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Microhardness of Ni-Cr alloys under different casting conditions

Microdureza de ligas de Ni-Cr fundidas sob diferentes condições

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ABSTRACT: This study evaluated the microhardness of Ni-Cr alloys used in fixed prosthodontics after casting under different conditions. The casting conditions were: (1-flame/air torch) flame made of a gas/oxygen mixture and centrifugal casting machine in a non-controlled casting environment; (2-induction/argon) electromagnetic induction in an environment controlled with argon; (3-induction/vacuum) electromagnetic induction in a vacuum environment; (4-induction/air) electromagnetic induction in a non-controlled casting environment. The 3 alloys used were Ni-Cr-Mo-Ti, Ni-Cr-Mo-Be, and Ni-Cr-Mo-Nb. Four castings with 5 cylindrical, 15 mm-long specimens (diameter: 1.6 mm) in each casting ring were prepared. After casting, the specimens were embedded in resin and polished for Vickers microhardness (VH) measurements in a Shimadzu HMV-2 (1,000 g for 10 s). A total of 5 indentations were done for each ring, one in each specimen. The data was subjected to two-way ANOVA and Tukey's multiple comparison tests ($\alpha = 0.05$). The VH values of Ni-Cr-Mo-Ti (422 ± 7.8) were statistically higher ($p < 0.05$) than those of Ni-Cr-Mo-Nb (415 ± 7.6). The lowest VH values were found for Ni-Cr-Mo-Be (359 ± 10.7). The VH values obtained in the conditions induction/argon and induction/vacuum were similar ($p > 0.05$) and lower than the values obtained in the conditions induction/air and flame/air torch ($p < 0.05$). The VH values in the conditions induction/air and flame/air were similar ($p > 0.05$). The microhardness of the alloys is influenced by their composition and casting method. The hardness of the Ni-Cr alloys was higher when they were cast with the induction/air and flame/air torch methods.

DESCRIPTORS: Metal ceramic alloys; Dental casting technique; Hardness tests.

RESUMO: Este estudo avaliou a microdureza de ligas de Ni-Cr usadas em prótese fixa fundidas sob diferentes condições. As condições de fundição foram: (1-maçarico) chama composta por uma mistura de gás/oxigênio e centrífuga sem o controle do ambiente de fundição; (2-indução/argônio) indução eletromagnética com o ambiente controlado com argônio; (3-indução/vácuo) indução eletromagnética com o ambiente sob vácuo; (4-indução/ar) indução eletromagnética sem o controle da atmosfera. Foram utilizadas três ligas: Ni-Cr-Mo-Ti, Ni-Cr-Mo-Be e Ni-Cr-Mo-Nb. Foram realizadas 4 fundições com 5 espécimes cilíndricos de 15 mm de comprimento (diâmetro de 1,6 mm). Depois das fundições os espécimes foram embutidos e polidos para as mensurações de microdureza Vickers (VH) em um Shimadzu HMV-2 (1.000 g por 10 s). Um total de 5 indentações foram feitas por anel, uma em cada espécime. Os dados de VH foram avaliados pelos testes de ANOVA e Tukey ($\alpha = 0{,}05$) para contraste de média. A microdureza das ligas apresentou a seguinte ordem: Ni-Cr-Mo-Ti (422 ± 7,8) > Ni-Cr-Mo-Nb (415 ± 7,6) > Ni-Cr-Mo-Be (359 ± 10,7), sendo diferentes entre si. Os valores obtidos nas condições indução/argônio e indução/vácuo foram semelhantes entre si ($p > 0{,}05$) e menores que os obtidos nas condições indução/ar e maçarico, estes últimos semelhantes entre si ($p > 0{,}05$). A microdureza das ligas é dependente da composição da liga e do método de fundição. A dureza das ligas de Ni-Cr foi maior quando fundidas nas condições indução/ar e maçarico.

DESCRITORES: Ligas metalo-cerâmicas; Técnica de fundição odontológica; Testes de dureza.

INTRODUCTION

Changes in supply and demand of gold have spawned a diverse range of alternative alloys. In the sixties, basic alloys such as nickel-chromium (Ni-Cr) alloys were developed. Their good mechanical properties and low cost dramatically increased their popularity in the last decades.

The excellent properties of Ni-Cr alloys are due to their complex composition. Basically, these alloys are composed of Ni (68 to 80%) and Cr (11.9 to 26.3%)[4], but alloying with other elements is required to ensure the achievement of mechanical and corrosion resistance, castability and porcelain bonding. Iron, aluminum, molybdenum, silicon, beryllium, manganese, cobalt, carbon, niobium, copper, titanium, gallium, magnesium and tin are added to Ni-Cr alloys in the range of 0.1 to 14%[3].

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TABLE 1 - Composition of the alloys employed (% wt.)*.

Alloys	Ni	Cr	Nb	Mo	Be	Si	Al	Ti
Ni-Cr-Mo-Nb	Bal.	12.5	4.0	4.25	-	0.50	2.25	0.45
Ni-Cr-Mo-Be	Bal.	14.0	-	8.5	1.80	-	1.70	-
Ni-Cr-Mo-Ti	Bal.	13.5	-	6.0	-	-	-	4.0

*Data provided by the manufacturers.

Despite their complex composition, the commercial nickel-base alloys are very versatile and relatively inexpensive; they possess excellent mechanical properties and high corrosion resistance[13]. The casting of these alloys is easily performed by the use of a gas-oxygen flame with a blowtorch, and it is essentially the same procedure introduced by Taggart in 1907[26]. This fact has made the Ni-Cr alloys widely used for fixed prosthodontics (e.g. metal crown and bridge, metal base of porcelain fused to metal)[15].

Nevertheless, the gas-air combustion in the blowtorch exposes noble, nickel-chromium and other basic alloys[10,24] to oxidation through the inclusion of carbon, which might change the physical properties of the Ni-Cr alloys[2]. This is due to the low atomic radius of the carbon atom, which allows its diffusion into the lattice, and the formation of an interstitial solution[17]. The carbon can also alter the physical properties of the Ni-Cr alloys through the formation of carbides. Carbon reacts with several elements alloyed with nickel, such as chromium, molybdenum, titanium and niobium[1].

The use of casting machines supplied with atmosphere control, such as the ones for titanium casting, can cover and protect the melt from oxidation and dissolution of other chemical elements, such as nitrogen and oxygen[10,25]. The dissolution of gases in the melt is due to a reaction between the liquid and the surrounding gases during the melting and is extremely dependent on the heating time, alloy composition and casting method[27].

Therefore, the objective of this study was to evaluate the Vickers microhardness of three Ni-Cr alloys with different compositions under different casting conditions.

MATERIAL AND METHODS

Three nickel-based alloys were employed in this study: VeraBond (Aalba Dental, Cordelia, Calif. USA); Suprem Cast-V (Talladium, Valencia, Calif., USA) and Tilite (Talladium, Valencia, Calif., USA) . The composition of the alloys is shown in Table 1.

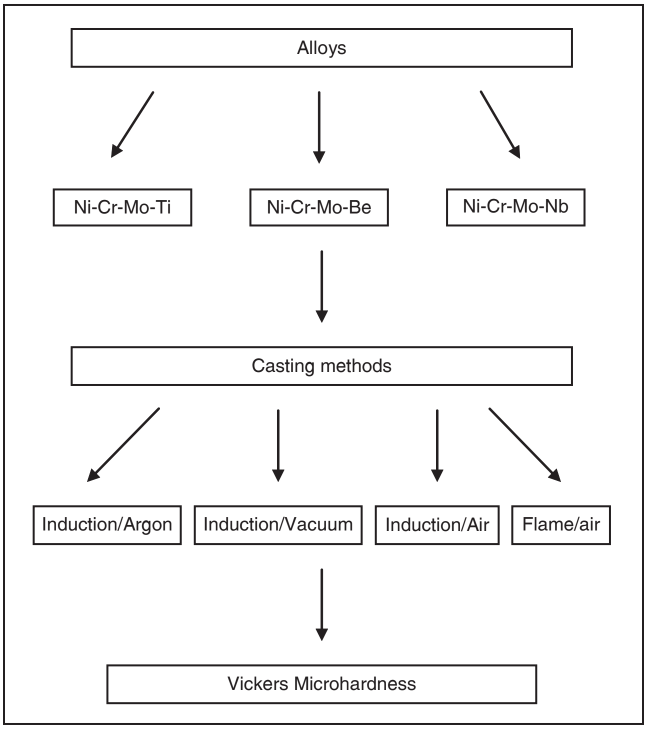


FIGURE 1 - Experimental design.

These alloys were melted in four different conditions:

1. (flame/air): torch melting with gas/oxygen and centrifugal casting machine (Keer, Michigan, USA) in a non-controlled atmosphere;
2. (induction/Argon): induction furnace and electrical centrifugal machine (F.lli Manfredi, San Secondo di Pinerolo, Toscana, Italy) in an Argon atmosphere (N-50, 99.999% pure - Air Liquide do Brazil, SP, Brazil);
3. (induction/vacuum): induction furnace and electrical centrifugal machine in vacuum;
4. (induction/air): induction furnace and electrical centrifugal machine in a non-controlled atmosphere.

Twelve groups resulted from the combination of three alloys and four casting conditions (Figure 1). Alloy in the as-received condition was used for comparison purposes.

Five metallic wires 15 mm-long and with a diameter of 1.6 mm were invested in metallic rings with phosphate investment (Micro-fine 1700, Talladium, Valencia, Calif., USA). After the investment setting, the wires were removed and the mould was used for casting the alloys, under the experimental conditions of this study. Four casting rings were prepared for each experimental condition. After the casting procedure, the specimens were removed, cleaned, and embedded in phenolic resin. The specimens were polished in ascending grits of SiC paper (#180 to #2,000, Norton, São Paulo, Brazil) and ultrasonically cleaned for 5 min, with 0.05 µm silica colloidal solution (Struers, Rodovre, Denmark).

The polished specimens were etched with a solution of nitric and acetic acid, mixed in the proportion of 1:1 for 15 s. This procedure allows hardness measurement in heterogeneous areas (Figure 2), avoiding indentation in alloy porosities and also permits the visualization of the alloy microstructure. The prepared etched surfaces of all alloys were examined using a stereomicroscope (Shimadzu HMV-2, Tokyo, Japan) under 400 X magnification. Photomicrographs were also taken.

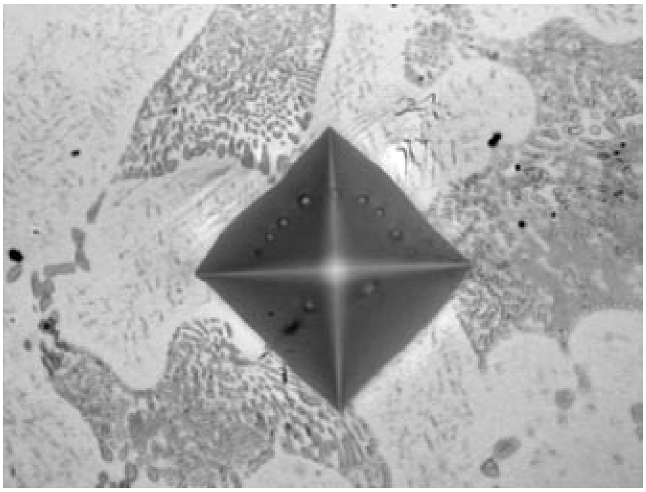


FIGURE 2 - Indentation on multiple phases of the Ni-Cr-Mo-Ti alloy. (Original magnification – 400 X).

The microhardness was measured with a Vickers indenter tester (Shimadzu HMV-2, Tokyo, Japan) with a load of 1,000 g and a loading time of 10 s[27]. One measurement was made in each cast wire and the mean value of all specimens ($n = 5$) from the same ring was used for statistical purposes. The data was subjected to a two-way ANOVA (alloy *vs.* casting condition) and Tukey's test for pair-wise comparisons ($\alpha = 0.05$).

RESULTS

The means and standard deviations of the microhardness values are shown in Table 2.

The results of two-way analysis of variance suggested a non-significant effect of the interaction Alloy *versus* Casting ($p = 0.10$). A significant effect of Alloy ($p = 0.0001$) and Casting methods ($p = 0.0001$) was detected. Graph 1 and 2 present the estimated average VH values under a reduced model that includes only the main factors Alloy and Casting method, respectively.

The hardness of the Ni-Cr-Mo-Ti was statistically higher ($p < 0.05$) than that of Ni-Cr-Mo-Nb (Graph 1). The lowest VH values were found for Ni-Cr-Mo-Be (359 ± 10.7). In regard to the casting methods, it can be seen from Graph 2 that the induction/air and flame/air casting methods led to higher hardness values, which were statistically different from the induction/Argon and induction/vacuum methods. On the other hand, the two latter methods were statistically similar ($p > 0.05$). All casting methods increased the hardness of the alloys, when they were compared to the as-received condition.

All tested specimens presented solidification dendrites with a laminar eutectic structure before and after casting (Figure 3).

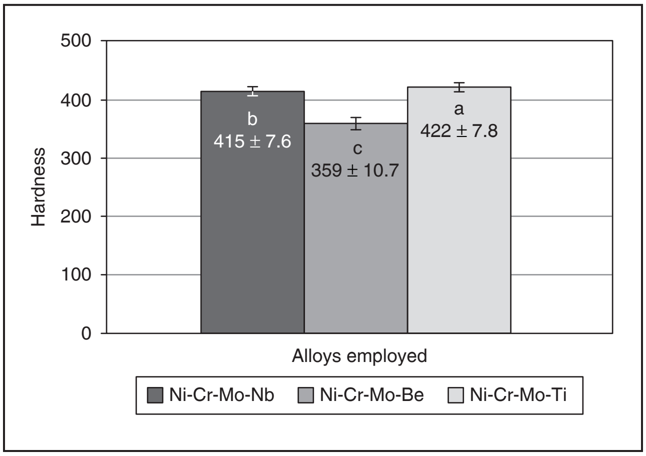
DISCUSSION

The microhardness test is an excellent way to evaluate the effect of variables for metals, mainly

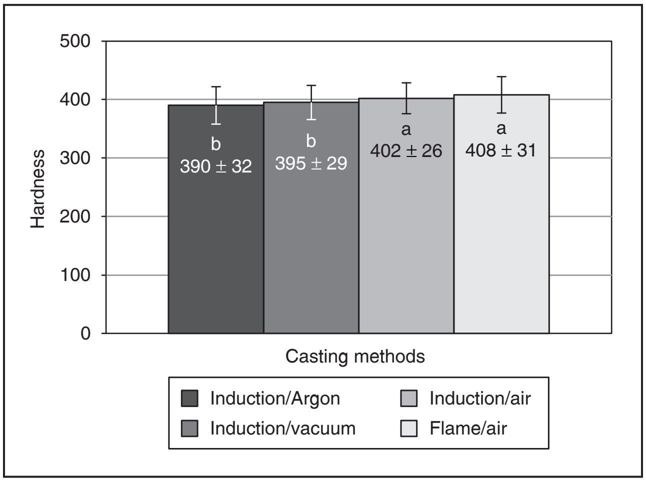
TABLE 2 - Means and standard deviations of Vickers hardness values for all experimental conditions (*).

Alloys	Casting methods				As-received*
	Induction/Argon	Induction/Vacuum	Induction/Air	Flame/Air	
Ni-Cr-Mo-Nb	406 ± 3.1^{c}	413 ± 5.2^{b,c}	418 ± 6.2^{b,c}	423 ± 3.7^{a,b}	392 ± 12
Ni-Cr-Mo-Be	348 ± 13^{d,e}	356 ± 3.7^{d}	366 ± 2.9^{d}	366 ± 4.6^{d}	311 ± 4.9
Ni-Cr-Mo-Ti	416 ± 1.6^{b,c}	415 ± 2.2^{b,c}	422 ± 2.5^{a,b}	433 ± 2.3^{a}	373 ± 1.6

(*) The values of the as-received condition were not included in the statistical analysis.



GRAPH 1 - Means and standard deviations of the Vickers hardness for the alloys employed.



GRAPH 2 - Means and standard deviations of the Vickers hardness for the casting methods.

after surface etching. This procedure allows the selection of areas free of porosities and allows indentions on heterogeneous areas (Figure 2). This is particularly important because it is known that the microhardness of the "light" fcc phase is higher than that of the "dark" hcp phase[19].

Several other advantages can be listed for hardness measurement. It is a property with a low coefficient of variation (7.53% in this study) when compared to other mechanical properties tested, it allows the evaluation of alloys in the as-received condition, which serves for comparison purposes for all casting conditions and it closely matches with other mechanical properties[16].

The results of this study demonstrated that the alloys in the as-received condition showed lower hardness values than that of the respective alloys after casting. It is likely that the as-received alloys are subjected to some heating treatment before commercialization, which increases the softness of the alloy and reduces the values of its mechanical properties[7,21]. Unfortunately, the manufacturers do not provide this information, which prevents us from confirming this hypothesis.

In regard to the casting conditions, the hardness values were higher when the casting procedures were performed in a non-controlled atmosphere (flame/air; induction/air). As the only variable between these two methods was the heat source, it can be concluded that Ni-Cr alloys are more susceptible to contamination by gas uptake from the atmosphere (like oxygen, hydrogen and nitrogen) than from heat source elements itself.

On the other hand, Tajima *et al.*[27] (1984) have not observed similar findings to the ones shown in this study. The authors reported that casting under argon atmosphere tended to increase the hardness of Ni-Cr alloys when compared to casting with flame/air and induction/air. The same authors showed that casting with flame/air allows the lowest uptake of oxygen and nitrogen. However, another investigation showed that the casting of Ni-Cr alloys with flame/air induced an increase in roughness in comparison with castings made under controlled atmosphere[5] which the authors considered as an indirect evidence of oxidation provoked by the flame. No apparent reason was found to explain the controversy among the findings of the reported and the present study. Further studies on this topic are required in order to elucidate this phenomenon.

Several Ni-Cr alloying elements in the Ni-Cr alloy can form oxides and nitrites with gases from the atmosphere at high temperatures that can alter the mechanical properties of the alloys[27]. In another study, Au-Pd-Ag alloys showed less reactivity with the investment material when the casting procedure was performed in an argon controlled atmosphere compared to a non-controlled atmosphere[28]. It is evident that the atmosphere control could avoid the reaction of the alloying elements with gases.

It is likely that the higher hardness values reached by the alloys when cast with the blowtorch (flame/air) are due to the ability of some alloying elements, such as chromium, titanium, niobium, silicon, molybdenum, in forming carbides like MC, M_6C, M_7C_3, $M_{23}C_6$ e M_2C_3[23]. The formation of carbides can occur because carbon can be released during the flame/air combustion[18,25]. The amount of carbon absorbed by the alloy can be even higher

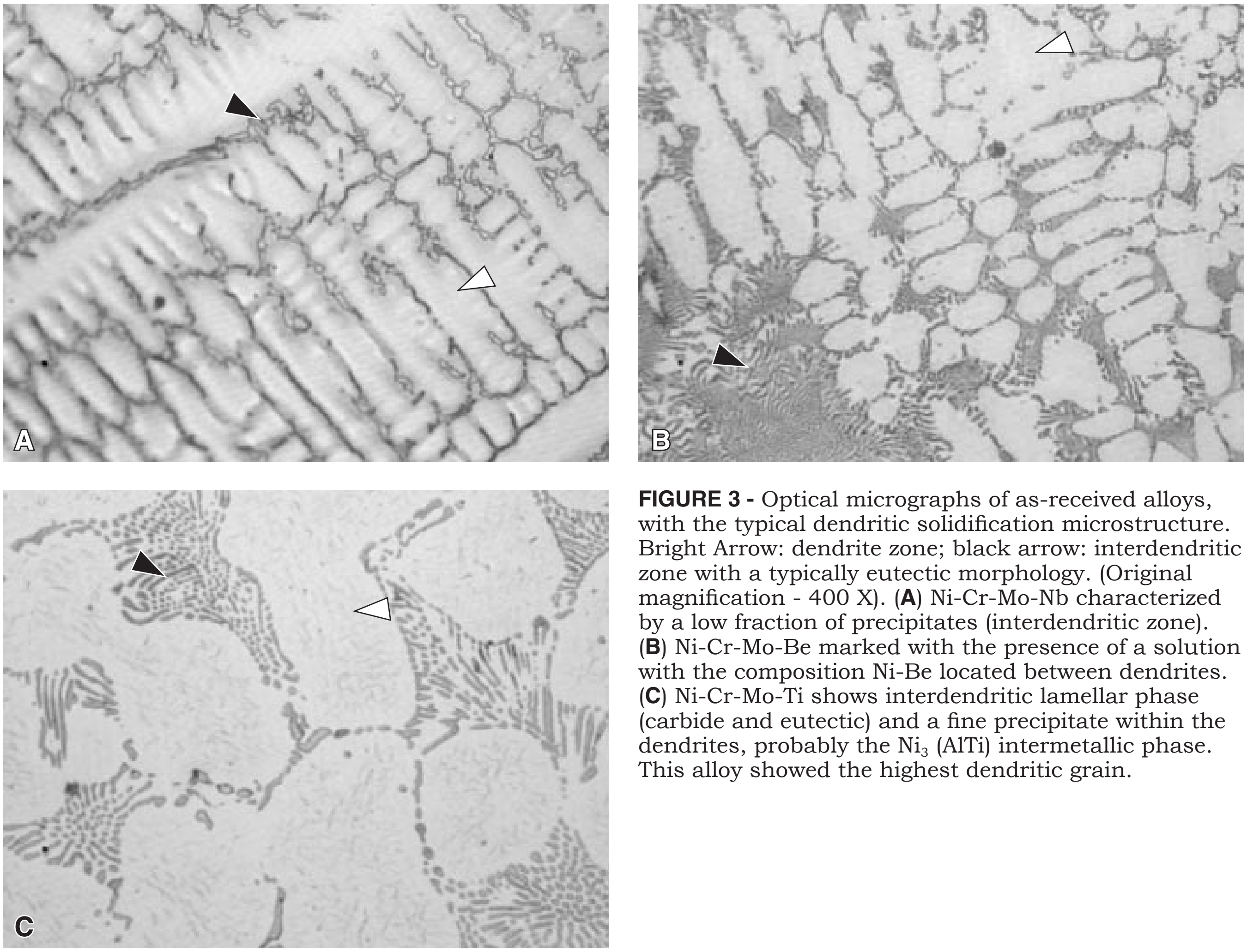


FIGURE 3 - Optical micrographs of as-received alloys, with the typical dendritic solidification microstructure. Bright Arrow: dendrite zone; black arrow: interdendritic zone with a typically eutectic morphology. (Original magnification - 400 X). (**A**) Ni-Cr-Mo-Nb characterized by a low fraction of precipitates (interdendritic zone). (**B**) Ni-Cr-Mo-Be marked with the presence of a solution with the composition Ni-Be located between dendrites. (**C**) Ni-Cr-Mo-Ti shows interdendritic lamellar phase (carbide and eutectic) and a fine precipitate within the dendrites, probably the Ni_3 (AlTi) intermetallic phase. This alloy showed the highest dendritic grain.

when the alloy is overheated or when the oxidizing zone of the flame is used during casting. This uptake of carbon modifies the alloy microstructure and its mechanical properties[22].

This also explains why the Ni-Cr-Mo-Ti showed the highest hardness mean. The presence of Ti in this alloy can provide the formation of more carbides and nitrites, since this element is very reactive to carbon, which in turn, increases the values of the mechanical properties of alloys[1]. The Ni-Cr-Mo-Nb showed an intermediate hardness mean, which is likely due to the formation of the gamma prime or intermetallic phase (Ni_3Al and Ni_3Nb), a solution hardening phase that also increases the alloy strength[20].

The Ni-Cr-Mo-Be showed the lowest hardness. This alloy does not have alloying elements that promote the formation of precipitates and strengthening solutions on the Ni solid-solution matrix[3]. Previous studies also observed similar findings to those of the present investigation. Comparing the hardness of Ni-Cr alloys with or without beryllium it was observed that the presence of beryllium decreased the hardness of the alloy. Contrary to what was observed, one author claimed that a small amount of beryllium is supposed to function as a hardener and grain refiner[9]. However the role of this element on the alloy hardness is not completely understood yet[4,6].

Be has been included in Ni-Cr alloys due to its ability to increase the castability of the alloy[8] and enhance the bonding strength between porcelain and metal[29,30]. However, beryllium is an extreme allergen as well as an accumulative toxin and also reduces the corrosion resistance of Ni-Cr alloys[11,14].

Irrespective of the alloys' composition, all of them showed hardness values similar to that of enamel and superior to that of noble alloys. This represents a drawback of this alloy during the finishing and polishing procedures[12]. The high hardness of Ni-Cr alloys can also be attributed to the phase called P, an intermetallic phase of unknown structure presented on the Cr-Mo-Ni phase diagram[21].

Microstructure examination was performed to explain the possible differences between the alloys, but all of them showed the same microstructure, which consisted of dendrites (light) and an interdendritic region (dark).

Further studies should be conducted in order to evaluate composition changes of the alloys after different casting conditions in order to support the hypothesis raised in the discussion of the present study.

CONCLUSIONS

The microhardness of the alloys was lower in the as-received condition when compared to that of the alloys after the different casting methods were carried out. The microhardness of the alloys was influenced by their composition and casting method. The Ni-Cr-Mo-Be alloy showed the lowest hardness values. The microhardness of the alloys was higher when they were cast with the induction/air and flame/air methods.

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