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Comparative Study of the Effect of Sn and Co Content on the Density and Hardness of Sintered Copper Systems

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Abstract. This present work consists of studying the synthesis and the effect of Sn and Co content on the density and hardness of binary systems (Cu100-x-Snx, Cu100-x-Cox). In this work we have study the influence of the addition of tin and cobalt (X = 5, 10 and 12 % by weight) in the metastable domain. The hardness of the Cu-Sn and Cu-Co alloys becomes high with the increase of the content of these two additive elements, the compacting pressure and the sintering temperature and even the effect of these on the increase of the density in an almost linear way. The porosity rate is proportional to the compaction pressure. SEM observation shows that the dispersion and particle size of tin and cobalt in the copper matrix is irregular.

Introduction

Metallic alloys manufactured by powder metallurgy (PM) [1, 2] still occupy a serious place for many advantages such as low energy consumption, minimal loss of raw powder, minimization of secondary operations [3]. PM was developed as a means of limiting conventional (fusion) production and has the ability to synthesize a variety of alloys.

The Cu-Sn and Cu-Co binary systems [4] elaborated and developed by PM The Cu-Sn and Cu-Co binary systems [4] developed by PM is the aims of several research [5, 6]. These alloys are used for many applications due to their high quality of friction, their resistance to corrosion and their high resistance and high electro / thermal conductivity [7-9]. It appears that much of the work has been done on copper-based alloys [10-16].

Cobalt and tin are elements used to enhance the mechanical properties of resistance to wear, heat and corrosion especially for parts used in the naval or aeronautical sector. Cu-Sn are used in the production of hard alloys for the manufacture of saw teeth, drills and drill bits. Copper alloys share the characteristics of density and hardness with the addition of cobalt (Co) or tin (Sn) leads to the formation of the rich areas of these two elements. These are mainly located between the copper particles. For these reasons, we try to contribute to the study of the effect of tin (Sn) and cobalt (Co) content on the characterization; in particular the microstructure, the density and the hardness of the bimetallic systems.

Therefore, the main objective of this work is to elaborate and characterize of Cu-Sn and Cu-Co copper-based binary alloys obtained by unilateral compaction followed by sintering (liquid sintering for Cu-Sn and solid sintering for Cu-Co), focusing particularly on the influence of several parameters (the content of Sn and Co additions, the compaction pressure and the sintering temperature) on the elaboration of these alloys and to make a comparison between these two results obtained.
Experimentation

1/ Raw material

The objective of our study is the development and characterization of Cu-Sn and Cu-Co metal systems. For the synthesis of these, we chose the technique of (PM) from the raw materials that were in the form of oxides. The reduction of these oxides is carried out in a hydrogen furnace at a temperature of 500 °C to 550 °C in order to obtain powders with purity higher than 97.5%. Three materials are used in the manufacture of pellets: Copper, Tin and Cobalt (Fig. 1).

2/ Characterization of the powders used

Observation using a scanning electron microscope (SEM) equipped with an energy dispersion spectrometer (EDS) makes it possible to specify the morphology and purity of the powders used: Copper (Cu), Tin (Sn) and Cobalt (Co) (Fig. 1).

Fig. 1. Images (SEM) of the morphology of the powders, a) Copper, b) Tin and c) Cobalt.

Figures 2 (a), (b) and (c) showed percent purity and collect spherical shaped particles having an average size of between 38 and 63 μm (Fig. 2).

Fig. 2. SEM of the quantitative purity analysis of the powders, a) Copper, b) Tin and c) Cobalt.

The properties of the materials used are shown in Table 1.

Table 1. Properties of the powders used.

<table>
<thead>
<tr>
<th>Type of powder</th>
<th>T$_{\text{melting}}$ (°C)</th>
<th>Density (g / mm)</th>
<th>Purity (%)</th>
<th>Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (Cu)</td>
<td>1 084</td>
<td>8.96</td>
<td>97.60</td>
<td>&lt; 63</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>232</td>
<td>9.42</td>
<td>98.50</td>
<td></td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>1493</td>
<td>8.57</td>
<td>98.50</td>
<td></td>
</tr>
</tbody>
</table>
3/ Homogenization of mixtures

Two types of samples (Cu-Sn, Cu-Co) were prepared with three levels of (5%, 10%, 12%) wt. The constituents are dosed using a digital scale. The homogenization of the mixture is carried out with a porcelain mill rotating at a speed of 120 rpm for 3 hours and controlled by means of an optical microscope. In order to obtain a pasty mixture of 15 g of mass for each sample, powder is wet and kneaded with 50 ml of acetone.

Table 2. Composition of samples (Cu-Sn, Cu-Co).

<table>
<thead>
<tr>
<th>Samples</th>
<th>% wt Cu</th>
<th>% wt Sn</th>
<th>% wt Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95</td>
<td>5</td>
<td>/</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>10</td>
<td>/</td>
</tr>
<tr>
<td>3</td>
<td>88</td>
<td>12</td>
<td>/</td>
</tr>
<tr>
<td>4</td>
<td>95</td>
<td>/</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>/</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>88</td>
<td>/</td>
<td>12</td>
</tr>
</tbody>
</table>

4/ Synthesis Samples

We have prepared two different groups of samples (Cu-Sn and Cu-Co), the first group is compacted by a constant pressure \( P = 96 \text{ MPa} \) and sintered in different temperatures \( T_{\text{Cu-Co}} = 275, 300 \text{ and } 350 \degree C \) and \( T_{\text{Cu-Sn}} = 850, 900 \text{ and } 950 \degree C \). The second group is compacted by three different pressures \( (P = 48, 75 \text{ and } 96\text{MPa}) \) and is sintered in a constant temperature \( T = 950 \degree C \).

The samples are uniaxially compressed with a heavy-duty steel punch in a hydraulic press. They are exposed to the open air for 24 hours to evaporate acetone.

The sintering took place in a sintering furnace; the holding time is 60 min (Figure.3)

![Fig. 3. Different types of samples, A) green sample and B) sintered sample.](image)

5/ Shrinkage in Dimensions

Shrinkage is a very interesting element to study; therefore, it must be considered in order to have a product free of defects. The dimensions of the samples after sintering have a linear shrinkage in both directions (the diameter and the thickness of the sample) of the order of 7 to 9% for the alloys (Cu-Sn) and 18 to 21% for alloys (Cu-Co).

Results and Discussions

1/ Microscopic analysis

The optical images (optical microscope) of the Cu -x% Co and Cu -x% Sn binary systems are composed of several phases (Figure 4): dark parts represent the sintered particles of copper and the light areas correspond to the particles of cobalt and tin.
a) 350 °C sintering temperature of (Cu-Co)

b) 950 °C sintering temperature of (Cu-Sn).

Figure 4. Microstructure of Cu-Co and Cu-Sn alloys compacted at 96 MPa.

Figure 4 also shows the microstructures of the alloys (Cu-Co and Cu-Sn) at different levels of cobalt additions and tin (5%, 10%, 12%) compacted at 96 MPa and sintered at a temperature of 950 °C and 350 °C, respectively. The microstructure of these alloys shows a slight size difference of cobalt and tin grains in the copper matrix. It is noted that there is a structural change with the increase of cobalt and tin content, which explains a redistribution of the mixture grains under the effect of this content and sintering temperature which affect the porosity and the density of the alloys obtained.

2/ SEM microscopic analysis

The results of SEM metallographic analysis of samples of different compositions are shown in Figures 5 and 6. The presence of pores is clearly indicated. The nature of these pores is closed and multiform result of the deployment of the sintering mechanisms and the compaction pressure. It may also be noted that the Co or Sn content of the composition affects the rate and shape of the porosity in the alloy structure, it varies proportionally to the proportion of these two cobalt and tin addition elements.

Then, the comparison between the Cu-Sn and Cu-Co alloys which are illustrated in Figures 5 (a, b and c) and 6 (d, e and f) show the microstructural aspects of these alloys, also indicates the improvement of the diffusion and formation of the alloy structure resulting from liquid phase sintering for the Cu-Sn alloy and in the solid phase for the Cu-Co alloy. Also, the dark phase is rich in Cu and the shining Sn (Figure 5) and Co (Figure 6), the pores appear black. At a compression pressure of 96 MPa, we can observe the evolution of the microstructure, the reduction of the porosity and the grain content of the Sn and Co additive elements increased in the copper matrix when the contents of these elements increase from 5 to 12%. Moreover Sn and Co are immiscible in Cu, it is deduced that there is a quasi-pure formation of Cu-Cu, Sn-Sn and Co-Co solid solutions.
3/ Density results

The density variation as a function of the sintering temperature ($T_{Cu-Sn} = 275$, 300 and 350° C, $T_{Cu-Co} = 850$, 900 and 950°C) and under a constant compaction pressure ($P = 96$ MPa); for different Cu-x% Sn alloys; Cu-x% Co ($x = 5$, 10% and $x = 12$); is shown in Figure 7. It is found that the density increases almost linearly in the indicated temperature field. This increase can be explained by the rearrangement of the powder particles under the effect of sintering temperature change, so the contact surfaces expand, the grains deform plastically to densify the powder compact and thus reduce the porosity rate. It is also deduced that the temperature has a greater effect on the density of the copper alloy without taking into account the element of addition (Sn and Co); in this case it is noted that the value of the density increases from 6 g / cm$^3$ ($T_{sintering} = 275$ ° C,) to 33 g / cm$^3$ ($T_{sintering} = 950$°C).
4/ Hardness study (Hv)

Figure 8 shows the effect of the sintering temperature on the change in the value of Vickers hardness such that the compaction pressure is constant (the same values of previous temperatures and pressures). The hardness of the samples and the temperature are proportional.

The increase in hardness values is noticeable for Cu-x% Sn alloys relative to their density values. For Cu-x% Co alloys, both values are high (density and hardness), resulting in some resistance to surface penetration. The effect of the cobalt content on the hardness is observed at more than 12% compared to the effect of tin on this property when its content is less than 10%. In addition, the sintering temperature has an impact on the hardness value, particularly in the case of 12% cobalt and the sintering temperature of 950 °C is 72 Hv. In this case, it can be concluded that the energy consumed is significant (950 °C); while in the case of 5% tin, the value obtained for the hardness is 66 Hv and the energy consumed (300 and 350 °C) is less than three times 950 °C.
Conclusion

The objective of this work is to characterize from a microstructural and mechanical point of view a new Cu-Sn and Cu-Co alloys developed by cold compression. This work meet with few industrial conditions required in certain industrial fields, taking into account the parameter of density, the latter reflects the effect of the processing parameters, namely the compaction pressure, the sintering temperature, the concentration of tin and cobalt. For the elaboration of these alloys, we take into consideration the morphological characterization of the powders used, the microstructural study (SEM / EDS and optical microscope), and mechanical properties of the elaborated samples. Thus, we can conclude that:

- The microstructure shows that there is a heterogeneity of distribution of the addition elements in the copper matrix, which explains the inhomogeneous structural hardening.
- Note that there is almost pure formation of Cu-Cu, Sn-Sn and Co-Co solid solutions, which implies that tin and cobalt are immiscible in Cu.
- The density increases linearly with the addition elements (Co and Sn) and the temperature values. Hardness growth is noticeable for Cu-Sn samples compared to their density values.
- The temperature has a greater effect on the density of the copper alloy without taking into account the addition element (Sn and Co).
- The density has a small effect on the hardness. Indeed, the increase in hardness depends on the sintering temperature and the composition of the mixture for Cu-Sn alloys, while the addition element (Sn) decreases the hardness of Cu-Sn alloys.
- In the case of 5% tin, a hardness of 66 Hv is obtained with an energy consumption of: 300 and 350 °C is less than three times 950 °C.

Then, it is deduced that the Cu-Sn alloys are more usable in the industrial field, in particular the aeronotic and the naval sector because they are light and the sintering temperature is low than the Cu-Co alloys for rather large contents.

References

