Materials Research. 2014; 17(3): 627-631
DOI: http://dx.doi.org/10.1590/S1516-14392014005000018

Microstructural Evidence of Beryllium in Commercial Dental Ni-Cr Alloys

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Received: July 11, 2013; Revised: January 17, 2014

The focus of this work was to determine microstructural features in commercial Ni-Cr alloys which could be used to identify indirectly the presence of beryllium. Thus, eight commercial alloys were characterized by chemical analysis, thermal analysis, X-ray diffraction (XRD), scanning electron microscopy – back-scattered electron images (SEM/BSE), energy-dispersive spectroscopy (EDS). The results indicate that the presence of beryllium can be inferred from microstructural analysis via XRD and SEM/BSE. The X-ray diffractograms of the beryllium-containing alloys showed clearly the existence of the NiBe intermetallic phase. SEM/BSE images of these alloys show a very characteristic eutectic microstructure which also indicates the presence of this element. These characteristics are not observed in the beryllium-free alloys.

Keywords: *dental materials, Ni-Cr alloys, microstructural characterization*

1. Introduction

The use of metallic infrastructure for dental prosthesis is a well established method of patient rehabilitation that brings appearance, phonetic, functional, nutritional and psychological benefits for patients that have lost a tooth. Nowadays, there are two groups of dental alloys in use for prosthetic restoration: noble metals (Au, Pd, Pt and Ag) and base metal alloys (Ni-Cr, Co-Cr and Ti).

The base metal alloys increased in market share after 1970, when the gold price started to rise. Among these alloys, the Ni-Cr alloys became popular for fixed partial dentures because of its low cost, good corrosion resistance and good mechanical properties that enable thinner and lighter prostheses than the gold alloy type IV[1]. However these alloys have higher allergenic potential, higher melting point, and are more difficult to weld[2]. To improve its castability, as well as its interaction with dental ceramics, some commercial Ni-Cr alloys include beryllium[3-5]. However, beryllium and its compounds have high toxicity potential[6]. The main contamination risk is due to its vapor, which is a problem for the prosthetic technicians, especially in workplaces without adequate ventilation and exhausting system[1]. In addition, inhalation of dust or fumes containing beryllium can also cause chronic beryllium disease (CBD), generating progressive shortness of breath, and may be, in some cases, fatal[7,8].

The purpose of this work was to investigate the microstructural characteristics of commercial Ni-Cr base dental alloys, which could indicate the presence of Be. The different microstructures may also affect the corrosion and adhesion to ceramics and resin cements. In addition, this investigation also aimed the comparison of several properties presented by beryllium-free and beryllium-containing commercial alloys such melting point and hardness, which can influence the castability and machinability respectively.

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2. Material and Methods

The chemical compositions of the commercial alloys were determined via X-ray fluorescence - wavelength-dispersive X-ray spectroscopy (XRF-WDS) in a PANalytical - Axios Advanced equipment and via optical emission with inductively coupled plasma (ICP-OES) using a Varian – Vista equipment. The latter was used specifically to determine the beryllium contents of the alloys. All the characterizations were carried out from the alloys in the as-received condition.

Differential thermal analysis (DTA) measurements were performed in order to obtain the *solidus* (T_{Sol}) and *liquidus* (T_{Liq}) temperatures of the alloys. The measurements were carried out under high purity argon (min. 99.999%) flux in a Setaram - LABSYS equipment using cylindrical specimens with dimensions of 3 mm diameter and 2 mm height, which were machined from the ingots. The samples were subjected to one DTA cycle of heating/cooling as follow: 20 °C → 100 °C at 5 K/min, isotherm at 100 °C/300s, 100 °C → 800 °C at 20 K/min, isotherm at 800 °C/180s, 800 °C → 1400 °C at 20 K/min and 1400 °C → 20 °C at 20 K/min.

Microscopy analysis were performed on a scanning electron microscope (SEM - TM3000, Hitachi), in the backscattered electron mode (BSE) coupled with energy-dispersive spectroscopy (EDS - Swift ED3000, Oxford Instruments). The samples were cut under oil with a low speed diamond saw, hot mounted using phenolic resin, ground under water with SiC abrasive paper of grit size # 320=>2400 and finally polished with a colloidal silica suspension.

X-ray diffraction (XRD) experiments were carried out to complement the SEM measurements in order to identify the phases present in the microstructure. Bulk samples were used due to the impossibility of powder production. The experiments were performed in an X-ray diffractometer SHIMADZU model XRD 6000, using Cu-Kα radiation under the following condition: $10° < 2\theta < 90°$, 0.05 step, 2 s counting time. The phases were identified with the aid of the software Powder Cell[9], using the crystallographic information reported in Villars and Calvert[10].

Vickers Hardness tests were carried out in a Buehler equipment, model Micromet 2004, with 300 gF load during 30 seconds. The results are the average of fifteen random measurements in one sample of each composition.

3. Results and Discussion

The chemical compositions, measured by XRF-WDS and ICP-OES of the commercial alloys studied in this work are presented in Table 1. The alloys are based on Ni, Cr and Mo, with intentional additions of Si, Ti, Al, Be, Co, Nb, Fe and Cu. The beryllium-containing alloys had beryllium contents from 1.34 to 2.15 mass.%. It should be mentioned that the manufacturer of the commercial alloys *Tilite V* and *Dan Ceramalloy* do not report the presence of Be in their compositions, but the ICP-OES analysis indicated the presence of this element.

The DTA curves of all alloys exhibited similar behavior with two endothermic peaks during heating as shown in Figure 1. The temperatures of the thermal events for each alloy are shown in the Table 2 and Figure 2. The T_{Sol} of the beryllium-containing alloys is in the range of 1149 °C to 1161 °C and T_{Liq} in the range of 1237 °C to 1320 °C. For the beryllium-free alloys the T_{Sol} is in the range of 1112 °C to 1215 °C and the T_{Liq} in the range of 1301 °C to 1325 °C. *Tilite V* has the highest beryllium content and lowest T_{Liq}, while *Verabond* has the lowest beryllium content and its T_{Liq} value is close to those of beryllium-free alloys. The effect of beryllium lowering the melting point of the alloy is well known and it is one of the reason to add beryllium to

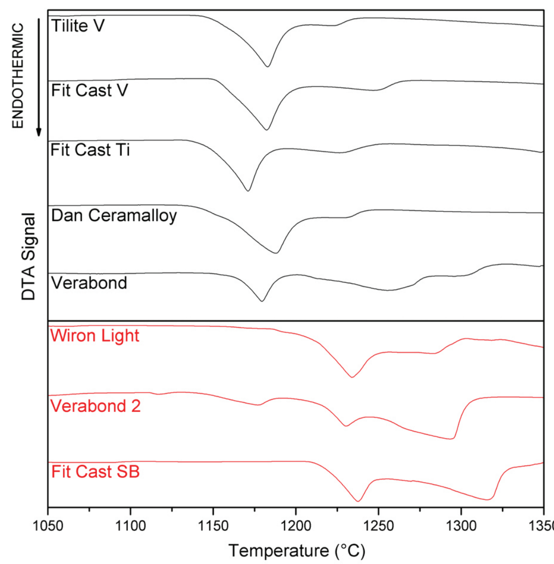

Figure 1. DTA curves: in black the beryllium-containing alloys and in red the beryllium-free alloys.

Table 1. Alloys compositions, given by the manufacturers and measured by XRF-WDS and ICP-OES in this work.

Alloy		Contents (mass.%)												
		Ni	Cr	Mo	Si	Ti	Al	Be	Co	Nb	Fe	Mn	Cu	Others
Tilite V	ICP+XRF	72.8	13.8	8.0	0.1	0.5	2.2	2.1	0.4	-	0.1	-	-	-
	MANUF.	76-60	21-12	14-4	-	6-4	-	-	-	-	-	-	-	-
Fit Cast V	ICP+XRF	73.3	15.1	7.5	-	0.6	1.5	1.7	0.3	-	-	-	-	-
	MANUF.	73	14	8.5	-	-	1.7	1.80	-	-	-	-	-	-
Fit Cast Ti	ICP+XRF	75.8	11.4	7.2	0.3	1.4	2.1	1.7	-	-	0.1	-	-	-
	MANUF.	74	14	8.5	-	1.8	-	1.7	-	-	-	-	-	-
Dan Ceramalloy	ICP+XRF	58.2	18.5	4.5	0.1	0.6	1.9	2.0	11.9	-	0.6	-	1.7	-
	MANUF.	56	20	5	-	2	-	-	12	-	-	-	-	5
Verabond	ICP+XRF	79.2	11.1	4.4	0.5	0.2	2.7	1.3	0.4	-	0.2	-	-	-
	MANUF.	77.95	12.6	5.0	-	0.35	2.9	1.95	0.45	-	-	-	-	-
Wiron Light	ICP+XRF	67.0	21.0	8.6	2.2	-	0.4	-	-	0.4	0.2	0.2	-	-
	MANUF.	64.5	22.0	10.0	2.1	-	-	-	-	-	-	-	-	1.4
Verabond 2	ICP+XRF	76.2	10.0	2.9	4.1	0.3	2.4	-	-	4.1	-	-	-	-
	MANUF.	77.05	12.50	4.25	0.50	0.45	2.25	-	-	4.00	-	-	-	-
Fit Cast SB	ICP+XRF	63.8	21.9	9.6	2.1	-	0.6	-	-	-	1.8	0.2	-	-
	MANUF.	60.75	25	10	2	<1	-	-	-	-	-	-	-	-

The element beryllium was measured via ICP-OES. All others elements were measured via XRF. Maximum standard deviation per element: Al: 0.1%, Si: 0.2%, Ti: 0.1%, Cr: 0.5%, Ni: 1.0%, Nb: 0.1%, Mo: 0.2%, Be: 0.1%, Co: 0.4%, Fe: 0.1%, Mn: 0.2, Cr: 0.2%.

Table 2. Temperatures of the thermal events measured by DTA.

Alloy	T_{Sol} (°C)	T_{Liq} (°C)	ΔT (K)
Tilite V	1148.9	1236.9	88.0
Fit Cast V	1151.8	1264.8	113.0
Fit Cast Ti	1144.6	1249.3	104.7
Dan Ceramalloy	1148.7	1243.5	94.7
Verabond	1160.7	1320.2	159.5
Wiron Light	1207.0	1300.9	93.9
Verabond 2	1112.0	1304.3	192.3
Fit Cast SB	1214.8	1325.0	110.1

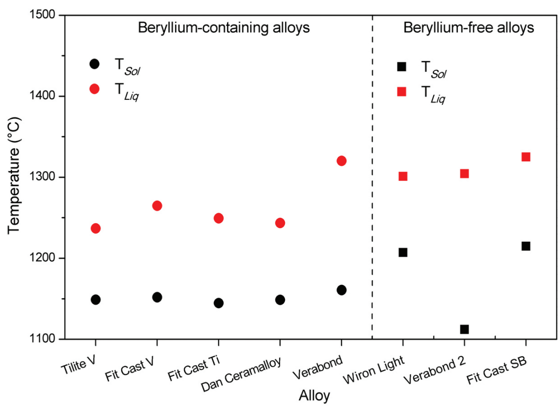

Figure 2. T_{Sol} and T_{Liq} of the alloys studied in this work.

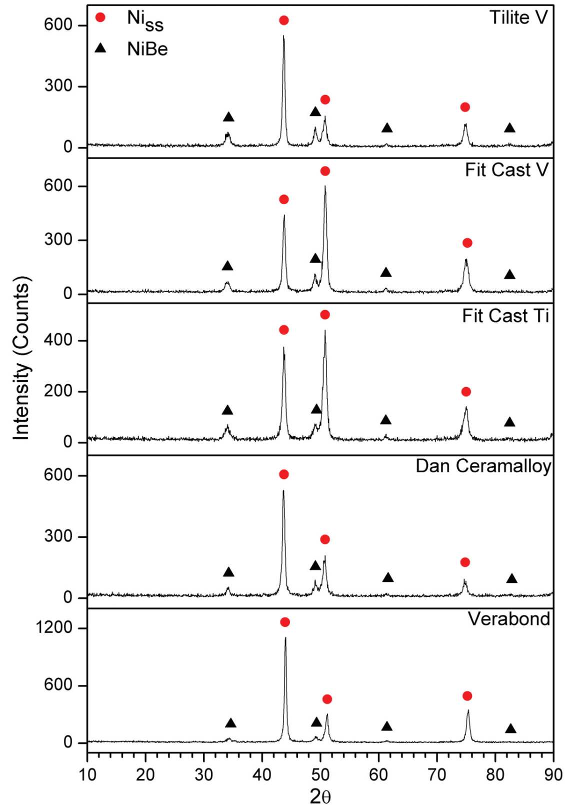

Figure 3. X-ray diffractograms of the beryllium-containing alloys.

these alloys[3,4,5]. The T_{Sol} of the beryllium-containing alloys are very close to each other and to the temperature of the Ni-rich eutectic in the Ni-Be phase diagram (1150 °C)[11]. As expected, the beryllium-free alloys show higher T_{Liq} compared to those of beryllium-containing alloys. *Verabond 2* has distinct composition compared to the other two beryllium-free alloys (*Wiron Light* and *Fit Cast SB*) and shows the lower T_{Sol}. Note that this alloy presents high contents of Si and Nb.

Figures 3 show the X-ray diffractograms of the beryllium-containing alloys. All the diffractograms are very similar and indicate the presence of Ni_{SS} (ss- solid solution) and the intermetallic NiBe phase. The characteristic presence of the NiBe phase is the first microstructural evidence of the presence of beryllium in certain Ni-Cr base alloys. Geis-Gerstorfer and Passler[12] have characterized beryllium-containing Ni-Cr-Mo alloys and have shown the appearance of diffraction peaks of the NiBe phase for Be contents higher than 0.6% (mass %). The X-ray diffractograms of the beryllium-free alloys are shown in Figure 4. As expected, all the alloys presented the Ni_{ss} phase. No extra peaks were observed in alloy *Fit Cast SB*. Low intensity peaks in the alloy *Wiron Light* could not be identified. *Verabond 2* alloy presents peaks of the $Ni_{16}Nb_6Si_7$ phase likely associated to the high concentration of Si and Nb in this alloy.

Figures 5 and 6 show micrographs (SEM/BSE) of the beryllium-free alloys and beryllium-containing alloys respectively. The micrographs of the beryllium-free alloys show primary precipitation of Ni_{SS} and an interdendritic

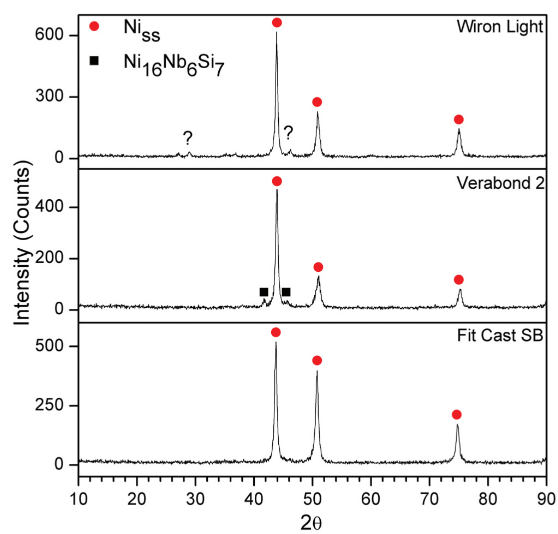

Figure 4. X-ray diffractograms of the beryllium-free alloys.

secondary phase. The SEM/BSE contrast suggests that during solidification there is an important segregation of the heaviest elements (ex. Mo, Nb) for the interdendritic region. The compositions of the interdendritic phases could not be accurately measured due to their small sizes. Anyhow, in the case of the alloys *Wiron Light and Fit Cast SB* were observed higher contents of molybdenum, chromium and silicon in this region compared to the matrix. This

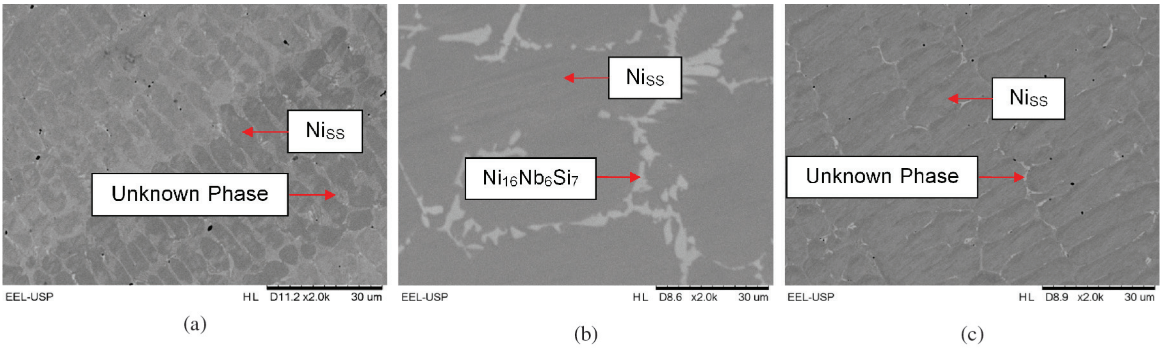

Figure 5. SEM/BSE micrographs of beryllium-free alloys: (a) Wiron Light, (b) Verabond 2 and (c) Fit Cast SB.

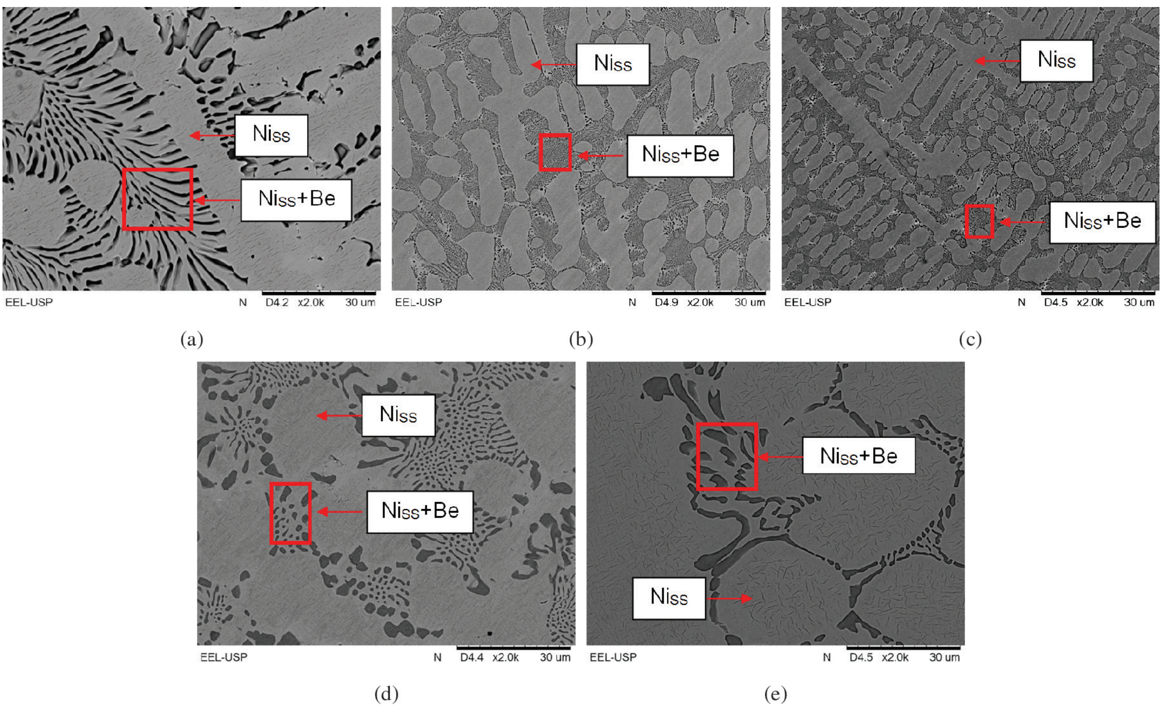

Figure 6. SEM/BSE micrographs of the beryllium-containing alloys: (a) Tilite V, (b) Fit Cast V, (c) Fit Cast Ti, (d) Dan Ceramalloy and (e) Verabond.

characteristic is also reported in other studies of this kind of materials[13]. The micrograph of all beryllium-containing alloys indicates a primary solidification of Ni_{SS} and a very characteristic eutectic region containing Ni_{SS}+NiBe. Among all five alloys containing beryllium, different sizes of primary dendrites and of the eutectic regions were noted, which may be associated to the different cooling conditions during processing of these alloys. In the case of alloys *Tilite V*, *Dan Ceramalloy* and *Verabond*, a needle-shaped phase was observed in the interior of the primary dendrites. This phase presumably has been formed via a solid state reaction during cooling and should correspond to the intermetallic NiBe phase, based on the work of Hero et al.[14]. Thus, the presence of this very characteristic eutectic is also a microstructural evidence of beryllium in the Ni-Cr base alloys, in agreement with results found in other papers[12,14-16]. Bauer et al.[15] found a lamellar eutectic

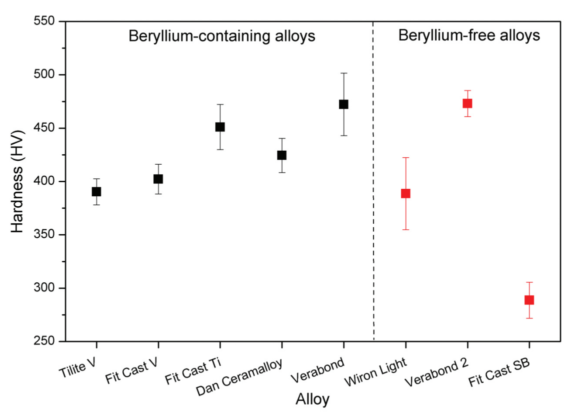

Figure 7. Hardness values (Vickers) of the alloys studied in this work.

in the microstructure of a certain alloy and suggested the possible existence of Be in its composition, although the manufacturer claimed the absence of Be in that alloy. We consider that this typical eutectic microstructure observed in beryllium-containing Ni-Cr commercial alloys cannot be reproduced without the presence of this element. This statement should be valid at least in the case of commercial alloys, where there are restrictions in terms of the chemical elements and their quantities, to satisfy simultaneously low cost, good castability, good mechanical properties and good metal-ceramic adhesion.

The Vickers Hardness values of all alloys evaluated in this work are shown in Figure 7. The presence of Be cannot be inferred based only on the hardness values. For example, in the case of alloy *Verabond 2*, its hardness values are intermediate among the hardness values of the beryllium-containing alloys. However, there is a trend of the beryllium-containing alloys to present higher hardness values, which might be associated somehow to the precipitates embedded in the interior of the Ni_{ss} dendrite phase.

4. Conclusion

In this work, eight dental Ni-Cr alloys were characterized in terms of chemical analysis, thermal analysis, X-ray diffraction and scanning electron microscopy. Three of the alloys were beryllium-free and five of them had beryllium contents between 1.34 and 2.05 mass.%, as measured by ICP-OES analysis.

The presence of beryllium can be inferred from microstructural analysis via XRD and SEM/BSE. The X-ray diffractograms of these alloys showed clearly the existence of the NiBe intermetallic phase. SEM/BSE images of these alloys show a very characteristic eutectic microstructure which allows identifying the presence of beryllium.

In spite of the generally higher hardness of the beryllium-containing alloys, this property cannot be used to indicate the presence of beryllium in this class of material.

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