EFFECT OF MICROWAVE SINTERING ON THE MECHANICAL AND STRUCTURAL PROPERTIES OF PEWTER ALLOY

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ABSTRACT

97%Sn 2%Cu 1%Sb (pewter) alloys were examined to determine the effect of green density, sintering time and sintering temperature on the mechanical and structural properties of the conventional and microwave sintered compacts. Two compaction loads; 30kN and 40kN were used to produce the samples with different green densities. Eight different time-temperature combinations were used for each heat treatment. Samples with a higher green density resulted in a higher sintered density and higher hardness. Longer sintering time and higher sintering temperatures resulted in higher densities, larger grain size and higher hardness for both sintering methods. However, the microwave sintered samples in general have finer microstructures, higher densities and higher hardness compared to the conventional sintered samples in a much shorter duration. Better mechanical and structural properties were achieved by microwave sintering in 15 minutes compared to 120 minutes by conventional sintering.

Keywords and phrases: microwave sintering, conventional sintering, mechanical & structural properties, pewter

INTRODUCTION

Microwave sintering is a method of heating that involves energy conversion which is different from the conventional sintering that concerns energy transfer. In microwave sintering, the heat is generated internally within the material instead of originating from external sources. In the process of microwave heating, the materials absorb microwave energy themselves and then transform it into heat within the sample volume [Sorescu 2007, pg410]. The energy is directly transferred to the material through the interaction of electromagnetic waves with molecules leading to heating [Ebadzadeh 2007, pg1]. Microwave sintering is much more uniform at a higher heating rate. This results in a reduction of processing time and energy consumption.

Microwave heating is a function of the material being processed, and there is almost 100% conversion of electromagnetic energy into heat, largely within the sample itself, unlike conventional heating where there are significant thermal energy losses [Agrawal 1998, pg480]. While it is well recognized that bulk metals are opaque to microwaves and good reflectors, metallic materials in powder form are very good absorbers of microwaves and can be heated very rapidly since unsintered alloys will couple in a microwave field very efficiently and effectively to produce highly sintered bodies [Agrawal 1998, pg483].

Background.

Since 1984, the Materials Research Institute at The Pennsylvania State University has been a pioneer institution in the microwave processing of a whole range of ceramics, composites, and metallic materials. The 1980s saw successes in sintering and synthesizing many traditional ceramics such as alumina, zirconia, ZnO, hydroxyapatite, silica, etc [Agrawal 2006, pg37].

Many electroceramics and transparent ceramics were successfully synthesized, fabricated and sintered in microwave fields. Following this, many successful programs in sintering non-oxides, especially WC/Co based products led to the innovative approach of continuous microwave sintering, which made it possible to successfully commercialize the developed technology for WC/Co based products applied in the cutting and drilling industry. Another advancement in 1996 was the successful sintering of powder metal parts (steel) with improved performance and better mechanical properties, which opened up completely new avenues of research and commercial exploitation of microwave technology in new applications [Agrawal 2006, pg37].

Project Goals.

Pewter has been traditionally produced by the casting process where tin, copper and antimony are melted and mixed in the liquid phase to form the pewter alloy. This does consume a tremendous amount of energy, cost and time for the furnace. This paper investigates the possibilities of modern pewter production through a powder metallurgy process and extends this by exploring the possibilities of implementing microwave sintering as a substitute for conventional sintering.

METHODOLOGY

A. 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 97%wt Sn 2%wt Cu 1%wt Sb powder. These powders were weighed accordingly and placed into cylindrical containers which were then evacuated in a glove box prior to mixing by using a roller mixer (ABB:ABS 100) for about 12 hours at a frequency of 40Hz.

B. Preparation of green compacts.

Sixteen 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. Two different pressing pressures (30kN and 40kN) with a holding time of 5 minutes were used to prepare samples for this study by using a 10 ton Hydraulic Floor Press Machine (D2003K).

C. Sintering.

8 samples were sintered using the vacuum furnace and the other 8 sintered using the microwave furnace with varying experimental conditions at two different temperatures (160°C and 220°C) and different durations. A conventional furnace with cavity size of 5cm x 110cm under vacuum condition (10^{-6} MPa) with a heating rate of 6ºC/min was used for the conventional sintering. A Panasonic Thermwave Mod.111 multimode microwave system (1.3kW, 2.45GHz, 47cm x 61cm x 64 cm) with water cooling system was also used for this study. The green compacts were placed in a cylindrical thermal pod made from ceramic fibre and were sintered with graphite pellets which functioned as susceptors to ensure that excessive heat and energy did not build up in the system. The crucible was filled with argon gas prior to sintering and maintained a flow rate of 50mL/min during sintering.

D. Density measurement.

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

E. Grinding and Polishing.

Grinding with worn abrasive papers with grits of 2000 and 4000 was carried out using the rotary polishing and grinding machine (Struers RotoPol – 21) in order to avoid loose particles from silicon carbide from being easily embedded in tin alloys which are very ductile in nature. Polishing was carried out with nap cloth impregnated with 0.3µm agglomerated alpha alumina suspension. Finally, etching of tin alloy was performed by using 2% nital optimum (2mL HNO_3 + 98mL ethanol) for 2 to 5 minutes.

F. Microhardness test.

The Microhardness Tester (LM 700) was used where the diamond indenter is forced into the surface of the material using a calibrated machine with a test load of 25 gf with a dwell time 15 seconds to give a micro-indentation.

G. Microstructural Analysis.

Scanning Electron Microscopy (S-4000 Hitachi) was used to generate digital images from the specimens which were already polished and etched. Optical micrographs were used to calculate grain size through Lineal Intercept Method. The SEM images were also used to produce a virtual elemental map of a sample's surface. X-Ray Diffraction (XRD) was performed using Philips X'PERT System. The patterns were used to characterize the sintered samples and to observe if any changes in phases occurred.

FORMULAE

Equation (1).

To take into account the influence of the variation in the initial as-pressed density, the compact sinterability was also determined through a densification parameter, *d'*, which is expressed as:

$$d' = \frac{sintered\ density - green\ density}{actual\ density - green\ density}$$

A negative value implies compact swelling.

Equation (2).

The volume of open and closed pores can also be calculated using Archimedes' measurements. The volume of open pores, V_O, is given by [Fahrenholtz 2004, pg5]:

$$V_o = \frac{w_{sat} - w_{dry}}{density_{liq}}$$

Equation (3).

The volume of closed pores can be calculated only if the theoretical density, TD of the material is known. The dry weight divided by the TD gives the true volume, V_t. True volume is the volume of solid in the pellet. The volume of closed pores, V_{cp}, is then [Fahrenholtz 2004, pg5]:

$$V_{cp} = V_b - V_o - V_t$$

Where: Bulk volume (V_b) = $(w_{sat} - w_{susp})/\rho_{liq}$.

RESULTS

A. Mechanical Properties.

The green compacts pressed at 30kN load had an average green density of 80.5% while those pressed at 40kN load had an average green density of 84.4%. Higher green densities produced samples with higher bulk density and less porosity. Table 1 clearly shows that by increasing the sintering time from 60 to 120 minutes for the same compaction load, the bulk density had increased by about 3% for the conventional sintering. However, for the microwave sintering, the bulk density had increased by 1 to 2% when the sintering time had increased from 15 to 30 minutes under the same compaction load.

Table 1. Summary of Sintered Samples

Sample Name	Sintering Condition	ρ(sintered) (g/cm^3)	%Theoretical density	Densification Parameter	Porosity (%)	Hardness (HV)	Grain Size(μm)
97CS1	30kN/160°C/60min	6.1	83.40	0.16	16.71	12.92	23
97CS2	30kN/160°C/120min	6.33	86.64	0.31	13.48	13.98	26
97CS3	30kN/220°C/60min	6.53	89.38	0.42	10.75	14.24	27
97CS4	30kN/220°C/120min	6.92	94.65	0.72	5.48	17.18	29
97CS5	40kN/160°C/60min	6.19	84.94	0.02	15.38	14.88	23
97CS6	40kN/160°C/120min	6.41	88.10	0.21	12.48	15.96	25
97CS7	40kN/220°C/60min	6.59	91.05	0.36	9.94	16.92	26
97CS8	40kN/220°C/120min	7.18	98.28	0.88	1.86	19.14	27
97MW1	30kN/160°C/15min	6.78	92.76	0.63	7.37	17.32	17
97MW2	30kN/160°C/30min	6.83	93.48	0.67	6.65	17.86	18
97MW3	30kN/220°C/15min	6.88	94.13	0.70	6.00	20.16	22
97MW4	30kN/220°C/30min	6.96	95.15	0.76	4.98	22.10	25
97MW5	40kN/160°C/15min	6.74	92.26	0.50	7.87	19.70	16
97MW6	40kN/160°C/30min	6.89	94.24	0.63	5.89	23.30	18
97MW7	40kN/220°C/15min	7.11	97.28	0.82	2.85	23.72	20
97MW8	40kN/220°C/30min	7.22	98.71	0.92	1.43	23.96	24

Both microwave and conventional sintering produced higher density samples when the sintering temperature was increased from 160ºC to 220ºC. Nevertheless, the densities for microwave sintered samples at 160ºC were still higher when compared to conventional sintering at 220ºC. By doubling sintering time for the conventional sintering at 220ºC, the bulk density had increased by about 5 to 7%. Meanwhile, the sintering time did not have a significant impact on the increase in density when microwave sintered at 220ºC. On comparing the corresponding densification parameters, it is interesting to note that both sintering methods exhibited shrinkage for all sintering conditions. Swelling was not present at all.

Microwave sintering had produced samples with higher hardness values compared to conventional sintering even at lower temperature (160ºC). The hardness value for microwave sintering was generally about 25 to 28% higher than conventional sintering. The conventional sintering had only an average increase of about 12% in hardness values while microwave sintering had an increase of about 13 to 30% in hardness values under varying conditions.

As the compaction load, sintering temperature and sintering time increased, higher hardness were achieved. This is a result of diffusion of Cu into Sn which was clearly observed from X-ray maps shown in Figure 2. It is well established that the diffusivity of Sn in Cu is greater than that of Cu in Sn at high temperatures as reported by Upadhyaya and Sethi [6] for bronze which is a Cu enriched alloy. Whereas, experiments carried out by Acharya and Mukunda [7] with Cu-Sn couples indicate that at all temperatures it is predominantly Cu that diffuses into Sn, though at 700ºC and above, very slow diffusion of Sn into Cu can be detected.

In this study, diffusion of Cu into Sn was found visible at 220 ºC. Furthermore, XRD data shows that for both microwave and conventional heating, the degree of Cu diffusion into Sn increases with sintering time and temperature. Since microwave heating takes less time, the amount of diffusion of Cu relatively lower than conventionally sintered samples as evidently seen in Figure 2 (a) and (c) for the same compaction load.

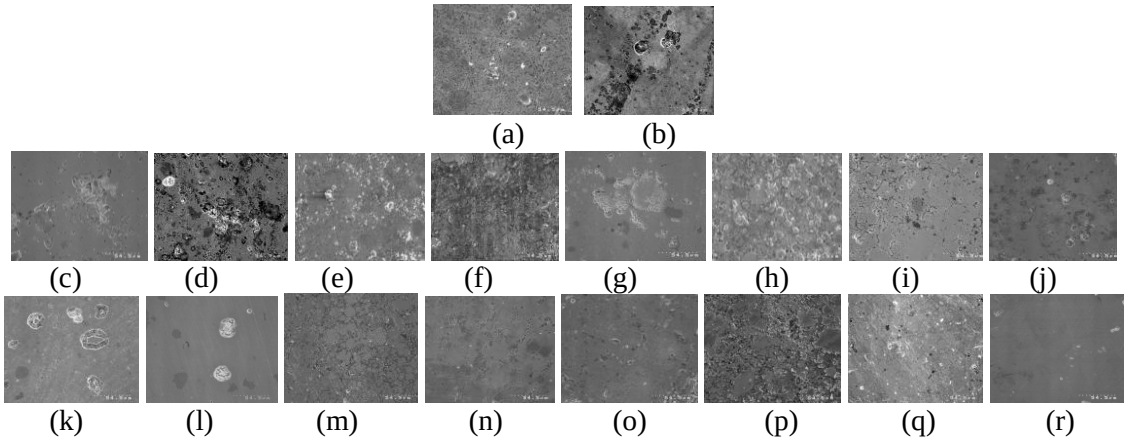

Figure 1. SEM images of: (a)Green compact (30kN) (b)Green compact (40kN) (c)CS1(160°C 60min) (d)CS2(160°C/120min) (e)CS3(220°C/60min) (f)CS4(220°C/120min) (g)CS5(160°C 60min) (h)CS6(160°C 120min) (i)CS7(220°C/60min) (j)CS8(220°C/120min) (k)MW1(160°C/15min) (l)MW2(160°C/30min) (m)MW3(220°C/15min) (n)MW4(220°C/30min) (o)MW5(160°C/15min) (p)MW6(160°C 30min) (q)MW7(220°C/15min) (r)MW8(220°C/30min)

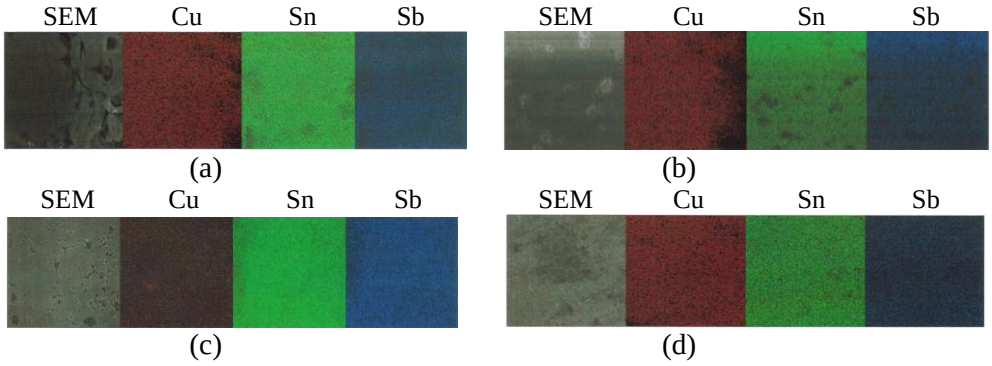

Figure 2. X-Ray map of selected samples: (a)CS4(30kN, 220°C, 120min) (b)CS8(40kN, 220°C, 120min) (c)MW4(30kN, 220°C, 30min) (d)MW7(40kN, 220°C, 15min)

B. Structural Properties.

The samples with lower green densities, when conventionally sintered, had somewhat more, larger and irregular shaped pores as shown in Figure 1. The conventional sintered samples with higher green densities had less porosity and smaller sized pores. By increasing the sintering time and temperature, the porosity decreased for both compaction loads.

The microwave sintered samples with lower green densities produced fewer larger sized pores when sintered at 160ºC compared with conventional sintering. However, when microwave sintered at 220ºC, the size and quantity of pores significantly decreased for both compaction loads. Microwave sintering produces samples with fewer pores and more uniformly distributed porosity compared with conventional sintering, even at a lower temperature. Moreover, the pores were more regularly shaped. As the sintering temperature increased from 160ºC to 220ºC, the sample appeared to have minimal porosity and to have almost achieved full density; 97.28% and 98.71% at 15 and 30 minutes of sintering time respectively. Microwave sintering has produced samples with finer microstructure compared to conventionally sintered samples since rapid heating has affected the normal growth of the grains.

XRD peaks from Figures 3 to 6 show that with increasing sintering time and temperature, Cu and Sb peaks gradually broaden and eventually disappear. Sn peaks were broadened and their intensities increased and decreased accordingly. Sb atoms were shown to have partially diffused into the Sn lattice early on during the blending process and were completely diffused later during sintering. This explains why Sb peaks were not visible at all. Meanwhile, Cu atoms gradually diffused into the Sn lattice and formed a Sn based solid solution with tetragonal structure.

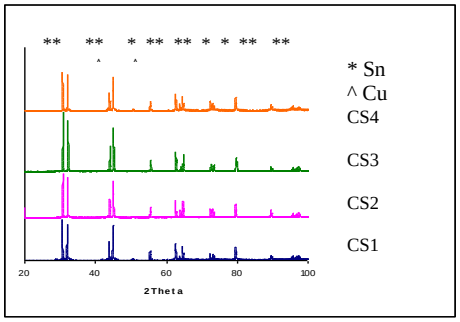

Figure 3: XRD peaks for CS at 160ºC

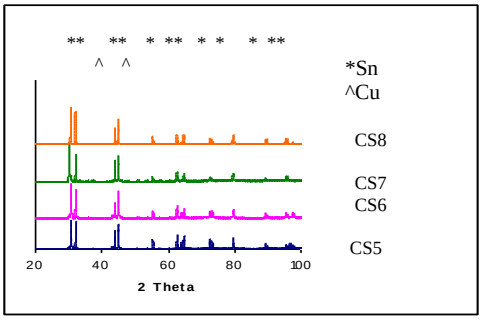

Figure 4: XRD peaks for CS at 220ºC

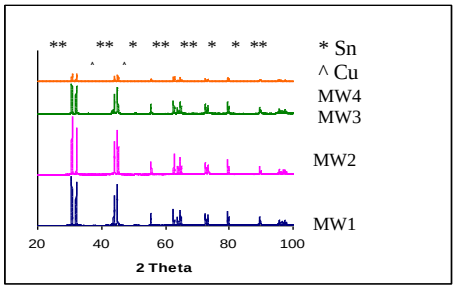

Figure 5: XRD peaks for MW at 160ºC

CS: Conventional Sintering

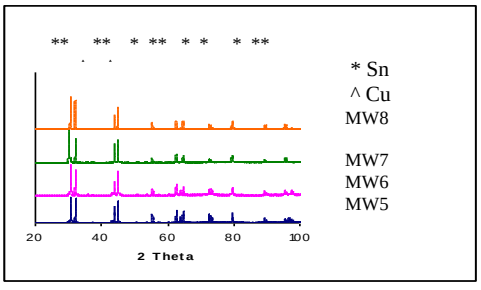

Figure 6: XRD peaks for MW at 220ºC

MW: Microwave Sintering

CONCLUSIONS

This study shows that 97Sn2Cu1Sb pewter can be consolidated through microwave sintering with a significant reduction in processing time. Higher green strength, longer sintering time and higher sintering temperature resulted in improved densities, porosities and hardness values for both conventional and microwave sintering. Microwave sintering produced better mechanical and structural properties at lower processing temperature and with shorter (~87%) processing time. To ensure better mechanical properties are achieved, encapsulating the sample into a vacuumed bottle prior to sintering should be done in order to prevent oxidation.

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