

Effect of the Remelting on Transformations in Co-Cr-Mo Prosthetics Alloy

B. Kacprzyk, T. Szymczak^{a,*}, G. Gumienny^a, L. Klimek^b

^aDepartment of Materials Engineering and Production Systems, Lodz University of Technology
Stefanowskiego 1/15 Street, 90-924, Łódź Poland

^bDepartment of Dental Technology, Division of Dentistry, UM Pomorska 251 Street

*Corresponding author. E-mail address: tomasz.szymczak@p.lodz.pl

Received 29.05.2013; accepted in revised form 04.06.2013

Abstract

In the article we were studying the impact of the remelting on transformations in Co-Cr-Mo prosthetics alloy. The TDA curves were analyzed, the microstructure was examined, the analysis of the chemical composition and hardness using the Brinell method was made. It was found that the obtained microstructure of the alloys that we studied do not differ significantly. In all four samples, microscopic images were similar to each other. The volume, size and distribution of the phases remain similar. Analysis of the chemical composition showed that all the samples fall within the compositions provided for the test alloy. Further to this the hardness of the samples, regardless of the number of remeltings did not show any significant fluctuations and remained within the error limit. After analyzing all the results, it can be concluded that the remeltings of the alloys should not have a significant impact on their properties. Secondly melted alloys can be used for prosthetics works.

Keywords: Theory of crystallization, Remelting, Thermal and derivative analysis, Microstructure, Composition, Alloys properties, Prosthetics alloys

1. Introduction

Foundry practice plays a very important role in dental prosthetics. Castings are an integral part of the filling manufacturing process. Their quality depends largely on the technology inter alia melting temperature. In order to fully assess clinical and laboratory usefulness of the alloys, it seems important to analyze the problem from the metal science, i.e. from the microstructure and its effect on material properties.

In the case of non-precious alloys used in dentistry (which include Co-Cr-Mo alloys), it is assumed that these materials should not be remelted. According to the manufacturer remelting can result the deterioration of i.a. their mechanical properties and corrosion resistance. It is to be said, that both economic, as well as ecological factors play an important role in the remelting of the materials used in dentistry.

Economic factor are associated with financial savings whilst the ecological factor are connected to the environment. Recycling, which often involves the re-use of secondary raw materials, should also be made applicable to biomedical materials. Considering the high cost of Co-Cr-Mo alloy and the fact that due to the small dimensions of the prosthetic components as well as the fact that every such component is made to individual order, a very large part of the material (sometimes up to 70%) is irretrievably lost.

Taking into account modern requirements for recycling and environmental protection, the problem of re-use of cast residues (which includes the gating system) should consider examining the effect of the addition of such material to new alloys. Adding the remelted alloy is even more notable, that and metallurgy a scrap addition is common. There are not unequivocal opinions on the impact of the remelting on dental alloys properties [1, 9]. According to some authors, there are no significant differences

that might suggest that the remelting could have an impact e.g. on chemical composition and corrosion resistance [4, 6, 2].

Since it is well known, that alloys properties largely depend on their chemical composition and microstructure resulting from transformations taking place, the goal of this article is to examine the transformations which take place during the cooling of the remelted alloys and the microstructure and hardness of the alloys obtained during this process.

2. Work methodology

The kind of prosthetic alloy used for the purpose of this story is called Biosil F. It is a patented Co-Cr-Mo prosthetic alloy used for frame dentures casting. It is especially recommended when performing skeletal work with long arms of the clasp retention brackets and flexible structures exposed to high tension. One of the main characteristic of the Biosil F alloy is its high biocompatibility as well as the fact, that it does not cause an allergic reaction in the patient's mouth. By using materials of high purity and an appropriate technology an extremely low content of Ni (0.05%) in Biosil is achieved. Biosil F meets the standards DIN 13 912 and ISO 68 71. Chemical composition of tested alloy is given in Table 2.

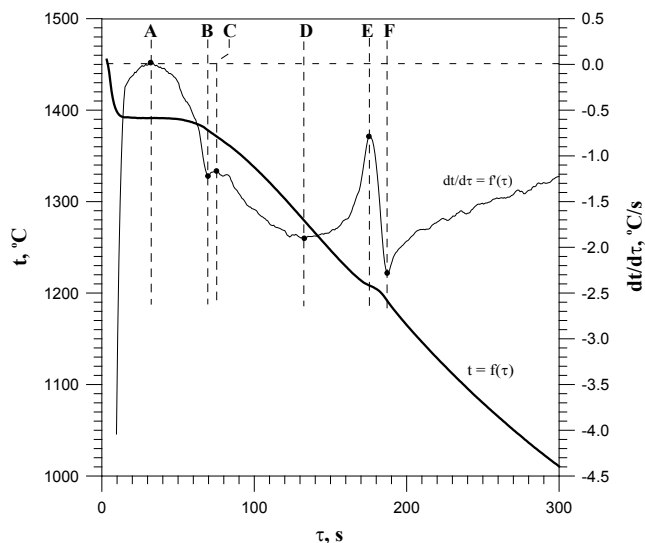
In order to determine the type of transformations taking place during the cooling operation an analysis of crystallization process was performed by TDA method. For this purpose, an examined alloy was melted in the laboratory crucible induction furnace with a capacity of 5 kg. The total weight of stock mass was 1 kg. In order to fully melt Co-Cr-Mo alloy blocks the furnace was heated to a temperature of 1500°C. The liquid alloy was poured into a sampler made of shell mass, with a thermocouple located inside it. The thermocouple was connected to a Crystallidigraph. An analysis was performed for four consecutive remeltings. After each melting and crystallization a sample was taken to metallographic studies, what was founded a series of a hardness tests. Metallographic studies were performed using a scanning electron microscope Hitachi S-3000N. Metallographic specimens (etched by Mi24Co) were observed using secondary electron imaging (SE) and backscattered (BSE). During the tests using a scanning electron microscopy a chemical analysis of selected areas was also performed with the use of EDS detector working with a microscope.

Hardness measurements concerning a ball of a diameter of 2.5 mm and load of 1840 N, were made on a Brinell hardness tester HPO-250.

3. Results and discussion

3.1. TDA method

Figure 1 shows an exemplary TDA curve registered during crystallization of the Co-Cr-Mo alloy o after its first remelting. All other curves were similar. There were the same thermal effects.



Point	τ , s	t , °C	$dt/d\tau$, °C/s
A	32	1391	0,02
B	70	1378	-1,22
C	75	1371	-1,16
D	133	1279	-1,90
E	175	1208	-0,79
F	187	1192	-2,28

Fig. 1. TDA curves registered after the first melt of investigated Co-Cr-Mo alloy and a description of the characteristic points

Three thermal effects can be observed on curves. They correspond to the crystallization of various phases in the tested alloy. The first thermal effect occurring at the highest temperatures is described by points AB. It corresponds to the crystallization of α phase which is mainly a solid solution of chromium and molybdenum in cobalt. According to studies of the chemical composition it contains: 70.24% Co, 24.97% Cr, 3.58% Mo, 0.83% Mn and 0.40% Si (Tab. 3, Fig. 2b). At the temperature $t_A = 1391^\circ\text{C}$ point A occurs. It shows the moment when the most heat was generated from α phase crystallization. Owing to the starting temperature of the measured liquids being too low, it can not be observed on curves. This temperature is also the beginning of the α phase crystallization. The end of the crystallization corresponds to point B on the curve, and takes place at a temperature $t_B = 1378^\circ\text{C}$. As a next δ phase crystallize. It is composed mainly of Cr, Co and Mo. Thermal effect derived from δ phase crystallization is described by BCD points. Compared to α solid solution it has increased concentration of Cr (49.57%) and Mo (21.65%) and decreased Co (27.81%). This demonstrates that pushing Cr and Mo atoms by crystallization of α solid solution to a liquid thereby forming suitable conditions for crystallization of this phase. The end of crystallization of this phase takes place at a temperature of $t_D = 1279^\circ\text{C}$. Starting from this temperature DEF the thermal effect begins on the TDA curves. It corresponds to the eutectic crystallization, which is composed of α phase and fine carbides. Based on literature reports it may be assumed that in this eutectic there are: $(\text{Cr}_{0,77}\text{Co}_{0,15}\text{Mo}_{0,08})_{23}\text{C}_6$ and CrC

[10, 11]. Eutectic crystallization finishes at 1192°C. At this temperature investigated Co-Cr-Mo alloy finishes its crystallization.

Exemplary microstructure of the investigated Co-Cr-Mo alloy, with different magnifications are shown in Figure 2 (a, b). Fig. 2a shows the dendritic structure of the α solid solution. Separations of the other phases crystallizing between the dendrites are shown in Fig. 2b. δ phase separations are shown as fine separations. The dark areas filled with very fine phases show eutectic solution composed of α and carbides. In all examined alloys microscope images were similar. There were the same structural components and its quantities and sizes were analogical.

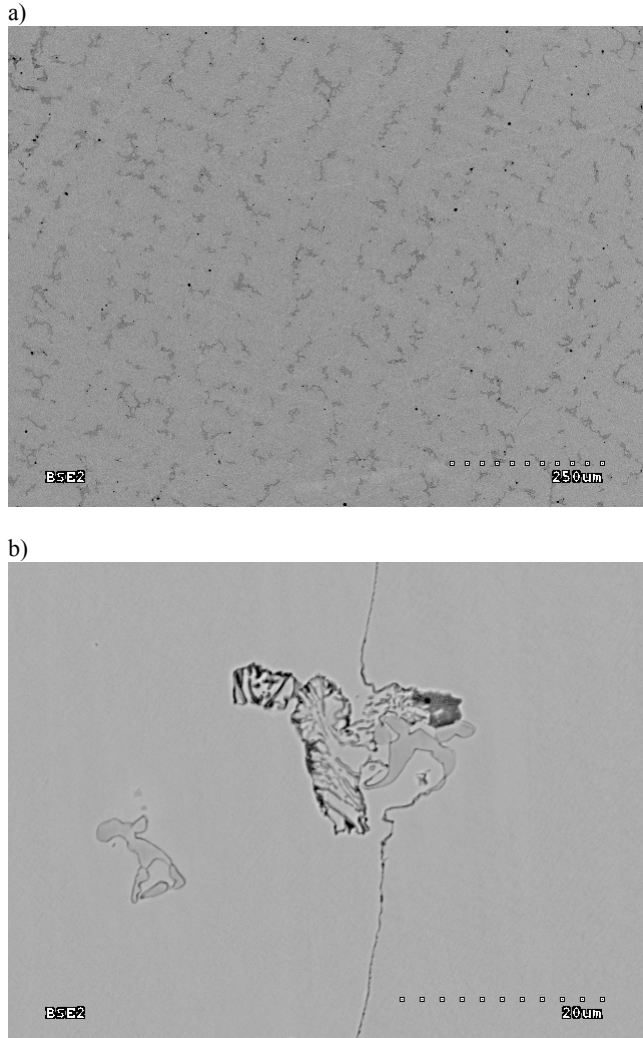


Fig. 2 (a, b). Microstructure of Biosil F single remelted, etching: Mi24Co (a – magn. $\times 120$, b – magn. $\times 2000$)
Dendritic microstructure. Phases: α -phase – solid solution cobalt based, δ phase, triple interdendritic eutectic

The presented microstructure is consistent with crystallization process presented by TDA curves.

3.2. Analysis of the chemical composition

Table 1 shows the alloy compositions of initial alloys and after subsequent remeltings. Figure 3 shows the microstructure of the alloy with points where analysis of the structural components was made, while Table 2 presents the chemical compositions of the particular components occurring in studied alloys. It is shown on the sample after two remeltings.

Table 1.
Chemical composition of the tested alloys

No. of remelting	Chemical composition (wt.%)				
	Cr	Mo	Mn	Si	Co
norm	26-30	5-7	max 1	max 1	rest
basic sample	28.3	6.0	0.6	0.8	rest
I	29.7	5.4	0.7	0.7	rest
II	28.5	5.5	0.4	0.7	rest
III	27.8	6.1	0.6	0.5	rest
IV	27.4	5.7	0.3	0.4	rest

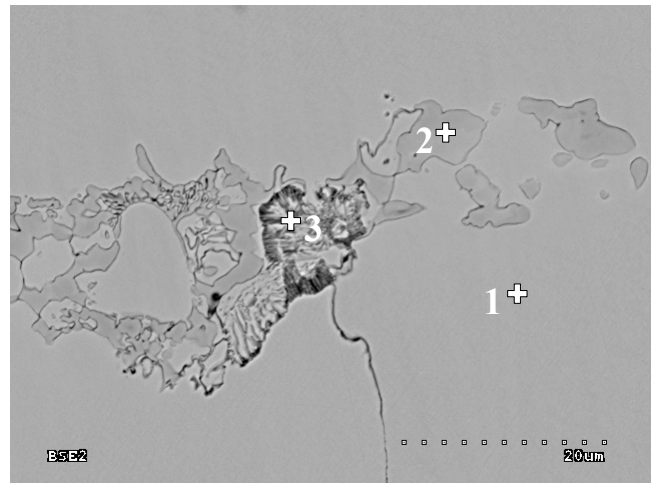


Fig. 3. Exemplary microstructure of the alloy and points analyzes the particular structural components, magn. $\times 2000$

Table 2.
Chemical compositions of the phases

Points	Chemical composition (wt.%)				
	Cr	Mo	Mn	Si	Co
1	24.97	3.58	0.83	0.45	70.24
2	49.57	21.65	0.41	0.57	27.81
3	29.62	7.81	0.63	0.53	61.41

3.3. Hardness testing

In Figure 4 results of the hardness tests after subsequent remeltings are presented.

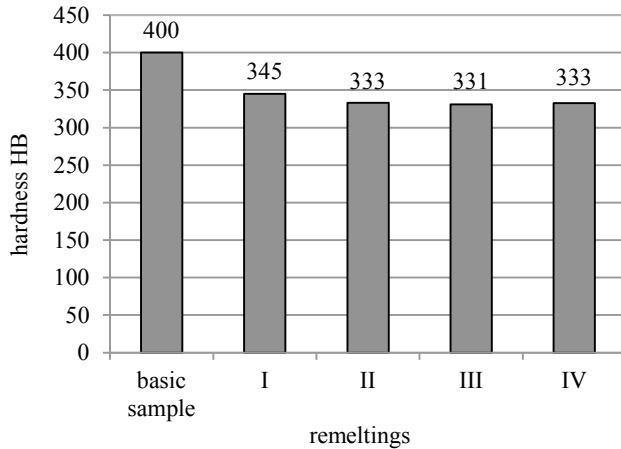


Fig. 4. The study of Brinell hardness – the average value of the individual samples

Hardness of the tested samples ranged from 345 HB for the I sample to 331 HB for III sample. There were no statistically significant differences between the hardness of the samples after subsequent remeltings.

4. Conclusions

This study shows that for all samples, regardless of the number of remeltings, the same changes occur in the composition of the alloy. Microstructures of the alloy did not differ significantly. The volume, size and distribution of the phases remain similar. The chemical compositions of all samples are in the range of compositions provided for the investigated alloy. Further to this the hardness of the samples, regardless of the number of remeltings did not show any significant fluctuations and remained within the error limit.

Taking this into account, it can be concluded that the subsequent remelting alloys should not have any significant impact on their properties and remelted alloys can be successfully used to execute prosthetic works.

References

- [1] Rajan, K. (1983). Thermodynamic assessment of heat treatments for a Co-Cr-Mo Alloy. *Journal of Materials Science*. 18, 257-264.
- [2] Bellefontaine, G. (2010). *The corrosion of CoCrMo alloys for biomedical applications*. M. Res. thesis. Birmingham.
- [3] Carek, A., Zivko Babic, J., Schauperl, Z. & Badel, T. (2011). Mechanical Properties of Co-Cr Alloys for Metal Base Framework. *International Journal of Prosthodontics and Restorative Dentistry*. April-June 1(1), 13-19.
- [4] Jakobsen, S.S, Larsen, A., Stoltenberg, M., Bruun J.M. & Soballe, K. (2007). Effects of as-cast and wrought Cobalt-Chrome-Molybdenum and Titanium-Aluminium-Vanadium alloys on cytokine gene expression and protein secretion in J774A.1 macrophages. *Eur Cell Mater*. 14, (45-55).
- [5] Marciniak, J. (2002). *Biomaterials*. Gliwice. Silesian University of Technology Press.
- [6] Klimek, L., Pierzynka, R., Błaszczuk, T., Burnat, B., Scholl, H. & Marciniak, S. (2009). The effect of re casting on corrosion of Ducinox prosthetic alloy. *Archives of Foundry Engineering*. 9(3). 67-70.
- [7] Khamis, E. & Seddik, M. (1995). Corrosion evaluation of recasting non-precious dental alloys. *International Dental Journal*. 45, 209-217.
- [8] Ozdemir, S. & Arıkan, A. (1998). Effects of recasting on the amount of corrosion products released from two Ni-Cr base metal alloys. *Eur. J. Prosthodont. Rest. Dent*. 6(4), 149-153.
- [9] Ameer, M.A., Khamis, E. & Al-Motlaq, M. (2004) Electrochemical behavior of recasting Ni-Cr and Co-Cr non-precious dental alloys. *Corrosion science*. 46, 2825-2836.
- [10] Klimek, L. & Pietrzyk, B. (2004). Electron backscatterer diffraction as a useful method for alloys microstructure characterization. *Journal of Alloy and Compounds*. 382, 17-23.
- [11] Klimek, L., Pietrzyk, B. (2004). Microstructural characterization of Co – Cr – Mo alloy. *Acta Metallurgica Slovaca*. 10, 866-869.