Effect of temperature on the microstructure of hot pressed Co based Co-Cr-Mo alloy

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In this study, biocompatible Co-based Co-Cr-Mo alloy powder produced by direct-resistant hot-pressing technique at different temperatures. The effect of pressing temperature on microstructure and mechanical properties of the samples produced were determined. The powder consisting of 67.5% Co (99.5% purity-325mesh), 27.5% Cr (99% purity-325mesh) and 5% Mo (purity 99.95%-325mesh) was homogeneously mixed by the adding polyethylene glycol lubricant. The powder mixtures prepared were directly hot pressed under 115 bar at 750, 800, 850, 900 ° C for 5 minutes. Density, microstructure and some mechanical characteristics of the samples produced were investigated. The density of the sintered specimens increased with the temperature, except the specimen at 850 °C in which porosity increased, due to the local microstructural segregation.

(Received October 1, 2012; accepted September 18, 2013)

Keywords: Hot Pressing, Orthopedic Implants, Co-Cr-Mo Alloy, Powder Metallurgy

1. Introduction

Co-Cr-Mo alloys are used widely to improve mechanical properties and increase corrosion resistivity of implant material [1]. Co based super alloys are used in the structural elements subjected to high temperatures such as commercial and military plane turbines due to their excellent tensile properties, weld ability, easy machinability and very good thermal corrosion resistively [2].

Implant production with metallic materials by PM techniques dates back to 1960s. The first studies were on porous Co-Cr-Mo hip prosthesis [3]. Powder metallurgy techniques made a big contribution to the improvement of the surgical implants in recent 30 years. These take place mainly in orthopedics and dentistry [4].

One of the most economic and fast PM techniques is hot pressing method. There is no need additional sintering since the process is performed by applying pressure and heat simultaneously in argon atmosphere and is completed in a short time. Preformed powder placed into graphite moulds can be compacted in a very short time such as 10 minutes. A homogenous and finished product with high density and low cost are among the advantages of hot pressing techniques. Non oxidizing ceramics can be produced by this technique. The physical properties of the products of this method are superior to the ones produced by the other PM techniques [5].

This study is focused on the production of Co based Co-Cr-Mo alloy by direct hot pressing technique and investigation of the effect of pressing temperatures on the microstructure.

2. Materials and method

In this study Co27Cr5Mo powder alloy was produced by direct hot pressing technique in four temperatures 750, 800, 850, 900 ºC. For this, metal powders 67.5 % Co (99.5 % pure 40 um), 27.5 % Cr (99 % pure 40 um), 5 % Mo (99.95 % pure 3-7 um) of Alfa Aesar-USA, were weighed by a 10^{-4} scale balance and blended. Compositions of powder blends are given in Table 1.

Table 1. Compositions of powder blends and sintering temperatures.

Sample Number	Compound (Percent %)	Sintering Temperature(ºC)
1	%67,5Co-%5Mo- %27,5Cr	750
2	%67,5Co-%5Mo- %27,5Cr	800
3	%67,5Co-%5Mo- %27,5Cr	850
4	%67,5Co-%5Mo- %27,5Cr	900

The powders were mixed in a mixer, which rotates spirally 360 degree, for 30 minutes after polyethylene glycol, in 1 % in weight, was added. Then ceramic balls were placed in the container and the mixture was mixed further 30 minutes thus obtaining a full homogenous granulated mixture.

Blended powder was placed into the graphite moulds shown in Fig. 2 to obtain specimens in the dimensions of 40×10×5. The upper compression graphite caps were placed on. Graphite moulds were then placed into the metal dies manufactured for this purpose. The die was put into the argon gas chamber of the hot press, Fig. 1.a. The

computer aided hot press was run by the procedure given in Fig. 3.

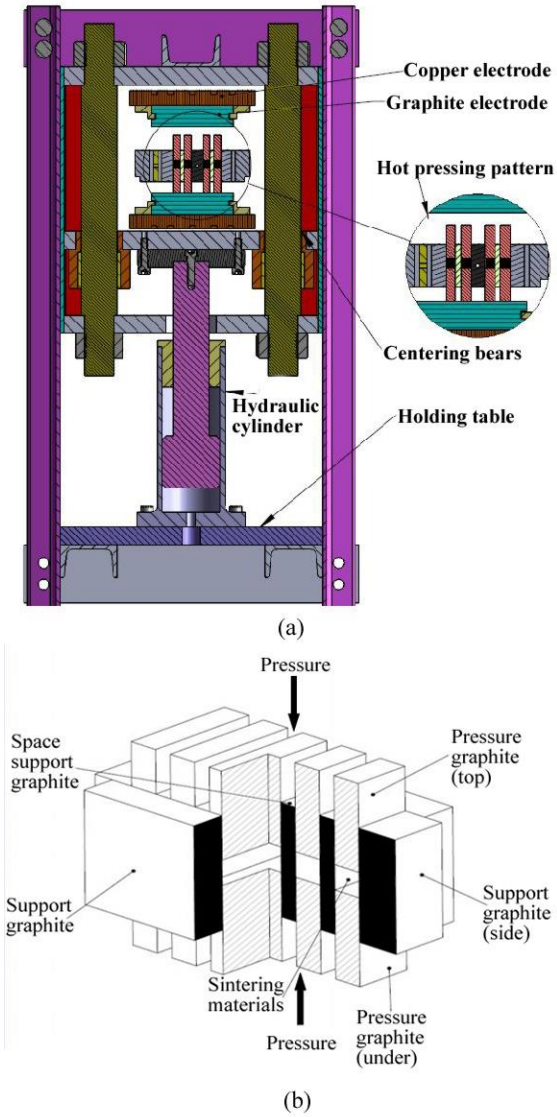

Fig. 1. (a) Hot press machine, (b) Graphite mould [7].

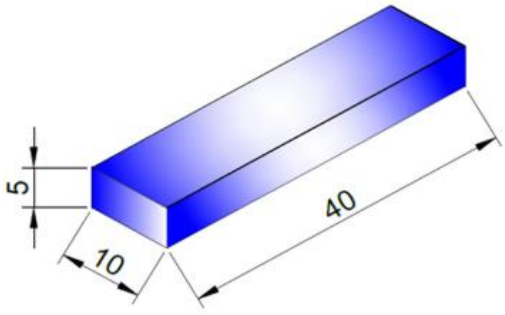

Fig. 2. The socket produced.

The first specimen was sintered at 750 °C while the second, third and fourth specimens at 800 °C, 850 °C and 900 °C respectively The lubricant within the compacts removed at 400-450 °C during hot pressing.

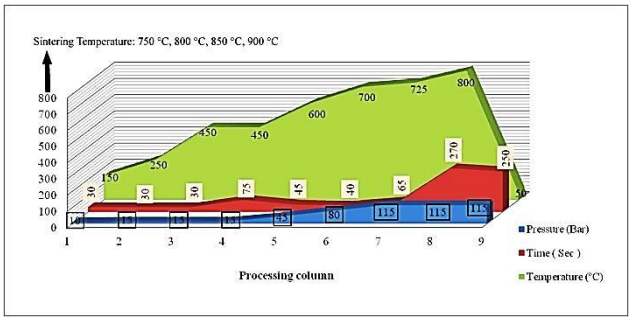

Fig. 3. Process parameters at 750 °C.

After hot pressing, the specimens were prepared for optical microscopy and SEM (JEOL JSM 7001F), and micro hardness measurements with the conventional metallurgical methods. Surface finish was performed by 1 µm diamond paste and the polished surfaces were etched in 5 ml HNO_3^+, 200 ml HCl^+, 65gr $FeCl_2$ solution electrolitically.

3. Results and discussion

3.1. Density measurements

Density and porosity rates given in Table 2 were calculated by Archimedes principle. The variations of porosity and density with temperature are shown in Fig. 4.

Table 2. The measured densities.

Density / Sample	Sintering Temperature(°C)	Measure Density gr/cm³	Theoretical Density gr/cm³	Porosity Amount (%)
1.	750	5.8451 gr/cm³	8.4877 gr/cm³	31.1344
2.	800	6.1195 gr/cm³	8.4877 gr/cm³	24.7204
3.	850	6.2410 gr/cm³	8.4877 gr/cm³	26.0812
4.	900	7.381 gr/cm³	8.4877 gr/cm³	13.0388

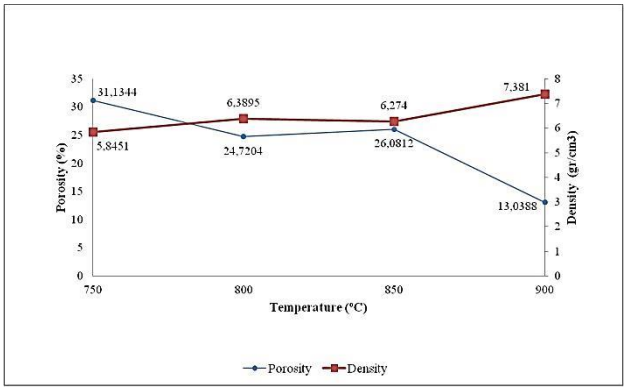

Fig. 4. Variation of porosity (%) and density with temperature.

The porosity rate was compared to the one of the ASTM F75-87 standard for the surgery applications of implants given in Table 3. It was seen that the porosity of specimen 4 had a very good consistency with the Standard values.

Table 3. Process parameters performed with water atomization (WA) powder [10].

Particle Form	All symbolic porosity	Pressure press (MPa)	Sintering Temperature (°C)
WAC	33	770	1150
WAM	20	770	1350
WAF	5	1235	1350

Note: C: total rough porosity (>30%), M: total average porosity (~20%), F: total good porosity (<10%) [10].

It was seen that density increased directly proportional with the temperature. Density reached up to 86.97 % at 900 °C, which is a very good value for PM parts.

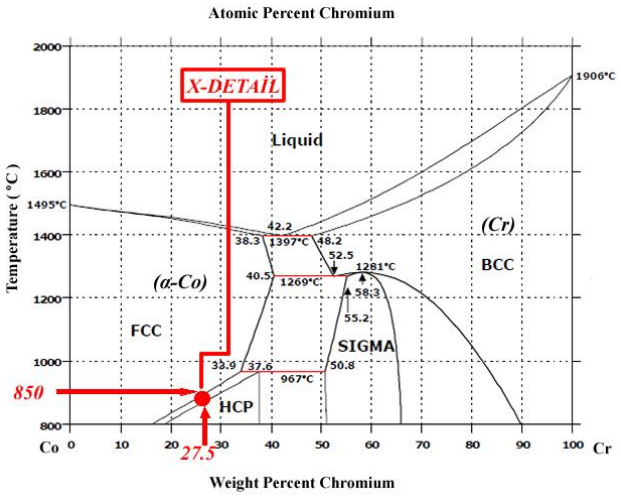

Fig. 5. Co- Cr binary phase diagram [8].

But it is also seen from Figs. 5 and 6 that porosity increases and density reduces at 850 °C. The composition of the phases formed at 850 °C is shown by X in Co-Cr binary phase diagram in Fig. 5. There are α Co and ε Co in that composition. This region is prone to segregations and makes the materials brittle [11]. It is also thought to cause decrease in density due to more pore occurring or slowing the bulk diffusion as a result of the zonal segregations [12] during the formation.

3.2 Micro hardness results

Microhardness values of the specimens are given by the temperature in Fig. 6. Microhardness values increase with temperature, twice between 750 °C and 900 °C from 101 HV to 204 HV as can be seen in Fig. 6. The mechanical properties improved with the increase in sintering temperature [6].

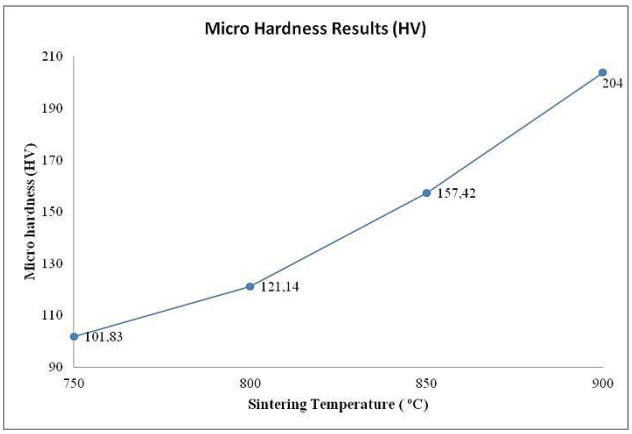

Fig. 6. Variation of microhardness with temperature.

3.3 Microstructures

3.3.1. Porosity

The highest porosity rate is in the specimen 1. This indicates that sintering temperature and time is not enough for a full consolidation. The porosity decreases with increase in sintering temperature. The morphology of the pores also changes to smaller and spherical and are distributed more homogenously (Fig. 7). The decrease in porosity naturally increases the densities of the specimens [6, 9] as the microhardness and density measurements prove this as can be seen in Fig. 4 and Fig. 6. The porosity decreased and density of the sintered specimens inceased with the temperature. Interestingly the specimen sintered at 850 °C exhibits a contradictory behavior. In this specimen pore rate increased and density decreased in an unexpected manner, Table 2. The specimen sintered at 850 °C has α-Co and ε-Co phases in Co-Cr binary phase diagram at the sintering temperature as can be seen in Fig. 5 and it was thought that the local microstructural segregation in this region causes an increase in porosity and forms voids inside the specimen as mentioned above.

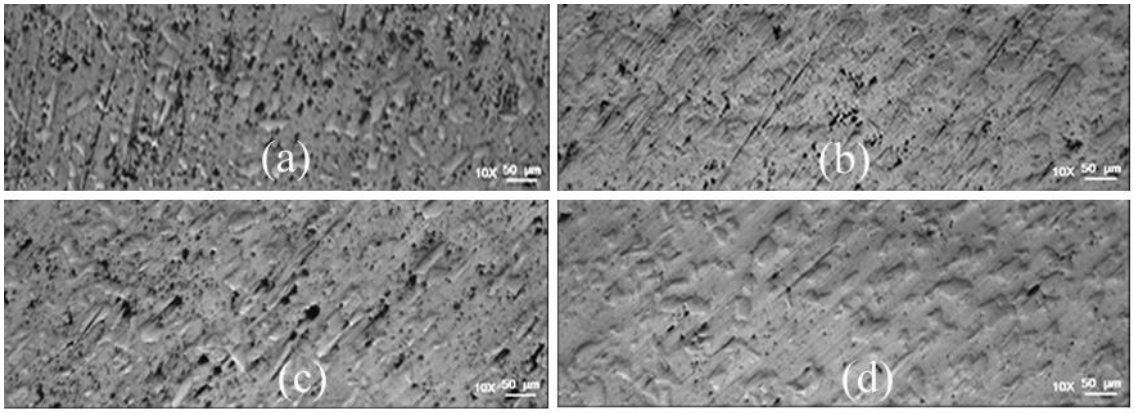

Fig. 7. Optical micrographs of the specimens sintered at a) 750 °C, b) 800 °C , c) 850 °C, d) 900 °C.

3.3.2. SEM images

SEM images of hot pressed specimens are given in Fig. 8. Since the sintering temperatures were chosen far below the melting points, there are no Co and Cr compounds but Mo and Co compounds due to the greater affinity of Mo to Co. The amount of this compound increased with the temperature. Sintering temperature of 750 ºC is seen to be insufficient from Fig. 8 while 800 ºC is more adequate and 900 ºC is the best of all of them.

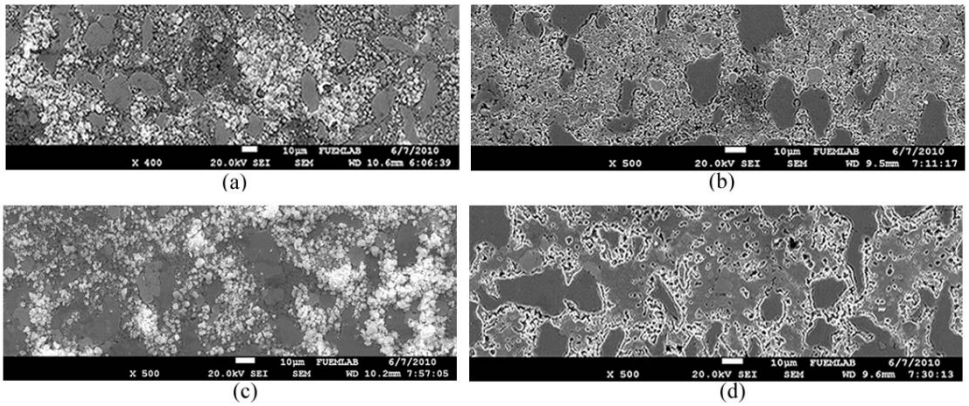

Fig. 8. SEM images of the specimens sintered at a) 750 ºC b) 800 ºC c) 850 ºC d) 900 ºC.

The best indication of sintering progress is the necking of the particles. This formation is insufficient in the specimen 1 and 3. The necking in the specimen 2 is better than the specimen 3 and the best in the specimen 4 sintered at 900 °C. Sintering temperature of specimen 3 corresponds to the two phase region, α-Co and ε-Co, at the hot pressing temperature in Co-Cr binary phase diagram. Due to the local segregation more pores can be seen from SEM photos of this specimen Fig. 9. SEM image taken from the specimen 4 shows that sintering temperature is sufficient for a good consolidation at 900 °C Figs. 8 and 9. The variations in the microstructures of the specimens sintered at 750 °C, 800 °C, 850 °C and 900 °C are given in the SEM micrographs in Figs. 9 all together.

The porosity is shown with a, b, c, d, and e points in Fig. 9. As can be seen from the figures, necking among the particles is increased with increasing sintering temperature and the numbers of pores are higher in the specimen hot pressed at 750 °C than the one at 900 °C.

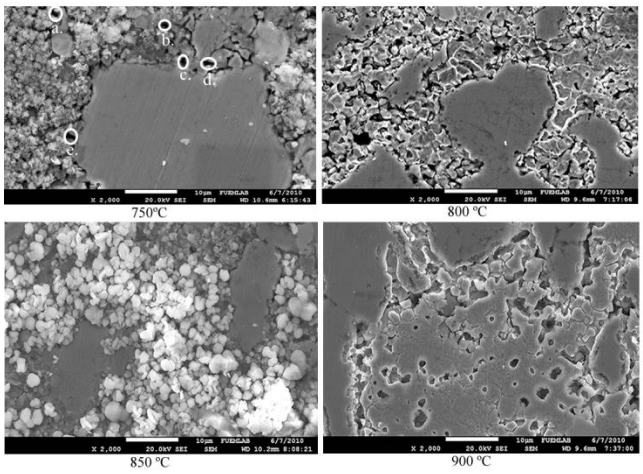

Fig. 9. SEM image of the specimen sintered at 750 °C, 800 °C, 850 °C and 900 °C.

4. Conclusions

In this study Co based Co-Cr-Mo powders were compacted and sintered in a numerical controlled hot pressing machine under argon gas atmosphere at 4 different sintering temperatures and the following conclusions were obtained.

-A mixing time of totally 60 minutes (30 minutes with lubricant followed by ball milling for 30 minutes) is enough to obtain a homogenous distributed powder mixture.

-Necking among the powder particles increases with the increase in temperature and naturally porosity decreases with temperature. A density of 86.97 % was obtained at 900 °C.

-Density decreased and porosity increased surprisingly at 850 °C compared with the specimens hot pressed at 800 °C. The sintering temperature of 850 °C corresponds to the dual phase region in Co-Cr phase diagram and the effect of sintering at this temperature on consolidation of the compact must be investigated considering the result obtained in this study.

-The effect of sintering temperature on the hardness is significant. The hardness increased in direct proportion to the sintering temperature. There is twofold different between the hardnesses of the specimens hot pressed at 750 °C and 900 °C. The temperature is found to be the most important parameter at constant pressure for a good consolidation of the powder and the best results was obtained at 900 °C when porosity and hardness are concerned.

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