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DENSIFICATION OF PRE-MIXED AND PREALLOYED Cu-12Sn BRONZE DURING MICROWAVE AND CONVENTIONAL SINTERING

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ABSTRACT

The present study compares the effect of microwave and conventional furnace sintering on bronze powder compacts. Cu-12 wt.% Sn compositions prepared by premix and prealloyed powder route were sintered in a range of temperature corresponding to solid-state, transient and supersolidus liquid phase sintering conditions. The compacts were characterized for sintered density and densification parameter. This study also examines the role of initial porosity variation on the microwave sintering and compares the densification results with those processed by conventional sintering.

INTRODUCTION

Microwaves are electromagnetic radiation with wavelength ranging from 1 mm to 1 m in free space, and frequency ranging from 0.3 GHz to 300 GHz [1]. However, only a narrow frequency range centered at 915 MHz and 2.45 GHz are permitted for research purposes [2]. Compared to conventional heating, where heat transfer occurs predominantly *via* radiative mode, in microwave heating the sample *per se* acts as a source of heat. In conventional heating, the heat transfer mode is from outside to inside. This poses a limitation of sample size and heating rate in order to minimize thermal gradient. In contrast, microwave heating is much more uniform at a rapid rate. The rapid heating by microwaves reduces processing time and results in energy saving. In addition, the uniform heating minimizes problems such as abnormal, localized microstructural coarsening, and thereby results in improved properties.

Nowadays, microwave processing is being applied for materials synthesis by sintering [3-5]. Until recently, most of the microwave sintering was restricted to ceramic materials [6]. Subsequently, the applicability of microwave sintering was extended to consolidate cemented carbides for cutting and drilling tools [7-10]. However, the microwave sintering of metal was not envisaged because metals tend to reflect microwaves. Recently, it was shown that metals too can couple with microwaves provided they are in powder form rather than monolithic [11]. Subsequently, microwave sintering of P/M steel was conducted [12,13]. Anklekar *et al.* [14] demonstrated higher sintered density, hardness and flexural strength in microwave sintered Fe-2Cu-0.8C (FC0208) steels as compared to conventional sintering. Microwave heating is a very sensitive function of the material being processed and depends on several factors, such as sample size, its mass and geometry. Though there have been attempts to explain microwave heating of metal powders, still there is not yet any consensus on a comprehensive theory to explain the mechanism [15].

In order to understand the interaction of microwaves with metal powders and compare the response of metal powder compact in microwave *vis a vis* conventional sintering, experiments are required with a simpler system. Copper-tin based bronze is one such alloy system. Figure 1 shows the phase diagram of the Cu-Sn system [16]. Powder metallurgy is an established processing technique for consolidating Cu-Sn bronzes containing up to 15% Sn and the conventional sintering response of Cu-Sn system has been extensively studied over the last several decades [17]. Tailored composition of Cu-Sn powders can be prepared by both premixing as well as prealloying route. Sintered bronzes are typically used for self-lubricating bearing and porous filters. Both these applications require controlled porosity in the sintered component. This is achieved by sintering the Cu-Sn alloys to a temperature above the melting point of Sn (232°C), typically between 450-650°C. At these temperatures, Sn has higher solubility in the Cu-matrix and consequently the Sn-melt diffuses into Cu and leaves behind porosity whose size and volume fraction corresponds to Sn powder size and content, respectively. Typically, the porosity ranges from 20 to 40%. This process is termed transient liquid phase sintering and requires premixed Cu-Sn powders. Nowadays, P/M bronzes are also being consolidated for structural applications by employing prealloyed powders. Use of prealloyed powder eliminates transient melt formation. The prealloyed powders are usually sintered in solid-state to relatively higher temperatures (up to 780°C). In prealloyed bronze, the predominant sintering mode is solid-state. In addition to the transient and solid-state sintering route, the Cu-Sn alloys can also be consolidated through super-solidus liquid phase sintering (SLPS). As the name suggests, in SLPS, the sintering temperature is above the solidus temperature, which results in melt formation preferentially at intergranular regions. The intergranular melt, contributes to densification by capillary-induced rearrangement [18-20].

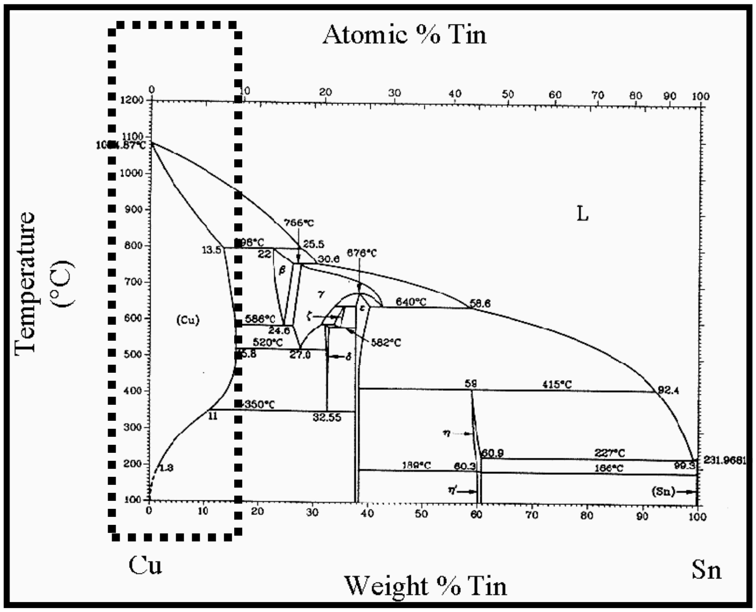


Figure 1. Phase diagram of Cu-Sn system [1].

From the above discussion, it is evident is that Cu-Sn alloys not only have a simple chemistry, but it also offer a unique opportunity to investigate solid-state, transient, and supersolidus liquid phase sintering all in one system at relatively lower processing temperature (< 1000°C). This study therefore aims at investigating the sintering response of Cu-Sn compacts as a function of powder condition, compaction pressure during microwave heating and comparing the same with conventional sintering.

EXPERIMENTAL PROCEDURES

For the present study, a Cu-12Sn (wt.%) composition was selected. The water-atomized Cu powder had an average size of 25 µm whereas the Sn powder (gas atomized) was spherical in shape with an average size of 15 µm. The details of powder characteristics is given elsewhere [21]. Both the powders were mixed together in requisite proportion in a Turbula mixer (Type 2C, Bachofen AG, Germany) for about 30 min. The composition so prepared is referred to as 'premixed'(PM) Cu-12Sn. In the second set of experiment, gas-atomized 'prealloyed' (PA) Cu-12Sn powder was chosen for investigation. The prealloyed Cu-12Sn powders had an average size of about 20 µm. Both the premixed and prealloyed powders were pressed to cylindrical compacts (12.7 mm diameter) in a 20 ton hydraulic capacity press (Apex Ltd., UK).

The as-pressed compacts were 'conventionally' sintered in a SiC-heated horizontal tubular furnace (Bysakh & Co., Kolkata, India) in forming gas ($95N_2$-$5H_2$) mixture. The furnace had a hot zone of about 75 mm. As described earlier, depending on the processing temperature, Cu-Sn alloys can be consolidated by solid-state, transient liquid phase or by supersolidus liquid phase sintering. Consequently, the Cu-12Sn alloys in the present study were sintered at 450°C, 775°C, and 830°C, respectively. In conventional sintering the compacts were heated at a constant heating rate of 5°C/min. A hold for 30 min was provided at the sintering temperature. The temperature was controlled to the accuracy of ± 3°C.

In another set of experiment, a 2 kW commercial microwave oven (Amana Radarange, model RC/20SE) with a 2.45 GHz multimode cavity was used to sinter the PM and PA Cu-12Sn alloys. The microwave setup was modified to keep the external body temperature of the oven close to the ambient by circulating cold water through the copper tubes fixed at the top and the sides of the double jacketed oven by brazing. A mullite tube 31.8 mm diameter and 914.5 mm in length was positioned at the center of the oven, by drilling holes on the side-faces, with ends projecting on both the sides. The schematic diagram of the microwave setup is shown in Figures 2a and 2b. As shown in Figure 2b, a mullite based insulation package made from Fiberfrax^{TM} boards was used to surround the mullite tube at the center of the cavity for containing the heat from dissipation during sintering. The design is so made that it could be used both with and without the use of suscepter or secondary coupler, which is either SiC rods or graphite coating on the outer surface of the alumina boat. The susceptors usually couple very well with the microwaves and are used for initially raising the temperature of the bronze to about 200°C. Above this temperature, the Cu-12Sn compacts start to couple with the microwaves. For the present investigation, graphite coating on the alumina boat was used as the susceptor. Thermocouples cannot be used for temperature measurement in microwave furnaces. Instead, the temperature of the sample was monitored using an infrared pyrometer (Raytek, Marathon Series) with the circular crosswire focussed on the sample cross-section. The infrared pyrometer was coupled to a data acquisition and display software on a personal computer. Further details of the experimental setup of microwave sintering is described elsewhere [14].

The sintered samples were characterized for the density. The sintered density was obtained both by Archimedes method as well as by dimensional measurements. The degree of densification during sintering was measured using a densification parameter, DP, which is expressed as:

$$DP = (\text{sintered density} - \text{green density}) / (\text{theoretical density} - \text{green density})$$

Tables 1 and 2 summarize the experimental variables.

Table I:

alloy	Cu-12Sn (wt.%)
condition	premixed (PM) and prealloyed (PA)
compaction pressure, MPa	150
sintering temperature, °C	450, 775, 830
sintering time, min	30

Table II:

alloy	Cu-12Sn (wt.%)
condition	premixed (PM) and prealloyed (PA)
compaction pressure, MPa	150, 300, 450, 600
sintering temperature, °C	775
sintering time, min	30

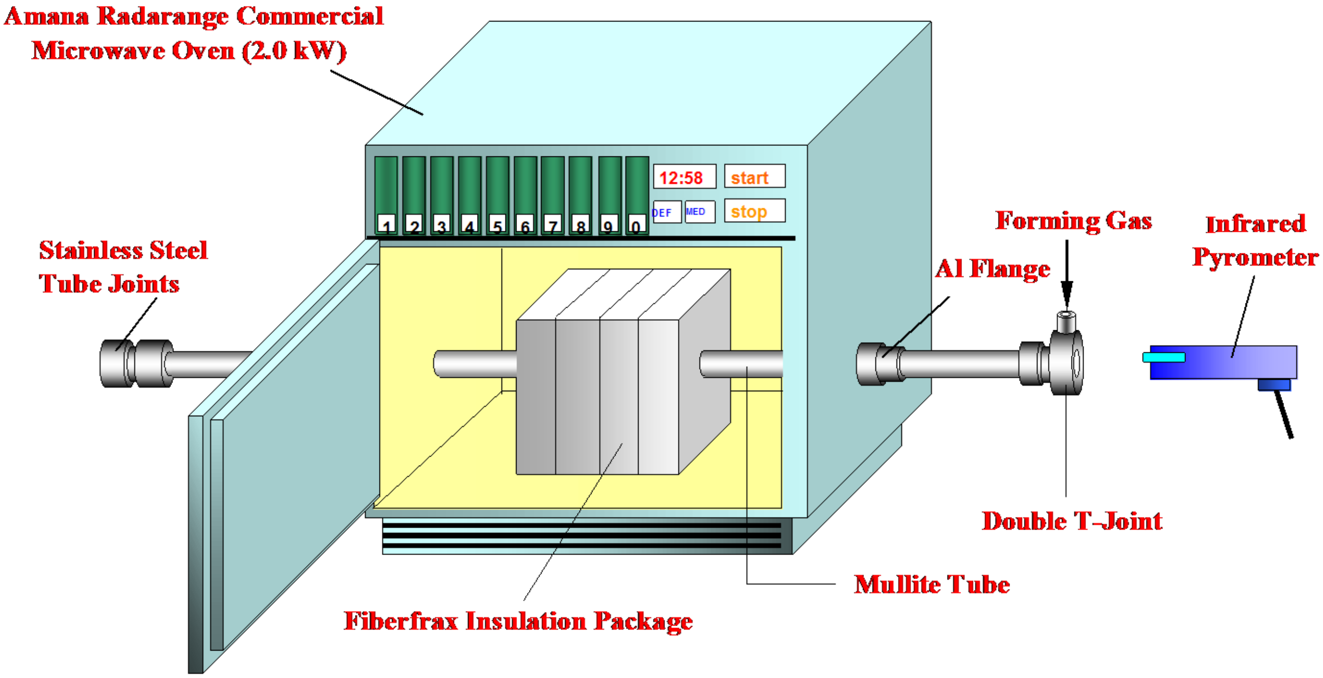
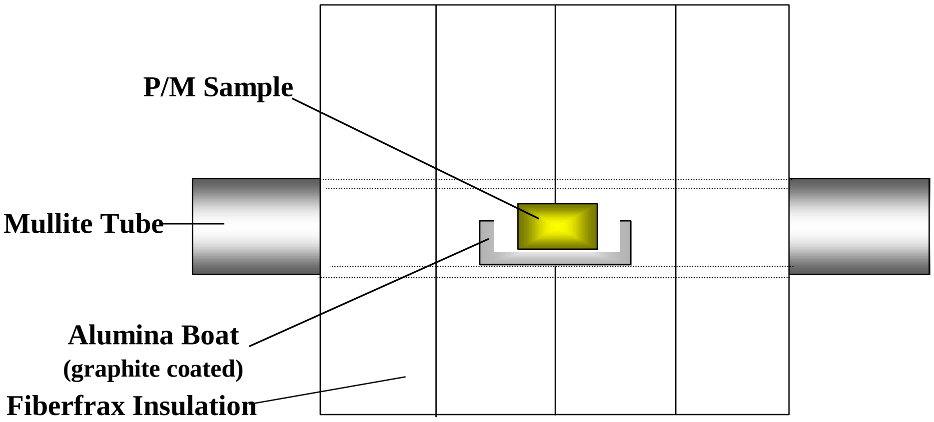


Figure 2a. Schematic diagram of the microwave furnace used for the present study.



Sintering Package Configuration

Figure 2b. Schematic diagram of the configuration of the sample during microwave sintering.

RESULTS AND DISCUSSIONS

Figure 3 compares the thermal profile of P/M bronze samples under microwave and conventional heating. Excluding the cooling time, it takes about 3 h for the sintering in a conventional furnace, whereas in a microwave furnace the sintering time is reduced by more than 50%. As the thermal mass is less during microwave heating, hence the microwave sintered samples cooled faster as compared to the conventionally sintered ones. During microwave heating, the temperature measurement was conducted using an infrared pyrometer, which is emissivity based, therefore temperature could not be measured below 350°C. From Figure 3, it is quite evident that both the premixed and prealloyed bronze samples couple with the microwave and do heat up. Interestingly, the prealloyed samples start to heat up slightly faster than the premixed samples.

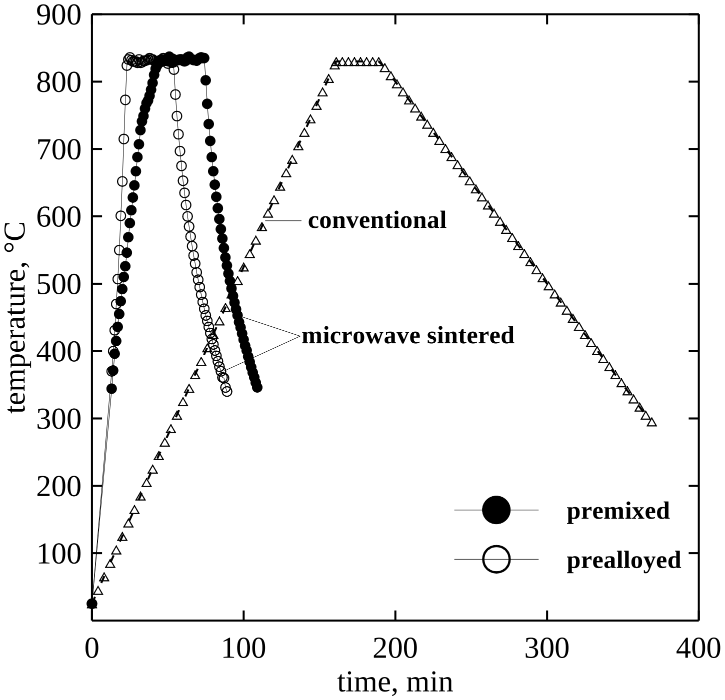


Figure 3. Thermal profile of conventional and microwave sintered Cu-12Sn alloy.

Effect of Sintering Temperature

Figures 4a and 4b show the variation in the sintered density and densification parameter with temperature during microwave sintering. For all the three sintering temperatures, the sintered density of premixed compacts is slightly higher than that of prealloyed ones. This can be attributed to the initially higher green density of premixed bronze as compared to the prealloyed sample at 150 MPa. Because of the solid-solution formation, the prealloyed bronze powders usually have lower compressibility as compared to the premixed ones. Sukanta [21] has shown that the green density of PM bronze is about 68% at 150 MPa, whereas that of PA samples is around 60%. Both the PM and PA microwave sintered samples show highest density at 775°C. During supersolidus liquid phase sintering (at 830°C), there is a density drop in both samples. For PM compacts, this can be attributed to the formation of transient Sn melt and its diffusion in the Cu matrix [22-24]. It is hypothesized that due to rapid heating in the microwave, there is very little time available for diffusion of Sn into Cu. Hence, most of the diffusion may be taking place during the sintering hold at 830°C. Usually, the diffusion of the 'primary' Sn-melt into the Cu will result in compact swelling. However, during supersolidus liquid phase sintering at 830°C, there will be a formation of Cu-Sn melt at the grain boundary and within the grains. Unlike the primary melt, this 'secondary' melt-formation will promote compact densification. Thus, during microwave sintering of PM bronze at 830°C, compact density will depend on the nature of melt and their volume fraction. In case of PA bronze, no primary (Sn) melt formation is expected at any stage, therefore, the compact is expected to show continued densification with increasing temperature. However, just like PM bronze, the density of the microwave sintered PA bronze is also lower at 830°C as compared to 775°C. This is possibly due to decoupling between microwaves and the bronze compact because of the formation of the secondary melt. The trend in densification parameter variation with temperature (Figure 4b) is similar to that of the sintered density.

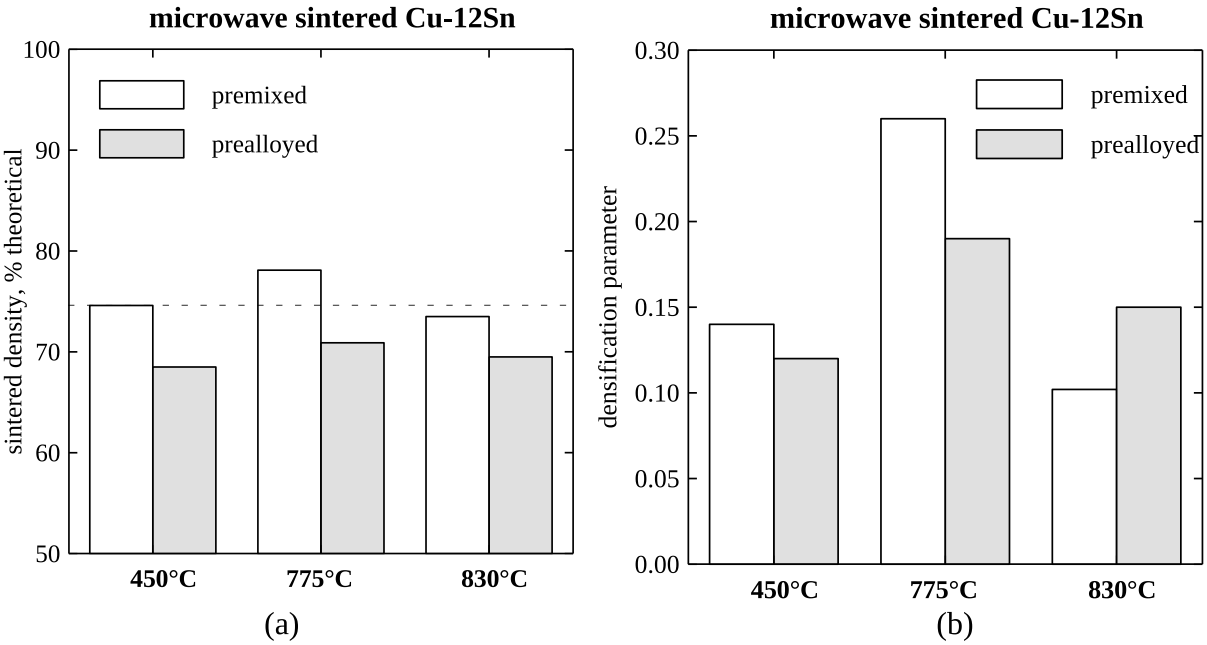


Figure 4. Effect of varying temperature on the (a) sintered density and (b) densification parameter of microwave sintered PM and PA Cu-12Sn alloy.

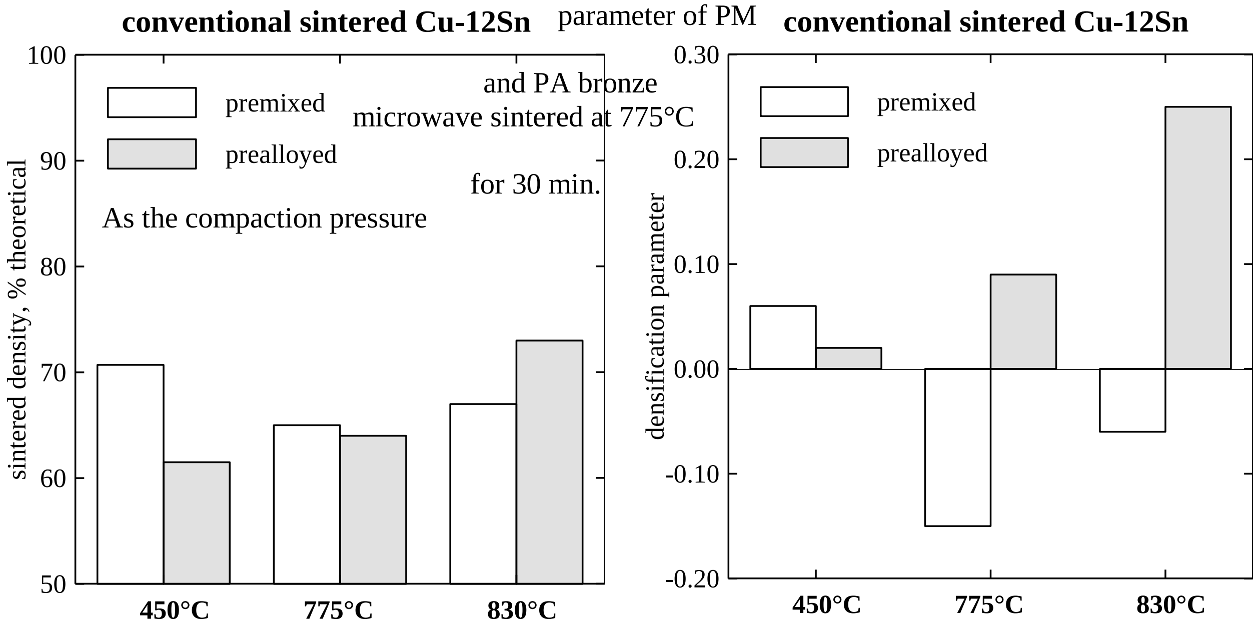
Figures 5a and 5b compare the variation in the density and densification parameter with temperature for conventionally sintered PM and PA bronze. Unlike microwave sintering, both the sintered density and densification parameter of conventionally sintered PA bronze increases with increasing temperature and is highest for supersolidus sintered condition. For PM bronze, the sintered density at 775°C and 830°C is lower than that at 450°C. From Figure 5b, the densification parameter of PM bronze at those two temperature is negative which implies compact swelling. As discussed earlier, compact swelling is attributed to the diffusion of the primary or transient Sn-melt into Cu and therefore is a characteristic of PM samples only. As indicated by the densification parameter, the compact swelling at 830°C is lower than that at 775°C. The decrease in compact swelling of PM samples at 830°C is because of the supersolidus sintering conditions which aids in densification, and thereby minimize the swelling tendency.

Figures 6a and 6b summarize the effect of powder condition (PM *vs* PA), sintering mode (conventional *vs* microwave) and temperature on the sintered density and the densification parameter, respectively. It is interesting to note at 150 MPa, none of the microwave sintered samples swell, whereas the conventionally sintered PM samples show dilation. Figures 7a and 7b show the PM Cu-12Sn compacts microwave and conventionally sintered at 775 and 830°C. Note that the microwave compacts are slightly smaller than the conventionally sintered ones. This is supported by negative densification parameter in the conventionally sintered PM bronze, which indicates swelling. For the same conditions, the microwave sintered samples have positive densification parameter implying shrinkage. Figure 8 shows the photograph of PA Cu-12Sn sintered conventionally and in microwave at 830°C for 30 min. Unlike the PM samples, here both samples show densification, as indicated by their positive densification parameter.

However, the microwave sintered sample has lower density as compared to the conventionally sintered samples.

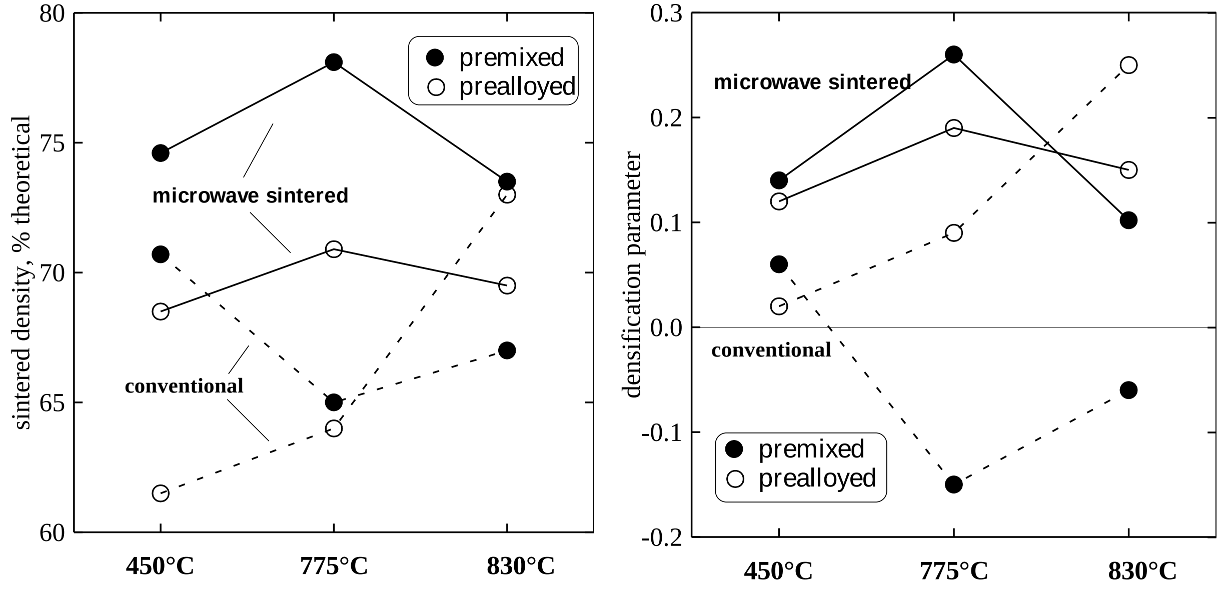
Effect of Compaction Pressure

Figures 9a and 9b show the effect of compaction pressure on the sintered density and densification parameter of PM and PA bronze microwave sintered at 775°C for 30 min. As the compaction pressure



(a) (b)

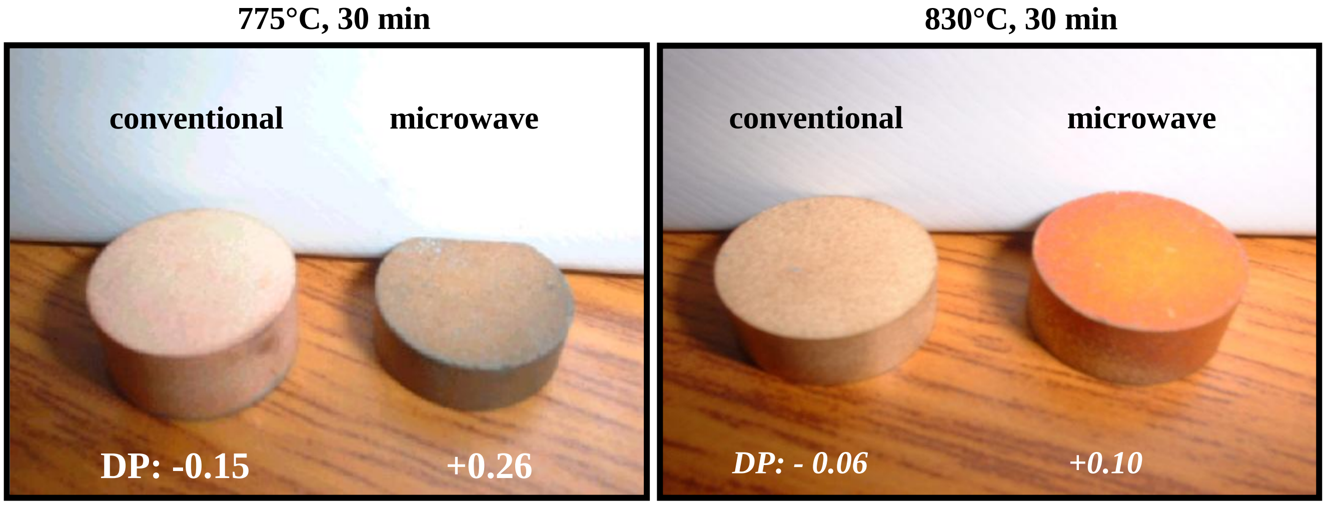
Figure 5. Effect of varying temperature on the (a) sintered density and (b) densification parameter of conventionally sintered PM and PA Cu-12Sn alloy.



(a) (b)

Figure 6. Effect of varying temperature and composition preparation route on the sintered density and densification parameter of conventionally and microwave sintered Cu-Sn alloy.

increases, the green density of Cu-12Sn alloy gradually increases. However, at higher pressures, there will be more variation in the green density of the compact from one region to another. From Figure 9a, the sintered density variation for both PM and PA samples is ± 3% which is of the same order of magnitude as the variation in the green density. Hence, comparison of just the sintered density may give confusing results. It is therefore more appropriate to compare the trend in densification parameter with varying compaction pressure for microwave sintered PM and PA samples (Figure 9b). For microwave sintered PA samples the densification parameter slightly increases with increasing pressure. Quite interestingly, all the PM microwave sintered samples show swelling, which increases with increasing compaction pressure. Similar results are also observed in the density and densification parameter variation in conventionally sintered PM bronze as shown in Figures 10a and 10b. The sintered density of



(a) (b)

Figure 7. Photographs of the PM Cu-12Sn compacts conventionally and microwave sintered at (a) 775°C and (b) 830°C for 30 min.

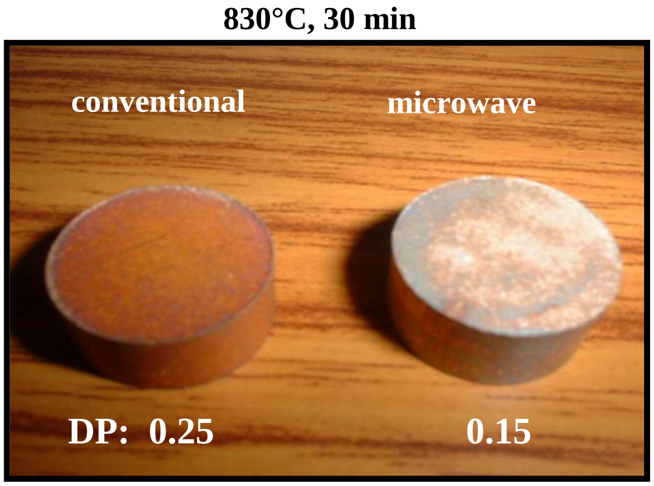
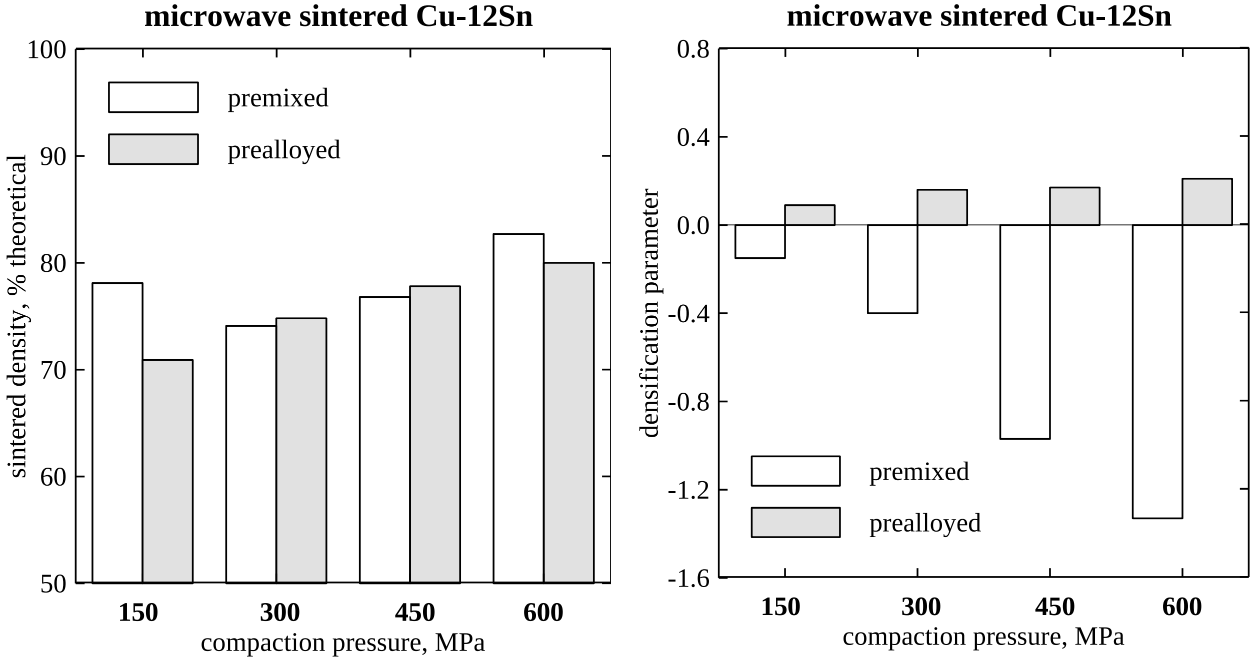


Figure 8. Photograph of the PA Cu-12Sn compacts conventionally and microwave sintered at 830°C for 30 min.

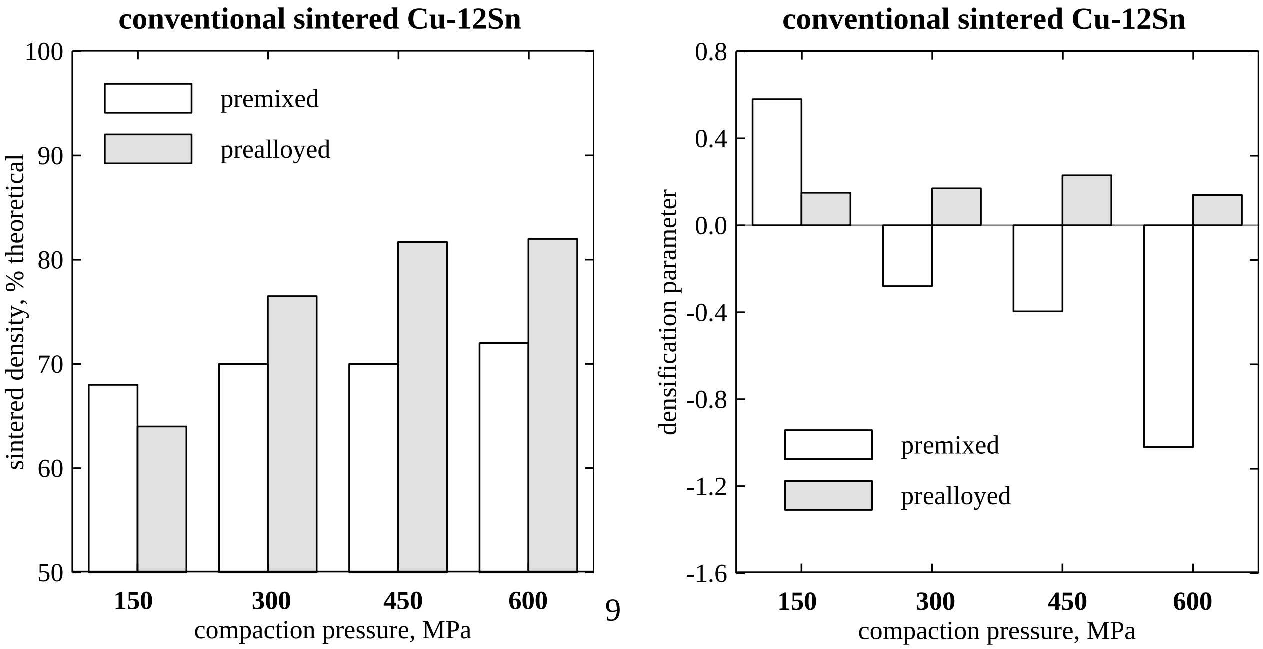
conventionally sintered PA Cu-12Sn increases with increasing compaction pressure (Figure 10a). However, this increase is due to the higher initial, as-pressed compact density. As evident from Figure 10b, there is no significant variation in the densification parameter of PA bronze with pressure during conventional sintering.

Figure 11 summarizes the effect of powder condition (PM *vs* PA), sintering mode (conventional *vs* microwave) and compaction pressure (green density) variation on the densification parameter of the bronze samples conventionally sintered at 775°C. As discussed before, the variation in initial porosity has no significant effect on the densification parameter of PA bronze sintered in both microwave and conventional furnaces. The PM bronze on the other hand swells with increasing pressure. This is in accordance with the well-documented observations of swelling in premixed bronzes [22-24]. A high



(a) (b)

Figure 9. Effect of varying compaction pressure on the (a) sintered density and (b) densification parameter of PM and PA Cu-12Sn alloy microwave sintered at 775°C for 30 min.



(a) (b)

Figure 10. Effect of varying compaction pressure on the (a) sintered density and (b) densification parameter of PM and PA Cu-12Sn alloy conventionally sintered at 775°C for 30 min.

compaction pressure results in lower porosity in green samples. Hence, the likelihood of Cu-Sn contact increases. During melt formation, this favors more effective diffusion of Sn-melt (primary liquid) into the Cu-matrix. This explains the increasing swelling in PM bronze with pressure. In addition, as the pore fraction reduces, the melt induced capillary stress also decreases proportionately [25]. Thus, such compacts will have lower structural rigidity and will be more prone to swelling. Microwave heating is usually more uniform as compared to conventional furnace heating. This will result in homogeneous melt formation and causes greater swelling of the microwave sintered PM Cu-12Sn compacts as compared to their conventionally sintered counterparts.

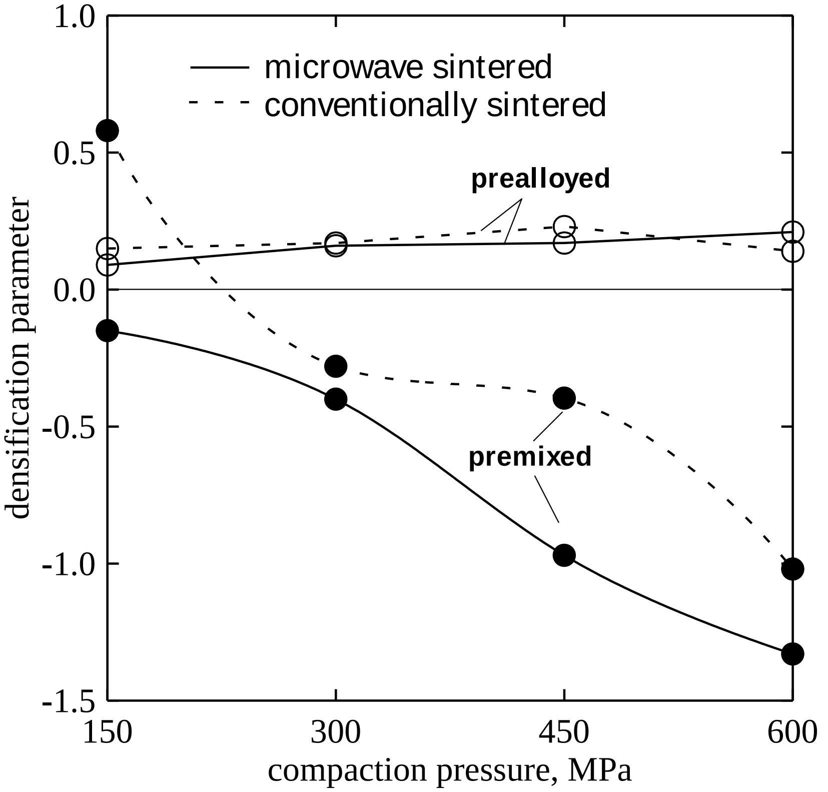


Figure 11. Effect of varying compaction pressure and composition preparation route on the densification parameter of Cu-12Sn alloy sintered in conventional as well as microwave furnace at 775°C for 30 min.

Recently, Upadhyaya *et al.* [26] have reported in detail the microstructural evolution in conventionally sintered premixed and prealloyed Cu-12Sn alloys. Work is underway to similarly characterize the microstructure of the microwave sintered samples and compare that with that with those obtained from conventional sintering.

CONCLUSIONS

For the first time, compacts prepared by using both premixed and prealloyed Cu-Sn bronze were sintered in microwave furnace for temperatures corresponding to transient, solid-state, and supersolidus sintering. As compared to conventional sintering, bronze was microwave sintered in significantly less time. In conventional sintering, the premixed bronze swells at 775°C and 830°C, whereas no swelling occurs during microwave sintering of both premixed as well as prealloyed compacts compacted at 150 MPa. Usually, the application of conventionally sintered premixed bronzes is restricted to making filters and bearings. However, the lack of swelling in premixed bronze during microwave sintering, offers an opportunity of extending their use for structural applications as well. This study also investigated the response of varying the initial porosity on the microwave and conventional sintering. In case of prealloyed bronze, the degree of densification remains unaffected by varying porosity (green density) for both microwave as well as conventional sintering. However, the premixed bronze samples show an increasing tendency to swell as the initial (green) porosity is reduced by increasing the compaction pressure. The swelling is more for microwave sintered samples as compared to conventionally sintered ones. Therefore, for fabricating bearing and filters with more porosity it is recommended to compact the premixed bronze at higher pressure, followed by microwave sintering.

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