INDIAN JOURNAL OF DENTAL ADVANCEMENTS
Journal homepage: www.nacd.in

ORIGINAL RESEARCH

Effect of Heat Treatment on the Corrosion Behavior of Nickel Chromium (Wiron 99) Alloys

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Article Info
Received: 20th October, 2009
Review Completed: 27th November, 2009
Accepted: 2nd December, 2009
Available Online: 18th April, 2010

Abstract

The purpose of this study was to evaluate the corrosion behavior of Nickel chromium alloys (Wiron 99) in the as-cast condition and when subjected to different firing temperatures. This information is important as the firing porcelain on the metal substructure of a restoration may produce changes in corrosion behavior that could influence an alloy behavior during long term use. This study was also designed to study comprehensively the clinical serviceability of these Nickel chromium alloys.

Key words: ***Nickel Chromium, Alloys & Wirons 99***

INTRODUCTION

Nickel chromium casting alloys have been used in dentistry since the 1930's.[1] These alloys are characterized as active or passive alloys and rely on a protective oxide coating for corrosion resistance in the oral environment. It has been suggested that 16-27% chromium provides an adequate protective oxide film for these nickel based alloys.[2]

Ni-Cr alloy is a class of base metal alloy system. The binary phase diagram for the Ni-Cr system shows extensive solid solubility of chromium in nickel.[3] As a result, the binary alloys are not precipitation hardenable. Approximately 37 wt % Cr may remain dissolved at room temperature in the matrix called gamma. Alloying elements are needed to strengthen the Ni-Cr alloys. Chromium provides corrosion resistance and some solid solution hardening, while other additives are used to provide more solid-solution hardening or precipitate formation. The presence of alloying additions is responsible for differences in castability, mechanical behavior and oxide formation.

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The electrochemical behavior of a dental alloy in 0.1N NaCl, citric acid and artificial saliva permits the estimation of the behavior of Ni-Cr alloy (Wiron 99) in the oral cavity. Ni-Cr alloys formed oxide layers approximately three times thicker when heated in air rather than in a furnace under vacuum.

The features of Ni-Cr,

FEATURES Periodic table	NICKEL (Ni) VIII group	CHROMIUM (Cr) VI B group
Atomic number	28	24
Atomic weight	58.7	52
Density g/cm^3	8.90	7.19
Atomic radius in picometers	162	185
Boiling point ^{0}K	3187	2945
Melting point^{0}K	1726	2130
Electron affinity	1.3	0.98
Electron negativity	1.91	1.66
Oxidation number	3+, 2+	6+, 3+
Ionic radius in picometers	62, 72	52, 69
Weight fraction	65%	22.5%

HEAT TREATMENT

Heat treatment is a process in which solid metals is heated beyond the critical temperature and cooled at controlled rates to get different microstructures and desired properties which are associated with heat treatment may affect the corrosion rate, nature, form and size.

CORROSION FUNDAMENTALS

Corrosion is the destruction or deterioration of a material by chemical or electrochemical reaction with its environment. It is theoretically equivalent to the reverse of extractive metallurgy, if the material deteriorating is a metal. It must be noted that the deterioration by physical cause is not corrosion and it is termed as erosion, galling, wear, etc. Loss of useful properties of a material by chemical or electrochemical reaction with its environment is also known as corrosion.

Recent research on dental casting alloys has been dominated by studies on corrosion. In vitro corrosion tests have evaluated number of variables, including effects of electrolytic media and artificial saliva, alloy composition, surface of the metal. The surface state of the metal is an important factor influencing corrosion because the surface composition is almost always different from that of the bulk alloy. Upto three times the mass of metal ions such as Ni and Be is released during occlusal rubbing in combination with corrosion than during corrosion alone for Ni-Cr alloys. No long term studies have been performed to monitor the impact of the release of such large concentrations of metal ions on the overall health of patients.

PROPERTIES OF WIRON 99

STANDARD VALUES	WIRON 99
Color	Silver
Density	8.2 g/cm³
Melting interval	1310-1250°C
Casting temperature	1420°C
Coefficient of expansion25-600°C	$140x10^{-6}$
Ductile yield	330 MPa
Elongation limit	25%
Modulus of elasticity	220 GPa
Vickers hardness (HV 10)	180
Specific mass	8.2

AIMS AND OBJECTIVES

The purpose of this study was to evaluate the corrosion behavior of Nickel chromium alloys (Wiron 99) in the as-cast condition and when subjected to different firing temperatures. This information is important as the firing of porcelain on the metal substructure of a restoration may produce changes in corrosion behavior that could influence an alloy behavior during long term clinical use. This study was also designed to study comprehensively the clinical serviceability of these Nickel chromium alloys.

MATERIALS & METHODOLOGY

MATERIALS

The Wiron 99 alloy (BEGO-WILCOS-BRASIL) is specifically applied for dental use in Fixed Partial Prostheses. This alloy has,

ELEMENT	PERCENTAGE
Nickel (Ni)	65%
Chromium (Cr)	22.5%
Molybdenum (Mo)	9.5%
Silicon (Si)	1%
Niobium (Nb)	1%
Iron (Fe)	0.5%
Cerium (Ce)	0.5%
Carbon (C)	0.02%

- Inlay Wax (Harvard, Pico)
- Phosphate Bonded Investment Material (BELLASUN-BEGO)
- Casting Ring (BEGO)
- Asbestos Ring Liner (Whip mix)
- Vacuum mixer (BEGO Motova SL)
- Vibrator (BEGO Vibroboy-S)
- Induction Casting Machine (BEGO FORNAX 35 EM)
- Furnace (Miditherm MP-EWL Type 5630)
- Sand Blasting Machine (BEGO- Korostar F)
- Polishing stones and discs (Dentaurum)
- Belt grinder
- Lathe machine

- Polishing machine with abrasive wheel discs(BAINPAL)
- Self cure acrylic powder and liquid
- Sodium chloride, Citric acid and Artificial saliva
- Potentiostat (Princeton, NJ, USA)
- Standard calomel electrode
- Auxiliary electrode

Nickel is main constituent. Chromium provides tarnish and corrosion resistance. Molybdenum is added to decrease the thermal coefficient of expansion and improves resistance against pitting corrosion and forms oxides on the alloy surfaces. A minor element such as Be is also sometimes added to influence the castability and oxide formation. As corrosion medium aerated solution of artificial saliva, sodium chloride and citric acid was used.

The compositions of artificial saliva includes,

Potassium dihydrogen phosphate	3.4025g
Sodium hydroxide	0.2436g
Distilled water	500ml

The artificial saliva is maintained at a pH=6.4, citric acid solution at pH= 6.35 and 0.1 N sodium chloride at pH= 6.45.

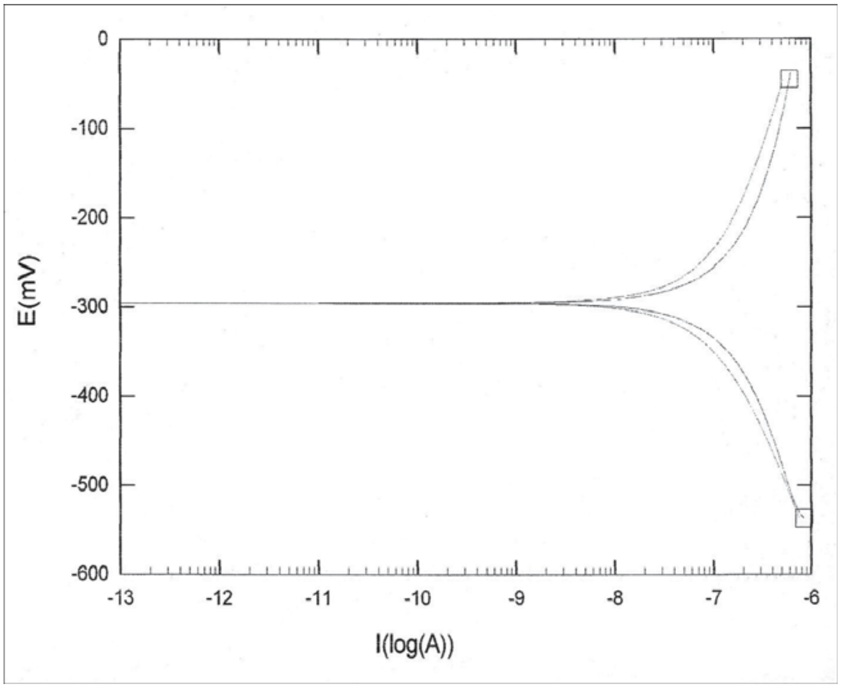
METHODOLOGY

A rod of 0.5cm in diameter and 10cm in length was prepared by injecting wax into split metal mould. The patterns were then oriented vertically in the casting ring with sprue former. The sprued patterns were then invested using phosphate bonded investment material. After bench set, burnout procedures were done and cast with Ni-Cr alloys (Wiron 99) using the centrifugal electromagnetic induction casting machine. After bench cooling, the casting was removed from the investment and sandblasted, and the sprues were removed using a cut-off disk mounted in a high speed dental lathe. Any slight surface roughness remaining was removed with a very fine mounted finishing stone, using light pressure. This rod was then cut into 5 samples of 0.5 cm diameter and 2 cm length each and belt grinding was done to get a smooth surface. One end of all these test samples were polished sequentially with 1/0 to 4/0 grit emery abrasive papers, diamond paste and fine alumina to get a polished even surface by using polishing wheel discs. Of these five samples, one of the sample 'A' namely as cast was kept for corrosion study. Second sample 'B' was selected for 650°C firing cycle. Subsequently the third sample 'C' for 750°C, fourth sample 'D' for 850°C and fifth sample 'E' for 950 °C firing cycle. Heat treatment (firing) was done in a closed electric furnace for one hour followed by air cooling to room temperature. Three cycles of heat treatment was done to all these samples and a corrosion study was carried out separately for each cycle of heat treatment or firing. The medium for corrosion study selected was 0.1 N NaCl, Citric acid and Artificial saliva at room temperature. Later on the graph was estimated which showed the corrosion rates.

The diameter of the sample was measured by using Vernier calipers. Later on the radius was calculated which is half the diameter and then the electrode area (EA) was calculated using the formula,

$$EA = \pi r^2$$

The determination of cyclic polarization curves recording were performed with the electrochemical system which consists of a potentiostat, a three electrode cell, an electrochemical interface and a PC. Corrosion tests were performed using EG & G Princeton Applied Research Potentiostat/ Galvanostat Model 273 (Princeton, NJ, USA) and a corrosion cell standardized to ASTM G5. The Reference Electrode was Standard Calomel Electrode (SCE) and the Auxiliary Electrodes were Platinum. Experimental data were acquired, Tafel extrapolation and Stern Geary fits (SoftCorr III, EG & G PAR) were used to obtain the corrosion rates. The working electrode made from alloy sample was processed into cylindrical shape and mounted in an acrylic support and polished mechanically by using different abrasive discs. Then washed with water, dried and with the help of the sample holder the as cast sample is immersed into the corrosion medium like 0.1 N NaCl, Citric acid and Artificial Saliva. Under these conditions the surface exposed to corrosion was a one dimensional circular area.



Cyclic Polarization Curves UsingTafel extrapolation and Stern Geary fits

Results

The objective of this study was to estimate the degree of modification of corrosion tendency of Ni-Cr alloy (Wiron 99) by thermodynamic methods, by placing the alloy in 0.1 N NaCl, Citric acid and Artificial Saliva.

The values have been tabulated below and the corrosion rate in expressed as –mpy

SAMPLE	SOLUTION	NO FIRING	1ST FIRING	2ND FIRING	3RD FIRING
A	0.1 N NaCl	36.66	-	-	-
	Citric acid	45.47	-	-	-
	Artificial saliva	63.62	-	-	-
B	0.1 N NaCl	-	3.325	14.93	26.64
	Citric acid	-	4.414	5.143	13.44
	Artificial saliva	-	4.045	6.043	10.07
C	0.1 N NaCl	-	1.398	3.035	8.418
	Citric acid	-	16.10	7.924	4.010
	Artificial saliva	-	4.630	5.008	12.04
D	0.1 N NaCl	-	7.328	3.057	2.936
	Citric acid	-	3.667	5.529	7.481
	Artificial saliva	-	3.259	4.770	8.302
E	0.1 N NaCl	-	11.37	14.93	15.08
	Citric acid	-	4.904	7.245	12.59
	Artificial saliva	-	19.06	18.91	9.467

The composition and integrity of the oxide layer on Ni-Cr casting alloys are critical to their performance as dental restorative materials

DISCUSSION

Results indicated that, the nickel based alloys were weakened by the heat treatment. The results of the present study are in contrast to the findings of investigators who found that the nickel base alloys can also be used for the casting of thin copings, retainers and for construction of long span fixed partial dentures.

NaCl is more ionic (100%) therefore more dissociation. Citric acid is less ionic which are less than that of acetic acid and therefore less dissociation. Artificial saliva is also less ionic so less dissociation. Higher temperature causes the oxidize layer to form and form corrosion.

NaCl was used as a corroding media to find out whether the gradual intake of food can cause any corrosion with Ni-Cr alloys (Wiron 99) and citric acid was used specially in cases of prognosis towards hyperacidity and artificial saliva to find out whether Ni-Cr alloys (Wiron 99) has any influence on corrosion rate and might affect the oral mucosa and the fixed prosthesis.

According to the table given above, it was found graphically that the sample 'A' showed maximum corrosion in artificial saliva when compared to 0.1 N NaCl and citric acid and consequently there was a decrease in the corrosion rate when the samples 'B, C, D and E' were heat treated at 650°C, 750°C, 850°C and 950°C for 1st, 2nd and 3rd firing cycle.

For sample 'B' at around 650°C, there was maximum corrosion rate at the 3rd firing when compared to 1st and 2nd firing with NaCl, citric acid and artificial saliva as the corroding medium.

For sample 'C' at 750°C, there was tremendous increase in the corrosion rate at 3rd firing with NaCl and artificial saliva and with gradual decrease in the corrosion rate with citric acid from 1st firing to 3rd firing cycle.

For sample 'D 'at 850 °C, there was increase in corrosion rate with citric acid and artificial saliva from 1st firing to 3rd firing but with NaCl there was decrease in the corrosion rate from 1st to 3rd firing cycle.

For sample 'E' at 950°C, there was a gradual increase in the corrosion rate with NaCl and citric acid as the corroding medium from 1st firing to 3rd firing cycle and there was gradual decrease in corrosion rate with artificial saliva from 1st to 3rd firing cycle.

CONCLUSION

Ni-Cr alloys (Wiron 99) continue to be an important part of dental restorative materials. Introduction of new alloys almost presents an educational challenge to the entire profession.

The increased corrosion rate demonstrated with Artificial Saliva by sample 'A' (as cast condition) may be due to the decreased passivating effect than in NaCl or Citric acid.

The decrease in corrosion rate may be attributed (for samples 'B, C, D & E') at increased temperature due to the fact that heat treatment alters the rate of dissociation of elements of the alloy.

The firing cycles for the alloys used may have rendered the particular alloy more prone for corrosion with different media selected. This is due to the change in the microstructure (phases) that have occurred at high temperature during heat treatment.

The cumulative effect of corrosion rate with saliva has not shown much change which may be due to pH value close to 7.

It is also known that high temperature to which the alloys are subjected have an effect on electrochemical properties differently and hence this is reflected in the variation in the corrosion rate at different temperatures.

Rate of corrosion with saliva may be of varying nature because saliva is associated with subtle changes with systemic variation constantly, where as other agents consumed a constant composition and temperature relatively.

The values corresponding to this alloy tested increased in time, leading to the conclusion that the alloys are passivated which has been established graphically by Tafel extrapolation technique.

In summary, in this investigation, the corrosion properties were not only dependent on composition of Ni-Cr alloy (Wiron 99) but surface oxide characteristics as well.

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