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Study of a dental cobalt-base alloy used in prosthetic dentistry. part 1: Microstructure and thermophysical properties

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ABSTRACT

Among the dental alloys used in prosthetic dentistry, besides the ones rich in noble elements as gold or platinum, there are also cheaper chromium-rich nickel-base and cobalt-base alloys. In this study the microstructure and the properties of a cobalt-base alloy containing 30 wt.% of chromium and other alloying elements was characterized. In this first part of the work, the microstructure of the alloy in its as-cast state or in its heat-treated state, and its thermo-physical properties were examined. The results showed that the chemical composition, the hardness, the melting temperature range and the thermal expansion behaviour were not exactly the ones which were expected. The heat-treatments applied to the alloy for simulating the possible consequences on its constitution did not considerably change neither the microstructure of the alloy nor its hardness. In the second part of this study this will be the corrosion behaviour of the alloy in artificial saliva which will be characterized. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Dental cobalt-base alloy;
Heat-treatment;
Microstructure;
Hardness;
Melting range;
Thermal expansion.

INTRODUCTION

In odontology dental prostheses (e.g. bridges) are placed in mouth instead natural teeth to insure the same functions. Mastication induced rather intense mechanical stresses and, often, ceramic cannot be used alone. In the specific case of the multiple assemblage called “bridge” an alloy is present inside the ceramic to help it resisting cyclic flexural solicitations. Such alloy must be resistant enough, not only to mechanical stresses but also to aqueous corrosion.

The alloys involved as structural materials for frameworks present various chemical compositions. They can

be classified (American Dental Association, 1984)^[1] as “high noble”, “noble” or “predominantly base”. The “high noble” alloys must contain more than 40 wt.% gold and more than 60 wt.% of gold, palladium and platinum together (i.e. Au+Pd+Pt > 60 wt.%, in which Au > 40 wt.%). The “noble” alloys must contain at least 25 wt.% in noble metal (but without any minimal value for Au). The “predominantly base” alloys are defined as containing less than 25 wt.% of noble metal, without further precision about their chemical composition. In practice many of the “predominantly base” alloys are based either on nickel or on cobalt. They also contain chromium in quantity high enough to achieve high cor-

rosion resistance by favouring the development of a protective passivation layer^[2].

Among the cobalt-based alloys corresponding to the “predominantly base” family of dental alloys, there are cobalt-chromium-tungsten alloys and cobalt-chromium-molybdenum alloys. It was for example demonstrated that the “Vitallium” alloy for example brought an interesting resistance against body fluids^[3]. With such base chemical compositions these alloys have some similarities with other cobalt-based alloys, for example to the ones used for high temperature applications as the hottest parts of aero-engines or industrial processes working at high temperature^[4-7] and which are called superalloys. Indeed these ones also contain heavy elements such as W and Mo which strengthen them by solid solution strengthening and high quantities of chromium to resist not aqueous corrosion but high temperature oxidation and hot corrosion^[8-9].

Here this is another alloy which is under interest, the dSIGN30 alloy. This first part of the study consists in the characterization of the microstructures and thermal behaviour of this alloy, as earlier done for other dental alloys destined to similar applications with nickel-chromium alloys among them^[10]. In a second part this will be the corrosion behaviour which will be explored^[11].

EXPERIMENTAL

The studied alloy

The studied alloy, called dSIGN30, is a commercial cobalt-based alloy the chemical composition of which is given in TABLE 1.

TABLE 1 : Chemical composition of the dSIGN30 alloy (commercial data); all contents in weight percent^[12]

Co	Cr	Ga	Nb	Mo	Si	B	Fe	Al	Li
60.2	30.1	3.9	3.2	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0

Concerning its physical properties^[12] its density is 7.8 g cm⁻³, its melting temperature range 1145-1165°C, its Young’s modulus 234 GPa, its 0.2% conventional tensile stress 520 MPa, its elongation to rupture 6.0% and its Vickers hardness 385. Its thermal expansion coefficient should be 14.7×10⁻⁶ °C⁻¹ between 20 and 600°C. Devoted to the association with the IPS d. SIGN fluorapatite glass-ceramic, its applications con-

cerns short- and long-span bridges, partial dentures, implant superstructures or crowns. For that its advantages are presented as being a reduced hardness, an easiness of casting and processing, slow oxidation, a certified biocompatibility.

Obtaining the pieces

In this work the samples were realized by investment casting. A pattern resin (GC, Tokyo, Japan) was injected in a machined stainless steel mould, in order to obtain the models. These ones thereafter allowed obtaining the final mould in which the liquid alloy was finally injected using a centrifugal casting machine and a gas/oxygen torch. All samples were then separated from the cast-rod.

Heat treatments

One of the as-cast pieces (parallelepipeds 10 mm × 10mm × 1mm) was cut in two equal parts with a precision saw. The first part was kept in as-cast state while the second one was subjected to a heat-treatment reproducing the “oxidation treatment” and the different steps of heat-exposure generally applied to the ceramic part which ought to cover the metallic structure. This was carried out in a ceramic furnace Programat X2 (Ivoclar Vivadent) with as thermal cycles: oxidation (TABLE 2), alumina cleaning, steam cleaning, first “opaque”, second “opaque”, “dentine” (two times), glazing (TABLE 3). The samples were each time air-cooled between two successive treatments.

Metallographic characterization

The as-cast part and the heat-treated one were embedded in a cold resin mixture (Araldite CY230 + hardener HY956, ESCIL), then ground with SiC-papers from grade 120 to grade 2400. After ultrasonic cleaning the sample was polished with textile enriched with 1 µm hard particles to obtain a mirror-like state. The sample preliminarily coated with ultra-thin carbon

TABLE 2 : Thermal cycle of oxidation

Service temperature (B)	403 °C
Heating rate (T↑)	80 °C/min
Temperature / vacuum beginning (V1)	404 °C
Temperature / vacuum end (V2)	925 °C
Baking temperature (T)	925 °C
Time spent at baking temperature (H)	5 min

TABLE 3 : Thermal cycles reproducing the baking conditions of the IPS dSIGN ceramic (Ivoclar Vivadent)

	B	T↑	V1	V2	Final T	H
Opaque 1	403°C	60°C / min	450°C	899°C	900°C	1 min
Opaque 2	403°C	60°C / min	450°C	889°C	890°C	1 min
Dentine 1	403°C	60°C / min	450°C	869°C	870°C	1 min
Dentine 2	403°C	60°C / min	450°C	869°C	870°C	1 min
Glazing	403°C	60°C / min	450°C	830°C	830°C	1 min

layer was observed with a Scanning Electron Microscope (SEM) JEOL JSM 6010 LA in Back Scattered Electrons (BSE) mode.

The same SEM was also used with its attached Energy Dispersive Spectrometry (EDS) device to semi-quantitatively analyse the chemical composition of the alloy. Further, a SX100 CAMECA microprobe was employed for more accurate chemical measurements by Wavelength Dispersion Spectrometry.

A third technique was additionally used for completing the microstructure characterization: X-Ray Diffraction (XRD) with a Philips X'Pert Pro diffractometer.

Hardness measurements

Micro-hardness tests were realized on the embedded samples with a Reichert D32 apparatus, according to the Vickers method and under a 32g load: 5 indentations in the matrix and 5 indentations on the precipitates.

Macro-hardness tests, still according to the Vickers method but under a load of 10kg, were carried out with a Testwell Wolpert apparatus: 5 indentations on the as-cast alloy and 5 indentations on the heat-treated alloy.

Thermal and thermo-mechanical characterization

The solidus and liquidus temperatures of the alloy were deduced from the temperatures of melting start, melting end, solidification start and solidification end determined by Differential Thermal Analysis (DTA) using a SETARAM TG-ATD 92-16.18 apparatus. The thermal cycle was composed by a first heating at +20K/min up to 950°C, a slower second one (+5K/min), a first cooling at -5K/min down to 950°C, followed by a faster second one at -20K/min down to ambient temperature.

The thermo-dilatometric behaviour of the alloy was characterized using a SETARAM TMA 92-16.18 apparatus with programmed thermal cycle reproducing the successive steps of ceramic baking. A sample was

especially cut in one of the dSIGN30 pieces (5 mm × 10mm × 1mm) which was cut in two parts. The following successive cycles were applied, under a flow of 2L/h of pure Ar (1bar):

- Stage of 300s
- Heating at +20K/min up to T_1
- Stage of 600s
- Cooling at -20K/min

With $T_1=900^\circ\text{C}$, $T_2=890^\circ\text{C}$, $T_3=870^\circ\text{C}$, $T_4=870^\circ\text{C}$ too, and $T_5=830^\circ\text{C}$.

RESULTS AND DISCUSSION

Microstructure of the studied alloy as-cast and after heat-treatments

TABLE 4 displays the general chemical composition of the obtained alloy. Its as-cast microstructure is illustrated in Figure 1 (SEM/BSE micrograph) while the corresponding XRD spectrum is shown in Figure 2. The general composition of the alloy (TABLE 4) well corresponds to the announced one concerning cobalt and chromium. In contrast niobium is well present but seemingly with lower content than given in TABLE 1 (four times lower), while no gallium was really detected. One can see that the as-cast alloy is mainly constituted of a matrix – seemingly dendritic – and of precipitates of two types. These ones appear either in white or in black when the SEM is used in the BSE mode.

TABLE 4 : Chemical compositions of the dSIGN30 (SEM/EDS)

Elements (wt.%)	Co	Cr	Nb	Mo	Si
Whole alloy	(bal.)	28.8	1.0	0.6	0.7

The precipitates, which are rich in Nb and Mo for the white ones and in Cr for the black ones seem being carbides, maybe of the MC type in the first case and of chromium in the second case. Unfortunately their sizes and their volume fractions were not high enough to al-

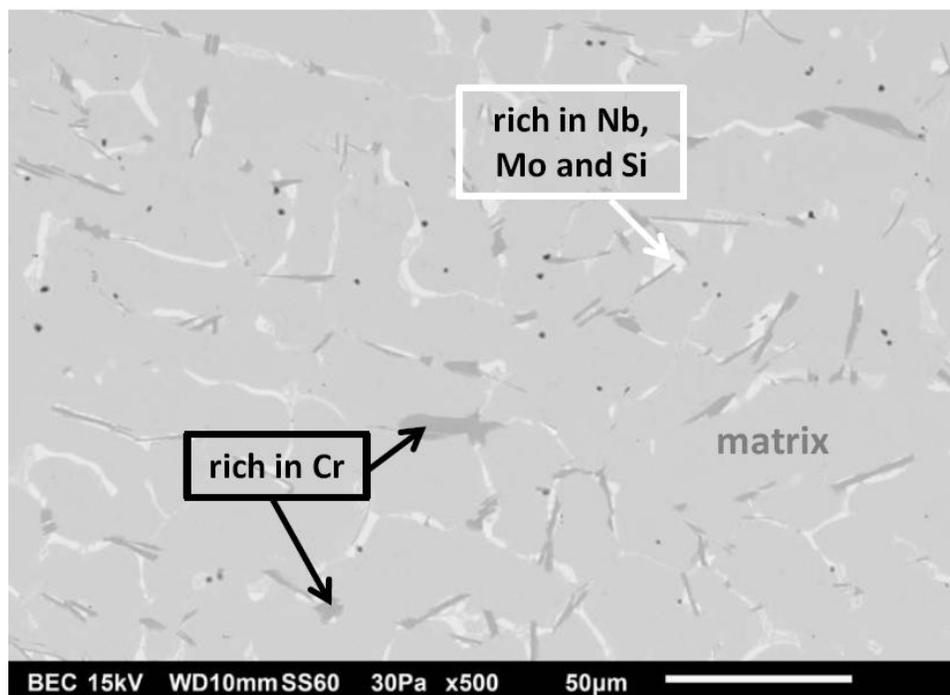


Figure 1 : Microstructure of the dSIGN30 alloy in its as-cast condition

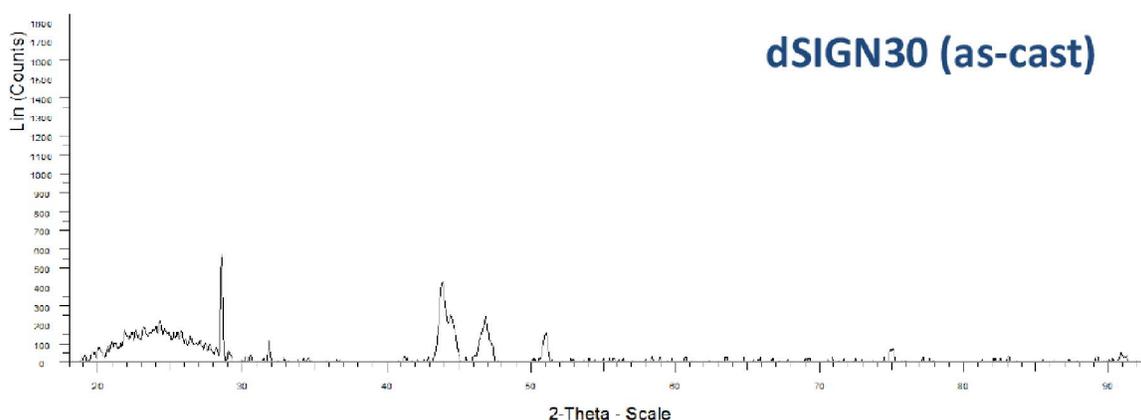


Figure 2 : XRD spectrum acquired on the as-cast dSIGN30

low identifying them by EDS spot analysis and by XRD respectively. The XRD result (Figure 2) only shows that matrix is maybe double constituted: a part still austenitic (Face Centred Cubic, high temperature variety) and a part become Hexagonal Compact (HC, low temperature variety).

The successive heat-treatments induced no significant changes in the microstructure. Indeed there are only minor modifications of the particles in the dSIGN30 microstructure, as illustrated in Figure 3 by a second SEM/BSE micrograph, and in Figure 4 by a second XRD spectrum.

Hardness measurements

The macro and micro-Vickers indentations led to the following values:

- Macro-hardness (10kg-load): 340 ± 40 in the as-cast state, and 317 ± 26 in the heat-treated state.
- Micro-hardness (32g-load), matrix: 351 ± 80 in the as-cast state, and 278 ± 30 in the heat-treated state.

The values of macro-hardness are lower than the one claimed by the manufacturer (385Hv). Indeed, it is here about fifty Hv degrees lower in the as-cast state while heat-treatments induced a slight softening with as result new values about twenty Vickers degrees lower. It is possible that the cooling conditions obtained in the

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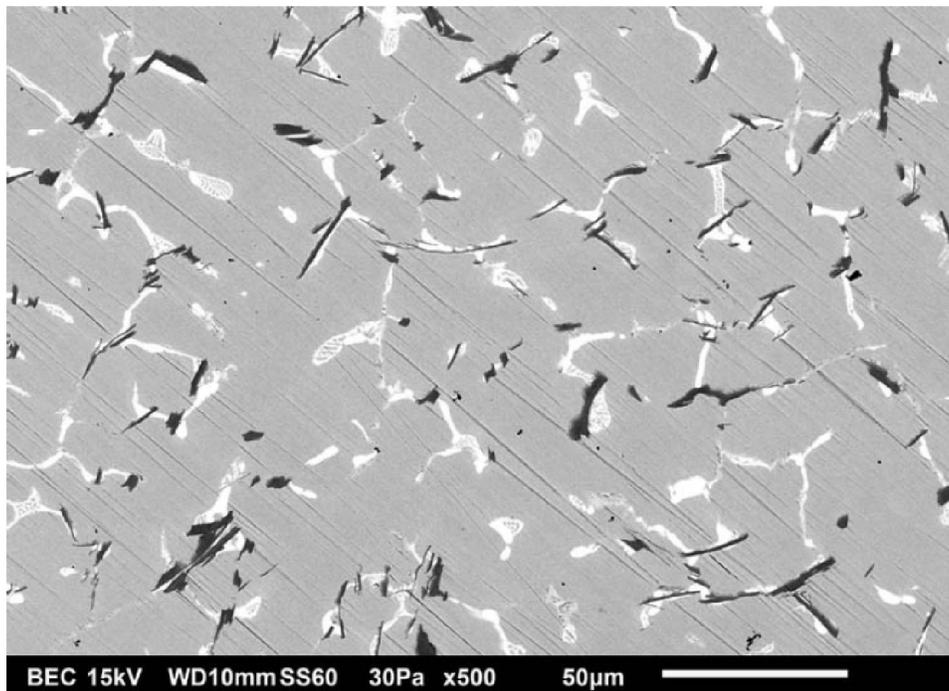


Figure 3 : Microstructure of the dSIGN30 alloy after heat-treatments

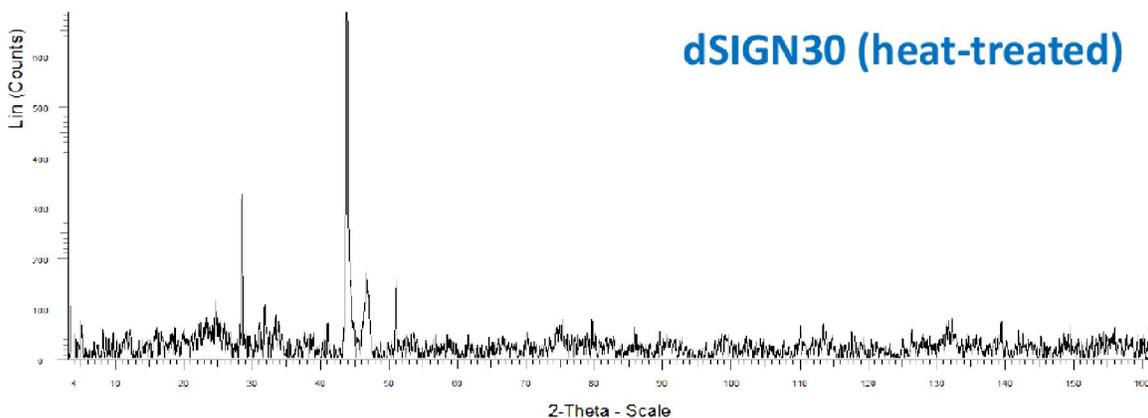


Figure 4 : XRD spectrum acquired on the heat-treated dSIGN30

present work were not the same as by the manufacturer, but it is also possible that the chemical composition a little different may be at the origin of this not very good correspondence. As for the macro-hardness the heat-treatment induced also a decrease in micro-hardness. The rather great scattering of the micro-hardness values (especially in the as-cast state: standard deviation of about the quarter of the average value), may be explained by some of the indentations which reached may be hard precipitates while the others concerned the softer matrix.

Melting and solidification temperature ranges

Differential Thermal Analysis runs were carried out.

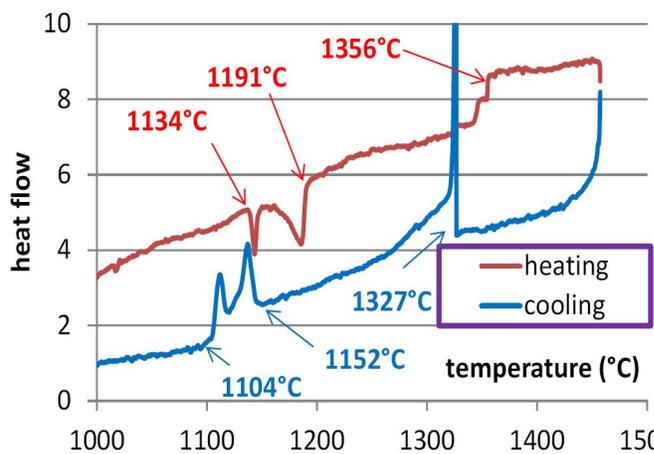


Figure 5 : Thermal analysis curve acquired on the dSIGN30 alloy

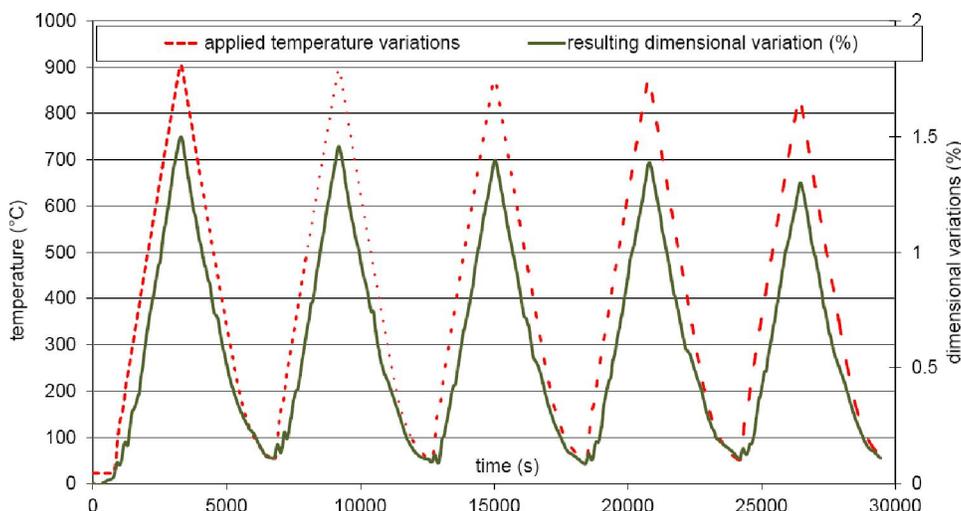


Figure 6 : Dimensional variations of the dSIGN 30 alloy during the multi-cycles dilatometry test

TABLE 5 : The successive values of the average thermal expansion coefficient measured during the heating phases of the five following cycles

Heating number	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Average value of TEC ($\times 10^{-6} \text{ }^\circ\text{C}^{-1}$)	21.9	20.8	19.5	18.7	18.1

The heat-flow curves at heating (in red) and at cooling (in blue) are drawn together in Figure 5. They present three endothermic peaks in the heating parts and three exothermic ones in the cooling parts.

By considering the microstructure of the as-cast alloy one can guess that, despite the not really interpenetrated morphologies, chromium carbides and matrix constitute a eutectic compound which is the first part of the alloy to melt, at about 1135°C . Analogously the MC carbides and a part of matrix may be themselves a second eutectic compound which melts at a higher temperature, about 1190°C . Thereafter matrix is the single solid to remain and its melting progresses up to about 1360°C , temperature at which the alloy is now totally liquid. During the cooling matrix is the first phase to crystallize, here at about 1330°C , followed by the {MC + matrix} eutectic (near 1150°C). Solidification finishes with the {chromium carbides + matrix} eutectic, at about 1100°C . Classically, the melting start temperature and the solidification end one are slightly different from one another and the melting end temperature and the solidification start one are also not the same. This hysteresis usually observed is due to heating rate and cooling rates still a little too high to allow phases transformations progressing according to the thermodynamic equilibria (e.g. the well-known problems of nucleation and undercool-

ing...), these ones being then delayed to higher temperature at heating and lower temperatures at cooling. One can consider that the values during heating (1134°C and 1356°C), eventually the average value of the melting start and solidification end temperatures (1119°C) and the one of the melting end and solidification start (1341.5°C), can be taken as solidus temperature and liquidus temperature.

If these values show acceptable agreement for the minimal temperature of the melting range claimed by the manufacturer (1145°C) this is not the case for the maximal values: the DTA experiment clearly showed that the melting end temperature is much higher than the maximal temperature of this melting range (1165°C).

Thermo-dilatometry behaviour

During the successive heat-treatments separated by coolings and re-heatings the alloy may evolve dimensionally, what may induces stresses in the alloy-ceramic prosthesis. The thermo-dilatometry test following the thermal history of the alloy led to the curves plotted in Figure 6. The increases and decreases in temperature (dotted red curve) effectively induced expansions and contractions of the alloy. The deduced values of average thermal expansion coefficients (TEC) are displayed in TABLE 5. Seemingly the TEC are slightly decreasing with the number of thermal cycles. However, the

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obtained values are all higher than the about $15 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ announced by the manufacturer.

General commentaries

This metallography characterization of the dSIGN dental cobalt-base alloy allowed to better know its microstructure which is composed of a dendritic matrix of cobalt solid solution containing a part of the other elements and of particles, some ones rich in heavy elements and the others rich in chromium. The morphologies and the decrease in melting start temperature that they seem inducing (which led to values to which the presence of chromium carbides and tantalum carbides provoke in 30 wt.%Cr-containing cobalt-base superalloys) seems designating these particles as being carbides. Since no carbon is claimed in the chemical composition of the dSIGN30, this hypothesis is to be confirmed, but by other means than EDS spot measurements and XRD runs since these techniques were not able to respond this question because of the too small size and too low volume fractions of these particles. Still concerning the melting range it seems that the manufacturer did not know that the alloy was not completely liquid above 1165°C since the DTA experiments carried out in this work showed melting end and solidification start temperatures much higher. In fact, as demonstrated in the present work, melting and solidification occurred three times during heating and during cooling respectively. In addition, the measured hardness was a little lower than claimed by the manufacturer, in the as-cast state as well as in the heat-treated state. But this is maybe important for the mechanical strength of the alloy since the hardness is rather high in both cases (data from manufacturer and values issued from the present work). To finish, the thermal expansion behaviour which was characterized here is not so interesting than the one announced by the manufacturer.

CONCLUSIONS

The dSIGN30 dental cobalt-base alloy which was available for this work appeared thus a little different

than described by the manufacturer, in term of chemical composition as well as in term of thermo-physical properties. Its castability is maybe not so good in reality as suggested by the too narrow melting range announced by the manufacturer, and the thermal expansion behaviour is probably farer from the ceramic's than announced. In contrast, its mechanical strength is seemingly of high level even if the hardness is not as high as expected. In the second part of this study, the dSIGN30 alloy will be soon studied in corrosion in solutions simulating the buccal milieu, with electrochemical measurements.

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