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# The effect of powder sintering method on the densification and microstructure of pewter alloys

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**Abstract.** Pewter alloys made from tin, copper and antimony powders were sintered using microwave and conventional vacuum sintering. Three different compositions of the pewter alloy were used; 91Sn6Cu3Sb, 94Sn4Cu2Sb and 97Sn2Cu1Sb. The effect of densification and microstructure of the pewter alloys from varying sintering time and sintering mode were examined and compared. Samples were compacted at 40kN and sintered at 220°C. Samples in the conventional furnace were sintered 60 minutes and 120 minutes, while samples in the microwave furnace were sintered for 15 and 30 minutes. Samples sintered at longer sintering times resulted in higher density for both sintering methods. Microwave sintering produced samples with slightly smaller grain size than the conventionally sintered samples resulting in a better densification. There were no new phases formed from the sintering of pewter alloy.

*Keywords: microwave sintering, conventional sintering, pewter alloy, grain size and densification*

## 1. Introduction

Microwave processing has been applied to a wide variety of materials [1-4]. Microwave heating is fundamentally different from conventional furnace heating. The latter involves radiant/resistance heating followed by transfer of thermal energy via conduction to the inside of the body being processed. Microwave heating, on the other hand, is a volumetric process involving instantaneous, rapid and highly efficient conversion of electromagnetic energy into thermal energy. Thus, the use of microwave energy for materials processing has major potential and advantages over conventional heating. For example, microwaves allow enhanced densification at lower processing temperature and with shorter processing time. In the process of microwave heating, the materials absorb microwave energy themselves and then transform it into heat within the sample volume [5]. The energy is directly transferred to the material through the interaction of electromagnetic waves in the form of heat [6].

A review of the research undertaken in the field of microwave sintering reveals a significant amount of work on oxide ceramics and semi-metals like carbides and nitrides. The applicability of microwave sintering to metals has been overlooked because most metals are known to reflect microwaves [7]. Roy *et al.* [8] discussed the use of microwave sintering and noted that few experiments have been done with metal powders. Green laboratory and commercial compacts were microwave sintered, typically, at 1100°C to 1300°C for 5 to 30 minutes. The sintered compacts were reported to have uniformly distributed porosity with improved properties in comparison with conventionally processed materials. Roy *et al.* [8, 9] were the first to prove that metallic materials can be coupled with microwaves as long as they are in powder form. Rodiger *et al.* [10] reported that sintering of hardmetal with microwaves leads to a finer microstructure because of lower sintering temperatures and shorter processing times compared to conventional sintering.

Manufacturing industry in the 21st century will have to reduce its consumption of energy in order to protect the environment. Since the pewter industry uses traditional casting processes to make its products, the use of high temperatures requires large quantities of energy. However, a significant proportion of the energy is consumed in maintaining the temperature of the surrounding furnace material or container rather than being used in product manufacturing. If energy can be efficiently used in the manufacturing of products by improving the sintering process, less energy will be consumed, which will in turn save energy.

## 2. Experimental method

### 2.1 Mixing of powder

Tin powder with 99.5% purity (-100 mesh), copper powder with 99% purity (<75µm) and antimony powder with 99.5% purity (-100 mesh) were used to prepare samples of three different compositions; 97%wt Sn 2%wt Cu 1%wt Sb, 94%wt Sn 4%wt Cu 2%wt Sb and 91%wt Sn 6%wt Cu 3%wt Sb powders. These powders were weighed accordingly and placed into cylindrical containers which were then evacuated in a glove box. The evacuation process was repeated until the oxygen content was down to about 40 ppm. They were then mixed using a roller mixer (ABB:ABS 100) for about 12 hours at a frequency of 40Hz.

### 2.2 Preparation of green compacts

Twelve samples from 80g of powder were prepared from the same die to produce samples with a cross section of 10.1 mm in width and 30.8 mm in length with the height of 42mm in average. The samples were pressed at 40kN load in a 10 ton Hydraulic Floor Press Machine (D2003K) with a holding time of 5 minutes. Between these limits, samples were defect-free and had sufficient green strength for handling.

### 2.3 Sintering

Two samples from each composition were sintered using the conventional vacuum furnace for two different sintering times; 60 and 120 minutes. The other six were sintered using the microwave furnace for 15 and 30 minutes. All these samples were sintered at 220°C. A conventional furnace with cavity size of 5cm x 110cm under vacuum condition was used. A heating rate of 6°C/min was maintained for the conventional sintering. The vacuum pressure was always allowed to reach 10<sup>-6</sup> MPa before sintering. A Panasonic Thermwave Mod.111 multimode microwave system (1.3kW, 2.45GHz, 47cm x 61cm x 64 cm) with water cooling system designed for the high temperature processing of materials in a laboratory or small-scale industrial manufacturing was used for this study. The green compacts were placed in a cylindrical thermal pod made from ceramic fibre. The sample was sintered with graphite pellets which were used as susceptors to ensure that excessive heat and energy did not build up in the system. It helps to give a better control of temperature at the low sintering temperatures used. The power dial at the controller was adjusted to 50% input energy level and the microwave unit was set to 70% output power level to allow high and uniform heating rates of 15°C/min. The crucible was filled with argon gas prior to sintering and maintained a flow rate of 50mL/min during sintering since the

furnace was not designed for vacuum conditions. However, since short sintering times were used, the effects of using argon during sintering were neglected.

#### 2.4 Density Measurement

The density of as-pressed pellets was calculated from the sample mass and volume. Meanwhile, a liquid displacement method, Archimedes's technique, was used to determine the density of the sintered samples.

#### 2.5 Microstructural Analysis

Scanning Electron Microscopy (S-4700 Hitachi) was used to generate digital images from the etched specimens. The SEM images were also used to produce a virtual elemental map of a sample's surface. Grain size was calculated using the Lineal Intercept Method from images obtained using the optical microscope (Olympus BX60). X-Ray Diffraction (XRD) was performed using Philips X'PERT System. The patterns were used to characterise the sintered samples and to observe if any changes in phases occurred.

### 3. Results

#### 3.1 Density

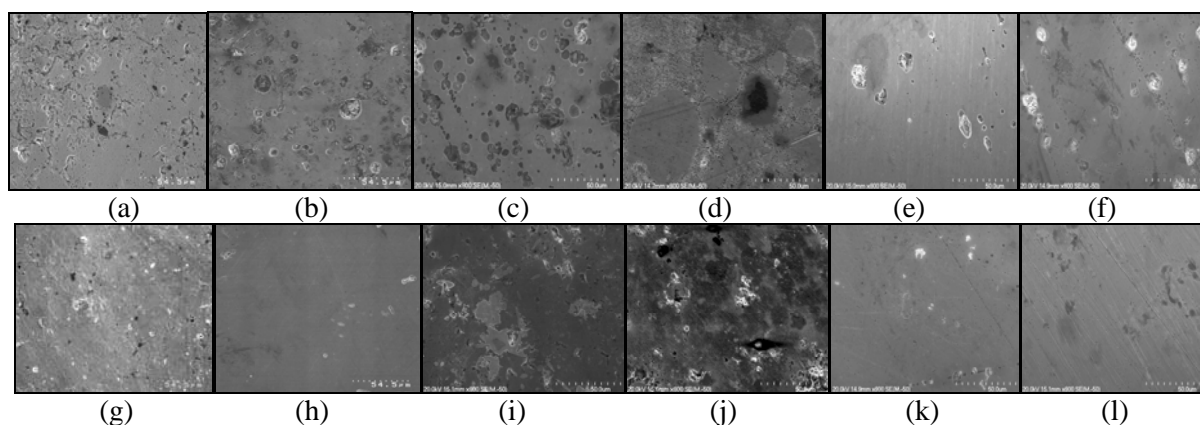
There are significant increases in density for all three compositions when the sintering time and temperature are increased. By increasing the sintering time for the conventional sintering from 60 to 120 minutes at 220°C, the bulk density for the composition of 97Sn2Cu1Sb increased from 91.05% to 98.28%. The composition of 94Sn4Cu2Sb showed a more significant increase in the density values upon sintering. Doubling the sintering time from 60 to 120 minutes has produced samples with bulk densities of 94.33% and 98.46% respectively. Similarly, the 91Sn6Cu3Sb composition has also shown comparable results with respect to change in bulk density. The samples for the 60 minutes and 120 minutes achieved densities with 94.39% and 98.51% of theoretical density respectively. Meanwhile, microwave sintering produced samples with higher densities when compared with conventional sintering as can be seen from Table 1. However, the percentage increase from doubling the sintering time from 15 minutes to 30 minutes appeared to be smaller than the percentage increase obtained from a conventional sintering process. However, the densities obtained from microwave sintering for 15 minutes is relatively higher than the densities obtained from conventional sintering for 60 minutes. The 97Sn2Cu1Sb, 94Sn4Cu2Sb and 91Sn6Cu3Sb alloy compositions reached theoretical densities of 98.71%, 98.75% and 98.79% respectively when sintered for 30 minutes. By increasing the copper and antimony content, the density values for the microwave sintering are similar but increased more significantly after conventional sintering.

**Table 1.** Summary of the measured theoretical density and the grain size values

Sample Name	Sintering time (min)	Sintering mode	% Theoretical Density	Grain Size (µm)
97Sn2Cu1Sb	60	CS	91.05	26
	120	CS	98.28	27
	15	MW	97.28	20
	30	MW	98.71	24
94Sn4Cu2Sb	60	CS	94.33	25
	120	CS	98.46	26
	15	MW	97.33	20
	30	MW	98.75	24
91Sn6Cu3Sb	60	CS	94.39	24
	120	CS	98.51	26
	15	MW	97.61	20
	30	MW	98.79	23

### 3.2 Grain Size

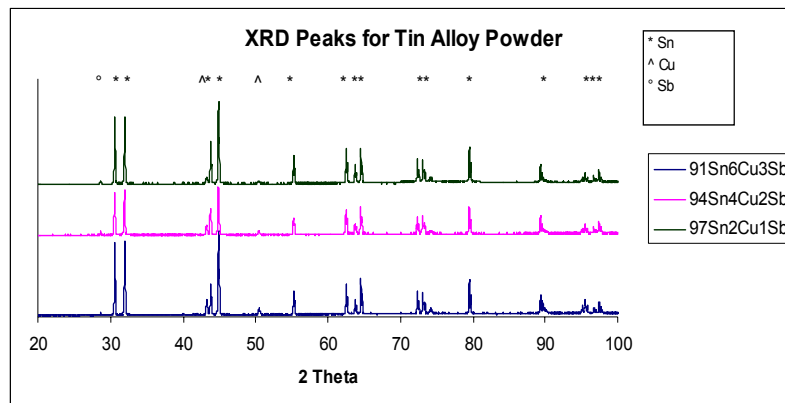
When compared with conventional sintering, microwave sintering resulted in less grain growth but better densification. SEM images from Figure 1 revealed that pores are generally smaller in size as the sintering time increases. This is noticed in all the three compositions; 97Sn2Cu1Sb, 94Sn4Cu2Sb and 91Sn6Cu3Sb. The grain size (Table 1) appeared to be similar with increasing percentages of copper and antimony in the tin alloy for the same sintering duration. On the other hand, conventional sintering gives more grain growth when compared with microwave sintering as a result of lower heating rates in conventional furnace. Thus, larger grain sizes appear in conventionally sintered samples than in microwave sintered samples. This grain coarsening in conventionally sintered material leads to lower hardness and tensile strength compared with the microwave sintered samples. Grain coarsening is driven by the grain boundary energy. Large grains tend to grow at the expense of smaller ones, leading to an increase in the mean size and a net reduction in the total amount of grain boundary per unit volume of material. Changes in pore size and grain size were evidences of microstructural change for both conventional and microwave sintering. No exaggerated grain growth occurs although a significant amount of porosity still exists between the grains for microwave sintered samples.



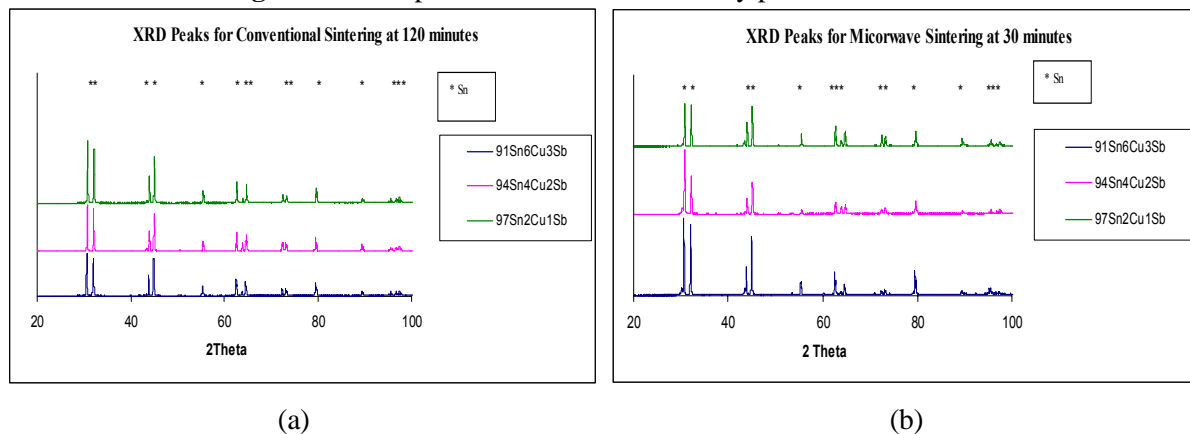
**Figure 1.** SEM images showing porosities in conventional sintered 97Sn2Cu1Sb samples (a)CS 60 min (b)CS 120 min, 94Sn4Cu2Sb (c) CS 60 min (d) CS 120 min, 91Sn6Cu3Sb (e)CS 60 min (f) CS 120 min and microwave sintered 97Sn2Cu1Sb samples (g)MW 15 min (h)MW 30 min, 94Sn4Cu2Sb (i)MW 15 min (j) MW30 min, 91Sn6Cu3Sb (k)MW 15 min (l)MW 30 min

### 3.3 X-Ray Diffraction

Sn peaks are the most prominent ones for all the three compositions since it is a Sn-based alloy. However, Sb and Cu peaks appear to be visible in all the green compacts for the three types of composition. Cu and Sb still exist as elemental Cu and Sb at this stage, since the Sb and Cu atoms have not been diffused during the compaction process. Similar peaks were obtained for the mixed tin alloy powder for all three compositions even before compaction as shown in Figure 2. Sb and Cu atoms were completely diffused during the sintering process. This explains why Sb and Cu peaks were not visible at all in the sintered samples. A longer sintering time results in better diffusion of Cu into the Sn lattice to form a solid solution with a tetragonal structure. This is further verified by the X-Ray maps in Figure 3. Unlike cast pewter, in which the intermetallic phase  $\text{Cu}_6\text{Sn}_5$  forms, there are no new phases formed from the powder sintering of pewter alloy because of the small amounts of copper and antimony and the low sintering temperature.



**Figure 2.** XRD peaks for the mixed tin alloy powder



**Figure 3.** XRD peaks for (a) conventional sintering at 120 minutes and (b) microwave sintering at 30 minutes

#### 4. Conclusions

Microwave sintering produced a more uniform structure with enhanced densification after shorter processing time when compared with conventional sintering. Longer sintering time resulted in improved density, fewer pores and higher hardness for both conventionally and microwave sintered material. Microwave sintering for 30 minutes gives similar densification to that obtained after conventional sintering for 120 minutes. Microwave sintering has the potential to contribute to a more energy saving and cleaner process compared with traditional casting.

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