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Mechanical properties of hot pressed CoCrMo alloy compacts for biomedical applications

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ABSTRACT

This study aimed at investigating the influence of the processing conditions on the mechanical properties of hot pressed compacts of a CoCrMo biomedical alloy.

Several hot pressed CoCrMo compacts were processed in vacuum (10^{-2} mbar), at a pressure of 60 MPa with different temperatures (900 °C, 1000 °C and 1100 °C) and different times (10 min, 30 min and 60 min). Compacts were examined by SEM/EDS. The transverse rupture strength, Young's Moduli and hardness were determined. The fracture surface of compacts were also examined.

The compacts hot pressed at 900 °C exhibited lower TRS than those processed at 1000 °C and 1100 °C, which showed similar strength values, regardless the sintering time. The 900 °C compacts showed also lower YM and higher porosity. Lower hardness values were registered for 900 °C compacts while 1000 °C compacts exhibited the highest values. The fracture surface analyses revealed fragile fracture for 900 °C compacts (10 min and 30 min) and 1000 °C (10 min). The remaining compacts exhibited ductile fracture.

A full characterization of the mechanical properties of hot pressed CoCrMo compacts has been made and the selection of the processing parameters according to the desired mechanical properties is now possible.

1. Introduction

Co–Cr–Mo alloys are one of the most important biomaterials used in the production of implants and dental prosthetic infrastructures due to its high stiffness, strength, wear and corrosion resistance [1–7]. The tarnish and corrosion resistance of these alloys are provided by the presence of chromium in the alloy, which should not greatly exceed 30% for ease of casting. Molybdenum contributes to the strength of the alloy [8]. The structures made of these alloys are mainly obtained by casting. However, they should undergo thermal treatment to overcome the drawbacks of the undesired formation of M_7C_3 carbides (M = Co, Cr or Mo) and σ–sigma brittle phase at the inderdentritic regions [9,10]. These elements reduce the strength and ductility of the alloy. Porosity defects are also associated with cast Co–Cr–Mo parts. A tight control of the thermal treatment parameters should exist since the grain growth negatively impacts the strength and fatigue properties of the alloy. In order to overcome the limitations in terms of mechanical properties of the cast CoCrMo alloys, wrought parts have been used due to its finer and more homogeneous microstructure. The Powder Metallurgy (PM) route is also an option when the fine grain microstructures and high mechanical properties are requested. Additionally, more attention should be paid to this route as it is highly related to the Powder Metallurgy (PM) based Computer Aided Design/Computer Aided Manufacturing (CAD/CAM) systems that allow the production of customized parts [11,12]. These systems offer further advantages such as short production times and the ability of processing materials with special properties like gradient porous materials [13] or composite materials [14–21].

The properties of the compacts are highly influenced by the PM route that is used in their production [1]. Hence, components obtained by press and sinter technique often exhibit porosity, which negatively affects its mechanical and electrochemical

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behavior [22,23]. On the other hand, routes that include hot consolidation of powders such as hot pressing (HP) and hot isostatic pressing (HIP) address these problems by the simultaneous application of temperature and pressure to the compact [6,24].

Little attention has been given to the hot pressing of CoCrMo alloys and to the mechanical and electrochemical properties of compacts thus obtained. Thus, few studies can be found on this topic in literature. Chen et al. [6] and Doni et al. [5,25] performed studies on the wear properties of CoCrMo hot pressed compacts. Sato et al. [26,27] and Naoyuki et al. [28] reported some results on the mechanical properties of dense and porous CoCrMo compacts.

With this study, authors aimed to investigate the influence of the hot pressing parameters, namely time and temperature, on the mechanical properties of a CoCrMo alloy used in biomedical applications.

2. Material and methods

A CoCrMo dental alloy (Nobil4000, Nobilmetal, Villafranca d'Asti, Italy) was used in this study in the form of air atomized powder. The composition of alloy is presented in Table 1. The powder particles have spherical shape (Fig. 1) and the following size distribution: $D_{10} = 4.44$ µm; $D_{50} = 8.27$ µm and $D_{90} = 12.76$ µm.

Rectangular CoCrMo compacts (40 mm × 6 mm × 1 mm) were produced by hot pressing CoCrMo powders in a graphite die at three selected temperatures (900 °C, 1000 °C and 1100 °C) during three selected times (10 min, 30 min and 60 min). The graphite die was painted with zirconium oxide paint in order to impede carbon to diffuse to metal substrates. Hot pressing was performed under vacuum (10^{-2} mbar). All compacts were ground until mirror finishing for microscope observation. Afterwards, they were ultrasonically cleaned in an alcohol bath for 10 min and rinsed in distilled water for another 10 min to remove contaminants.

Table 1
Chemical compositions of the powders (wt.%).

Co	Cr	Mo	Si	Impurities
62	31	4	2.2	Mn–Fe–W

Microhardness evaluation (Microhardness tester, type M, Shimadzu, Japan) was performed along the length of the compacts. The mean value and standard deviation was then calculated.

The transverse rupture strength (TRS) of the HP samples was obtained by the means of three-point flexural tests. Transverse rupture strength (TRS) was calculated as follows:

$$\sigma_{TRS} = \frac{3FL}{2bh^2}$$

where σ_{TRS} is the transverse rupture strength of the compacts (MPa), F is the force required to rupture the compacts (N), L is the length of compacts span relative to fixture (35 mm), b is the width of the compacts (mm) and h is the thickness of compacts (mm).

After flexural tests the fracture surface of the compacts were examined by the means of scanning electron microscopy – SEM (JSM-6390LV, JEOL, Tokyo, Japan). Before SEM examination, fracture surfaces were coated, by sputtering, with a layer of 10 nm of 80Au20Pd.

3. Results

Fig. 1 shows the Young's Moduli (YM) of the hot pressed compacts. The 900 °C compacts exhibited lower YM than the 1000 °C and 1100 °C compacts. They showed increasing YM with increasing hot pressing stages. All the 1000 °C and 1100 °C compacts exhibited the same YM, except the 1000 °C sintered during 10 min.

The results of the transverse rupture strength (TRS) tests are presented in Fig. 2. The 900 °C compacts exhibited low strength values when compared to other compacts, with the latter showing similar results. Longer hot pressing times showed to have a great impact on the strength of the 900 °C compacts. On the other hand, the strength of 1000 °C and 1100 °C compacts did not show to be significantly influenced by longer hot pressing stages. Hence, after a 10 min stage, the compacts hot pressed at 1000 °C and 1100 °C have achieved their maximum strength and longer sintering times did not result in further strengthening. The 1000 °C compacts exhibited slightly higher strength than the 1100 °C compacts.

The analysis of porosity is plotted in Fig. 3. The hot pressing time showed to have a positive impact on the reduction of porosity in the three temperatures tested. The highest porosity registered was observed in the 900 °C compacts hot pressed during 10 min. All compacts hot pressed during 60 min were considered fully dense with some of them exhibiting a residual level of porosity.

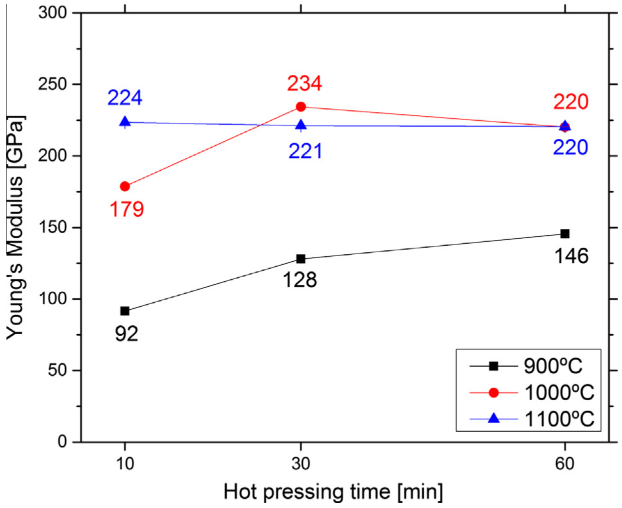

Fig. 1. Young's Moduli of the CoCrMo compacts hot pressed at different conditions of temperature and time.

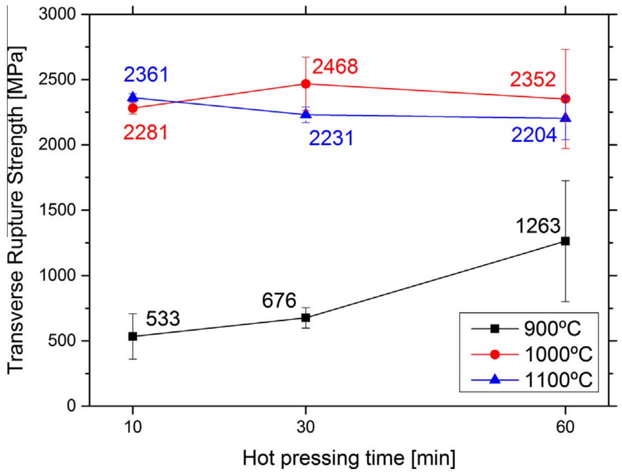

Fig. 2. Transverse rupture strength (TRS) of the CoCrMo compacts hot pressed at different conditions of temperature and time.

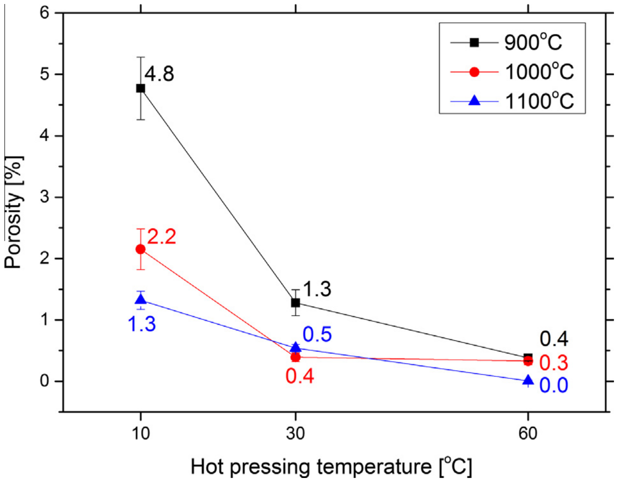

Fig. 3. Porosity of the CoCrMo compacts hot pressed at different conditions of temperature and time.

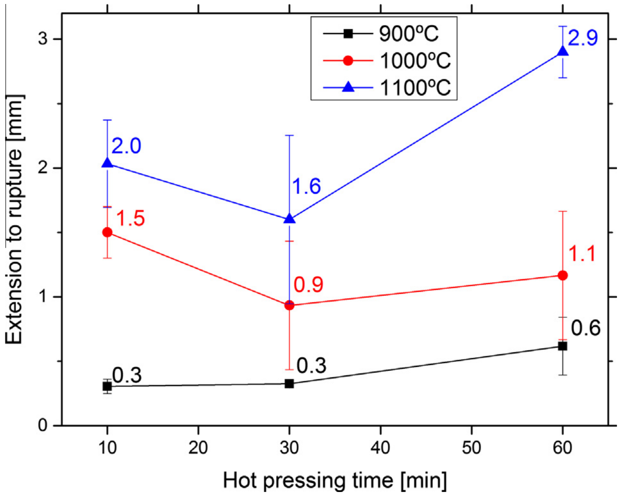

Fig. 5. Extension to rupture of the CoCrMo compacts at different conditions of temperature and time.

The hardness values are plotted in Fig. 4. The 900 °C compacts exhibited the lowest values and their hardness increased sharply with the increase of hot pressing time. The 1000 °C and 1100 °C compacts exhibited higher hardness values with the former compacts being harder than the latter. The increase of the hot pressing times resulted in a relative increase in the hardness values for these two types of compacts.

The extension to rupture of compacts was also examined and the results are presented in Fig. 5. The 900 °C compacts exhibited very low extension to rupture, regardless the hot pressing time, revealing a brittle behavior. The 1000 °C compacts showed higher values relative to the former compacts. The higher extension to rupture values were registered for the compacts hot pressed at 1100 °C, revealing a markedly ductile behavior.

In Fig. 6 the micrographs of the compacts obtained after the different hot pressing conditions are depicted, with the porosity and microstructure being visible. Fig. 7 shows the fracture surface of the compacts after the three point flexural test. It is seen that bonds between powders were very weak in the 900 °C compacts hot pressed during 10 min and 30 min. Necks between particles were in a early stage and starting to form. At the same temperature, compacts hot pressed during 60 min revealed a significant improvement in the bonds between powders, with deformation of the particles being noticed at the fracture surface. The level of deformation of the particles verified in the 1000 °C, hot pressed for 10 min, is similar to that exhibited by compacts hot pressed at 900 °C during 60 min. The remaining compacts exhibited extensive deformation of the powders at the fracture surface, evidencing good bond between them and an advanced stage in the sintering process.

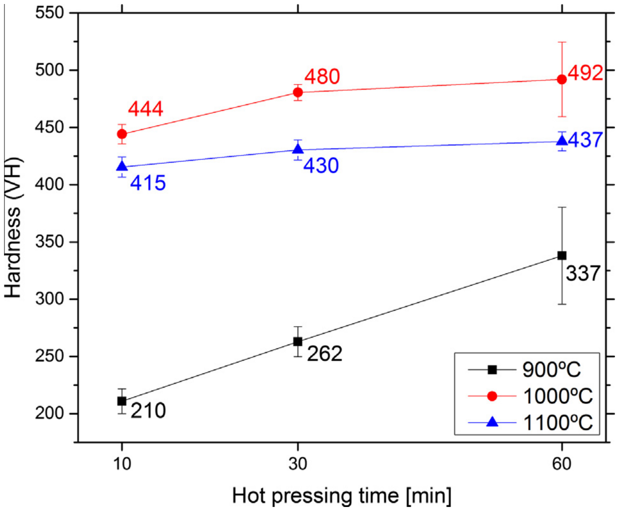

Fig. 4. Hardness vickers of the CoCrMo compacts hot pressed at different conditions of temperature and time.

4. Discussion

Before discussing the results, some considerations on the CoCrMo alloy used in this study must be made. It is a Co-Cr biomedical alloy that fulfills the ANSI/ADA Specifications No. 14 (ISO 6871) in terms of chromium and cobalt weight, which should be no less than 20% and 85%, respectively (Table 1). Cobalt is the major element in the alloy and its content in the alloy is regarded for the elastic modulus, strength and hardness [10]. Chromium is the second major element in the alloy (Table 1) and is responsible for its corrosion resistance. Its content in the alloy should not exceed significantly 30% because it turns casting more difficult and due to the formation of a brittle (σ–sigma) phase [10,26–28]. The chemical composition and microstructure of the hot pressed CoCrMo compacts using this alloy can be found in another study performed by the same authors [16]. The same study showed that hot pressed compacts revealed greater corrosion resistance than cast compacts.

The temperatures range used in this work (900–1100 °C) was in line with temperatures used in other studies on hot pressed Co–Cr alloys [24,26,27]. The temperature of 900 °C has produced the compacts with the lowest mechanical properties, especially when the hot pressing time of 10 min and 30 min were used. The compacts thus produced showed high porosity, low stiffness, low strength, low hardness and exhibited very fragile behavior. When the hot pressing time was extended to 60 min, a great reduction in porosity was observed followed by a significant improvement of the mechanical properties. Nevertheless, the properties exhibited by the compacts sintered at 900 °C during 60 min were roughly the same as those obtained for the compacts hot pressed at 1000 °C during 10 min.

The properties obtained for the compacts hot pressed at 1000 °C and 1100 °C did not show significant differences, except for the

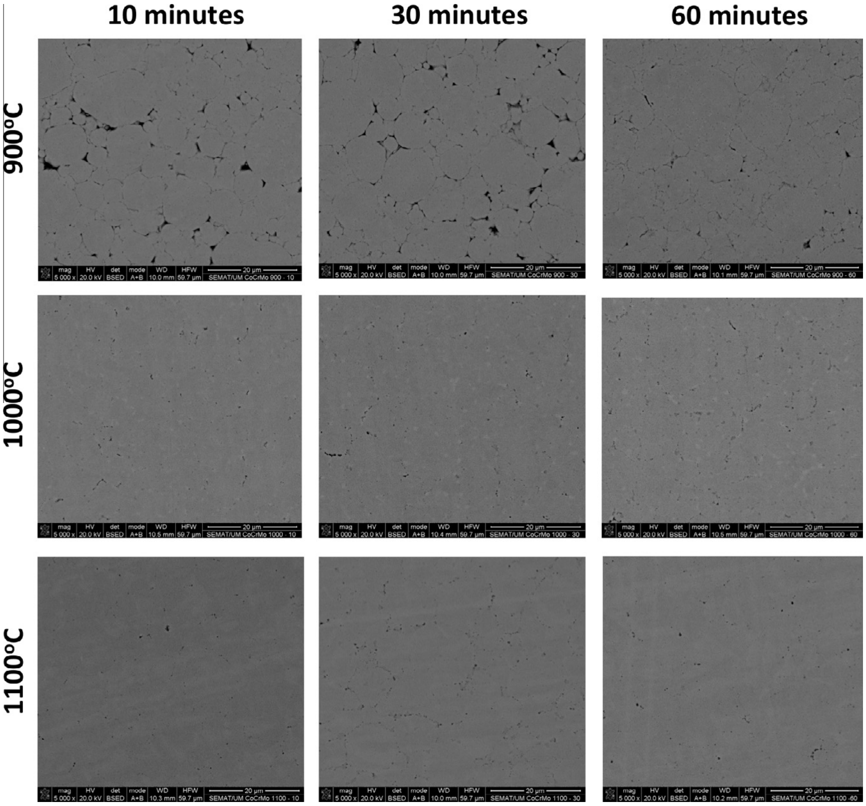

Fig. 6. Micrographs of the CoCrMo compacts hot pressed at different conditions of temperature and time.

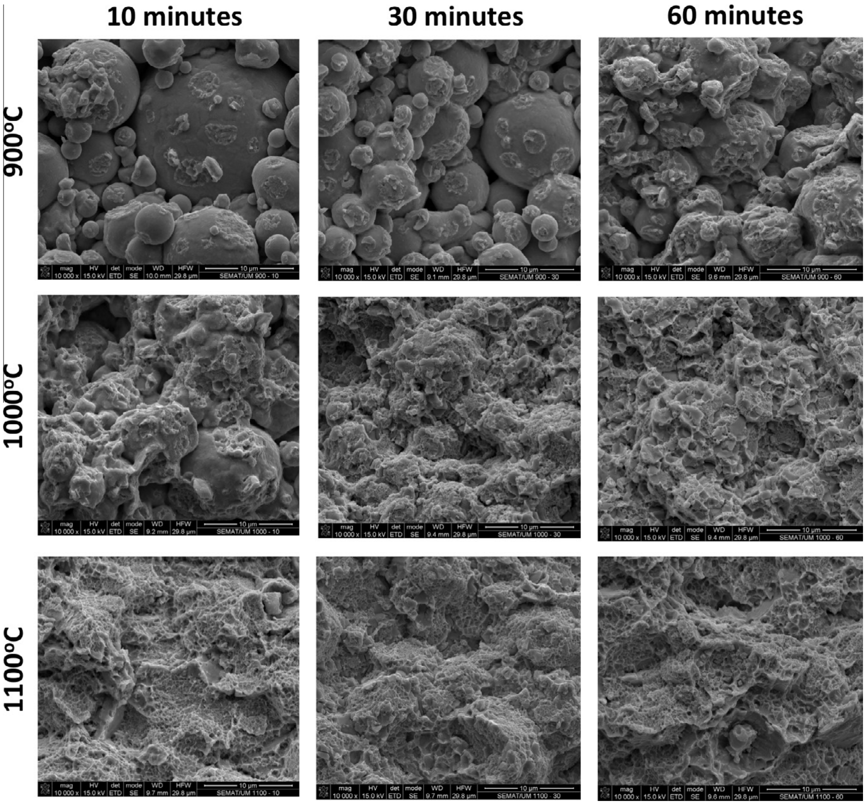

Fig. 7. Fracture surface of the CoCrMo compacts hot pressed at different conditions of temperature and time.

hardness values. The temperature of 1100 °C produced softer compacts than the temperature of 1000 °C, for all the hot pressing times tested (Fig. 4). The synergetic effects of two factors explain this: the grain growth occurring at a higher temperature and the absence of σ-sigma precipitates at the grain boundaries. Sato et al. [26] showed that CoCrMo compacts hot pressed at 1100 °C did not show precipitates from σ–sigma phase, conversely to those hot pressed at lower temperatures. The absence of σ-sigma phase favors the grain growth, which impacts the strength, ductility and hardness of the compacts. Hardness is an important characteristic in a way that hard alloys, combined with high elastic modulus, allow the manufacture of longer prostheses [10]. The higher hardness, thought, may impact the ability to finish/polish the alloy clinically.

A good correlation between the Young's modulus values and the level of porosity of the compacts could be observed, with higher porosity being related to lower stiffness of the compacts. Hence, compacts hot pressed at 900 °C revealed the lowest stiffness while those hot pressed at 1000 °C and 1100 °C for hot pressing times of 30 and 60 min showed maximum stiffness (Fig. 1). Sato et al. [27] reported a significant reduction in porosity with increasing hot pressing temperatures, despite the discrepant values relative to the present study.

The transverse rupture strength (TRS) measured for the compacts hot pressed at 900 °C was significantly lower than that exhibited by the remaining compacts. Again, the best results obtained for this temperature was observed when the 60 min hot pressing stage was used. The differences observed for the TRS of compacts hot pressed at 1000 °C and 1100 °C were very small, regardless of the hot pressing time used, with the 1000 °C compacts exhibiting slightly higher values for the hot pressing time of 30 and 60 min. On the other hand, significant differences were observed in the ductility of the compacts, measured by the extension to rupture in the TRS test. The 900 °C compacts exhibited a fragile behavior while the 1100 °C compacts exhibited the highest plastic elongation (Fig. 5). These results are in accordance with Sato et al. [26] findings, which reported the highest strength values for the compacts hot pressed at 1000 °C (explained by the smallest grain size) and the highest plastic elongation for the 1100 °C compacts (explained by the dissolution of the σ–sigma phase).

The analysis of the fracture surfaces of the compacts is a useful tool to relate the sintering stage resultant from each hot pressing condition to the mechanical properties obtained. Hence, the weak bonds between powders displayed mainly by the 900 °C compacts, resulted in low Young's modulus, low hardness, low strength and fragile behavior. On the other side, the effective bonds between the metallic particles, proved by the extensive tearing of the particles at the fracture surface, are related to the higher YM, higher hardness, higher strength and ductile behavior displayed by the compacts hot pressed at higher temperatures.

Some correlations between the properties of the specimens and their processing parameters were evaluated as shown in Figs. 8, 9 and 10.

Correlation between hardness and strength is shown in Fig. 8. As expected more hard materials have also higher strength values. It is also seen that processing time has a major effect only at 900 °C (blue points – size reflects time), where longer time leads to better results. For 1000 and 1100 °C, this effect however is rather minor.

Links between TRS and elongation at rupture are shown in Fig. 9. For solid materials, normally higher strength means less ductility, but when materials are partially porous (or not well sintered), the link is more complex. Here one can see that the solid materials "rule" is valid for high-temperature processed specimens (1000 and 1100 °C), where indeed higher strength is associated with lower elongation. Processing time in this case has no clear effect, as higher strength might be found at intermediate or lower time, on the contrary to 900 °C.

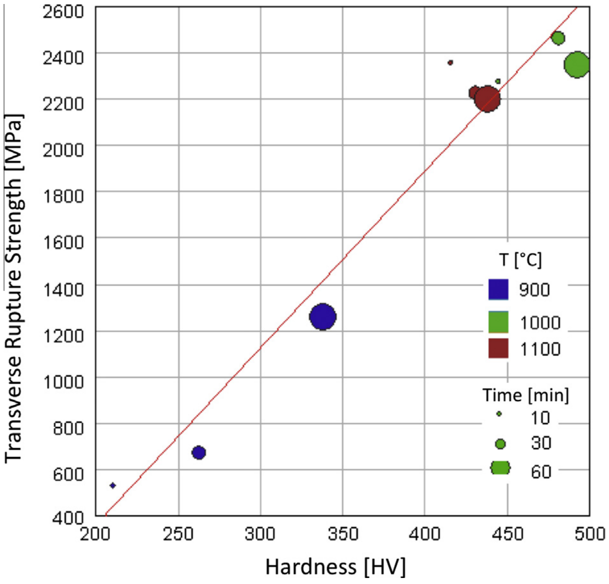

Fig. 8. Correlation between hardness (HV) and strength (TRS).

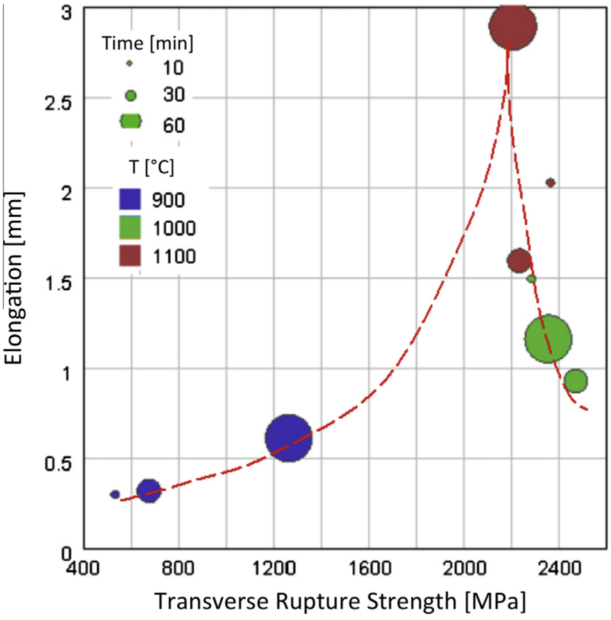

Fig. 9. Correlation between strength (TRS) and elongation at rupture.

Effect of porosity on Young's modulus is shown in Fig. 10. Dashed lines indicate trends, connecting the experimental points with the same processing time (10, 30, 60 min). One can observe that temperature increase has the most of effect for short time (10 min), but for 30 and 60 min the increase of the modulus is only seen vs. values obtained at 900 °C.

The conclusions, which could be made of these plots, can be used for recommended processing selection. It is clear that 900 °C is too low temperature to cope with higher demand for properties, as even at longer processing time (lower porosity), the modulus, elongation and hardness are still of an average level. The value of 1000 °C and 30 min seem to be a good compromise to achieve reasonably low porosity, high modulus and strength with ~1% elongation. If higher ductility is required, temperature of 1100 °C and 60 min time possibly will be a better option.

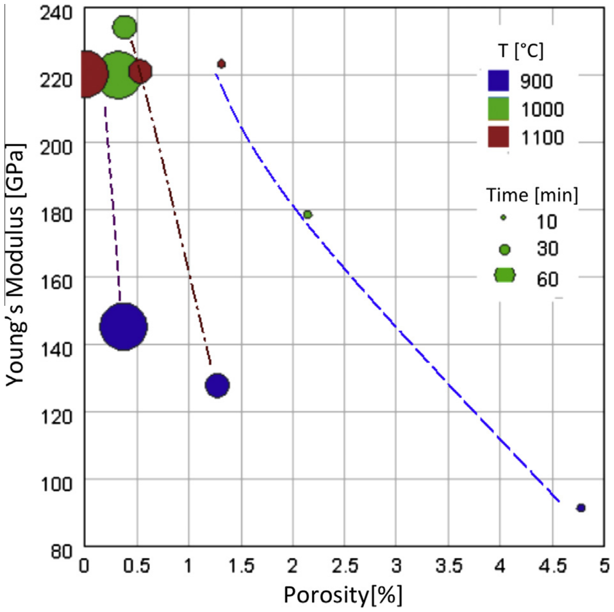

Fig. 10. Plot of the effect of porosity on Young's modulus (YM).

5. Conclusions

From this study, the following conclusions can be drawn:

1. The properties of the CoCrMo compacts showed to be significantly affected by the processing conditions, namely the temperature and time;
2. The hot pressing temperature of 900 °C showed to impart to compacts high porosity, low mechanical strength, low hardness and low Young's modulus, particularly using short sintering times;
3. The hot pressing temperatures of 1000 °C and 1100 °C showed to result in compacts with similar mechanical strength, porosity and Young's moduli. However, higher hardness values were registered for 1000 °C compacts when compared to those hot pressed at 1100 °C.
4. The 900 °C compacts exhibited brittle behavior while 1000 °C and 1100 °C compacts exhibited increasing ductility with increasing hot pressing temperature;
5. This study has shown that hot pressing is a feasible technique for the production of CoCrMo compacts for biomedical applications with adequate mechanical properties. The mechanical strength, porosity, Young's moduli and hardness can be adjusted by tuning the processing conditions.

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