Influence of the Casting Conditions on the Structure and Properties of a Co-Cr-Mo Dental Alloy

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The paper aims to investigate the influence of the casting conditions and in particular of the mold temperature (T_{mold}) - as the main parameter of the solidification process - on structure, corrosion resistance and mechanical properties of a Co-Cr-Mo dental alloy. The alloy has been cast at T_{mold} = 500 and 900 °C and the solidification structure has been investigated by using optical and scanning electron microscopy (SEM). Corrosion of the as-cast alloy in two different artificial salivas having pH = 6.0 and 7.7, and mechanical testing revealed that casting Co-Cr-Mo dental alloy at lowest permissible temperature (500 °C) does not adversely affect the structure and properties of the alloy. Due to the highest melt solidification rate, an improvement in structure and corrosion resistance while maintaining the mechanical properties was found.

Keywords: Co-Cr-Mo dental alloy, casting, mold temperature, corrosion, artificial saliva

Co-Cr-Mo alloys are typically indicated for construction of metal frameworks for removable partial dentures due to their adequate properties, such as good castability, dimensional accuracy, corrosion strength, surface smoothness, low modulus of elasticity and ductility [1]. In addition to a lower cost, Co-Cr-Mo alloys, as metal-ceramic restoration alloys, should have good mechanical properties, high flow rate, accurate cast adaptation, ease of handling, finishing and polishing, weld strength and, above all, biocompatibility [2,3]. Other major advantages of these alloys are their lower thermal expansion coefficient and higher thermal stability during porcelain firing at high temperatures. But all these properties can undergo dramatic changes if the chemical composition and technological parameters are modified [4,5]. Contents of chromium and of the other elements are so selected that the matrix is composed of solid solution of chromium and molybdenum in cobalt (γ) [6,7]. An important factor that decides the structure of these materials is the high solubility of the alloying elements in γ. This gives the possibility of not only solution hardening but also of its controlled decomposition that leads to stable phases resulting in precipitation hardening. Both molybdenum and tungsten – often present in these alloys – are added to obtain the solution hardening effect. These two element are usually applied interchangeably. Depending on concentration of carbon - which can reach 0.40 % - and the alloying elements, precipitating can take place due to the eutectic reaction or simple precipitation [8,9]. Precipitation hardening in such alloys is caused by interdendritic precipitates of carbides of the alloying elements. Because of the presence of chromium, the $M_{23}C_6$-type carbides dominate in the cobalt-based alloys [10], but the chromium-rich carbides (M_7C_3 and M_3C_2) can be also found. Thermal processing has been commonly used in Co-Cr alloys to modify the potential carbide precipitation reactions, so the solidification rate can play a similar role as the chemical composition [11].

Together with alloy composition, the type of investment and the investing technique have great influence on the final quality of casts. Silica-based investments provide good castability, but the surface quality is pledged by the formation of nodules. On the other hand, phosphate-agglutinated investments produce excellent superficial quality but give lower castability because the gases are not easily released from the mold. In the first case, the mold temperature (T_{mold}) can be decreased, but in the second case, it has to be higher [12].

The castability of an alloy is often associated with its ability to fill the mold [13], and mold filling is dependent on numerous factors other than the metal or alloy, such as T_{mold}, superheat of the melt, applied pressure, type of machine, and chemical stability of the investment against molten alloy.

An improvement in the structure and mechanical properties of a biomedical Co-Cr-Mo alloy under as-cast condition could be the positive effect of the grain refinement, which requires an extensive nucleation and the inhibition of crystals growth. The major advantage of finer grained materials is a reduced scatter in the properties [14-17].

All above mentioned suggest that T_{mold} can influence – as effect of the solidification rate – both the structure, corrosion resistance and mechanical properties [18]. Many results are divergent because most research has been conducted on samples / ingots with sizes and masses certainly different from those of dentures.

Considering that conventional preheating furnaces have low accuracy (more than 10°C plus/minus from the nominal temperature shown in the display) and usually it takes more than 1 min before casting is completed after the removal of molds from the oven, it is difficult in practice to determine the real temperature of the mold at the moment of casting, which could be considered a limitation of the casting procedure [18]. Finally, a question remains standing: is T_{mold} a technological parameter that has to be strictly keeped? And related to this, how much influence does this parameter have on the final result of the casting?

The paper aims to investigate the influence of the casting conditions and in particular of T_{mold} - as the main parameter of the solidification process - on structure,

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Table 1
THE CHEMICAL COMPOSITION OF THE
Co-Cr-Mo ALLOY BEFORE CASTING

Cr	Mo	Si	Mn	C	Fe	Co
28.91	5.12	0.52	0.44	0.38	0.27	balanced

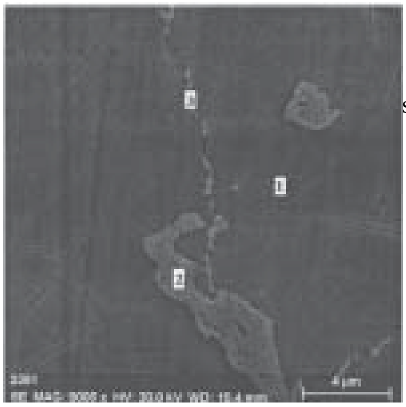


Fig. 1. The initial structure of the Co-Cr-Mo alloy and the EDX analisys results for the nominated points 1 ... 3 as Co:Cr:Mo ratio:1) 9 : 2.7 : 1; 2) 3.5:1.8:1; 3) 4.8 : 2 : 1

corrosion resistance and mechanical properties of a Co-Cr-Mo dental alloy. The alloy has been cast into the mold having 500 and 900 °C, respectively and the solidification structure has been investigated by using SEM. Corrosion of the as-cast alloy in two different artificial salivas having ph = 6.0 and 7.7, and mechanical testing revealed that casting Co-Cr-Mo dental alloy at lowest permissible temperature (500 °C) does not affect substantially the structure and properties of the alloy. However, as effect of the highest melt solidification rate, a slightly improvement in corrosion resistance while maintaining the mechanical properties takes place.

Experimental part

Co-Cr-Mo alloy

The chemical composition of the Co-Cr-Mo alloy (Bredent F400) determined by using spectrometry analysis (Foundry Master 1J0013 Spectrometer) is shown in table 1.

The initial structure of the alloy consists in solid solution γ and dominant M$_{23}$C$_6$-type carbides (fig.1). Despite the high amount of Cr, no hard and brittle Cr-rich s-phase which decreases corrosion resistance due to local Cr depletion around the s-phase precipitates, was present. This will be confirmed later by XRD.

Investing

An ultrafine phosphate-bonded precision investment material (Feguravest) was used. To control the expansion of the mold by corresponding contraction of the casting alloy, the ultrafine investment powder was stirred with the diluted Feguravest liquid (performing a dilution of 100% with demineralized water). The lower the concentration of the mixing liquid, the higher the overall expansion of the investment material. After manual premix with a spatula in a mixing bowl and stir for around 60 s under vacuum, the casting ring placed on a lab vibrator was poured out carefully and then left to harden for 30 min. The casting ring was preheated to the end temperature (950°C) in three stages using standard stepwise heating shown in table 2. The three stages correspond to the transformation of the cristobalite and quartz, and sintering of quartz, respectively.

Series of three rectangular cross-section samples for tensile testing and four disc-shaped samples for corrosion testing having dimensions described in subsequent subsections have been invested as above mentioned. The gating system consists in sprues and air vents of 3 and 1 mm in diameter, respectively.

Table 2
THE STEPWISE HEATING PROGRAM

Stage	Heating rate [°C/min]	T [°C]	Holding time [min]
1st	5	280	40
2nd	7	580	30
3rd	9	950	60

Melting and casting

The Co-Cr-Mo ingots as cylinders with 15 mm in height and 8 mm in diameter were melted in an inductive furnace into an alumina crucible and then centrifugally cast before the oxide skin tears up ($T_{melt} \approx 1350°C$) in molds having two different temperatures: 500 and 900°C, respectively. The temperature of 500°C was reached with the furnace cooling rate, so the mold doesn’t leave the oven during slowly cooling. For the latest case, the temperature of 900 °C was reached by air cooling, so the melting must precede the removal of the mold from the oven therefore the casting takes place precisely at the prescribed temperature.

Structural investigations

The structure of as-cast Co-Cr-Mo alloy was investigated by using optical microscopy (Zeiss Axiobserver AIM) and SEM (Vega Tescan II). The samples previously polished were prepared by electrochemical etching (AX-D1/150 W cell) using a solution of 10% H$_2$SO$_4$ + 90% ethyl alcohol (vol %) and a current of 1.5 A.

The XRD analysis of the samples were carried out using a Philips X-ray diffractometer (PANalytical X’Pert MRD) operating with a monochromatized Cu Kα radiation (λ = 1.54056 A) in the Bragg–Brentano schema. The diffraction patterns were obtained in the 2θ range of 35–100 °, using a step size of 0.0131 ° and a scan speed of 0.05471 °/s.

Corrosion testing

To evaluate the Co–Cr–Mo alloy stability, open-circuit potential (ocp), potentiodynamic and cyclic polarization measurements were recorded in two different artificial salivas Fusayama (KCl (0.4 g/L), NaCl (0.4 g/L), CaCl$_2$.2H$_2$O (0.906 g/L), NaH$_2$PO$_4$.2H$_2$O (0.690 g/L), Na$_2$S.9H$_2$O (0.005 g/L), Urea (1 g/L)) having *p*H = 7.7 and 6, respectively. The *p*H-values were corrected by addition of NaOH (*p*H = 7.7) or lactic acid (*p*H = 6).

The ocp measurements were conducted for 15 mins. For the potentiodynamic polarization, the range of the potential was swept from -1800 to +1500 mV at a scanning rate of 1 mV/s. For the cyclic polarization, the measurements were performed from the anodic to cathodic region by sweeping the potential at 5 mV/s from -1500 to +2000 mV and back to 0 mV, respectively. Three replicates of the electrochemical experiments were performed on different samples and representative results are presented: ocp, corrosion potential (E_{corr}), corrosion current density (i_{corr}), passivation potential (E_{pas}), breakdown potential (E_{bd}), and passivation current density (i_{pas}) measured at 0 mV potential.

The tests were carried out using a Voltalab 21 (PGP 201) potentiostat/galvanostat from Radiometer, with automatic data acquisition. The electrochemical cell having a satured calomel electrode as reference electrode, a Pt counter electrode and Co-Cr-Mo discs as working

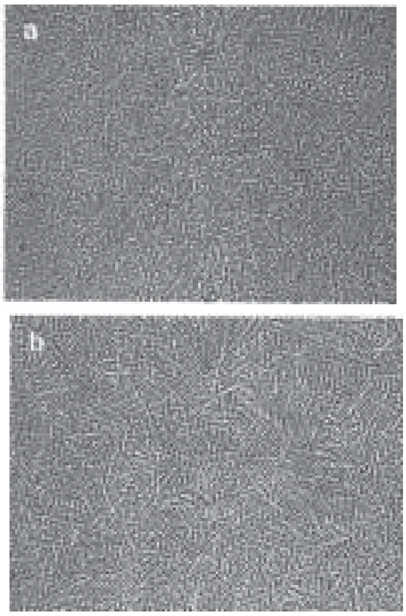


Fig. 2. The optical micrographs of samples cast at different T_{mold}: a) 500 °C; b) 900 °C (× 100)

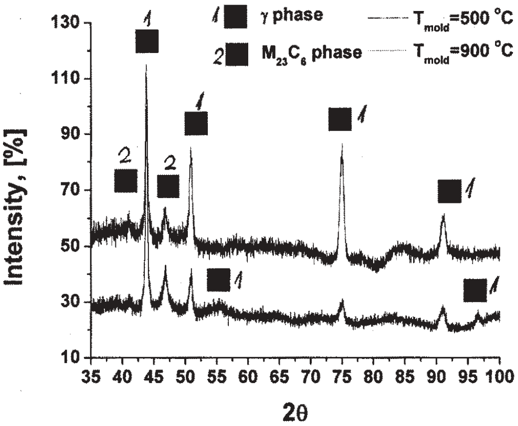


Fig. 3. XRD patterns of the Co-Cr-Mo alloy cast at T_{mold} = 500 and 900 °C

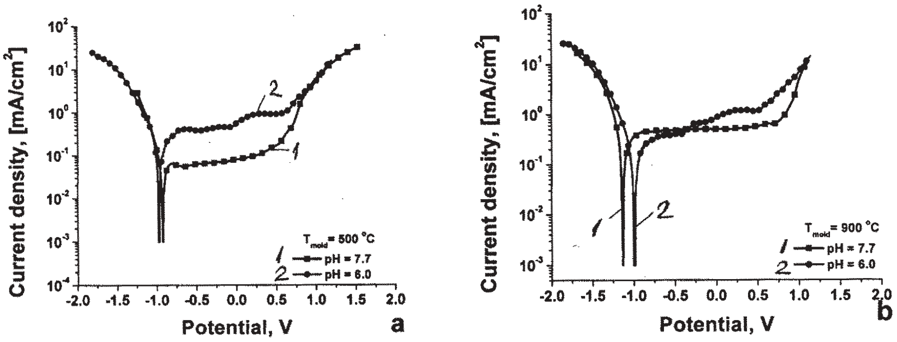


Fig. 4. Potentiodynamic polarization curves for the cast Co-Cr-Mo alloy: a) 500 °C;b) 900 °C

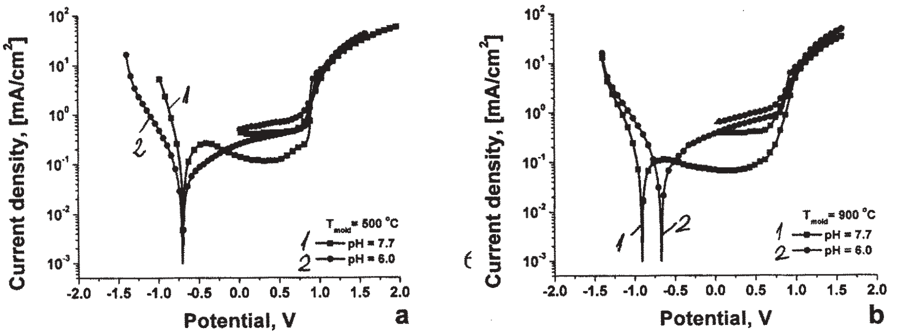


Fig. 5. Cyclic polarization curves for the cast Co-Cr-Mo alloy: a) 500 °C;b) 900 °C

electrodes was used. After casting in the above mentioned conditions, the discs with an exposed surface area of 1 cm^2 and 0.7 mm in thickness were mechanical polished by using 0.3 micron alumina suspension. Finally the corrosion samples were subjected to ultrasonic cleaning. After the cyclic polarization, all samples were investigated by SEM.

Testing of the mechanical properties

To evaluate the mechanical properties after casting at different T_{mold}, tensile testing was carried out according to ISO 6892-1: 2009. Proportional test samples with rectangular cross-section (0.7 × 4 mm), gauge length of 20 mm and total length of 44 mm were tensile tested to determine the proof strength (Rp), the tensile strength (Rm) and elongation at fracture (A). All specimens were obtained by casting as was above mentioned. The tensile tests were conducted at room temperature using a computer-controlled testing machine (Instron 3382) with a constant crosshead speed of 1 mm/min.

Results and discussions

Figure 2 shows the optical micrograph of the as-cast Co-Cr-Mo alloy at 500 and 900°C, respectively. It is obvious that for T_{mold} = 500 °C (fig. 2a), which implies a higher nucleation rate due to the increased temperature gradient, a grain refinement took place. Because there is no any change in chemical composition between the two cases and the structural form factor of dendritic arms (defined as length to width ratio) remains constant, the grain refinement is the result of the solidification conditions [18,19].

XRD patterns shown in figure 3 confirm the presence of γ-phase and $M_{23}C_6$-type carbides without significant changes in γ to $M_{23}C_6$ ratio for both Co-Cr-Mo alloys cast at T_{mold} = 500 and 900 °C, respectively. And what is the most important, for both cases, no brittle Cr-rich s phase was identified. This will be later certified by the achieved elongations at fracture get from the tensile tests.

In figures 4 and 5 are shown the potentiodynamic and cyclic polarization curves for the Co-Cr-Mo alloy cast at different T_{mold}. It was found that no matter the considered casting conditions, the corrosion process was similar. The evolution of the current density in cyclic polarization highlights that during the electrochemical process the pitting occurs. However, there are some differences of the corrosion parameters as shown in table 3. Both the higher ocps and lower i_{corr} indicate a better stability of the Co-Cr-

Parameter \ Conditions	T_{mold} = 500 °C		T_{mold} = 900 °C	
	pH = 7.7	pH = 6.0	pH = 7.7	pH = 6.0
ocp	-279.9(83.297)	-364.0(24.041)	-392.5(14.849)	-405.0(32.527)
E_{corr}, mV	-868.5(241.901)	-981.5(9.758)	-1091.9(40.800)	-991.8(6.930)
i_{corr}, mA/cm^2	0.127(0.0045)	0.085(0.0025)	0.193(0.0408)	0.186(0.0334)
E_{pas}, mV	-807.0(2.828)	-700.5(3.536)	-879.0(19.799)	-850.0(1.414)
E_{bd}, mV	624.0(127.279)	541.0(9.899)	638.0(107.480)	534.0(38.891)
i_{pas}, mA/cm^2	332.5(115.709)	710.0(285.671)	640.0(117.380)	615.0(264.458)

Tabel 3
THE CORROSION PARAMETERS OF THE AS-CAST Co-Cr-Mo ALLOY

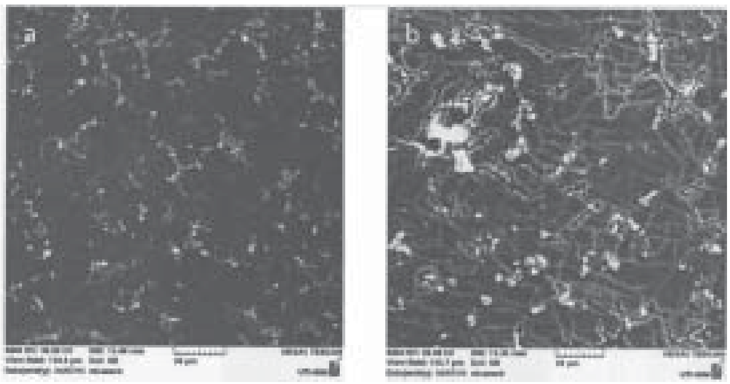


Fig. 6. SEM images for as-cast Co-Cr-Mo alloy immersed in artificial saliva having *p*H = 6: a) T_{mold} = 500 °C; b) T_{mold} = 900 °C

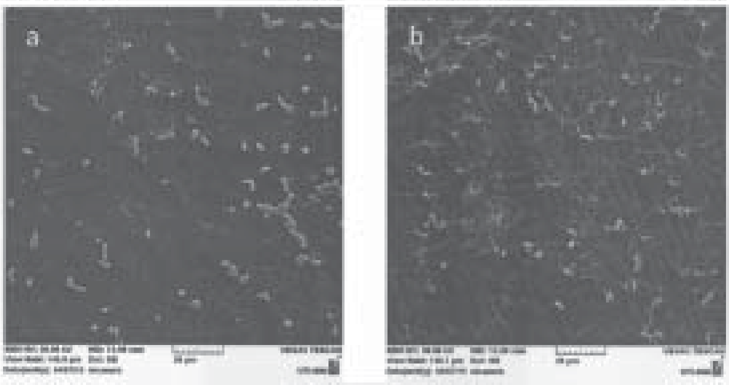
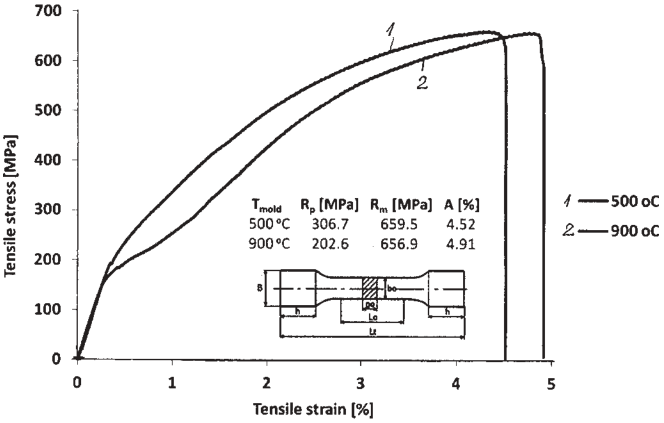


Fig. 7. SEM images for as-cast Co-Cr-Mo alloy immersed in artificial saliva having *p*H = 7.7: a) T_{mold} = 500 °C; b) T_{mold} = 900 °C



T_{mold}	R_p [MPa]	R_m [MPa]	A [%]
500 °C	306.7	659.5	4.52
900 °C	202.6	656.9	4.91

Fig. 8. Tensile stress vs. tensile strain for cast Co-Cr-Mo alloy and the main mechanical features

Mo alloy cast at T_{mold} = 500 °C. In other words, for this case, the passivization takes place at lower current density which shows a better corrosion resistance of the alloy in basic environment [20-22].

From figures 6 and 7 it can be seen the accelerated pitting corrosion when immersing the alloy in acid saliva. But the stability of the as-cast alloy corresponding to T_{mold} = 500 °C is better.

Tensile testing aims to confirm the mechanical behavior of the material as response to the possible changes in structure. Because there is no significant changes in the g to $M_{23}C_6$ ratio for both cast Co-Cr-Mo alloys it is expected that there is no spectacular diferrences in tensile stress vs. tensile strain curves. Figure 8 shows the results of tensile testing from which it appears that the Young modulus (as the slope of the linear portion) and R_m are practically identical, with a slightly modification of A due to the supplimentary precipitation of carbides in the alloy cast at T_{mold} = 500 °C. As a result, A decreases with aproximatelly 0.4%, which is perfectly normal, therefore the alloy doesn't get supplementary brittleness. A difference in R_p appears because of changes in tensile strain at yield (0.84% for T_{mold} = 500 °C vs 0.56% for T_{mold} = 900 °C). That is happens because of carbide precipitation in the first case. So, casting at lower temperature preserve the initial strength and global plasticity of the alloy.

Conclusions

This study aimed to evaluate the effects of the casting conditions on the structure and properties of a Co-Cr-Mo dental alloy. Corrosion of the as-cast alloy in two different artificial salivas having *p*H = 6.0 and 7.7, and mechanical testing revealed that casting at the lowest permissible temperature (500 °C) does not adversely affect the structure and properties of the Co-Cr-Mo dental alloy. XRD patterns have confirmed the presence of γ-phase and $M_{23}C_6$-type carbides without significant changes in γ to $M_{23}C_6$ ratio for both Co-Cr-Mo alloys cast at T_{mold} = 500 and 900°C, respectively and no brittle Cr-rich s phase was identified. As effect of the highest solidification rate, a slightly improvement in corrosion resistance especially in basic environment while maintaining the mechanical properties, takes place. A positive refinement of the structure as effect of the higher solidification rate is reported. The weakness of the lower temperature casting remains the possible worsening of the castability that requires special designing of the gating system such as ledge and melting reservoir dimensioning.

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