CORROSION BEHAVIOR AND ROUGHNESS OF NI-CR/AL_2O_3 COMPOSITES AS DENTAL RESTORATIVE

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ABSTRACT :

This work investigated on the corrosion behavior and roughness of Ni-Cr alloy as dental restorative. Alumina with three weight percentages (1, 5 and 10%) added as reinforcement to fabricate Ni-Cr/alumina composites. Corrosion behavior was tested in artificial saliva at 37$\pm$1 ^oC and pH=4.4. The data of corrosion indicated that the addition of alumina led to reduce the dissolution of metals in base alloy due to the enhancing of Cr_2O_3 passive film and producing Ni_3Al phase in matrix. The roughness of surface was reduced for composites compared with base alloy (Ni-Cr) which is important factor to reduce the accumulation of bacteria on restorative materials in mouth; this reduction is due to the formation of ductile Ni_3Al compared with brittle Ni_2Cr_3 in composites.

KEYWORDS : Dental materials; Ni-Cr alloy; Saliva; Roughness; Corrosion .

السلوك التآكلي والخشونة لمتراكبات $Ni\text{-}Cr/Al_2O_3$ كمواد تعويضية في الاسنان

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الخلاصة :

يتضمن البحث الحالي التقصي عن السلوك التآكلي والخشونة لسبيكة نيكل – كروم، كما اضيفت الالومينا بثلاث نسب وزنية 1 و5 و 10% كتقوية للسبيكة الاساس. اجري فحص التآكل في محلول اللعاب الصناعي عند اس هيدروجيني 4.4 ودرجة حرارة 37$\pm$1 درجة مئوية وقد اظهرت النتائج بان اضافة الالومينا يؤدي الى تقليل الذوبان المعدني للسبيكة الاساس بسبب تعزيز طبقة اوكسيد الكروم الحامية وتكوين الطور Ni_3Al. كما بينتْ نتائج فحص الخشونة السطحية بان المواد المتراكبة تمتلك خشونة اقل من السبيكة الاساس وهذا ما يعد عامل اساسي لتقليل تجمع البكتريا على المواد التعويضية المستخدمة داخل الفم. ان النقصان الحاصل في الخشونة سببه تكوين Ni_3Al اللدن مقارنة مع الطور Ni_2Cr_3 الهش.

الكلمات المرشدة : مواد طب الاسنان، سبيكة نيكل – كروم ، اللعاب ، الخشونة ، السلوك التآكلي.

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INTRODUCTION :-

Historically, the management of dental caries was based on the belief that caries was a progressive disease that eventually destroyed the tooth unless there was surgical and restorative intervention (Silver 1994). It is now recognized that restorative treatment of dental caries alone does not stop the disease process and restorations have a finite lifespan.

Consequently, contemporary management of dental caries includes identification of an individual's risk for caries progression, understanding of the disease process for that individual, and active surveillance to assess disease progression and manage with appropriate preventive services, supplemented by restorative therapy when indicated. The restorative materials include metals and ceramic (Silver 1994). The limitations of metals and alloys in dental application are susceptible to chemical and electrochemical degradation; therefore there are attempts to use composites. Composites are materials obtained by combining two or more materials or phases with a view to take advantage of the salient features of each constituent. It is essential that each component of the composite be biocompatible to avoid degradation between interfaces of the constituents (Silver 1994).

Nickel is found in many alloys used in dental treatment to provide improved physical and chemical properties, such as strength and durability, as well as to reduce the cost of using precious alloys such as gold. The amount of nickel in any dental alloy can vary from a few per cent to over 60%. Nickel alloys are recognized for their ability to withstand the harsh oral environment and have a long-standing history of successful use in dentistry. Nickel dental alloys are used in the construction of long-term restorations designed to remain in clinical service for many years, including crowns, fixed bridges and removable partial dentures. They are also used for shorter-term applications, such as in orthodontic appliances to move and straighten teeth **.**
Many researchers focused on Ni alloys as dental materials (Hartmut et al. 1989 and Viswanathan et al. 2009) and using Ni-based WC/Co/Cr composite coatings (Andrea et al. 2013).

Corrosion of Ni-Cr-Mo alloys in an aqueous solution of 0.05% NAF and in commercial mouthwashes also studied **(**Nilo et al. 2013 and Sousa et al. 2014). While others researchers highlighted using SS 316L (Kahtan et al. 2012 and Rana 2013) as dental alloy. The effect of laser surface modification on dental alloys was investigated (Ataiwi et al. 2013). Microhardness, compressive strength and other physical properties of functionally graded Ti/HA biomaterials were tested (Jawad et al. 2015), in addition to investigate the properties of functionally graded coating of Al_2O_3/ZrO_2/HAP on SS 316L (Rana 2015 and 2016).

The current work aims to study the effect of addition alumina in three weight percentages to Ni-Cr alloy and investigate the corrosion behavior in artificial saliva and roughness test to know the ability of using these composites as restorative materials in mouth.

EXPERIMENTAL PROCEDURE :-

Materials and Chemicals

Nickel and chromium powders were used as started materials to fabricate Ni-Cr alloy, where Ni powders (Johnson Matthey, USA) with main particle size < 55 μm and Cr powders with purity 99.9% and particle size 25-75μm. α-alumina (Baikowski, USA) with an average particle size of < 85 μm and purity of 99.8% was used as reinforcement and the XRD of alumina is shown in Fig. (1) which was good agreement with JCPDS card (46-1131) indicating the

tetragonal shape of particles. The analysis of fabricated alloy was (73.78 Ni, 21.3 Cr, 2.08 Co, 2.02 Mo, 0.22 Mn, 0.18 Si, 0.17 Ti, 0.15 W and 0.10 Fe wt%) obtained by XRF analysis.
For corrosion test, the electrolyte of modified Fusayama artificial saliva was prepared (Geis and Weber, 1985), which closely resembles natural saliva, with composition of (0.4 g/l KCl, 0.4g/l NaCl, 0.906 g/l $CaCl_2.2H_2O$, 0.69 g/l $NaH_2PO_4.2H_2O$, 0.005g/l $Na_2S.9H_2O$ and 1g/l urea). Lactic acid was added to adjust the pH of the solution equal to 4.4 (Zhang et al., 2009).

Fabrication and Characterization

Powder metallurgy method was used to fabricate the Ni-Cr/alumina composites with three weight percentages (1, 5 and 10%) which added to Ni base alloy. The fabrication was achieved by weighting, pressing at 50-51 kN (after try and error for variable loads) and sintering in vacuum furnace at 950^{o}C for 4 hrs. XRD was carried out with Cu as target at scan rate 40.0 (kV) and current= 30.0 (mA). The preparation of specimens and test the XRD were achieved at Babylon University – College of materials engineering. SEM images were recorded at magnified 20 µm at University of Technology – Nanotechnology and Advanced Materials Center.

Corrosion Test

Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 3 mV.sec^{-1}. Polarization experiments were started when the rate at which open circuit potential (E_{oc}) changed was less and more 200mV. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) by Tafel extrapolation method. This test was achieved at University of technology – materials engineering department .
Three electrodes were used in electrochemical cell include reference electrode (SCE), auxiliary electrode (Pt) and working electrode (specimens).

Roughness

The roughness was tested by TA 620 measuring platform with TR200 hand-holding roughness gauge and TR240 portable roughness gauge. The samples were mounted on the tester. The diamond point stylus runs back and forth onto the samples and readings of the maximum surface roughness (maximum departure from perfection over a prescribed length) and average roughness (average departure of the surface from perfection over a prescribed sampling length) is displayed on the screen. The roughness value is selected as an average of three records. This test was achieved at University of technology – materials engineering department.

RESULTS AND DISCUSSION :-

Characterization

XRD analysis of Ni-Cr alloy is presented in Fig. (2). The most intensive peak in the XRD spectrum for the Ni-Cr is at $2\theta = 44.064^o$ which can be the result of matching of two peaks corresponding to Ni (111) ($2\theta = 44.508^o$ according to JCPDS card (04-0850)) and Cr (110) ($2\theta = 44.393^o$ according to JCPDS card (06-0694)) (Feng et al. 2012). In base alloy, Ni_2Cr_3 phase is still distributed along the grain boundaries of Ni matrix, but becomes small and discontinuous, this phase appears as lath-shaped precipitates and agreement with JCPDS card (26-0430). All standard XRD patterns are shown in Figure (3). XRD patterns for of Ni-Cr/alumina composites indicate the overlapping peaks of formed phases with peaks of nickel and chromium. Where some of alumina can be dissolved and then the aluminum reacts with base metals to form phases such as NiAl according to JCPDS card (44-1188) and Ni_3Al phase according to JCPDS card (21-0008) which exists as lath-shaped precipitates in the NiCr matrix. $AlCr_2$ phase also formed according to JCPDS card (21-0008). The characterization of fabricated composites by SEM images is shown in Fig. (4), this figure indicates the distribution on the micrometer scale. Fig. (4-b, c and d) shows the SEM photomicrographs of the composites at different weight percentage of reinforcement. In base alloy, can be seen a network-shaped brittle Ni_2Cr_3 phase in α-Ni and Cr particles. The SEM of composites indicates two main regions, dark phase is alumina and the light phase is nickel. All the specimens are very homogenous with few pores and an even distribution of Ni inclusions. Generally in composites, the lath-shaped and spherical precipitates which are identified as Ni_3Al and α-Cr phases respectively. The following explanation related to SEM of composites with different percentages of alumina.

A sufficient uniform reinforcement distribution is observed when the weight percentage of reinforcement is 1 wt. %. For higher reinforcement content, reinforcement clusters are observed but the distribution of reinforcement is quite homogeneous. A uniform distribution of reinforcement becomes impossible when the content of reinforcement is higher because of inadequate ratio of the surface areas of matrix alloy particles and reinforcement particles. The reinforcement clustering depends on the reinforcement concentration. The effect of reinforcement clustering on the composite is a decrease in the bulk density and an increase in porosity (Saidatulakmar et al. 2008).

Corrosion Behavior

Fig. (5) shows the Tafel plots of base alloy and its composites in saliva at pH=4.4 and 37^oC. These plots indicate the cathodic and anodic regions, where the reduction and oxidation reactions can occur as follow:

$2H^+ + 2e \rightarrow H_2$ (At Cathode) …… (1)

$Ni \rightarrow Ni^{2+} + 2e$ (At Anode) (2)

Corrosion properties of nickel-chromium alloys depend on their bulk composition, microstructure and development of protective surface oxide, in addition to composition of surrounding electrolyte selected for the study (Kedici et al. 1998; Bumgardner and Lucas 1995).

In these alloys Cr plays important role to protect surface by formation Cr_2O_3 film which leads to passive these alloys. But these passive films may be destroyed by corrosive ions in saliva. Addition of alumina to base alloy shifts corrosion potential (E_{corr}) to more active direction with decreasing corrosion current density especially in presence 1 and 10 wt% Al_2O_3. The later percents also affect cathodic and anodic Tafel slopes.

The presence of alumina acts as cathodic regions which reduce the dissolution of nickel from alloy and reduce the corrosion rate as shown in Table (1) in addition to enhancing the presence of Cr_2O_3 passive film. The added alumina incorporates with nickel in matrix to reduce the dissolution of this metal and then allows for Cr_2O_3 to be continued.

Roughness

The addition of alumina to Ni-Cr alloy gave lower roughness compared with that for base alloy as shown in Table (2). In base alloy, there are brittle phase of lath-shaped Ni_2Cr_3 precipitates. This brittle phase gave more roughness during grinding. While in composites, it was found that the Ni_3Al precipitates embedded in NiCr matrix. This phase enhances the room temperature compressive plasticity and impact resistance (Russell 1972), where ductile lath-shaped Ni_3Al phase and α-Cr particles were precipitated leads to marked change in microstructure and gives rise to the improvement of the compressive properties. This is the reason of decreasing roughness in composites.

On the other hand, at surface irregularities, attached bacteria can survive longer because they are protected against natural removal forces and oral hygiene measures (Newman 1974). Moreover, roughening of the surface increases the area available for bacterial adhesion. Many studies were done about the effect of surface roughness of porcelain (Kawai et al. 2000) and of composite resins (Mei et al. 2011). The effect of surface roughness for denture acrylic on biofilm formation (Morgan and Wilson 2001; Azevedo et al. 2012; Park et al. 2012) has been studied. The increasing of roughness leads to accumulation of plaque (Sorensen 1989; Einwag et al. 1990).

The bacteria adhesion forces to composite increase with increasing roughness of its surfaces. Also the surface roughness affects biofilm formation. As restorative dental material, the lower roughness is favorite .

CONCLUSION :

The corrosion and roughness of Ni-Cr/alumina composites have been investigated to study the role of alumina in three percentages (1, 5 and 10 wt%) on reduction the corrosion rate and roughness and then reducing of biofilm which forms on restorative material surface. The experimental results showed that 10% alumina gave good reduction in corrosion rate and the lowest roughness. The reduction in corrosion rate is due to enhancing chromium oxide film and reducing Ni region to dissolve. While the reduction in roughness occurred by formation of ductile Ni_3Al phase compared with brittle Ni_2Cr_3 phase .

Table (1) Corrosion parameters of Ni-Cr alloy and its composites in saliva at 37°C .

Material	E_{corr} mV	i_{corr} $\mu A.cm^{-2}$	$-b_c$ mV.dec.$^{-1}$	$+b_a$ mV.dec.$^{-1}$	C_R mpy
Ni-Cr alloy	-210.1	43.36	89.3	99.1	17.32
Ni-Cr/1% alumina	-233.5	5.690	40.3	72.4	2.273
Ni-Cr/5% alumina	-312.3	32.37	83.9	86.2	12.93
Ni-Cr/10% alumina	-303.0	4.380	38.2	64.6	1.750

Table (2) Roughness values of Ni-Cr alloy and its composites.

Materials	Ra/ µm
Ni-Cr alloy	0.025
Ni-Cr/1% Alumina	0.023
Ni-Cr/5% Alumina	0.022
Ni-Cr/10% Alumina	0.021

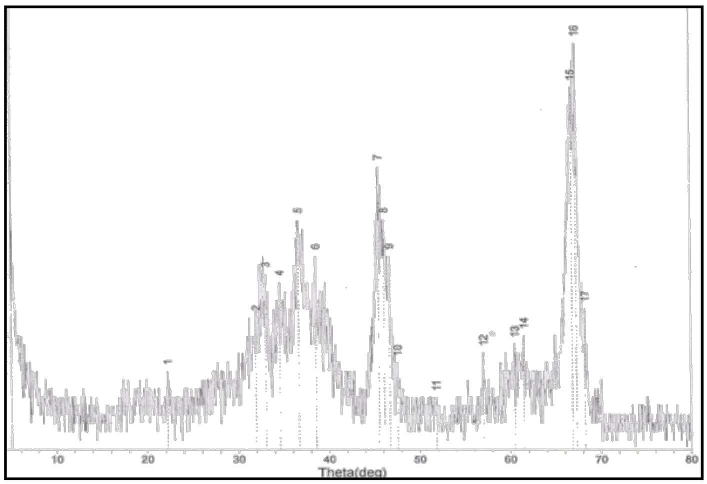

Fig. (1) XRD of alumina.

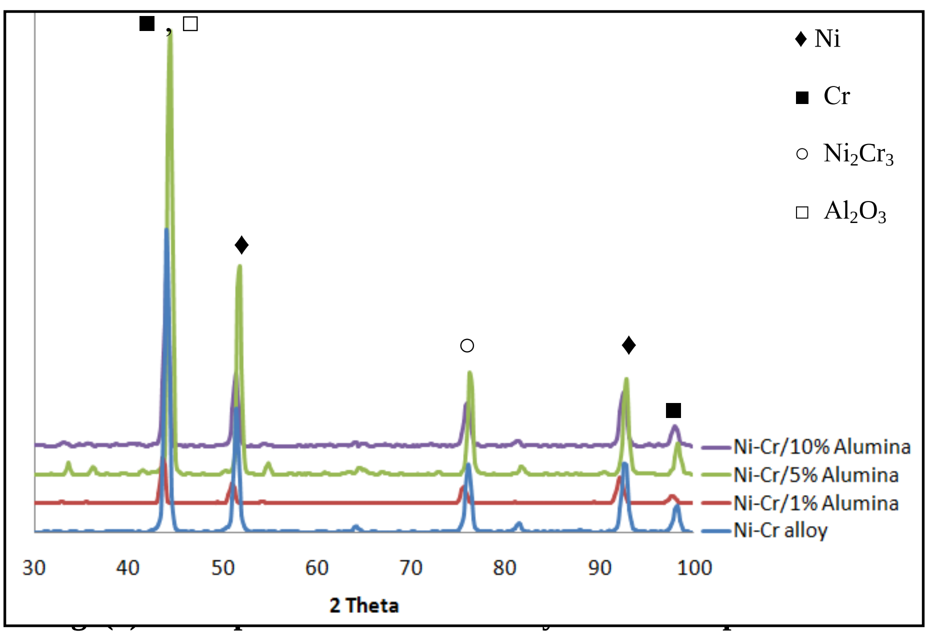

Fig. (2) XRD patterns for Ni-Cr alloy and its composites.

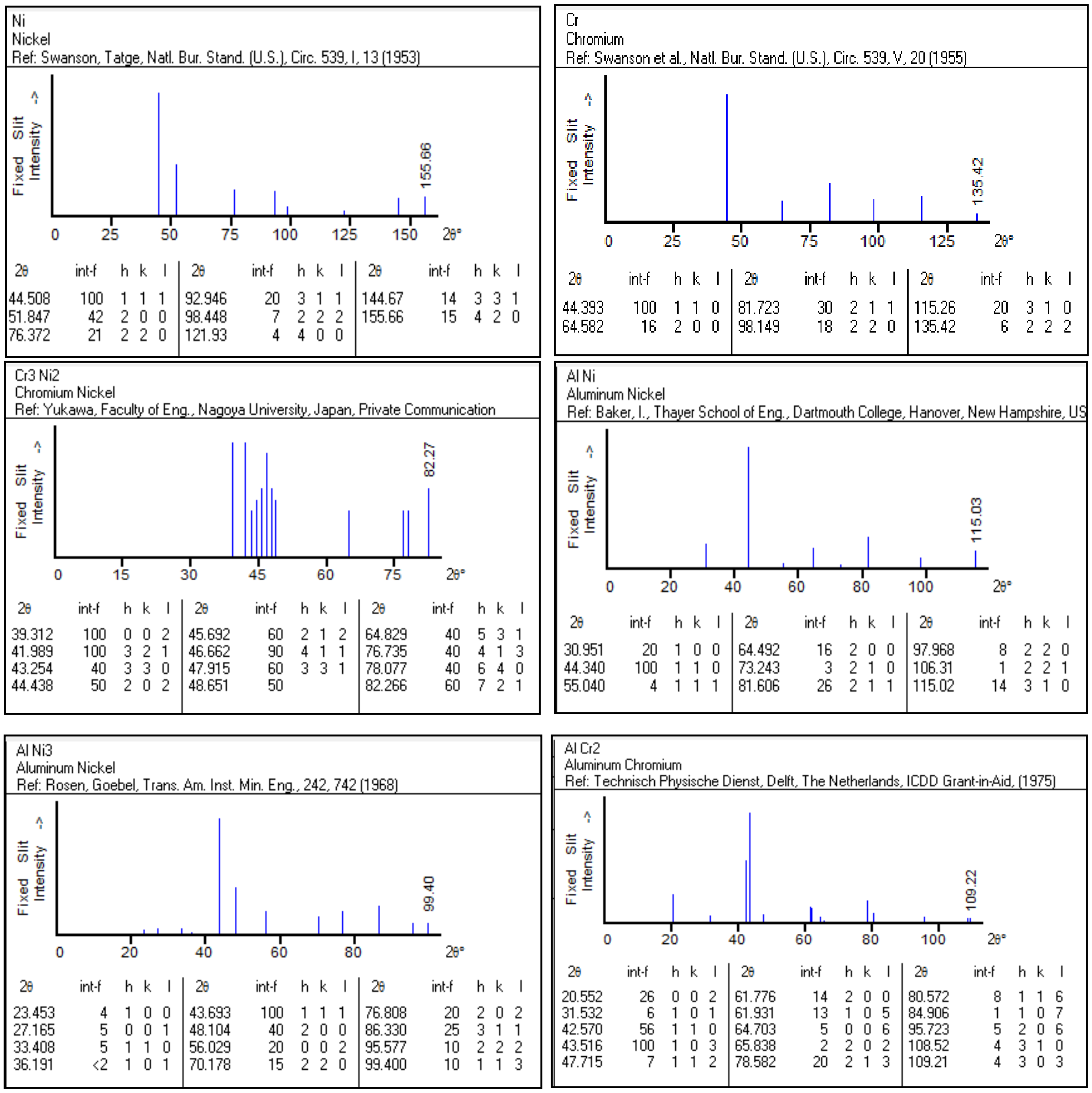

Fig. (3) Standard XRD for main intermetallic phases according to JCPDS cards.

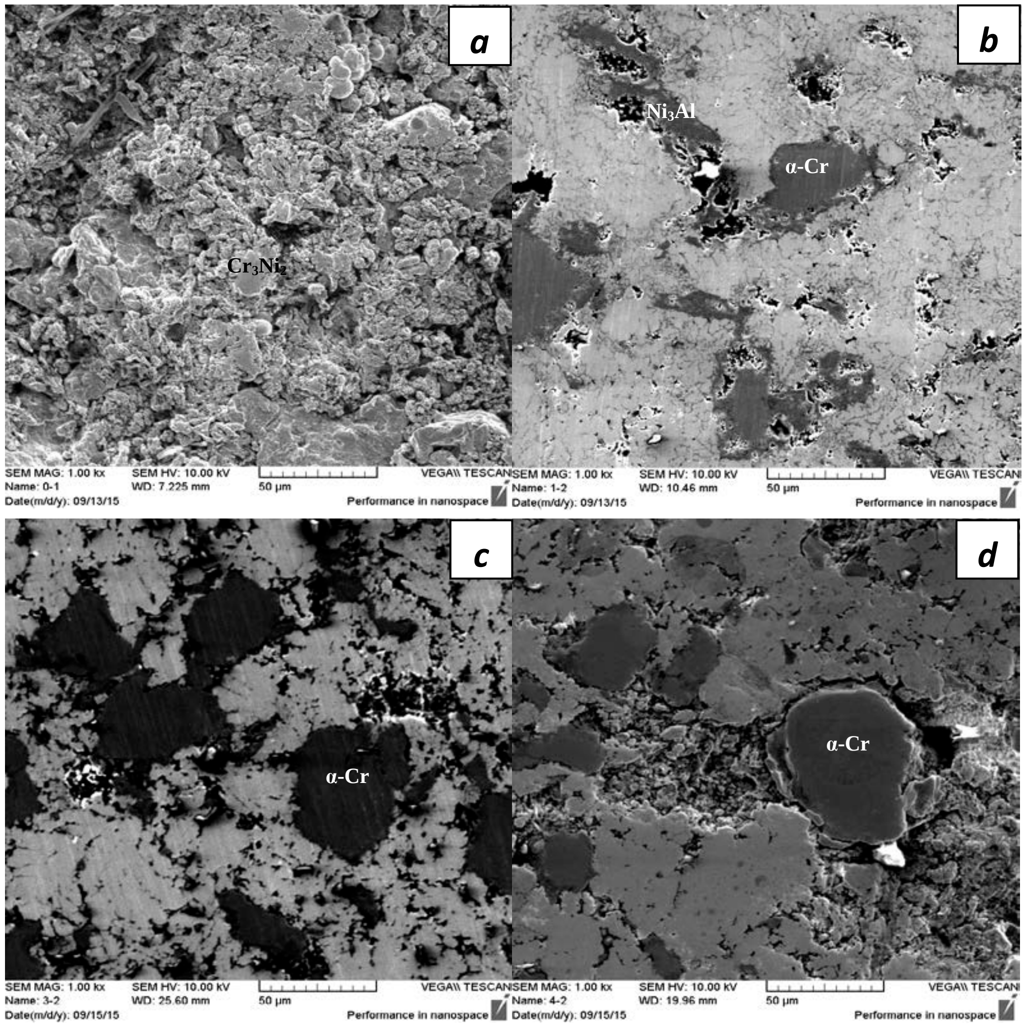

Fig. (4) SEM images of Ni-Cr alloy (a) and its composites reinforced by 1%Alumina (b), 5%Alumina (c) and 10%Alumina (d).

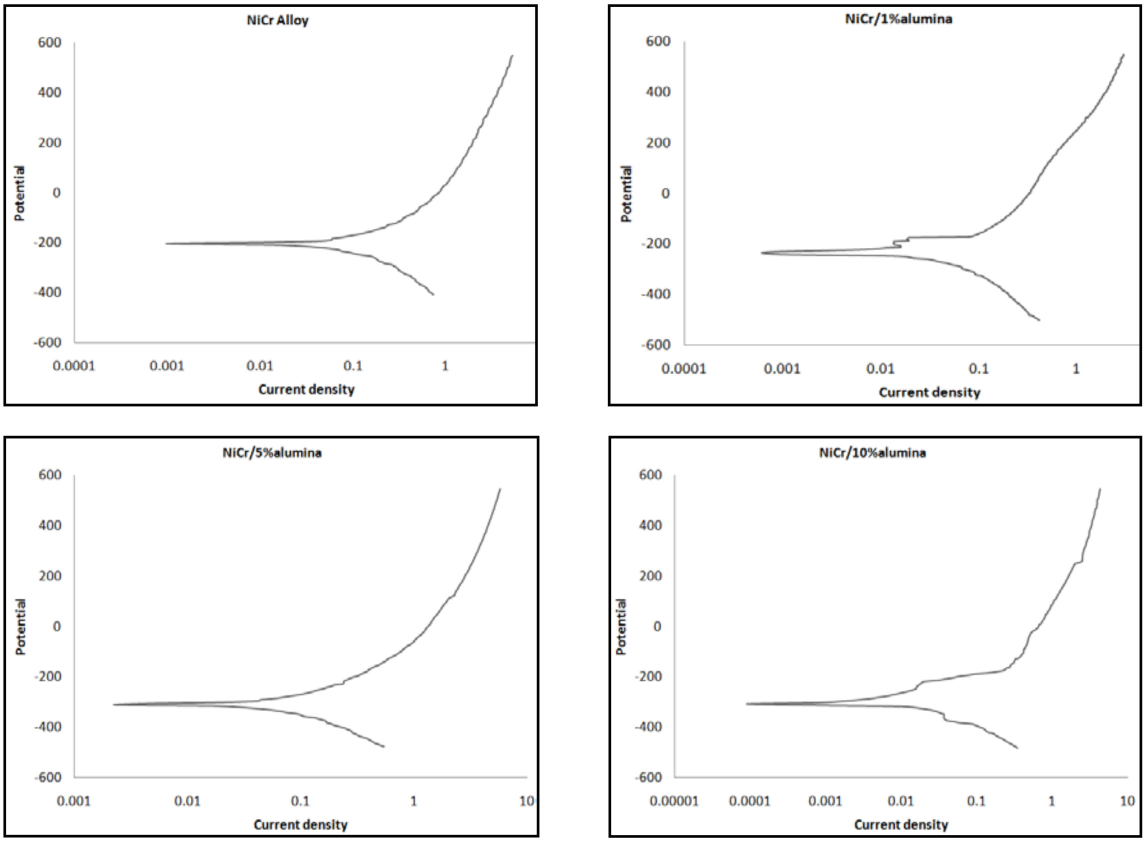

Fig. (5) Tafel plots of Ni-Cr alloy and its composites in saliva at 37^{o}C.

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