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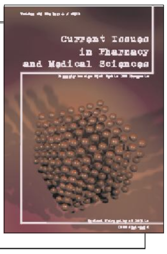

Effect of recasting of CoCrMoW dental alloy on its microstructure and corrosion resistance

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ABSTRACT

The procedure consisting in the recasting of previously cast alloy is frequently used in dental laboratories in order to reduce the cost of permanent partial dentures being produced. Such a procedure may result in changed chemical composition of newly produced alloy and may influence its microstructure and corrosion resistance. In this research, the dental alloy CoCrMoW with the trade name Remanium 2001 (Denaturum, Germany) was used. Three groups of dental alloys were prepared by mixing 50% brand new alloy with alloy remnants from previous castings. The first group used 100% brand new alloy and served as control one (R1). The second group (R2) consisted of equal amounts of brand new alloy and alloy remnants cast only once. The third group (R3) contained 50% brand new alloy and alloy cast twice. Microstructural analysis was performed as well as chemical composition and corrosion in artificial saliva environment. The following corrosion resistance has been demonstrated on the basis of electrochemical research for three cobalt alloys: R1R3R2. Furthermore, it has been demonstrated that new material should be used in casting, and if previously cast material is used, it should be mixed with new material in the ratio 50:50. The recasting procedure can be safely used in dentistry.

Keywords: recasting, cobalt alloy, durability of prosthetic devices, corrosion resistance

INTRODUCTION

Corrosion resistance is one of the most important features of prosthetic alloys. The corrosion processes occurring in prosthetic alloys have negative impact on their durability as well as harmful effect on the human organism [7].

Post process materials are used for recasting processes [13] in dental laboratories not only in case of noble metals alloys but also in case of cobalt alloys. From references [1,13], it appears that the properties of recasted alloy may differ from the properties of a new alloy purchased by the manufacturer. The differences may be associated with its chemical composition, castability as well as with mechanical properties. However, the opinions concerning changes of mechanical properties as a result of recasting are extremely divided. Some authors [1] state that these properties can increase or decrease compared with the new alloy [13]. However, there are experimental studies described in literature [9] which documented changed chemical composition of final products under the influence of successive recasting processes and development of new phases determining the changes in alloy properties. The deterioration in the scope of corrosion properties [3] or even cytotoxicity [2] is also possible after multiple recasting.

The impact of Co–Cr alloy recasting on its physical and chemical properties was investigated by Harcourt [4]. Its chemical analysis was carried out before the first recasting and after one, six, nine and thirteen recasting processes. The obtained results imply that castability is reduced and recasting process is more difficult as a result of changes in chemical composition after recasting [1].

However, Sheffick [12] found that the behaviour of Co–Cr and Ni–Cr alloys was less favourable than the behaviour of type III gold and that this behaviour was nonconforming with recasting procedures in the scope of chemical composition. Furthermore, Sheffick concluded that the first recasting process for these alloys should be carried out with the addition 50% of new alloy (w/w) in order to improve castability and percentage content of individual elements in these alloys [1]. Khamis and Seddik [6] investigated the impact of recasting (up to 4 times) on corrosion properties of Ni–Cr and Co–Cr technical dental

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alloys. They found that there was no effect of successive recasting on corrosion resistance of Co and Mo containing alloy.

The purpose of the present study was to evaluate the effect of addition of remelted materials on microstructure, chemical composition and corrosion resistance of CoCrMoW alloy.

MATERIAL AND METHODS

Remanium 2001 dental alloy (Dentaurum, Germany) with cobalt matrix consisting of 63% Co, 23% Cr, 7,3% Mo, 4,3% W, 1,6% Si and Mn% and N% (w/w in accordance with data furnished by the manufacturer) has been used in tests. This alloy is used for casting of denture elements (among others crowns and bridges). Three groups of identical dental alloys have been prepared in order to simulate standard applications used in dental laboratories. The first group was cast in 100% from brand new alloy as a control group (R1). The other groups were made of 50% brand new alloy and 50% remnants from the previous group (tab. 1). The second group (R2) was cast as the mixture of equal amounts of the new alloy and the alloy after previous recasting. The alloy used in the third group (R3) was prepared by adding new alloy and 50% remnants from second group (R2).

Table 1. Different recast alloy groups used in this study

Groups	Procedure
Control group (R1)	Cast from 100% new alloy
Cast once (R2)	Cast from 50% new alloy and 50% remnants from first group
Cast twice (R3)	Cast from 50% new alloy and 50% remnants from second group

The process associated with preparation of specimens made of Remanium 2001 alloy was carried out under conditions prevailing in the professional prosthetic dental laboratory in accordance with procedures applied in production of metal denture elements. The castings were produced in investment casting process by means of vacuum – pressure casting machine Nautilius (Bego, Germany) and ceramic crucibles.

The specimens used for investigation of chemical composition were made as the discs with diameter of Ř 25 mm and thickness of 2 mm. The discs were subjected to grinding by means of water abrasive papers with grain size of 220, 600 and 1200 correspondingly. After grinding, the specimens were mechanically polished by means of diamond particles suspension 3 m and silica oxides particles suspension 0.05m as well as washed in acetone and dried thereafter.

The analysis of chemical composition was performed by means of Q4 Tasman 130spark emission spectrometer (Bruker, Germany) in detail Co130 testing channel used to complete five (5) analyses (sparking sequences) for each specimen.

Susceptibility to corrosion was determined for tested materials by means of accelerated electrochemical tests using potentiodynamic method. The preparation of the surface of specimens (cuboids with dimensions of 10×10×2 mm) for corrosion tests was identical to the preparation for analysis of chemical composition. The potentiodynamic measurements were carried out in artificial saliva solution (pH=5.3), at temperature 37°C, by means of Atlas 0531 set dedicated for corrosion tests. The composition of artificial saliva was prepared on the basis of ISO 10271:2001 standard: 0.4g NaCl, 0.4g KCl, 0.795g $CaCl_2 \cdot H_2O$, 0.78g $NaH_2PO_4 \cdot H_2O$, 0.005g $Na_2S \cdot 9H_2O$, 1g of urea and 1000 ml H_2O. The tests were carried out in electrochemical cell with three electrodes, with control electrode made of platinum and with reference electrode in the form of calomel electrode (SCE) placed in Lugin's capillary filled with artificial saliva solution. The surface area of electrode under test was equal to 1cm^2. The value of open circuit potential (E_{ocp}) without external polarization was recorded during the period of 18 h. After determination of E_{ocp} polarization curves were recorded with automatic scanning potential at 1 mV/s from –400 mV to +700 mV. The density of corrosion currents i_{corr} and potentials E_{corr} were determined from Tafel curves using potentiodynamic curves analysis with AtlasLab program. The surface structure of tested materials after completion of corrosion tests was evaluated by means of Phenom G2 pro desktop scanning microscope.

RESEARCH METHODOLOGY AND DISCUSSION

The microstructure of tested cast alloys is characterized by typical coarse grained dendritic structure (Fig. 1). Dendritic segregation areas were detected within cristalites as well as continuous primary precipitations in interdendritic spaces and along boundaries of cristalites. The microstructure of castings containing remelted material is similar to microstructure of brand new castings. There were no inclusions, which could originate from charge contamination in the form of the investment material. Furthermore, diversified shape of carbides was revealed in the course of SEM analysis. The carbide phases are characterized by dual structure i.e. occurring in the form of blocky precipitations as well as lamellar precipitations („pearlitic type"). In the opinion of some authors [10], the lamellar structure of carbides is caused by cooling rate variation between 8 and 16°C/min; 35°C/min [16] is the maximum cooling rate for the creation of eutectoid phase [11]. Dispersion carbide precipitations may have impact on increased reinforcement of an alloy and its reduced plasticity.

From the chemical composition analysis in microareas (Fig. 2) it appears that carbides are characterized by

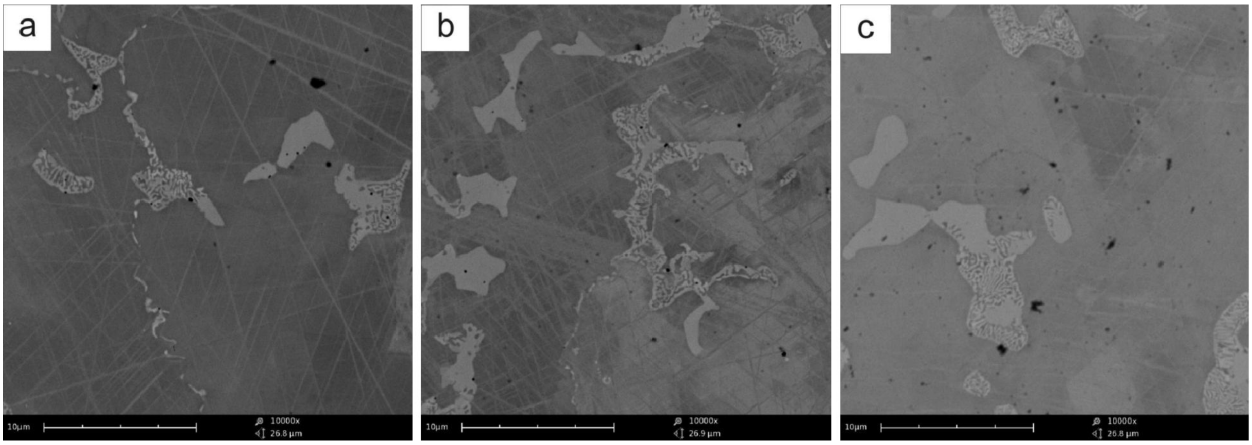

Fig. 1. SEM microstructure castings: (a) control sample R1, (b) recast R2, (c) recast R3

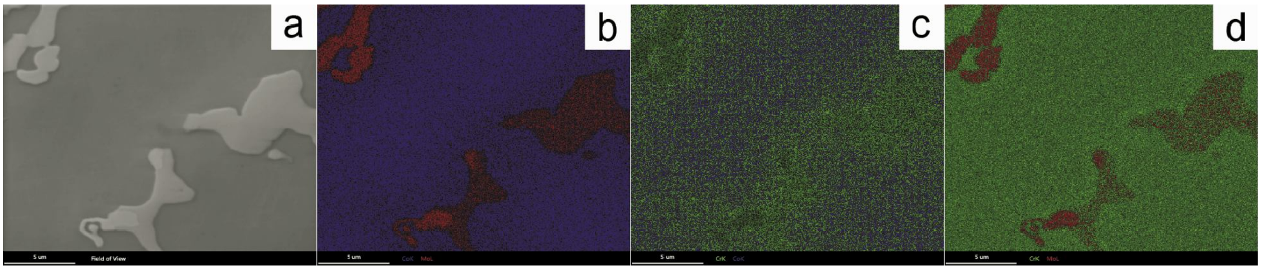

Fig. 2. Representative SEM microstructure of the as-cast Remanium 2001 and chemical composition maps of selected elements: (a) field of view, (b) maps of Co and Mo, (c) maps of Cr and Co, (d) maps Cr and Mo, legend colors: Mo – red, Co – blue, Cr green

high Mo and Cr content. XRD tests [14] demonstrated the coexistence of carbides in examined alloys, mainly $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2, causing the reinforcement of solid cobalt solution.

The changes in chemical composition of materials under test are illustrated in Tab. 2. It should be emphasized that there is information about elements concentrations under 1% indicated in manufacturer's data. It is extremely important to control the content of carbon, which occurs in various amounts and reacts with alloy components creating carbides depositing on grains boundaries. The carbon content for R1 and R2 groups is similar and similar alloy reinforcement can be expected. However, a significant change in carbon concentration has been denoted in remelted materials from R3 group which may result in increased hardness of alloy. The carbon content within 0.059÷0.073% indicates that materials under analysis belong to low carbon alloys group.

The electrochemical corrosion behaviour of Co-Cr dental casting alloys depends mainly on Cr and Mo contents in an alloy. The content of molybdenum is less important than chromium content in an alloy. However, in case of lower Mo content, the alloy is more susceptible to pitting corrosion. Hodgsoni et al. [5] indicate that passive layer on Co-Cr alloys predominantly consists of chromium oxides. The corrosion resistance of Co-Cr alloys varies depending on their chemical composition and on the uniformity of created passive layer. The differences in microstructure may affect the initial growth, density and uniformity of this passive layer. The thickness of passive layer spontaneously developing on Co-Cr alloys may reach 1÷4nm and it contains mainly chromium oxide (Cr_2O_3) and insignificant percentages of cobalt and molybdenum oxides [8]. Higher contents of Cr_2O_3 and MoO_3 in passive layer may lead to increased resistance to metal ions migration through the passive layer. Based on free corrosion potential curves (open circuit potential E_{ocp})

Table 2. Chemical composition of alloys test (only the main elements included) [wt. %]

Groups	C	Co	Cr	Mo	W	Si	Mn	N
R1	**0.059**	62.77	22.86	8.426	~4.299	1.136	0.152	0.192
Sd.	0.0076	0.111	0.125	0.085	0.034	0.013	0.0020	0.052
R2	**0.060**	62.52	22.84	~8.570	~4.320	~1.221	0.153	0.203
Sd.	0.0038	0.150	0.403	0.221	–	0.028	0.0022	0.071
R3	**0.073**	63.23	22.05	8.435	~4.315	1.199	0.146	0.184
Sd.	0.017	0.904	1.230	0.085	0.011	0.047	0.014	0.057
According to manufacturer	–	63	23	7.3	4,3	1,6	<1	<1

(Fig. 3a) it may be concluded that biomaterials under tests are characterized by very good corrosion resistance. The curves open circuit potential vs. time reflect the passive and stable state (open circuit potential vs. time maintaining a constant level) in metal and in passive layer in corrosive solution environment on the surface of materials under tests. The stabilization of corrosion potential can be seen after measurement time of about 1200 s. The highest values of E_{ocp} have been recorded for R1 alloy whereas R2>R3. Increased values of open circuit potential (E_{ocp}) may reflect better passivation of tested material and higher general corrosion resistance.

The value of corrosion current density (Fig. 3b) is used in electrochemical tests as the measure of corrosion process intensity. The lower is the value of corrosion current density, the higher the corrosion resistance. R1 specimen without any additives of recycled material (Tab. 3) is characterized by the highest corrosion resistance in our tests. The corrosion resistance of three base metals alloys is as follows: R1>R3>R2. Such corrosion behaviour may be associated with the open circuit potential, because corrosion potential in R3 alloy moves towards more positive values in comparison with R2 alloy because of the formation of passive layers consisting of chromium oxides that protect the surface and lead to the reduction of corrosion current density i_{corr} in R3 alloy.

Table 3. Corrosion parameters in artificial saliva

Groups	E_{corr} (V)	i_{corr} (A/cm^2)	R_{pol} ($\Omega\cdot$cm^2)
R1	$-39.511\cdot10^{-3}$	$81.091\cdot10^{-9}$	$529.321\cdot10^{3}$
R2	$-163.440\cdot10^{-3}$	$821.005\cdot10^{-9}$	$134.360\cdot10^{3}$
R3	$-118.960\cdot10^{-3}$	$480.425\cdot10^{-9}$	$115.240\cdot10^{3}$

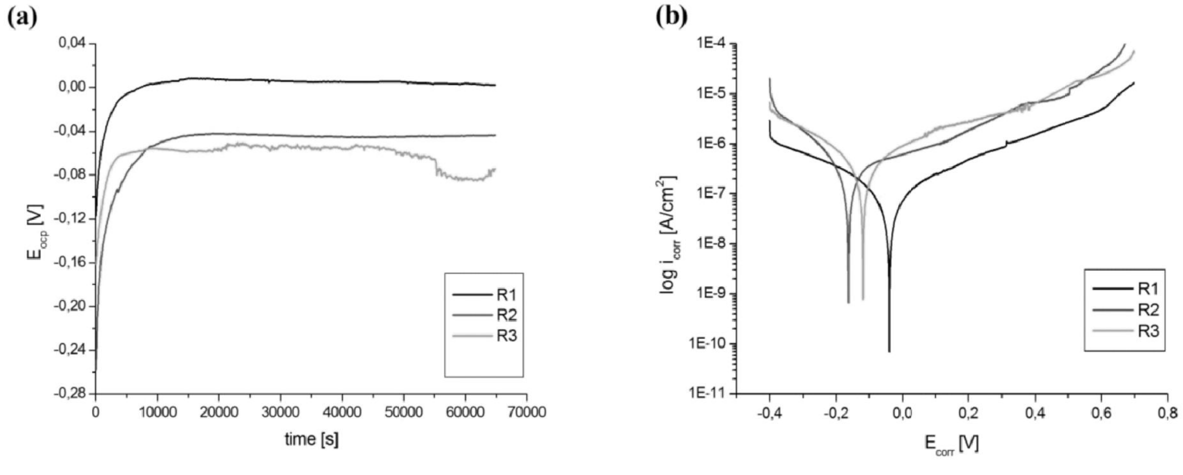

Fig. 3. Representative electrochemical curves of recast Remanium 2001 in artificial saliva: (a) open circuit potential curves after 18 h tests (b) the potentiodynamic polarization curves

According to data available in the literature [3] the values of corrosion potential in the oral cavity are between –300 and +300 mV referred to saturated calomel electrode. The rate of corrosion is reduced at this potential as a result of the formation of protective oxide layer on the surface and its further development. Irrespective of deteriorated corrosion resistance of R2 and R3 in comparison with R1 control group, it can be seen that electrochemical parameters obtained for these alloys are positive indicator of satisfactory corrosion resistance (potential within the range between –300 and +300 mV) in artificial saliva environment.

The carbides themselves are characterized by excellent corrosion resistance. During alloy solidification phase, carbon reacts with chromium or molybdenum forming carbides and devoiding the matrix of an element responsible for the corrosion resistance (Fig. 4). Chromium depleted zones occur in direct vicinity of the carbide as a result of this privileged chromium – carbon bond. These zones constitute corrosion attack areas.

SUMMARY

SEM microstructure analysis demonstrated that carbide phases in all alloys are characterized by dual structure and occur in the form of massive precipitations and lamellar precipitations. No significant differences have been found in chemical composition of the groups of tested alloys, except of carbon content in R3 group, which is about 20% higher than in R1 and R2 groups. Electrochemical tests have demonstrated that the corrosion resistance of three base metals alloys is as follows: R1R3R2 and open circuit potential measured in artificial saliva vs. SCE is included in the safe range between –300 and +300 mV. Chromium depleted zones in carbide vicinity are the corrosion attack areas. It has been demonstrated that new material should be used in casting, and if previously casted material is used, it should be mixed with new material. It appears from electrochemical tests and from chemical composition analysis that recasting procedure may be safely used in dentistry and may reduce the costs of CoCrMoW castings. The authors suggest

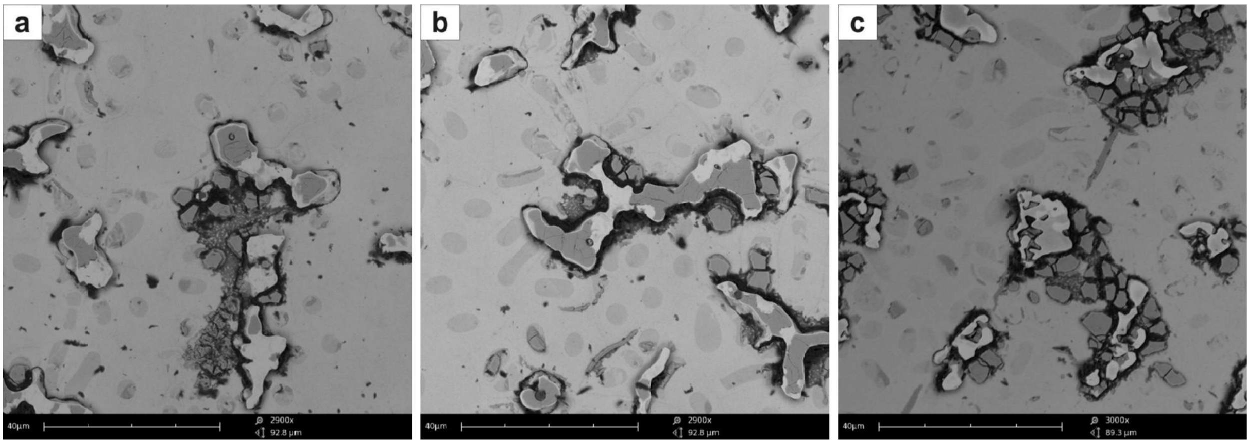

Fig. 4. SEM images of CoCrMoW alloy after polarization test: (a) control sample R1, (b) recasting R2, (c) recasting R3

investigating the effect of increased number of recasting processes on the alloy properties.

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