Microstructure and Densification Behavior of Liquid Phase Sintered Cu-28Zn Prealloyed Powder

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Abstract:
The present study investigates the effect of sintering temperature on densification behavior and properties of liquid phase sintered Cu-28Zn brass alloy. Microstructural evolution, chemical analysis and mechanical properties measurements have been studied in details. Obtained results allowed to accurately evaluating the sintering characteristic of this alloy. It is especially relevant in sintered samples that exhibits a pronounced variation of microstructure from top to down part of the specimens and consequently graded densification which was due to gravitational effect.

Keywords: Supersolidus liquid phase sintering, Gravitational effect, Graded densification

1. Introduction

Sintered brass parts are commonly made from prealloyed atomized powders with the composition of Cu-10, 20, and 30 wt% Zn with possible alloying additives [1]. Sintering of brass is normally performed in a temperature range from 815 to 925 °C depending on the alloy composition. The sintering process of brass components made from prealloyed powders includes liquid phase formation. However, in prealloyed condition, as there is no second phase available for melt formation, the powder melts during sintering above the solidus temperature. This mode of sintering characteristic to prealloyed powder system is referred to as Supersolidus liquid phase sintering (SLPS) [2-4]. The commonly observed liquid formation sites are the grain boundaries within particles, the interparticle neck region and the grain interior. Liquid forms inside the particles and spreads to the particle contacts, resulting in capillary force acting on the semisolid particles and enhancing the densification [4-9]. The SLPS process consists of several overlapping steps involving solid-state diffusion, particle rearrangement, solution-reprecipitation, and solid skeleton densification. After sintering the product is a composite of grains that were solid during sintering interlaced with a solidified liquid. Densification of brass during sintering by SLPS is sensitive to sintering temperature [10, 11]. With increasing sintering temperature and consequently enhancing liquid formation, the high diffusivity leads to progressive microstructural coarsening [12, 13]. A limitation of SLPS is that the condition necessary for densification is often very close to the condition resulting in compact shape distortion and microstructural changes due to interplay of capillary and gravity force, so that a high liquid formation results in rapid densification, but less dimensional precision [14, 15]. In fact, gravity force contributes to settling of liquid phase downward and graded densification of samples that depends on sintering time and time...
interval between formation and solidification of liquid. Though there is lack of information on supersolidus liquid phase sintering of brass components, recently Azadbeh et al. [16] has reported that the successful sintering of Cu-20Zn brass alloyed powder required controlling sintering temperature in the process of liquid phase formation to prevent graded densification and shape distortion during SLPS. The present study investigates the effect of sintering temperature on densification behavior and properties variations of Cu-28Zn brass alloy through SLPS process. In particular, physical and mechanical properties, microstructure and phase evolution on this alloy are detailed. To better determine the phase transformation and microstructural evaluation Differential scanning calorimetry (DSC), X-ray fluorescence (XRF) and X-ray diffraction (XRD) obtained from consolidated and unconsolidated samples.

2. Material and Experimental Procedure
2.1. Raw materials

A water-atomized prealloyed Cu-28Zn brass powder (made by Tabriz Powder Metallurgy Company) was used. Physical properties of started powder such as apparent density (based on ASTM B212) and flowability (based on ASTM B213) were measured for powder characterization. Particle size analysis by sieving method (according to ASTM E11 standard) was used to determine the particle size distribution of powder. Particle morphology (size and shape) was also studied using scanning electron microscopy. DSC was carried out under pure argon at a heating rate of 20 °C/min to study any changes in the material and formation of liquid phase which may occur during heating. The chemical composition of the as-received powder was analyzed by XRF.

2.2. Powder forming

The brass powder was mixed with 0.75 wt% lithium stearate as lubricant in a V shaped mixer at 65 rpm for a period of 60 minutes. The obtained powder, used as the base material for all compacts, was compacted into Charpy bars of 55 × 10 × 10 mm using a pressure of 600 MPa in a uniaxial hydraulic press, using a floating die. The green density was calculated by measuring the compact weight and dimensions.

2.3. Sintering

The heating cycle included a 30 min dwell at 540 °C for delubrication followed by sintering at different temperatures between 850 to 890 °C for 30 min in a small laboratory furnace (type, TFS/25-1250) with the constant heating rate of 15 °C/min and Argon flow of 2 l/min was maintained throughout the entire cycle.

2.4. Properties, microstructure and fracture surface of sintered materials

The sintered specimens were characterized by measuring density through water displacement by Archimedes method (DIN ISO 3369), since this technique is more precise than calculating the density from the dimensions as done with the green compacts. The degree of densification after sintering was measured using a densification parameter, \( \psi \), which is expressed as:

\[
\psi = \frac{\rho_t - \rho_g}{\rho_t - \rho_g}
\]

(1)

Where, \( \rho_g \) = green density and \( \rho_t \) = theoretical density which was calculated using the inverse rule of mixtures through the following formula:
\[
\frac{1}{\rho_t} = \sum_{i}^{N} \frac{w_i}{\rho_i}
\]  

(2)

Where \(N\) = the number of elements in the mixture, \(w_i\) = the weight fraction of \(i^{th}\) component, and \(\rho_i\) is the theoretical density of \(i^{th}\) element. The length of green and sintered compact was determined by a caliper with 0.02 mm precision, and the dimensional changes were calculated. The apparent hardness for all specimens was measured according to DIN ISO 4498 using a standard Vickers indenter at a load of 30 kgf. The recorded hardness values are the average of six readings taken at random spots throughout the metallographic sections. Impact energy was measured using a 300 J Charpy impact tester (type, ROELL AMSLER) according to ASTM En23-01 standard. The sintered specimens were sectioned in parallel to the pressing direction, polished and etched (8 g FeCl₃, 25 ml HCl, 50 ml H₂O). Microstructural characterization was carried out using an optical microscope, scanning electron microscope and image analysis system. The constituent phases and chemical composition of the sintered materials were analyzed by XRD and Energy dispersive x-ray (EDX) microanalyser.

3. Results and discussion
3.1. Powder characteristics

Table I and Fig. 1 represent the characteristics, chemical analysis, the particle size distribution and the scanning electron micrograph of as-received brass powder. The non-equilibrium nature of the powder production method makes it difficult to accurately predict sintering window using phase diagrams. Hence, DSC is employed to study the melting behavior of Cu-28Zn prealloyed powder.

![Fig. 1. Scanning electron micrograph of as-received powder.](image)

The sintering window and phase transformations of as-received powder which were calculated from the DSC curve as outlined in the thermal analysis book [17], is shown in Fig. 2.
Fig. 2. DSC plot showing melting behavior of as-received water atomized Cu-28Zn powder.

Tab. 1. Chemical composition and physical characteristics of the used brass powder in as-received condition.

<table>
<thead>
<tr>
<th>Chemical analysis (wt%)</th>
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<tbody>
<tr>
<td>Cu Balance</td>
</tr>
<tr>
<td>Zn  28.6</td>
</tr>
<tr>
<td>Al  0.14</td>
</tr>
<tr>
<td>Fe  0.085</td>
</tr>
<tr>
<td>S   0.062</td>
</tr>
<tr>
<td>Si  0.054</td>
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<tr>
<td>P   0.0084</td>
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<table>
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<tr>
<th>Properties</th>
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<tr>
<td>Flowability (sec/50g)</td>
</tr>
<tr>
<td>Apparent density (g/cm³)</td>
</tr>
<tr>
<td>Powder shape</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>21</td>
</tr>
<tr>
<td>3.2</td>
</tr>
<tr>
<td>Irregular</td>
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<table>
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<tr>
<th>Sieve analysis</th>
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<tbody>
<tr>
<td>Weight percentage</td>
</tr>
<tr>
<td>Particle size (µm)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>9.75</td>
</tr>
<tr>
<td>125 - 180</td>
</tr>
<tr>
<td>24.63</td>
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<tr>
<td>90 – 125</td>
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<tr>
<td>23.53</td>
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<tr>
<td>63 – 90</td>
</tr>
<tr>
<td>42.09</td>
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<tr>
<td>&lt;63</td>
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</table>

There are some endothermic peaks on the heating step in temperature range of 700 °C to 1100 °C. By comparing the peaks intensity, the first peak (≈890 °C) is related to the brass melting and based on the results the onset of liquid formation is about 860 °C. Also the second one (998.7 °C) according to its higher intensity can stand for the transformation of liquid to vapor, which due to evaporation temperature of zinc it can be concluded that zinc evaporation has occurred. Furthermore, since particle formation during atomization is far from an equilibrium solidification event; accordingly, liquids might form at temperatures
50 °C lower than indicated by the phase diagram [3]. Thus temperature window of 860 °C to 900 °C is suitable for performing experiments.

3.2. The effect of sintering temperature on properties, microstructural evolution and fracture surface

3.2.1. Physical and mechanical properties

The physical and mechanical properties (sintered density, dimensional changes, hardness and impact energy) are graphically presented as a function of the sintering temperature in Fig. 3. These properties demonstrate the progress of sintering. The calculated theoretical density according to equation (2), using the results of chemical analysis, was equal to 8.27 g/cm³. As well, green density of samples was calculated by measuring the dimensions and weight of each specimen, was 6.65±0.01 g/cm³. With sintering at 850 °C, the sintered density increases to 7.86 g/cm³ (Fig. 3a) and based on the equation (1), the densification parameter is 33%. By increasing the sintering temperature up to 870 °C, the sintered density reaches a maximum of 7.98 g/cm³, which corresponds to 44% densification. With further increasing sintering temperature above 870 °C, the sintered density decreases. So, for obtaining maximum density too high sintering temperatures are detrimental. It stands out clearly from the obtained microstructures (as will be shown below in Fig. 3), that the changes in density as a consequence of the sintering temperature can be related to microstructural evolution. The changes in length of the sintered samples are shown in Fig. 3b. The response of dimensional change to sintering temperature is in good agreement to that of the density. Accordingly, up to 870 °C with increasing densification there is a significant shrinkage (about 2.35%) of the sintered compact compared to the green one, while at 850 and 890 °C it is lower.

![Fig. 3.](image)

Fig. 3 shows the effect of sintering temperature on the macrohardness (apparent hardness) of Cu-28Zn. It is evident that with rising sintering temperature up to 870 °C the hardness increases, which apparently follows the same trend as the density. It is due to the fact that a high contiguity, as a consequence of optimum liquid phase formation, enhances the hardness. The hardness of the sintered sample reaches its maximum of 61.7 HV30 at 870 °C. High sintering temperature (>870 °C) results in decreasing hardness, since grain growth and
pore enlargement as a result of increasing sintering temperature are unfavorable. In addition, the values for impact energy, as the most sensitive property indicating the interparticle strength of Cu-28Zn obtained after sintering at different temperatures, is shown in Fig. 3b. As it is clear, the maximum value of impact energy (which is about 62 J/cm²) is achieved also at 870 °C, due to an increase in load bearing cross-section caused by liquid formation enhancement.

3.2.2. Structural analysis

Mechanical and physical properties of the materials are also depending on microstructural features as a result of the processing conditions. According to the Cu-Zn binary diagram, the chemical composition of the used powder is in the α phase area and its sintering between the solidus and liquidus temperatures results in a mixture of liquid and α phase.

Fig. 4. XRD pattern of (a) started powder, (b) sintered compact at 890 °C.

Fig. 4 compares the XRD patterns of the starting powders and of the samples sintered at 870 °C for 30 min in Ar atmosphere. The comparison reveals that the phase composition of the starting powders contains α phase, Copper Oxide and Zinc Oxide, but as might be expected from the Cu-Zn binary diagram, the XRD analysis of the sintered sample reveals only α phase.

Fig. 5. Schematic stages of supersolidus sintering processes in a narrow temperature window between solidus and liquidus, (a) initial particle packing, (b) formation of initial liquid with insufficient penetration of grain boundaries for densification, (c) viscous flow densification of semisolid particles, (d) final stage densification with closed, spherical pores[2].

As the powder used is prealloyed, the sintering process is of SLPS type, the schematic stages of which are shown in Fig. 5. By increasing the sintering temperature to a level
between solidus and liquidus, according to the schematic images of the binary diagram (Fig. 5), the amount of formed liquid is augmented and rearrangement of grains is developed.

![Fig. 6. Microstructure of specimens sintered at different temperatures for 30 min in Ar atmosphere followed by cooling in exit zone of furnace (top, center and bottom of broken cross sections at a distance of 1.6, 4.9 and 8.2 mm from upper surface of the sample), (a) 850 °C-top, (b) 850 °C-center, (c) 850 °C-bottom, (d) 870 °C-top, (e) 870 °C-center, (f) 870 °C-bottom, (g) 890 °C-top, (h) 890 °C-center, (i) 890 °C-bottom.]

When studying the microstructure of the sintered samples (Fig. 6), the main interest was focused on pore elimination. Grain growth and pore enlargement were also observed with increasing sintering temperature. In effect of increasing sintering temperature, rearrangement of fragmented grains of powder particles as a result of further liquid phase formation leads to higher densification and sphericity of grains. In spite of decreasing pore number, pore enlargement and grain growth occur concurrently with shape accommodation so that small grains are dissolved and reprecipitated on large grains through Ostwald ripening or grain coalescence. After sintering at 870 °C and above, the growth in grains and pores can be a good reason for a decrease of sintered density and impact energy. Regarding the declining pore number, increasing sintering temperature can be positive because of more sliding and grain repacking and more interfacial bonding. However, Considering the grain growth / pore enlargement, increasing sintering temperature has a negative effect. Between these two antithetical extreme effects there is an optimum state to achieve the highest density as a sound basis to obtain improved mechanical properties for high performance application. Comparing the microstructure of sintered parts, it is obvious, that a more uniform porosity, lower pore
number and smaller pore size can be achieved by sintering at 870 °C. Moreover, due to formation of excess liquid phase and the effect of gravity on it, some events such as settling of liquid occurred. This feature was evaluated by studying various regions of each fracture surface.

Fig. 7. Average grain size of specimens sintered at different temperature.

The average grain size as a function of sintering temperature is plotted in Fig. 7, for each part of the samples cross section, with standard deviation as error bars. As can be seen, increasing sintering temperature produces significant grain growth in this material, because grain coarsening as a result of diffusion is a thermally activated process. Furthermore, as a consequence of liquid settling due to gravitational force, the grain growth at the down part of sintered compacts is more than other parts which is clearly shown in Fig. 7.

3.2.3. Fractography

To give a good reference to the process taking place after an increase in sintering temperature, fractographic examination was done. Fracture surface images of sintered specimens show that the porosity decreases and grain size increases from top to bottom at each temperature (Fig. 8), which is due to liquid phase accumulating at the bottom of the sample as a result of gravity. Also, according to the research done by German et al [15], it was found that gravity causes a vertical force on the material. Pressure caused by each part mass is an effective factor in densification of the compact’s bottom (compared to its top) (Fig. 9). The stress at any point depends on the cumulative mass above it and is given by \( \rho gh \) value. Where \( \rho \) = density, \( g \) = acceleration due to gravity, and \( h \) = height between upper surface of the compact and the point. Accordingly, at compact’s bottom, higher pressure results in liquid settling and more densified structure. Detailed view of microstructure observed by scanning electron microscope (SEM) from the fracture surface of Cu-28Zn brass specimens (Fig. 8), broken by impact test, shows a ductile structure. Here, as shown in Fig. 8, the pores at fracture surfaces of the sintered compact at 850 °C, are open and nonuniform. In addition, fracture occurs at grain boundary regions, where the initial liquid phase forms, and apparently no transgranular fracture is observed. As the sintering temperature increases up to 870 °C more liquid phase form and the porosity decreases compared to 850 °C. Moreover, the
rearrangement of fragmented grains of powder particles as a result of liquid phase formation leads to a significant increase in load bearing cross section area.

Fig. 8. Fracture surface of specimens sintered at different temperatures for 30 min in Ar atmosphere followed by cooling in exit zone of furnace (top, center and bottom of broken cross sections at a distance of 1.6, 4.9 and 8.2 mm from upper surface of the sample), (a) 850 °C-top, (b) 850 °C-center, (c) 850 °C-bottom, (d) 870 °C-top, (e) 870 °C-center, (f) 870 °C-bottom, (g) 890 °C-top, (h) 890 °C-center, (i) 890 °C-bottom.

Fig. 9. Schematic image of liquid-phase settling to the bottom of the compact as a result of gravity force.
Fig. 10. Segregation of Zinc to grain boundaries of sintered specimens at; (a) 890 °C for 40 min, (b) and (c) 900 °C for 60 min in Ar atmosphere (different magnification).

Fig. 11. Linear analysis images of alloying elements distribution in the grains and grain boundaries of specimen’s fracture surface sintered at 890 °C; (a) Image of fracture surface, (b) Copper, (c) Zinc.

There is an almost full covering of melt in grain boundaries and particle contacts at 870 °C, while grain growth at higher temperatures results in coarser voids. Grain growth and voids widening at 890 °C due to the higher proportion of liquid phase are more than other temperatures. It should be taken into consideration that because of more porosity and lack of full densification at 850 °C, capillary force induces the melt penetration into the pores, but at higher temperatures and because of less porosity due to higher liquid formation, the capillary force decreases, and so, the gravity effect is dominant [15]. On micrograph of sintered sample at 890 °C (Fig. 10(a)), as well as samples sintered at 900 °C for 60 min in Ar atmosphere (Fig. 10(b) and (c)), segregated phase at grain boundary were observed, which was because of dezincification. The phase diagram of Cu-Zn provides an initial indicator of segregation due to alloying. The downward sloping liquidus and solidus lines indicate a tendency for Zn segregation at grain boundaries [6]. So, in order to investigate the changes in chemical composition caused by liquid phase formation, a linear analysis was done on the fracture surface of the compact sintered at 890 °C (Fig. 11). The difference in the chemical composition of grain boundary and grain interiors is clear, so that in the liquid formed at the grain boundaries the amount of Cu decreases but the Zn content increases. Such a change in chemical composition could be responsible for the different modes of fracture.

4. Conclusions

1. Sintering of Cu-28Zn prepared from prealloyed powder occurs along with liquid phase formation and is of supersolidus type.
2. Changes in physical and mechanical properties with rising sintering temperature agree well with each other, and the results of microstructural and fractographic analysis confirm them.
Based on the above mentioned changes, the optimum sintering temperature is approximately 870 °C.

3. An increase in sintering temperature results in decrease of pore number and causes sphericity as well as significant grain growth. As a result of grain growth, the pore size between them is increased. Moreover, at lower sintering temperatures, because of abundant porosity, the capillary force is the dominant factor and induces quick densification. While with filling voids by the liquid and decreasing porosity, the gravity force becomes dominant and induces the liquid to settle into bottom of the sample.

4. According to fractographic investigation and microstructural analysis it can be concluded that low sintering temperatures due to insufficient interparticle bonding and high sintering temperatures because of excess liquid phase formation are not favorable. There is an optimum temperature which can contribute to achieving improved physical and mechanical properties.

5. With increasing sintering temperature and liquid phase formation, as a result of gravitational force, the settling of liquid to bottom of the sample is enhanced and the number of pores decreases from up to down and graded densification occurs.

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References


**Садржај:** Проучен је утицај температуре синтеровања на денсификацију и својства течно фазног синтеровања месингане легуре Cu-28Z. До најситнијих детаља су проучаване микроструктурна еволуција, хемијска анализа и механичка својства. Резултати дозвољавају прецизно вредновање карактеристика синтеровања ове легуре. Пособно је важно да је у синтерованим узорцима изражена варијација микроструктуре од врха узорка према доњем делу и услед тога разлике у денсификацији што је утицај гравитационе силе.

**Кључне речи:** синтеровање у течној фази, гравитациони ефект, степенasta денсификација