Materials Research. 2014; 17(3): 664-671
DOI: http://dx.doi.org/10.1590/S1516-14392014005000022

Effect of Hot Pressing Variables on the Microstructure, Relative Density and Hardness of Sterling Silver (Ag-Cu alloy) Powder Compacts

Henriques, B.*, Soares, D., Teixeira, J.C., Silva, F.S.

Center for Mechanical and Materials Technologies, Universidade do Minho, Campus de Azurém, CEP 4800-058, Guimarães, Portugal

Received: August 9, 2013; Revised: January 15, 2014

The purpose of this work was to investigate the influence of the hot pressing variables, namely pressure, time and temperature, on the microstructure, density and hardness in a sterling silver alloy. Powders were hot pressed under different combinations of pressures (25MPa, 35MPa and 45MPa), times (10 min, 30 min and 60 min) and temperatures (250 °C, 300 °C, 400 °C, 500 °C and 700 °C). The microstructures of hot pressed compacts were analyzed by the means of SEM/EDS and optical microscopy. The density and hardness of specimens were assessed. The microstructure of all specimens consisted in Cu-rich precipitates of different sizes dispersed in a Ag-rich matrix. Of the variables that were examined, only temperature produced significant ($p<0.05$) differences in the density and hardness of the compacts. Full density of powders compacts was achieved for temperatures above 400 °C, irrespective of the hot pressing time. A hardness peak (~120HV) was observed for the specimens hot pressed at 400 °C.

Keywords: *sterling silver, powder metallurgy, hot pressing, microstructure, density, hardness*

1. Introduction

Pure silver exhibits a great color and luster, but it is too soft for the fabrication of artifacts, such as jewelry items. Therefore, it is common to add other metals (e.g. Cu, Al, Ga, Ge, Mn, Pt, among others) to produce an alloy with increased strength, hardness and wear resistance[1]. Copper is the most used alloying element of silver alloys, and its addition up to 10% is regarded for significant increase in strength and hardness[2]. Sterling silver is a silver alloy with 92.5% Ag, and 7.5% of other alloying elements, which is usually copper. The cast microstructure of sterling silver is characterized by a non-equilibrium structure of primary dendritic crystals of α-phase surrounded by a eutectic structure of finely dispersed mixture of small $\alpha + \beta$ crystals[2,3] that accounts for the mechanical improvement of the alloy. The β-phase is a Cu-rich phase that, also, precipitates on cooling and after solidification is complete. It occurs because the solubility of copper phase diminishes with decreasing temperature[2]. Besides alloy composition and cold work, another effective method for improving the strength and hardness in sterling silver alloys is age hardening[4].

Powder metallurgy (P/M) is a net or near net shape manufacturing method that involves the consolidation of powders into the required shape and a subsequent heat treatment (sintering) that causes particles to bond, thus imparting the necessary strength and metallurgical integrity to the manufactured part[5]. P/M is an alternative to conventional investment casting processes and competes with the later on a cost basis. Despite the higher metal powders costs relative to their cast and wrought counterparts, the savings in post-processing steps like machining operations and in scrap generation makes P/M methods very competitive. For a long time P/M has been used to produce parts for automotive, business machine, appliance, dental, medical, and other high-volume applications, with enhancement on quality standards. The jewelry and precious metal community introduced P/M more than 20 years ago. This topic has been presented and discussed at several jewelry forums, such as the Santa Fe Symposium[5-9] and World Gold Council Technical Conference[10,11], and at non-jewelry venues as well[12,13]. Among the P/M technologies, there are two that have shown to be more used in the jewelry industry, the P&S (Press and Sinter) and MIM (Metal Injection Molding). These are technologies that are well suited for large scale productions.

Hot pressing is another P/M technology that can be used in the production of jewelry items and it will be given attention in this paper when applied to the production of sterling silver powder compacts. Hot pressing combines die compaction and sintering in one step. Metal powders are loaded in a die (usually graphite) at high temperatures for a period of time that can range from several minutes to an hour, typically. The pressures involved are also lower than those used with conventional die compaction[14]. Full densities are typically achieved with this method as the high temperatures and applied pressure cause powder particle to undergo deformation, resulting in enhanced densification processes. Hence, the full density is thus achieved at lower temperatures and shorter times than would be required for conventional separate press and sinter operations. However, with regard to the production rate, hot pressing is much slower than the conventional press and sinter process and has lower tolerances[5]. Hot pressed products are restricted to simple geometries and they are often small billets to

*e-mail: brunohenriques@dem.uminho.pt

be machined to final shape. Hot pressing can also be used to produce products based in the mixture of two or more types of metal powders resulting in improved mechanical properties and/or unique aesthetical features. The same is applied to the mixture of metal powders with ceramic powders for the same end. In this way, it is important to know how materials behave when subjected to different hot pressing conditions. This study deals with the hot pressing of a sterling silver powder alloy. It was investigated the effect of hot pressing parameters on the microstructure, density and hardness of sterling silver powder compacts.

2. Material and Methods

2.1. *Powders*

The material used in this study was a silver alloy (94Ag6Cu). Powders were obtained by a process of solid-state reduction by the means of in-house equipment that uses a file to produce powders in a small scale. The morphology of the irregular powders thus produced is presented in Figure 1. The particle size distribution of powders was determined by using a laser diffraction particle size analyzer (Malvern HSD2600, Malvern Instruments Ltd, England). The particle size distribution (Figure 2) is the following: D_{10}=60µm; D_{50}=159µm and D_{90}=324µm.

2.2. *Processing conditions*

Powders were hot pressed under a range of selected conditions of pressure, time and temperature, which are displayed in Table 1. Hot pressing was performed under vacuum (10^{-2} mbar) using in-house equipment (Figure 3) based on a vacuum chamber and an induction heating furnace (Ameritherm Easyheat 5060). Powders were hot pressed in a graphite mold with a 4 mm diameter cavity.

Subsequently, the density of sintered compacts was measured accurately using distilled water by the Archimedes method and following the 42nd MPIF standard (A1)[15]. The relative density was calculated as the ratio between the measured density and the theoretical density. All specimens subjected to density measurements were ultrasonically cleaned in an alcohol bath for 10 min and rinsed in distilled water for another 10 min to remove contaminants. Then they were dried with adsorbent paper towels. The average random and systematic errors in the density measurements were quantified as 0.66%.

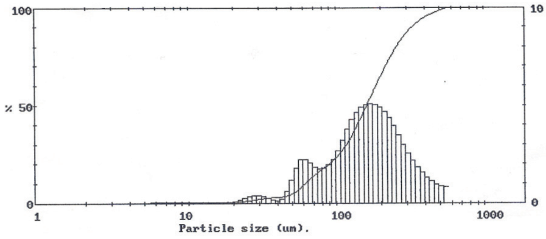


Figure 2. Size distribution of sterling silver (AgCu) powders.

Table 1. Hot pressing conditions of the silver alloy powders.

Pressure (MPa)	Time (min)	Temperature (°C)
25	10 30 60	250 300 400 500 700
35	10 30 60	250 300 400 500 700
45	10 30 60	250 300 400 500 700

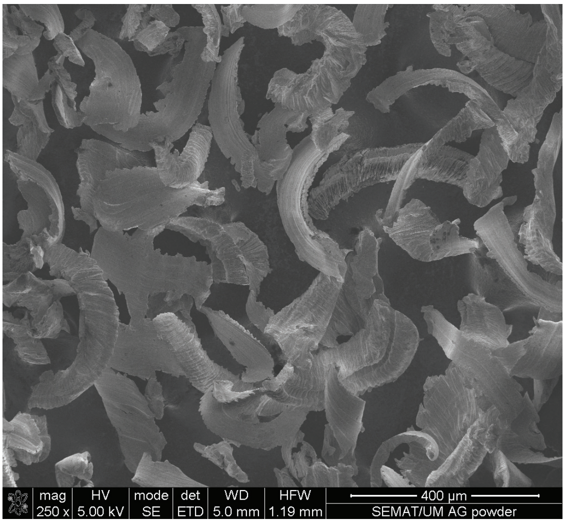


Figure 1. SEM micrograph showing the morphology of the silver alloy powders.

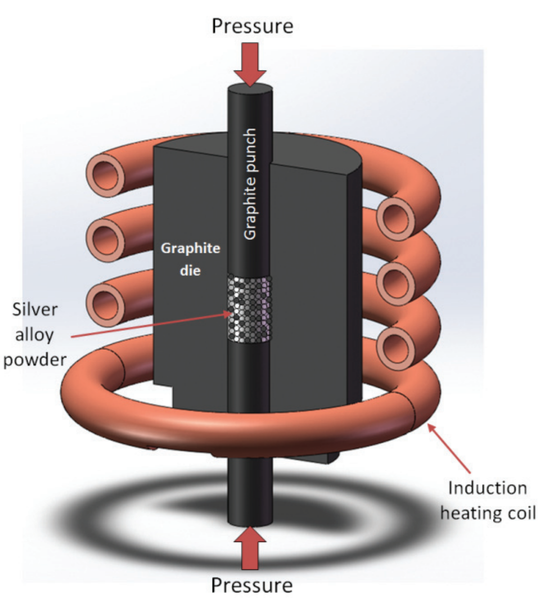


Figure 3. The hot pressing process: schematic of the apparatus.

The Vickers hardness evaluation (Microhardness tester, type M, Shimadzu, Japan) of the hot pressed compacts was conducted for all processing conditions. Five indentations were made in each type of substrate and the mean value and standard deviation was calculated. The load used was 1000 g and it was applied for 15s.

2.3. *Statistical analysis*

Data were analyzed using OriginPro statistic software (Version 8.5.1). The Kolmogorov_Smirnov test was first applied to test the assumption of normality. Differences between the various processing parameters (pressure, time and temperature) in terms of the relative density and hardness of specimens were tested using one-way ANOVA. P values lower than 0.05 were considered statistically significant in the analysis of the results.

2.4. *Microstructure and chemical analysis*

The hot pressed compacts were analyzed by optical microscopy (Axiotech, Carl Zeiss, USA) and SEM/EDS (Nova 200, FEI, Oregon, USA). For this, samples were embedded in auto-polymerizing resin, ground using SiC paper to successively finer grits to 1200-grit, and then polished, with first in 6µm and finally in 1µm diamond paste on felt discs. To analyze the microstructure, the hot pressed specimens were etched with a solution used for etching silver-copper alloys, chromic acid containing 7.6 g/L of CrO_3 and 8 g/L of sulfuric acid[3].

3. Results and Discussion

3.1. *Microstructure*

The microstructures of the etched, hot pressed sterling silver specimens are shown in Figure 4. The specimens hot pressed for different times exhibited different microstructures. The micrographs corresponding to lower hot pressing temperatures, namely 250 °C to 400 °C (Figure 4A-C), show the morphology of the original metallic particles, indicating that they were taken during an early stage in the sintering process. The colour contrast in Figures 4A-C is due to the etching treatment performed on the surface. The dark phase do not represent porosity. After hot pressing at a temperature of 500 °C (Figure 4D) the particles contours started to fade out, indicating an increase in sintering kinetics and solid state diffusion bonding. After hot pressing at a temperature of 700 °C (Figure 4E) the particles completely sintered and the boundaries between them could no longer be distinguished, resulting in a homogeneous etched surface.

It must be pointed out that the hot pressed specimens presented a microstructure distinct from the typical dendritic microstructure of the cast sterling silver alloys[15]. Nisaratanaporn et al.[16] reported that for cast materials, the presence of eutectic structures existing between dendrite arms (interdendritic regions). Despite exhibiting a different type of microstructure, the SEM micrographs of the hot pressed specimens also revealed the presence of eutectic structures mainly in specimens hot pressed at low temperatures (250 °C-400 °C). Figure 5A shows SEM micrographs of a specimen hot pressed at 300 °C where an eutectic type structure is presented. The chemical composition of this structure is 66%Ag-34%Cu (Table 2), which is close to the eutectic composition found in binary Ag-Cu phase diagram[3]. For higher temperatures (>400 °C), the eutectic structures tended to disappear and be replaced by Cu-rich precipitates (Figure 5B and Table 2).

Table 2. Chemical composition of the phases present in the hot pressed sterling silver compacts. Processing conditions: 700 °C; 30 min.

Region	Composition (wt%)	
	Ag	Cu
Eutectic structure	66	34
Z1 – Ag-rich phase (matrix) (α phase)	94	6
Z2 - Cu-rich phase (β phase)	31	69

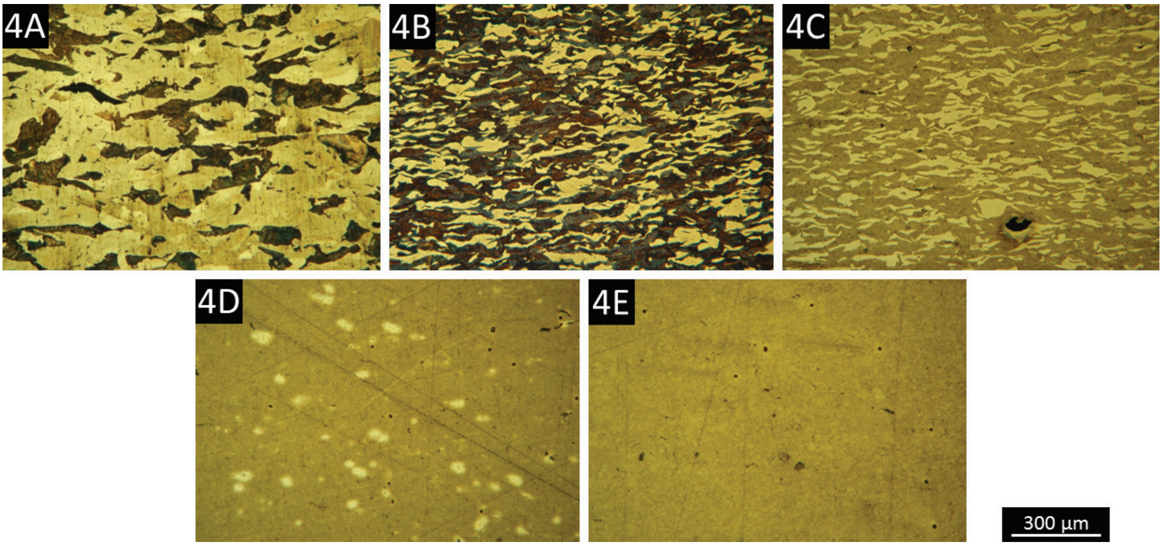


Figure 4. Microstructures of the hot pressed sterling silver processed at a pressure of 35MPa for 60 minutes at different temperatures: A) 250 °C; B) 300 °C; C) 400 °C; D) 500 °C and E) 700 °C.

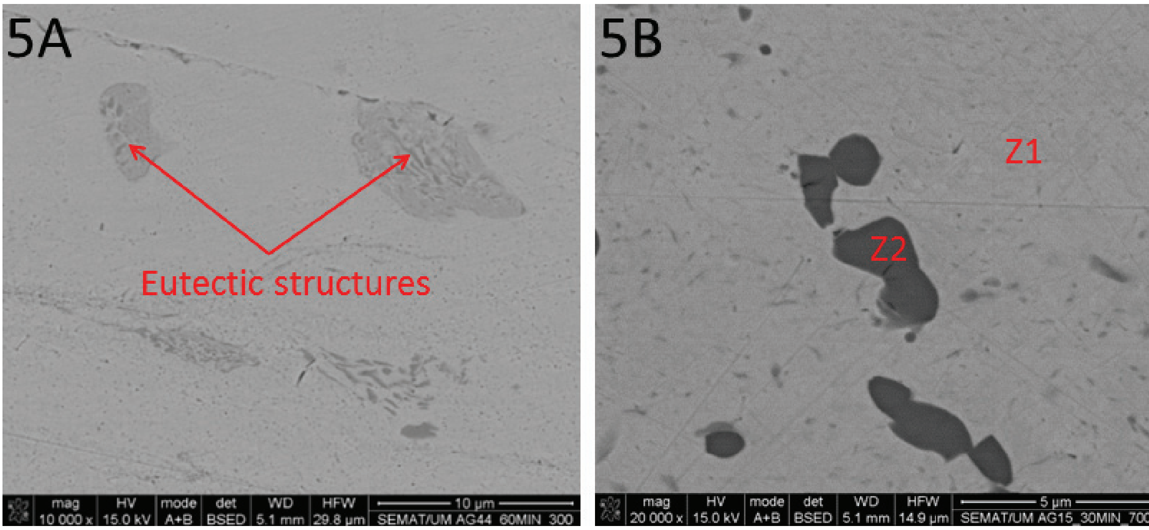


Figure 5. Micrographs of the hot pressed sterling silver compacts. A) 300 °C, 60min, 35MPa; B) 700 °C, 30min, 35MPa. The dark phase refers to a Cu-rich phase (β phase).

Figure 6 shows the SEM micrographs of hot pressed sterling silver specimens at different temperatures. Specimens hot pressed at low temperatures, namely 250 °C and 300 °C, exhibited extremely fine Cu-rich precipitates and some eutectic microstructures could also be observed. The specimens sintered at higher temperatures (400 °C, 500 °C and 700 °C) exhibited microstructures mainly composed by Cu-rich precipitates embedded in the Ag-rich matrix. The precipitates were found to be affected by the hot pressing temperature, i.e. they grew with temperature. In this way, the specimens hot pressed at 400 °C exhibited a larger number, but smaller, precipitates than those hot pressed at 500 °C. The same trend was observed for precipitates found in specimens hot pressed at 700 °C.

The formation of the eutectic structures that were found in specimens hot pressed at low temperature must have occurred at the casting process of the alloy. These structures remained in the powders after their manufacturing. The 250 °C and 300 °C hot pressing temperatures were found to be insufficient to promote the diffusion of the copper atoms towards the growth of Cu-rich precipitates as those found in specimens sintered at higher temperatures, namely at 400 °C, 500 °C and 700 °C (Figure 6). Higher temperatures means higher diffusion kinetics and this explains why the Cu-rich precipitates are bigger for higher temperatures.

3.2. *Relative density*

Figure 7 shows the effect of the hot pressing processing conditions, pressure, time and temperature, on the relative density of sterling silver powders compacts. The results show no significant differences ($p>0.05$) in terms of relative densities when pressures above 25MPa were used to hot press the sterling silver powders. This can be important because the use of low pressures in hot pressing can positively impact the life of the dies, resulting in economic benefits. The different hot pressing times used in this study also showed no significant ($p>0.05$) differences in the relative densities of the specimens. It was verified that the shortest hot pressing time, 10 min, generally resulted in the same relative densities of the specimens that were hot pressed for 30 minutes and 60 minutes. The hot pressing temperature was the variable that was found to produce significant ($p<0.05$) differences in the relative densities. The employment of hot pressing temperatures of 250 °C and 300 °C resulted in porous compacts. On the other hand, hot pressing temperatures equal or above 400 °C were found to produce fully dense compacts (d=~100%).

The presence of porosity in the samples showed to affect the sintering kinetics of the samples hot pressed at 250 °C and 300 °C (Figure 7). For temperatures above 400 °C this effect was not significant as in those situations high densities (full density in some cases) of compacts were promptly reached even for low sintering times.

3.3. *Hardness*

Hardness is perhaps the most important mechanical parameters among the mechanical properties assessed in jewelry alloys; first, because it is easy to measure and second, because it greatly impacts the fabrication and the performance of the jewelry item when worn by the costumer[17].

Figure 8 shows the effect of the hot pressing conditions, pressure, time and temperature on the hardness of hot pressed sterling silver compacts. The analysis of the hardness results showed that it was only significantly ($p<0.05$) affected by the hot pressing temperature. Neither pressure nor time resulted in significant differences in terms of hardness values. For all sintering times, the hardness values displayed an increasing trend until 400 °C, followed by a downward trend for higher temperatures. The first part, corresponding to the hardness increase until the hot pressing temperature of 400 °C, can be explained by the continuous densification of the powder compacts that was observed

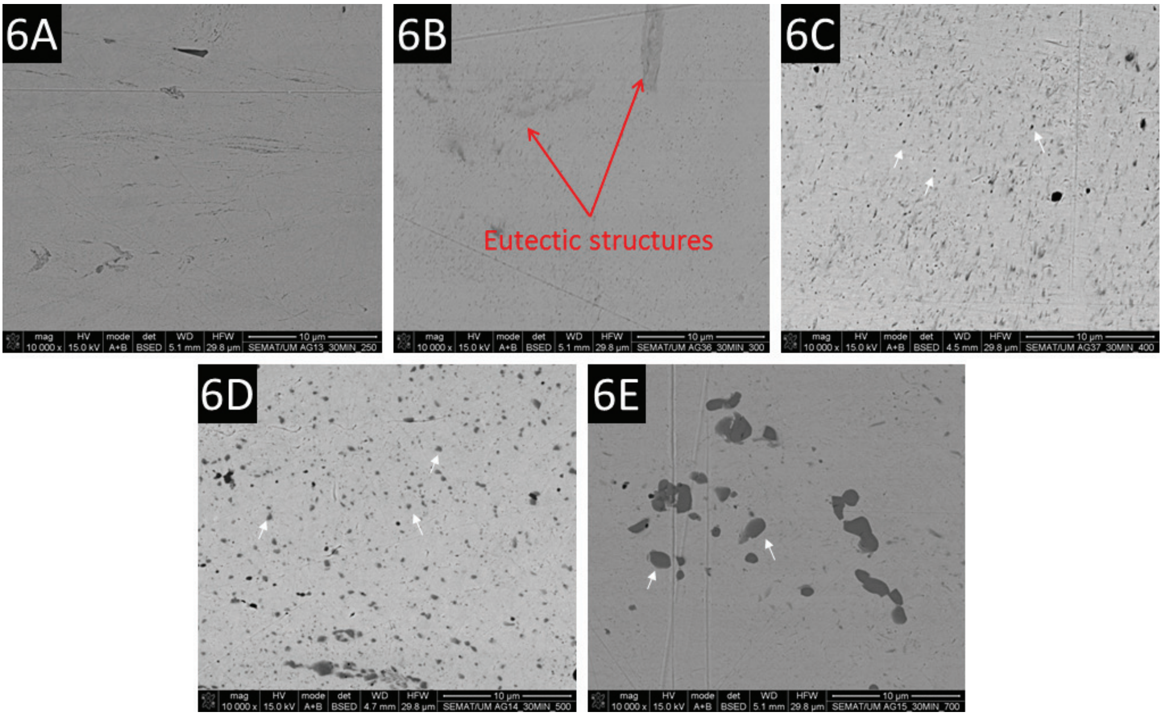


Figure 6. SEM micrographs of hot pressed sterling silver compacts processed at a pressure of 35MPa for 30min at different temperatures: A) 250 °C; B) 300 °C; C) 400 °C; D) 500 °C and E) 700 °C. White arrows indicate the Cu-rich precipitates (β phase).

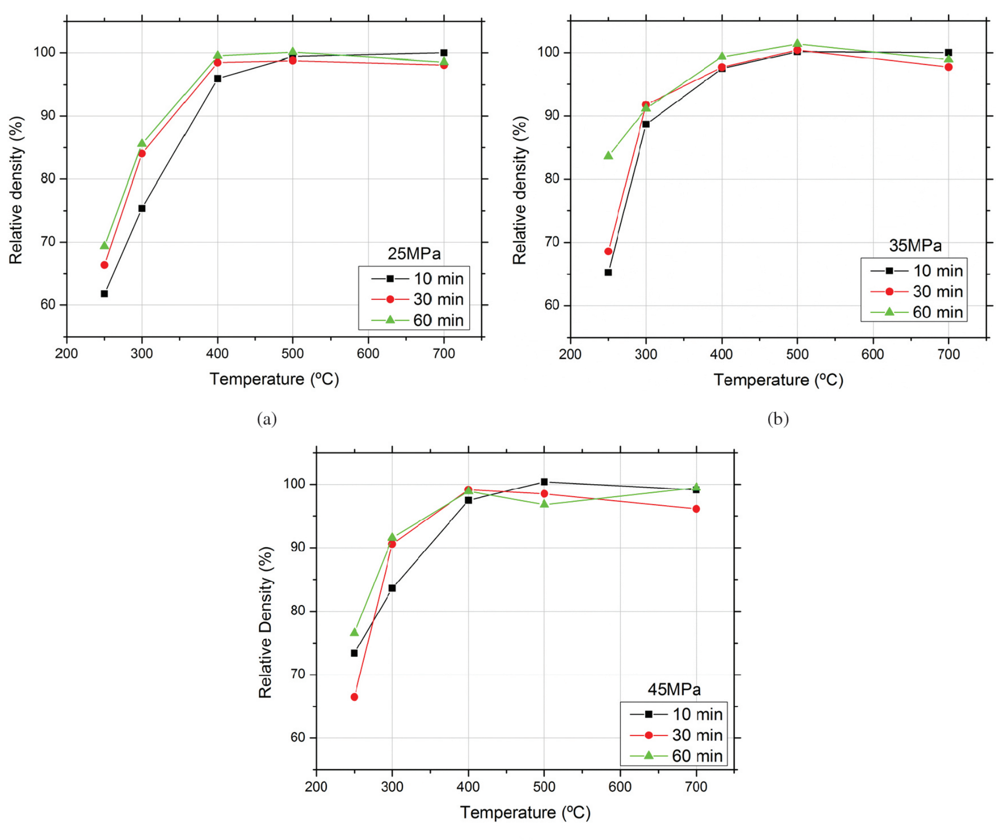
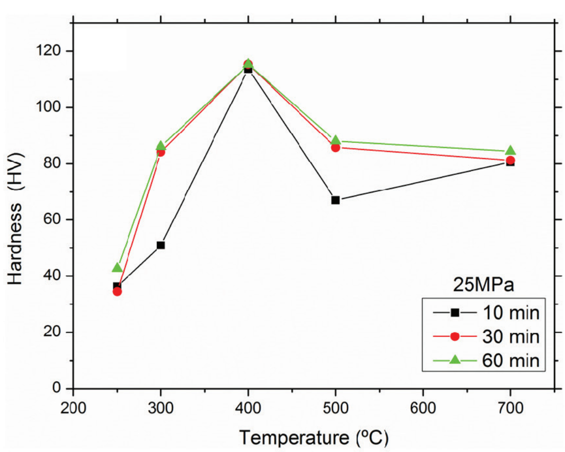
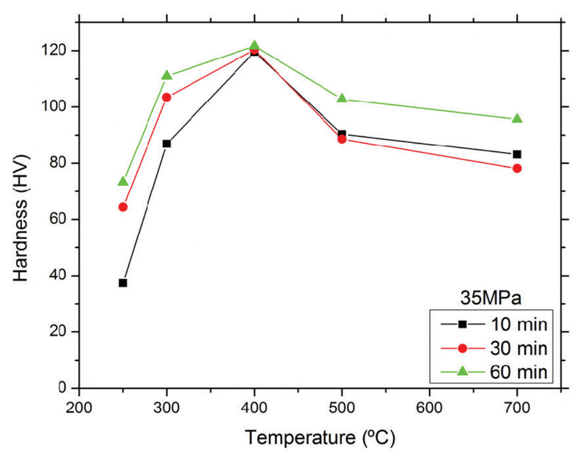


Figure 7. Influence of the processing parameters (pressure, time and temperature) on the relative density of the hot pressed sterling silver powder compacts.

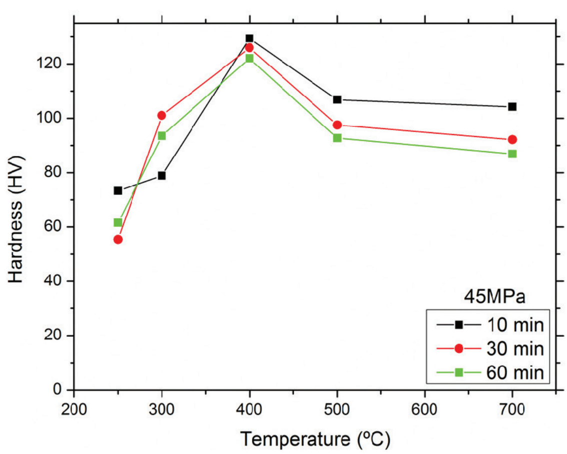
until the theoretical-like densities had been reached at this temperature (Figure 7). For higher sintering temperatures, namely 500 °C and 700 °C, a decrease in the hardness values was observed, despite the fact that the specimens were fully densified (Figure 7). There are some features occurring during the hot pressing cycles that explain such behavior, namely the occurrence of over aging mechanisms[2,4]. Age hardening is performed at low temperatures and increases the hardness of silver-copper alloys due to the formation of Cu-rich precipitates (β phase) out of the Ag-rich phase (α phase). The small precipitates are very effective in causing hardening. Figure 6 shows the formation of the Cu-rich precipitates (dark phase) within the Ag-rich matrix and their growth and coarsening with increasing hot pressing temperatures. In Figure 9 is shown the variation of the size of the Cu-rich precipitates with the hot pressing temperature along with the influence on the hardness, for the same hot pressing conditions shown in Figure 6. The analyses of Figure 6 and Figure 9 together shows that the precipitates formed at 400 °C are fine (0.22μm) and well distributed throughout the matrix, thus resulting in the maximum hardness (120HV). Conversely, the precipitates formed at 500 °C and 700 °C tend to be coarser in size (0.6μm and 1.75μm, respectively) and fewer in number as compared to those present in the specimens hot pressed at 400 °C. The overaging effect on the specimens lead to the formation of coarser microstructures that produced a decrease in hardness by releasing the coherency strains[18]. These findings are in good agreement with those reported by Seol et al.[18]. They have shown that the maximum hardness for a silver-copper alloy for dental application subjected to age hardening treatment was obtained with an aging temperature of 400 °C. They also verified that the maximum hardness values were registered for aging times between 10 and 100 minutes at this temperature. This finding is very important as it allows us to explain why no significant differences were found in hardness values of hot pressed compacts hot pressed at 400 °C for different times, namely 10, 30 and 60 minutes (Figure 8).



(a)



(b)



(c)

Figure 8. Influence of the processing parameters (pressure, time and temperature) on the hardness of the hot pressed sterling silver powder compacts.

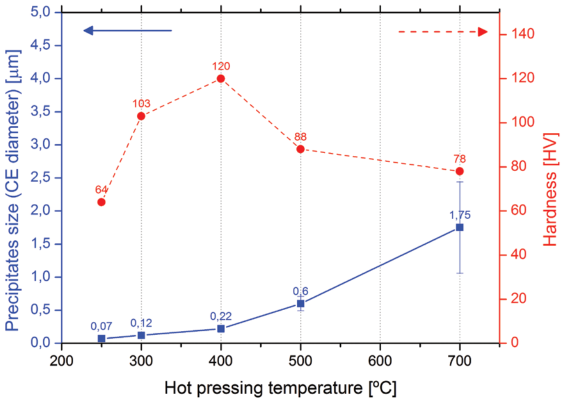


Figure 9. Plot of the relationship existing between the size of the Cu-rich precipitates (β phase) and the hardness measured in hot pressed sterling-silver compacts (Ag-Cu alloy) at a pressure of 35MPa for 30min and at different temperatures. CE = Equivalent Circular Diameter.

4. Conclusions

In this study, several processing parameters (pressure, time and temperature) involved in the hot pressing technique were investigated in terms of their influence on the microstructure, relative density and hardness of silver-copper powder compacts (sterling silver alloy). Within the limitations of this study, the following conclusions can be drawn:

- The hot pressing technique was shown to be a feasible process for producing full-dense silver alloy powder compacts;
- Of the parameters that were varied, temperature was shown to be the most important sintering parameter in the densification of the sterling-silver powders by hot pressing;
- The lowest temperature that lead to full-dense compacts was a sintering temperature of 400 °C;
- The sintering temperature of 400 °C resulted in the highest hardness with a value of 120HV;
- During low sintering temperatures (400 °C), the silver alloy underwent age-hardening caused by the formation of Cu-rich precipitates from the Ag-rich matrix, which lead to an increase in hardness. Higher sintering temperatures (500 °C-700 °C) resulted in overaging, i.e. the growth and coarsening of Cu-rich precipitates which decreased the hardness of the alloy;
- The microstructure of sintered silver alloy compacts produced at temperatures of 500 °C is composed by Cu-rich precipitates (β phase) dispersed in the Ag-rich matrix (α phase).

Acknowledgements

This work has been supported by Pos-doc grant of FCT (Portuguese Foundation for Science and Technology) with the reference SFRH/BPD/87435/2012.

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