

AN EXPERIMENTAL STUDY OF SINTERED Ni-Cr-xAl₂O₃ COMPOSITE

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Abstract

This paper deals with the Ni-Cr- xAl₂O₃ metallic composites (MCCs). The restraining of thermal expansion at adequate mechanical and corrosion properties is the main objective of this work. Composites are fabricated with four weight percentages of Al₂O₃ (x = 1, 2, 5 and 10 % Al₂O₃). Compacting and sintering has accomplished at 636 MPa and 1250 °C for seven hours. Allo sintered compacts were characterized by X-ray diffraction analysis (XRD) and Scanning Electron Microscopy (SEM). Results have indicated, the incorporation of Al₂O₃ with the matrix is due to the efficient sintering conditions, that diminishing the grain growth and increasing the softening temperature from 850 °C to become 1350 °C. Volume expansion appeared in the base sintered composites NiCr-xAl₂O₃ due to pores evolution according to SEM observation. With increasing of Al₂O₃ share, the microhardness and corrosion resistance have improved. DSC results indicate a clear two exothermic and one endothermic peak reaction has occurred during the heating cycle. Corrosion behavior of fabricated composites has estimated by polarization curves using Potentiostat at scan rate 3 mV·sec⁻¹. Potential-time measurements showed the formation of protective layer on surface composites compared with Ni-Cr base composite through an obtaining of the nobler open circuit potentials for composites. Corrosion parameters has estimated by the Tafel extrapolation method; these parameters indicated that the corrosion potential shifted toward a positive direction in addition to get lower corrosion current density especially for Ni-Cr / 5% alumina composite.

Keywords: Metal matrix composites, Ni-Cr-xAl₂O₃ composite, Thermal analysis and Corrosion in seawater.

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Introduction

Composite materials defined as macroscopic level mixtures of non-soluble constituents with two or more distinct compositions. The Nickel-based alloys show a wide range of engineering applications due to its remarkable properties that make it useful in parts industries that require retaining stability as well as an ability to resist the corrosion over a wide range of temperatures. Parts with Ni-Cr alloys are mostly manufactured by casting techniques. However, low production cost and lack of need for machining makes it necessary to produce these alloys using a powder metallurgy method [1,2]. The choice of better processing conditions can gain better subsequent properties of producing composite.

Metal matrix composites are very promising materials in obtaining excellent mechanical properties over the alloys and metals for multi aerospace, marine and automotive applications [3-7]. In the current work, an attempt has made to fabricate a new metal matrix composite material. This composite contains Ni, Cr and variable weight percentages of Al_2O_3 . The increases of variable percentages of ceramic constituents (i.e. Al_2O_3) is one of the feasible methods in improving the working properties of these composites. The using of high mixing technique besides vacuum sintering practices are of eminent importance in improving these composites. Ni-Cr- xAl_2O_3 composites, with either strengthened or modified microstructure using other alloying or strengthening techniques, offers a singular potential for creating new paradigms in material-structural interactions. Lately, a great deal of efforts passed in the direction of fabrication and characterization of new Ni-Cr metal matrix composite (MMCs). These efforts were concentrated on the development of corrosion resistance properties of these materials at high temperature applications.

Mykolas et al. [8], investigated the corrosion of the nickel metal matrix coating, composites containing B_4C , Al_2O_3 and SiC particles by corrosion test in neutral and acid salt fog, and also investigated the electrochemical behavior of MMC in neutral and acid solution by means of Voltammetry and impedance spectroscopy. J.F. Flores et al. [9], has assessed the erosion-corrosion and the corrosion processes of four MMCs in an experimental simulated cooling water environment. The MMCs were consisted of two Ni-base and two Fe-base matrices. Both of them were alloyed with different concentrations of Cr, Mo, Br, Si, and C. The produced matrices were reinforced with the WC particles. L.L. Sousa et al. [10], studied the electrochemical behaviour of the 59.6 % Ni, 24.0 % Cr and 9.8 % Mo alloy that used in dental prosthesis. The electrochemical study has revealed that the alloy has behavior similar to Chromium, displaying a broad passivity area due to the formation of a chromium oxide layer.

According to the above, it is little focus on the using of the high energy mixing technique to fabricate a modified Ni-Cr- xAl_2O_3 composite and examine the effect of alumina additions to the base material. This work is an attempt to complete the knowledge about the effect of Al_2O_3 additions to the behavior of sintered Ni-Cr composites.

Experimental procedure

Fabrication

Nickel (Ni) powder produced by (BDH Chemicals Ltd Poole England) with the (99.3% purity, average size: 20 µm); Chromium (Cr) powder produced by (Fluke Chemi AGCH-9470 Bucks) with (99.8% purity, average size: 35µm); and Al₂O₃ powder produced by (Acuro Organics Limited) with (99.9% purity, average size: 35 µm) were used as the starting materials. Mixing the initial powders has accomplished with the picobond high-energy mixer. It takes 90 minutes for each sample of Ni-Cr-xAl₂O₃ composites with the weight percent as listed in Table (1). Mixing has followed immediately by a pressing of samples at 636 MPa in a cylindrical punch and die. Sintering of the obtained samples was carried out in a well-calibrated vacuum furnace at 1250 °C for 4 hrs. Heating rate and cooling rate were both 5 °C·min⁻¹.

Table 1. Weight percentages of powders in composites.

Material	Composition wt. %		
	Ni	Cr	Al ₂ O ₃
Ni-Cr alloy	75	25	0
Ni-Cr/1% Al ₂ O ₃	74	25	1
Ni-Cr/2% Al ₂ O ₃	73	25	2
Ni-Cr/5% Al ₂ O ₃	70	25	5
Ni-Cr/10% Al ₂ O ₃	70	20	10

Characterization

The density of the green and sintered materials has measured by the Archimedeian principle according to ASTM B311-93. The porosity of composites has calculated according to the following formula:

$$V_p = 1 - \frac{\rho}{\rho_o} \quad 1$$

where, V_p is the porosity volume %, ρ is the density of sintered composite and ρ_o is the theoretical density of composites. The volumetric shrinkage has calculated for all sintered composite using the following equation:

$$\Delta V = \frac{V_o - V}{V} \quad 2$$

Where, V is the volume of sintered compact, and V_o is the initial volume of the sample. Phase identification of the sintered composites has achieved by X-ray diffraction (XRD) using Cu-K radiation.

Metallography's examination of the composites has made by Scanning electron microscope (Joel JXA-840). The microhardness has measured by a microhardness tester type microhardness Tester model Hv-1000 at room temperature. The compression strength of all sintered composites has performed according to ASTM (D95-85) at the room temperature with the crosshead speed of 1mm/min. Compression test was done using the universal testing machine model of Instron 5864.

DSC Analysis

High-temperature scanning calorimeter HTC (High-performance modular simultaneous TGA & DTA/DSC thermal analysers has used. The working temperature range has selected from ambient to 2400 °C in argon atmosphere. The test has achieved within the temperature range from ambient to 1300 °C with the constant heating 5 °C/min.

Thermal Expansion Test

The measurement of a material deformation as a function of either temperature or time is very important property. This test has accomplished by varying the temperature of the tested material according to calibrated software. Well calibrated TMA 402 Hyperion (produced by Netzsch) is used extensively in this work. The test sample is 20 mm in length and 5 mm diameter. The load was applied gradually to the tip of the gauge rod at 25 °C temperature; the temperature was first being lowered to 0 °C then raised to 1500 °C, and the displacement of the test sample is recorded. The rate of temperature increase shall not be more than 5 °C/min. Compressive stress that acting on the composite sample was around 4 MN/mm².

Corrosion Test

The electrochemical test was made by analysis of an open circuit potential - time measures Eoc that has altered to a less and more 200 mV. The measuring of the potential alongside them for a period of 12 hours and then locating the potentiodynamic polarization curves in 0.8 % NaCl solution, pH= 6.0 at 38 °C, by using a conventional glass cell thermostated. The reference is a saturated calomel electrode (SCE), an auxiliary platinum electrode and a working electrode using the potentiostat EG & G PAR 283, interfaced to a desktop computer HP through a GPIB interface fitted program (Softcorr III). The results achieved were stated in terms of the corrosion potentials E_{corr} and corrosion current density i_{corr} by Tafel extrapolation method.

Results and Discussion

Density and Volumetric expansion

Theoretical and sintered density values of a sintered composite with and without Al₂O₃ addition are shown in figure 1.

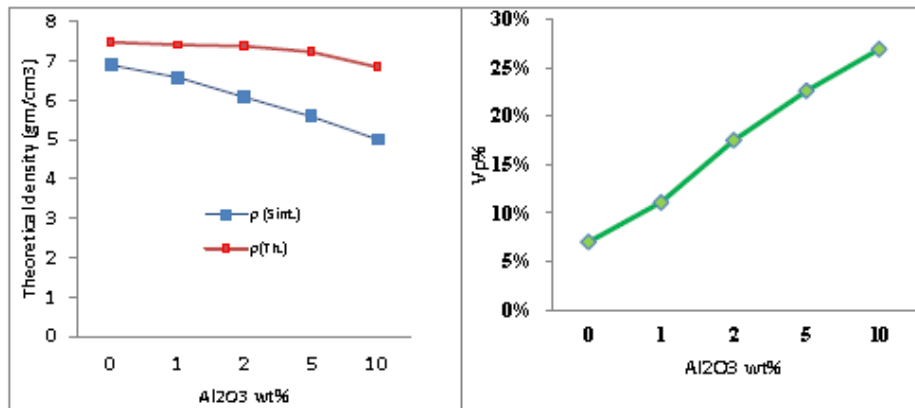


Fig. 1. (a) Theoretical vs. sintered density of compacts; (b) Effect of Al₂O₃ wt. % on porosity

The sintered density values of all compacts are decreasing from theoretical values by variable percentages (see figure 1-b). These percentages represent the porosity volumes for both base material and Alumina incorporated composites. As the weight percentages of Al₂O₃ increasing, theoretical and sintered densities are decreasing due to the substitution of high density particulate either Ni or Cr by low density particulate Al₂O₃. The grain size increase, obtained at a higher sintering temperature is easily achieved in composite without Al₂O₃ addition. Increasing of Al₂O₃ may diminish the grain growth in composites and increasing the volume percentages of porosity. In addition, porosity volume indicates the deficiency of sintering process; especially in composites with higher Al₂O₃ weight % (sintering temperature of Al₂O₃ is ~1700 °C). A similar trend has seen for the composites with Al₂O₃ addition. Nickel in all sintered materials produces shrinkage; therefore, increasing the density of sintered composites. Swelling after sintering has observed for the materials with the Al₂O₃ addition.

Microhardness and Compression Strength

The sintered composite indentation hardness has intensely affected by the presence of porosity, since the pores in the material do not contribute to the supporting of indenter. In this work, the composition and microstructure of all sintered composite is well recognized. Knowing that, there is a direct relationship between the density and the microhardness; the lower density, the lower apparent microhardness will be. Micro-indentation hardness techniques have suggested for determining the hardness of the MCCs, independent on the effects of the porosity.

As shown, in figure 2-a, the microhardness of free alumina composite is 306 MPa. This value indicates better efficiency of preparation practices, including the using of high energy mixer in blending powders and high temperature sintering in vacuum conditions. As, the weight percentage of Al_2O_3 increased the microhardness of composites linearly increased. The reason behind such increasing is the introducing of hard constituents (i.e. Al_2O_3) in the composite. It has distinctly recorded, that the improvement in MCCs microhardness depends mainly on the particles size and distribution, in addition to the indentation load. The addition of Al_2O_3 has enhanced the microhardness of base composite by 29 %.

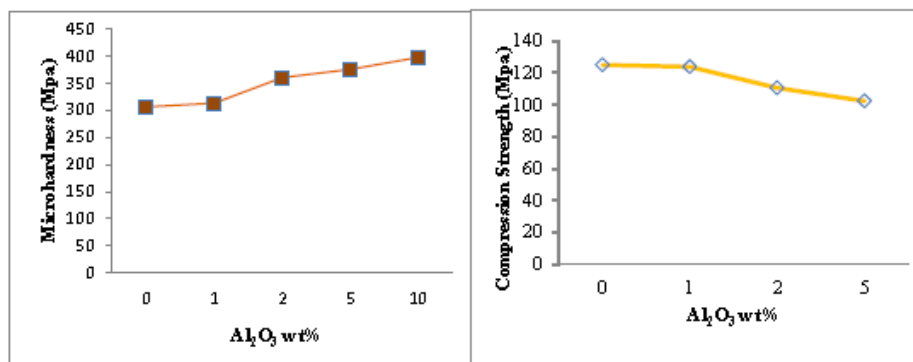


Fig. 2. (a) Effect of Al_2O_3 wt. % on microhardness; (b) Effect of Al_2O_3 wt. % on compression strength

According to figure 2-b, the compression strength of sintered composites is decreased as the weight % of Al_2O_3 increasing. The degradation in compression strength is due to the increasing in porosity volume percentage. In other words, as porosity volume is increased from 7 % at zero alumina composite, to 27 % at 10 wt. % of Al_2O_3 composite, the compression strength will be reduced from 125 MPa to 102.4 MPa respectively.

XRD-Results

The analysis of XRD has used to identify the sequence of reactions that occur between the composite constituents (i.e. Ni, Cr and Al_2O_3) during the sintering in vacuum furnace at 1250 °C. Figure 3 shows the X-ray diffraction analysis of the base and improved composites.

The X-ray patterns show a clear of $\alpha\text{-Al}_2\text{O}_3$ phase in all sintered composites. Achievements of such structure are due to the development of NiCr phase. This phase has presented because of the Al_2O_3 addition in different weight percentages. The maximum intensive peak in the XRD spectrum for the Ni(Cr) at $2\theta = 44.064^\circ$ which resulted in an overlapping of two peaks that corresponding to Ni (111) at $2\theta = 44.508^\circ$ from the JCPDS card (04-0850) and Cr (110) ($2\theta = 44.393^\circ$ from the JCPDS card (06-0694) [11]. XRD of Ni-Cr- $x\text{Al}_2\text{O}_3$ composites indicates the overlapping peaks of alumina with peaks of Ni and Cr.

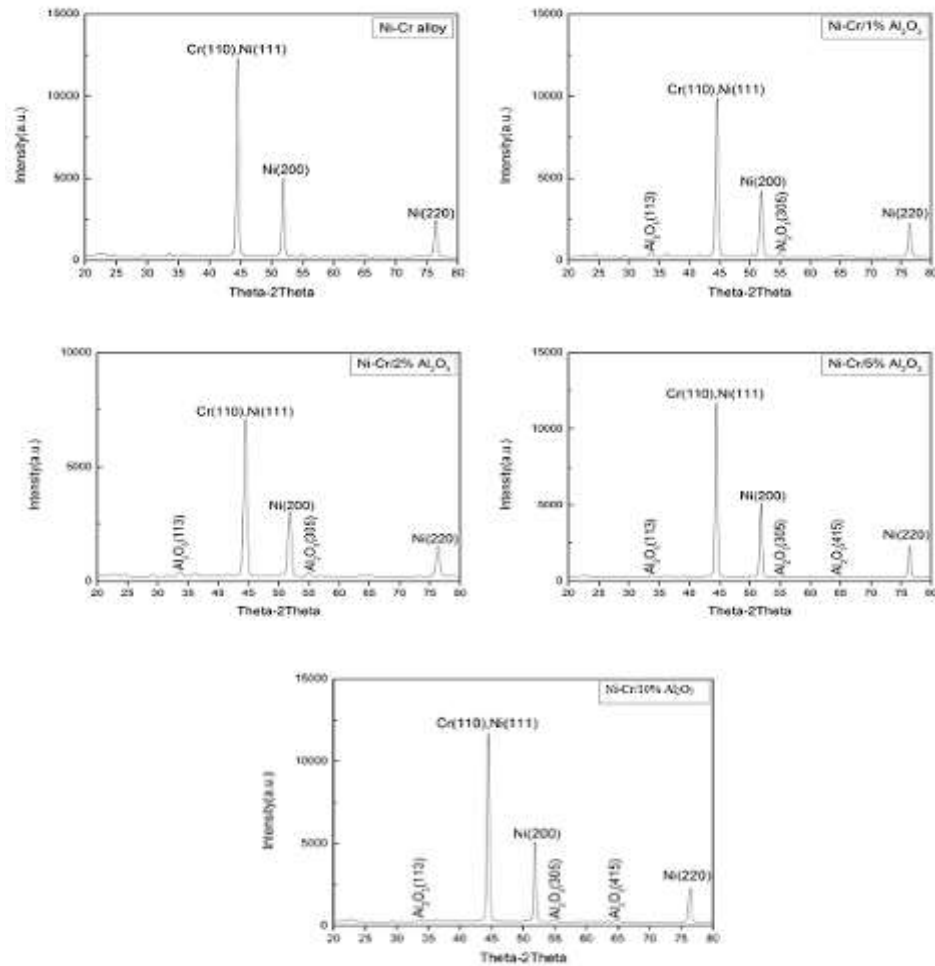


Fig. 3. XRD pattern of sintered composites

DSC Results

Results of DSC confirm the suitable procedure that followed in preparing and sintering of Ni-Cr and Ni-Cr-xAl₂O₃ composite. Figure 4 shows the results of DSC for the sintered Ni-Cr-10Al₂O₃ composite.

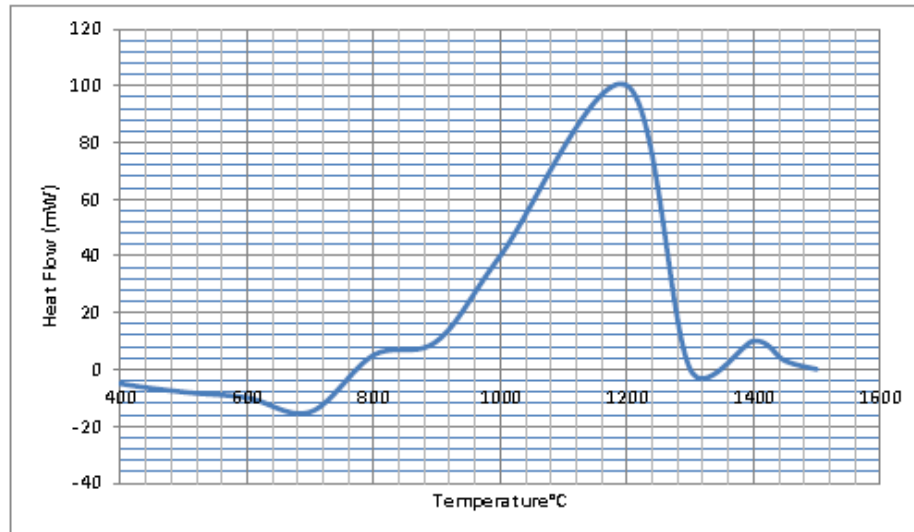


Fig. 4. DSC curves of sintered (Ni-Cr-10wt% Al₂O₃)

Two exothermic and one endothermic peak reaction has taken place during the heating cycle. The reason behind an exothermic reaction is the reaction between the nickel and oxygen that available in alumina during the heating cycle. While the endothermic reaction may be to some increments in some oxides unit cells axes. The exothermic peaks have observed at 700 and 1240 °C respectively. While endothermic peak observed at 640 °C.

Thermal Behavior Results

Accumulative diagram of the sintered composite thermal analyses has shown in figure 5.

In this figure, it is obvious that the composites exhibit different behaviors, according to their chemical compositions. As, the weight percentages of the Al₂O₃ increase, the thermal expansion percentages will decrease and the dimensions is withstanding the gradual increase of temperature. The reason behind such increment is the inhibition of grain growth of Ni and Cr by the composite third constituent Al₂O₃. If the weight percentage of the alumina is decreased, the softening temperature is decreased. The softening occurs at different temperatures, according to the weight percentage of added Al₂O₃. An early softening has occurred in composite with zero Al₂O₃ percentage at 850 °C during the heating and then increased as the percentage of Al₂O₃ increased until becoming 1360 °C in composite with 10 wt. % of Al₂O₃.

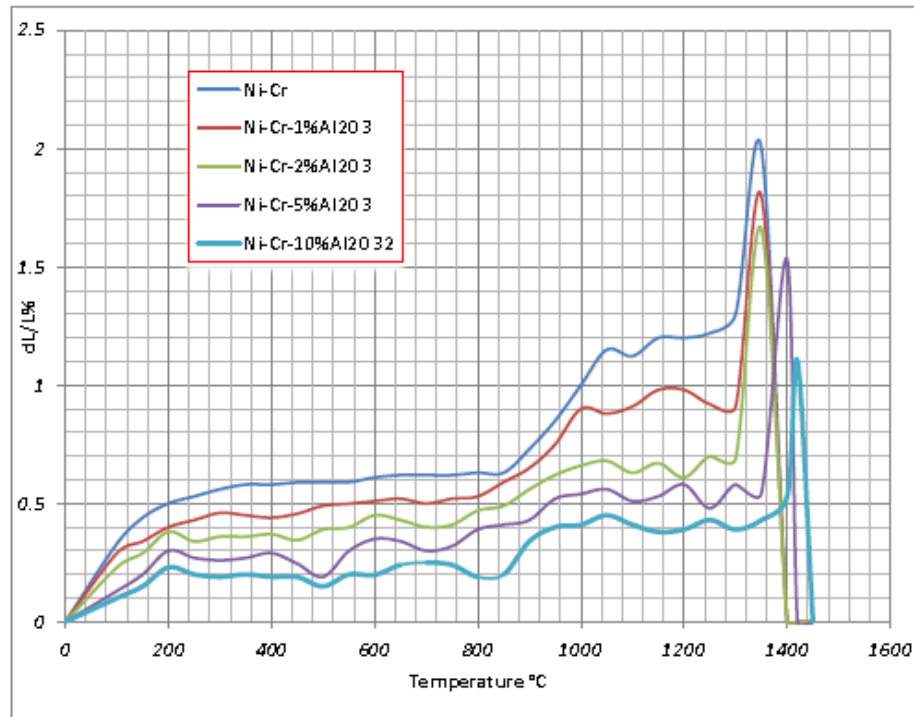


Fig. 5. Accumulative TMA of sintered composite.

SEM Observations

The characterization of fabricated composites by SEM images is shown in Figure 6, this figure indicates the distribution on the micrometre scale. Figure 6 a, b, c, d and e illustrates the SEM photomicrographs of the Ni-Cr-xAl₂O₃% composites at different weight percentage of Al₂O₃. The Ni looks light and the alumina is dark on the well-polished surface. All the composite specimens are very homogeneous with the little pores and an even distribution of Ni inclusions has occurred.

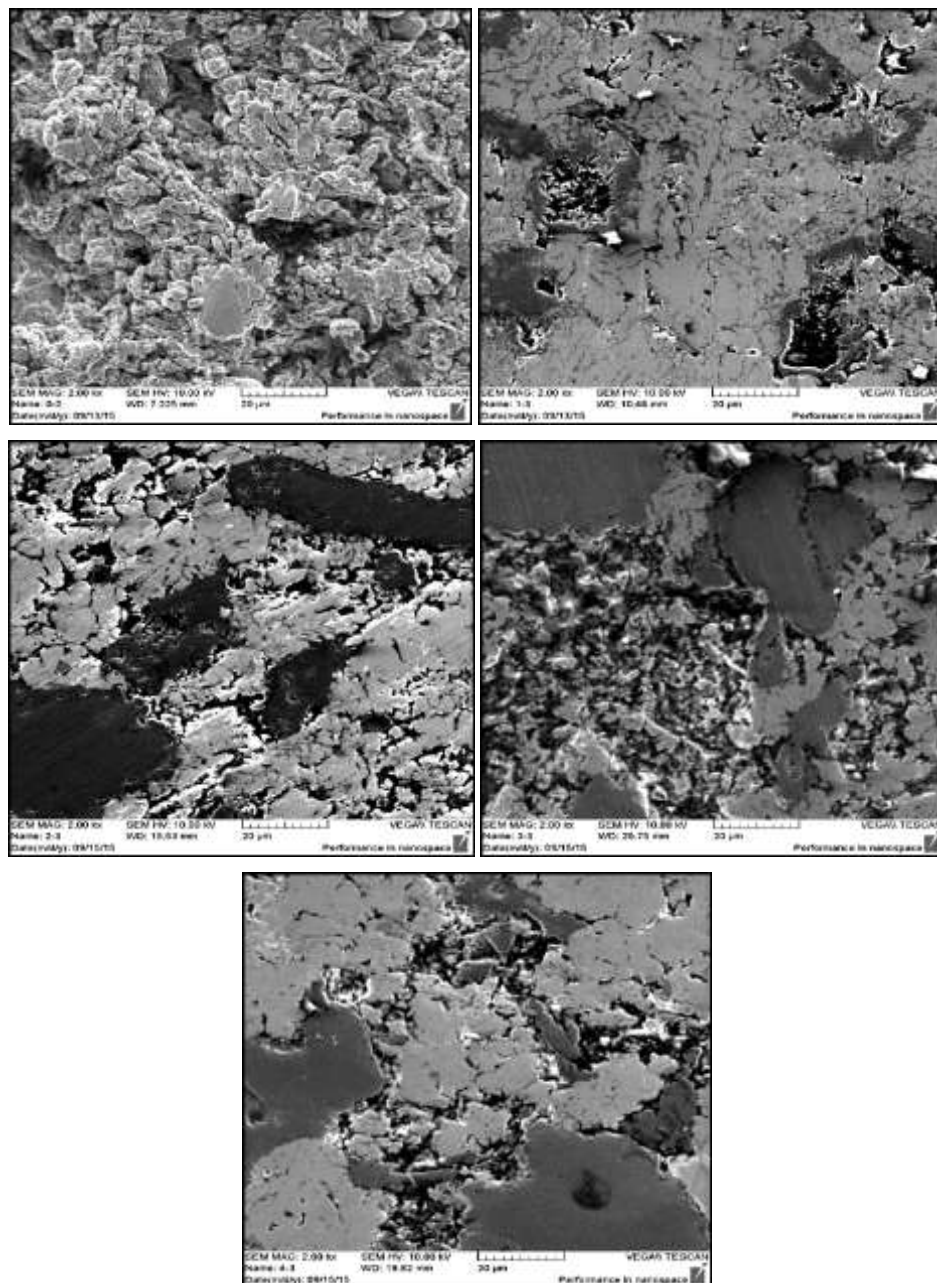


Fig. 6. SEM of composites (a) base alloy, (b) Ni-Cr/ 1 % alumina, (c) Ni-Cr/ 2 % alumina, (d) Ni-Cr/ 5 % alumina and (e) Ni-Cr/ 10 % alumina.

An adequate uniform distribution of reinforcement is detected when the weight percentage of Al₂O₃ is equal to 1 wt. %. As, the weight percentage of Al₂O₃ is increased, clusters are observed throughout the microstructure. However, the distribution of reinforcement (i.e. Al₂O₃) is homogeneous. A uniform distribution of reinforcement (i.e. Al₂O₃) becomes intolerable when the content of Al₂O₃ is higher (i.e. 10 wt. %) because of the inadequate ratio of surface areas of matrix composites particles and reinforcement particles. The reinforcement clustering depends extensively on the reinforcement concentration. Therefore, the using of high energy mixing during the composite preparations has minimized the clustering. Keep in mind, that as the clustering of Al₂O₃ has increased, bulk density and porosity will decrease [12].

Corrosion Results

Figure 7 shows the potential – time measurements of Ni-Cr alloy and its composites to evaluate the nature of the film formed at the material – medium interface.

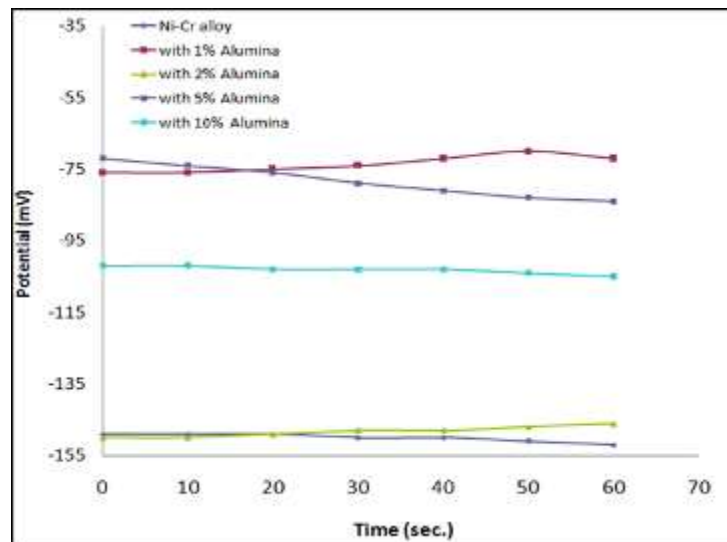


Fig. 7. Potential – time measurements for Ni-Cr alloy and its composites.

This figure indicates the potential shifting to more noble values than that observed at the instant of immersion. This specifies the formation of a protective surface film formation on the surface of composites in comparison with the base composite (i.e. without Al₂O₃).

Figure 8 shows the polarization curves of Ni-Cr alloy and its composites in seawater at room temperature.

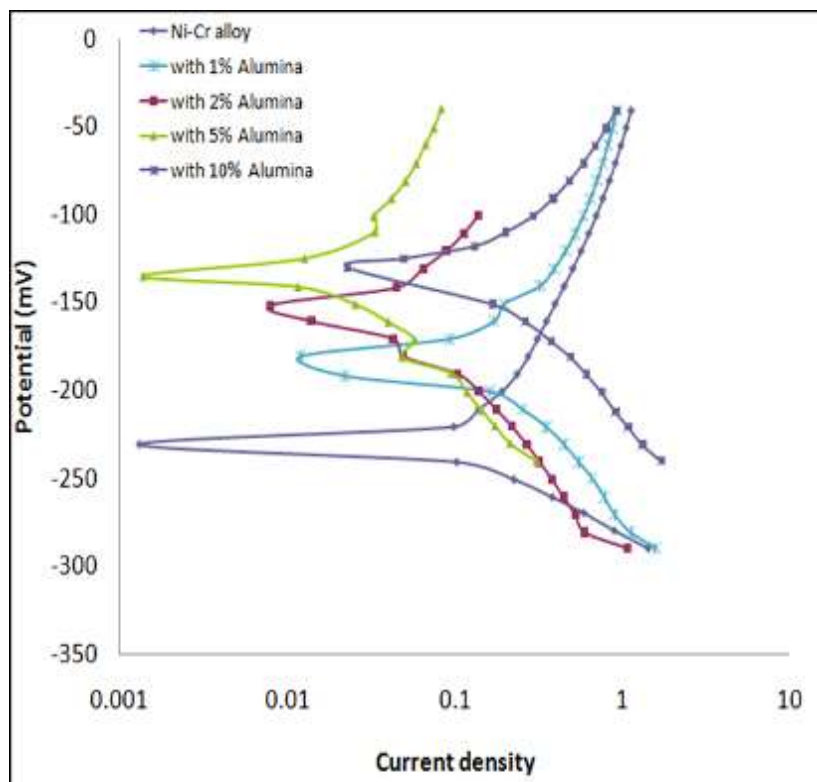


Fig. (8). Tafel plots for Ni-Cr alloy and its composites.

These curves indicate the cathodic and anodic regions. At cathodic sites, the diminution of oxygen takes place as follow:



while, at anodic sites, the dissolution of metals Ni and Cr takes place, followed by the passivation. This passivation has endorsed to an evolution of a chromium oxide layer formation, since the composite behavior is similar to the Cr behavior. Corrosion properties of Ni-Cr composites depend on their bulk composition, microstructure, growth of protective surface oxide and the composition of the surrounding electrolyte selected for the study [13, 14].

Addition of alumina to Ni-Cr composite has led to shifting polarization curves toward the lower current densities and nobler potentials. Corrosion parameters measured by potentiostat test indicate that the presence of alumina in bulk materials led to get lower corrosion current density especially in case of Ni-Cr-5%Al₂O₃ composite. While, the corrosion potential has become nobler with increasing weight % of alumina in bulk materials. This phenomenon indicates the role of Al₂O₃ particles in increasing the corrosion resistance of alumina reinforced composites by covering the anodic sites for alloy and enhancing the passivity of surface and reduces the dissolution of metals. This can be observed through the values of corrosion rate in (MPY) which listed in

Table 2. In general, the composites are further susceptible to corrosion attack than the matrix alloy. The effectiveness of all anodizing methods studied decreases with increasing reinforcement concentration.

Table 2. Corrosion parameters Ni-Cr/Alumina composites in Seawater at room temperature.

Material	E _{corr} (mV)	i _{corr} (μA/cm ²)	C _R (mpy)
Ni-Cr alloy	-231	117.22	23.97
Ni-Cr/1% Al ₂ O ₃	-181	62.45	12.77
Ni-Cr/2% Al ₂ O ₃	-152	20.41	4.17
Ni-Cr/5% Al ₂ O ₃	-135	14.88	3.04
Ni-Cr/10% Al ₂ O ₃	-130	89.73	18.35

Conclusion

The Ni-Cr-xAl₂O₃ composites with multi Al₂O₃ weight percentages has prepared by high energy mixing of Ni, Cr and Al₂O₃ and then sintered in vacuum conditions at 1250 °C. The dominant phase is the α-Al₂O₃, Ni, Cr solid solution with little amounts of Cr₂O₃ in composites with 10 wt. % of alumina. As the weight percentages of Al₂O₃ increasing, theoretical and sintered densities are decreasing due to the exchange of high density particulate either Ni or Cr by the lower density particulate Al₂O₃. The composite with 10 wt. % of alumina DSC results indicates a clear two exothermic and one endothermic peak reaction were occurred during the heating cycle. TMA analysis of sintered composites has augmented the idea behind the reinforcing of Ni-Cr composite with 10 wt. % of Al₂O₃. This weight percentage has increased the softening temperature to 1368 °C. Alumina addition has improved the corrosion resistance of Ni-Cr composites by covering the anodic sites of constituents (i.e. Ni and Cr) and enhancing the passivity of surface and reduces the dissolution of the metals.

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References

- [1] R. Asthana, S.T. Mileiko, and N. Sobczak, Bulletin of The Polish Academy of Sciences Technical Sciences, 54 (2006) 147-166.
- [2] José Roberto de Oliveira Bauer, Alessandro Dourado Loguercio, Alessandra Reis and Leonardo Eloy Rodrigues Filho, Braz Oral Res, 20 (2006) 40-46.
- [3] C. N. Tharamania and S. M. Mayannaz, Electrochemical and Solid-State Letters, 9, (2006) A412-A414.
- [4] Viswanathan S. SAJI, Han-Cheol CHOE, Trans. Nonferrous Met. Soc. China, 19, (2009) 785-790.

- [5] I. Lopez-Baez, E. Martinez-Franco, H. Zoz, and L.G. Trapaga-Martinez, *Revista Mexicana De Fisica*, 57 (2011) 176–183.
- [6] Tefvik Yavuz, Asli Acar, Serhan Akman and Atiye Nilgun Ozturk, *Materials Sciences and Applications*, 3 (2012) 163-167.
- [7] Z. Dong, X. Peng, Y. Guan, L. Li, F. Wang, *Corrosion Science*, 62 (2012) 147–152.
- [8] M. Gladkovas, V. Medelienė, M. Samulevičienė, E. Juzeliūnas, Corrosion study of electroplated nickel MMC with B_4C , Al_2O_3 & SiC , Institute of Chemistry, Lithuania, 36-40.
- [9] J. F. Flores, A. Neville, N. Kapur, A. Gnanavelu. *Journal of materials engineering and performance*, 21 (2012) 395-405.
- [10] L.L. Sousa, J.W.J. Silva, N.A.S. Sampaio, R.Z.Nakazato, H.A. Acciari, E.N. Codaro, *International Journal of Engineering Research and Development*, 10 (2014) 70-76.
- [11] Feng-Jiao Liu, Ming-Hao Fang, Zhao-Hui Huang, Yan-Gai Liu, Sai-Fang Huang, Xin Min, Mei-Ling Hu, and Hai-Peng Ji, *Materials Science and Engineering*, 554 (2012) 1– 5.
- [12] S. Shamsuddin, S.B. Jamaludin, Z. Hussain, Z.A. Ahmad, *Journal of Physical Science*, 19 (2008) 89-95.
- [13] S.P. Kedici, A. Abbas Aksüt, M. Ali Kılıçarslan, G. Bayramog Lu, K. Gökdemir, *Journal of oral rehabilitation* 25 (1998) 800-808.
- [14] J. D. Bumgardner, L. C. Lucas. *Journal of dental research*, 74 (1995) 1521-1527.