu,W.-L.,*Tribological properties of electroless Ni-P-SiC composite coatings in rolling/sliding contact under boundary lubrication.* Journal of University of Science and Technology Beijing, Mineral, Metallurgy, Material, 2007. 14(2): p. 167-172.

[2]. H. Chiriac, A.E.M., C. Gherasim, N. Lupu, *Synthesis and Characterization of of Fe-W and Ni-W Composite Coatings.* ROMANIAN JOURNAL OF INFORMATION SCIENCE AND TECHNOLOGY, 2008. Volume 11,Number 2: p. pp 123-132.

[3]. Anna Góral, E.B.-L., P. Indyka, *Structure Characterization of Ni/Al2O3 Composite Coatings Prepared by Electrodeposition.* Solid State Phenomena 2010. (Volume 163)(Applied Crystallography XXI): p. pp.64-67.

[4]. Zhou, Y., X. Peng, and F. Wang, *Size Effect of Al Particles on the Oxidation of Electrodeposited Ni–Al Composite Coatings.* Oxidation of Metals, 2005. 64(3): p. 169-183.

[5]. Zhao, G.-g., Y.-b. Zhou, and H.-j. Zhang, *Sliding wear behaviors of electrodeposited Ni composite coatings containing micrometer and nanometer Cr particles.* Transactions of Nonferrous Metals Society of China, 2009. 19(2): p. 319-323.

[6]. G. C. C. Gheorghies, I.V.S., *Preparation and structural characterization of nickel/ alumina nano-particles composite coatings.* JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, 2006. Vol. 8,No.3, : p. p.1234 -1237.

[7]. Sohrabi, A., et al., *Nanomechanical properties of functionally graded composite coatings: Electrodeposited nickel dispersions containing silicon micro- and nanoparticles.* Materials Chemistry and Physics, 2010. 121(3): p. 497-505.

[8]. Zanella, C., M. Lekka, and P. Bonora, *Influence of the particle size on the mechanical and electrochemical behaviour of micro- and nano-nickel matrix composite coatings.* Journal of Applied Electrochemistry, 2009. 39(1): p. 31-38.

[9]. Zhou, Y.-b., G.-g. Zhao, et al. , Fabrication and wear properties of co-deposited Ni-Cr nanocomposite coatings. Transactions of Nonferrous Metals Society of China 20(1): 104-109., 2010.

[10]. Gheoeghies, G.C., Preparation and structural characterization of nickel/ alumina nano-particles composite coatings. JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, 2006. Vol. 8,No.3, : p. p.1234 -1237.

[11]. Lin, C.S. and K.C. Huang, Codeposition and Microstructure of Nickel—SiC Composite Coating Electrodeposited from Sulphamate Bath. Journal of Applied Electrochemistry, 2004. 34(10): p. 1013-1019.

[12]. Susan D.F., M.A.R., Oxidation of Ni–Al-Base Electrodeposited Composite Coatings. II: Oxidation Kinetics and Morphology at 1000°C. Oxidation of Metals; Springer, 2002. Volume 57(Numbers 1-2): p. pp. 159-180.

[13]. Sheng-Lung Kuo , Y.-C.C., Ming-Der Ger , Wen-Hwa Hwu, Nano-particles dispersion effect on Ni/Al2O3 composite coatings. Materials Chemistry and Physics, 2003. 86 (2004) 5–10.

[14]. Wang, T.C., R.Z. Chen, and W.H. Tuan, Oxidation resistance of Ni-toughened Al2O3. Journal of the European Ceramic Society, 2003. 23(6): p. 927-934.

[15]. Pena-Munoz, E., et al., Electrolytic and electroless coatings of Ni-PTFE composites: Study of some characteristics. Surface and Coatings Technology, 1998. 107(2-3): p. 85-93.

[16]. Xue, Y., et al., Fabrication and Wear Resistance of Ni-Ce*O2 Nanocomposite Coatings by Electrodeposition*, in *Advanced Tribology*, J. Luo, et al., Editors. 2010, Springer Berlin Heidelberg. p. 695-696.

[17]. Thiemig, D. and A. Bund, *Characterization of electrodeposited Ni-TiO2 nanocomposite coatings.* Surface and Coatings Technology, 2008. 202(13): p. 2976-2984.

[18]. A. Jung, H.N., R. Hempelmann, *Nanocrystalline alumina dispersed in nanocrystalline nickel:enhanced mechanical properties.* J Mater Sci (2009) 44:2725–2735, 2009.

[19]. X.Peng, *Manufacture, Wet and Dry Corrosion, and Plasma Nitridation of Novel Nanocrystalline Ni-Cr Nanoparticle Nanocomposites: A Brief Review X. Peng.* Advanced Materials Research 32., 2008.

[20]. C. Zhang, X.P., J. Zhao, and F. Wang, *Hot Corrosion of an Electrodeposited Ni-11 wt % Cr Nanocomposite under Molten Na$_2$SO4–K$_2$SO$_4$–NaCl.* J. Electrochem. Soc., Volume 152, Issue 9, pp. B321-B326 (2005), 2005.

[21]. Park, H.-J.L.S.-W., *The Effect of Particle Size of Alumina Dispersions on the Oxidation Resistance of Ni-Cr Alloys.* Oxidation of Metals, , 1997. Vol. 48, Nos. 5/6.

[22]. Lim, H., S. Park, and S. Kang, *The effect of particle size of alumina dispersions on the oxidation resistance of Ni-Cr alloys.* Oxidation of Metals, 1997. 48(5): p. 391-415.

[23]. Zhang, Y., X. Peng, and F. Wang, *Development and oxidation at 800 °C of a novel electrodeposited Ni-Cr nanocomposite film.* Materials Letters, 2004. 58(6): p. 1134-1138.

[24]. Gül, H., et al., *Characteristics of electro-co-deposited Ni-Al2O3 nano-particle reinforced metal matrix composite (MMC) coatings.* Wear, 2009. 267(5-8): p. 976-990.

[25]. Thiemig, D. and A. Bund, *Influence of ethanol on the electrocodeposition of Ni/Al2O3 nanocomposite films.* Applied Surface Science, 2009. 255(7): p. 4164-4170.

[26]. Zhou, Y.-b., H.-j. Zhang, and Z.-t. Wang, *Effect of Y2O3 on microstructure and oxidation of [gamma] -Ni+[gamma]' -Ni3Al coatings transformed from electrodeposited Ni-Al films at 1[punctuation space]000 °C.* Transactions of Nonferrous Metals Society of China, 2008. 18(2): p. 297-302.

[27]. Yang, X., X. Peng, and F. Wang, *Effect of annealing treatment on the oxidation of an electrodeposited alumina-forming Ni-Al nanocomposite.* Corrosion Science, 2008. 50(11):

p. 3227-3232.

[28]. Nieh, T.G. and J.G. Wang, *Hall-Petch relationship in nanocrystalline Ni and Be-B alloys.* Intermetallics, 2005. 13(3-4): p. 377-385.

[29]. Schuh, C.A., T.G. Nieh, and T. Yamasaki, *Hall-Petch breakdown manifested in abrasive wear resistance of nanocrystalline nickel.* Scripta Materialia, 2002. 46(10): p. 735-740.

[30]. Trelewicz, J.R. and C.A. Schuh, *The Hall-Petch breakdown in nanocrystalline metals: A crossover to glass-like deformation.* Acta Materialia, 2007. 55(17): p. 5948-5958.

[31]. Giga, A., et al., *Demonstration of an inverse Hall-Petch relationship in electrodeposited nanocrystalline Ni-W alloys through tensile testing.* Scripta Materialia, 2006. 55(2): p. 143-146.

Table 1. Bath composition and deposition condition for Ni-Al$_2$O$_3$-Cr hybrid composite.

Component	Concentration (g/l)
NiSO$_4$.6H$_2$O	240
NiCl$_2$.6H$_2$O	40
H$_3$BO$_3$	350
CH$_3$(CH$_2$)11OSO$_3$Na	0.2
α-Al2O3 (50nm)	50
Cr (50nm)	50
Deposition Condition	**Value**
pH	4
Temperature (°C)	45
Current density (A/dm^2)	5