Effects of Different Mechanical Alloying Parameters on Microstructure of High Temperature Nanocrystalline Cu-Ta Alloys

Onur Dinçer¹,², M. Kaan Pehlivanoğlu¹, Arcan F. Dericioğlu²
¹TÜBİTAK SAGE, 06261, Mamak, Ankara, Turkey
²Middle East Technical University, Department of Metallurgical and Materials Engineering, 06800, Ankara, Turkey

Abstract

Copper (Cu) offers good machinability, good formability, and have high thermal and electrical conductivity for numerous applications such as thrust chamber of liquid rocket engine, nuclear reactor and electromechanical launch systems requiring high heat flux transfer. To improve mechanical properties without losing the thermal conductivity, nanocrystalline structures have been receiving substantial attention. Immiscible elements give accomplished method to the design of materials with astonishing structural stability and mechanical strength at high temperatures for metal alloying. Cu-Ta is a significant, immiscible system that has been considered as a candidate for high temperature stability applications. To produce immiscible Cu-Ta alloys severe plastic deformation methods are mostly preferred. In this study, the effects of the variation of mechanical alloying parameters like ball-to-powder weight ratio and process control agents (PCAs) on the densification of nanocrystalline Cu-Ta alloys have been studied. The base alloy was selected as 99.5 wt% Cu and 0.5 wt% Ta. Ball-to-Powder weight ratio (BPR) was varied from 15:1 to 5:1. Furthermore, methanol, toluene and hexane were used as PCA during high energy milling of Cu-Ta alloys. Density measurements and scanning electron microscopy characterization were conducted for both milled and sintered products.

1. Introduction

Copper (Cu) is a widely-used metal due to the advantages of high electrical and thermal conductivities, outstanding corrosion resistance and ease of production. However, in the pure form, mechanical properties of copper deteriorate dramatically at elevated temperature conditions. Based on the prevailing necessity for materials which possess high thermal conductivity coupled with high strength and provide resistance to softening and degradation, different copper alloys have been developed. As in the case of all other engineering metals, keeping mechanical properties optimized or maximized under relatively high temperatures is also hard for copper and its alloys. The challenging idea of developing a material with improved mechanical strength and conductivity for use in extreme temperature conditions is extended to copper alloys for tailoring the material properties by altering the general microstructural characteristics.

Nanocrystalline materials have received and continue to receive significant interest for their ability to reveal enhanced mechanical properties, specifically, strengthening via the Hall–Petch mechanism, compared to materials with a coarse-grained microstructure [1] [2].

Immiscible elements make it possible to design materials with surprising structural stability and mechanical strength at high temperatures as alloying elements. Immiscible elements tend to strongly segregate at grain boundaries (GBs), reducing their free energy and thus the driving force for grain growth. They can also reduce GB mobility through the solute drag effect. In addition, immiscible elements often form highly dispersed particles that effectively pinch GBs and create strong barriers to dislocation motion [3].

Cu-Ta is an important immiscible system that has been studied as a candidate for high temperature stability applications. The melting temperatures of Cu and Ta are very different; 1083 and 3017 °C, respectively. Cu-Ta alloys show high thermal stability at elevated temperatures in comparison to other Cu-based alloys. The increase in strength was attributed to the thermal decomposition of a non-equilibrium Cu rich Cu-Ta solid solution over a range of temperatures (700–900 °C), which led to the formation of high density, small coherent Ta-rich nanoclusters about 2 nm in size. The presence of these Ta-rich nanoclusters within grains and along grain boundaries resulted in strength levels as high as approximately twice those predicted by Hall–Petch hardening [4].

To produce immiscible Cu-Ta alloys, mostly preferred technique is high energy ball milling. Severe plastic deformation can be applied to the powder mixture by high energy milling operation.
In view of the above discussion, the main objective of this study is to understand the effect of varying mechanical alloying parameters like ball-to-powder weight ratio and process control agents (PCAs) on the densification of nanocrystalline Cu-Ta alloys. The base alloy was selected as 99.5 wt% Cu and 0.5 wt% Ta. Ball-to-Powder weight ratio (BPR) varied from 15:1 to 5:1. In addition to this, methanol, toluene and hexane were used as PCA during high energy milling of Cu-Ta alloys.

2. Experimental Procedure

1-3 μm average particle sized Cu (gas atomized, CPCN, China) and 50 μm agglomerated Ta (irregular, MIL-SPEC, USA) elemental powders were used in this study. The elemental powders were of 99.9 % and higher in purity, and average particle sizes were as specified by the suppliers. The shape and morphology of the powder particles were investigated using scanning electron microscope (SEM) (6400 JSM, Jeol, Japan). For the mixing of the powders, elemental Cu and Ta powders were weighted in a Sartorius CP3200S Model Precision Balance to ± 0.01 g accuracy. Powders were weighted separately and put into hardened steel jars. 0.5 grams of Methanol, toluene or hexane were used as PCA separately. Mechanical alloying (MA) was carried out in planetary ball mill (PM-400, Retsch, German) with hardened tool steel jars. In these operations 9 mm diameter steel balls (DIN 52100) were used. The speed of mixing was 200 rpm for all mechanical alloying operations. The jars were purged by argon gas before MA to minimize the oxidation of powder during the milling process. To understand the effect of BPR and PCAs, different powder mixtures were studied. The studied powder mixtures and alloy codes are given in Table 2. By changing BPR, powders were directly affected in terms of morphology. At lower BPR, powders are agglomerated and cannot be milled powders were pressed by a hydraulic press under 280 MPa using a 3-pieces steel die assembly. Compressed powders were sintered at 1000°C under hydrogen atmosphere for 1 hour in a horizontal tube furnace (TF1700, Protherm Furnaces, Turkey).

Milled powders and fracture surfaces of sintered alloys were characterized by scanning electron microscope (Evo, Zeiss, German). Densities of the alloys were measured by Archimedes’ immersion technique using xylene having a density of 0.865 g/cm³. The measured densities were divided by the theoretical densities and then multiplied by 100 in order to determine the percent relative densities (%RD) of the alloys. The theoretical densities were estimated using the rule of mixtures method.

3. Results and Discussion

In general, mechanical alloying (MA) involves loading the blended elemental or pre-alloyed powder particles along with the grinding medium in a vial and subjecting them to heavy deformation. During this process the powder particles are repeatedly flattened, cold welded, fractured, and rewelded. The methods of cold welding and fracturing, as well as their kinetics and predominance at any stage, depend mostly on the deformation characteristics of the starting powders. In the present study, starting powders are spherical Cu and agglomerated Ta. To understand the effect of Ball-to-Powder weight ratio (BPR) on mechanical alloying of Cu-Ta powders, BPR values of 15:1, 10:1 and 5:1 were studied. After 24 hours of milling, powders were separated from the balls. By naked eye, milled powders were observed to have varying characteristics by increasing order of BPR. During pressing, 5:1 BPR milled powders (CuTa5/1) could not be compacted, neither with mechanical press nor with cold isostatic press. CuTa5/1 milled powder can be seen in Figure 1. Milled powders were characterized by scanning electron microscope. Micrographs are given in Figure 3.
Table 1. Compositions, BPR and PCA of the Cu-Ta Alloys Investigated

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Powder</th>
<th>PCA</th>
<th>Ball (g)</th>
<th>Weight (g)</th>
<th>BPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuTa15/1</td>
<td>99.5</td>
<td>29.85</td>
<td>0.5</td>
<td>0.15</td>
<td>0.5 g Toluene</td>
</tr>
<tr>
<td>CuTa10/1</td>
<td>99.5</td>
<td>29.85</td>
<td>0.5</td>
<td>0.15</td>
<td>0.5 g Toluene</td>
</tr>
<tr>
<td>CuTa5/1</td>
<td>99.5</td>
<td>29.85</td>
<td>0.5</td>
<td>0.15</td>
<td>0.5 g Toluene</td>
</tr>
<tr>
<td>CuTa10/1-Met</td>
<td>99.5</td>
<td>29.85</td>
<td>0.5</td>
<td>0.15</td>
<td>0.5 g Methanol</td>
</tr>
<tr>
<td>CuTa10/1-Hex</td>
<td>99.5</td>
<td>29.85</td>
<td>0.5</td>
<td>0.15</td>
<td>0.5 g Hexane</td>
</tr>
</tbody>
</table>

All other milled powders could be compacted by the hydraulic press using 5 tons of pressure (280 MPa). Sintering operation was performed in a tube furnace at 1000 °C under hydrogen atmosphere for 1 hour. After sintering, density measurements were done by the aid of Xylene using Archimedes’ principle. The theoretical, measured and relative densities are given in Table 2. By changing BPR, powders were directly affected in terms of morphology. At lower BPR, powders are agglomerated and cannot be compressed. On the other hand, increasing BPR to 15:1 also affects the sintered density. As can be seen in Table 2, the relative density of CuTa15/1 is relatively lower than that of CuTa10/1. It is known that, at a high BPR, because of an increase in the weight proportion of the balls, the mean free path of the grinding balls decreases and the number of collisions per unit time increases. Consequently, more energy is transferred to the powder particles resulting in faster alloying. The more energy transferred to powder, the more temperature increases [5]. Therefore, by increasing temperature Cu-Ta powders which are highly ductile become agglomerated. To sum up, in this case, 5:1 and 15:1 BPR are not suitable for Cu-Ta milling. The optimized BPR value for this study is believed to be 10:1. As a process control agent (PCA) toluene, hexane or methanol were used. PCA is added to the powder mixture during milling to reduce the effect of excessive cold welding and as a carbon source for TaC formation. PCAs adsorb on the surface of the powder particles and minimize cold welding among powder particles, thereby inhibiting agglomeration. The surface-active agents adsorbed on particle surfaces interfere with cold welding and lower the surface tension of the solid material. By lowering surface tension, powders can be milled in shorter time and milled products can be finer [5]. In this study, toluene, hexane and methanol were used as PCAs at 10:1 BPR. From the sintered products, it can be understood that toluene added powders have higher density compared to others. Molecular weights of toluene, hexane and methanol are 92.14, 86.12 and 32.04 g/mol, respectively. Higher sintered density of both CuTa10/1 and CuTa15/1 may be attributed to the higher molecular weight of toluene.

After sintering operation fracture surfaces of studied alloys were investigated. The micrographs of fracture surfaces are given in Figure 4. These surfaces indicate that sintering occurred between particles; however, due to the flattened and irregular shape of the milled particles.
density could not reach to the respective theoretical density.

4. Conclusion

The effect of BPR and different PCA addition into Cu-Ta alloys were investigated in this study. The results of the study can be concluded as follows:

1. During mechanical alloying of Cu-Ta powder agglomeration was observed due to ductile nature of the constituent elements.

2. By increasing BPR from 5:1 to 15:1 powder microstructure turned from spherical morphology to flattened structure.

3. Optimum mechanical alloying parameter for this study can be regarded as 10:1 BPR with toluene as PCA addition.

4. Addition of different PCA into powder mixture affected the sintered relative density.

Table 2. The theoretical, measured and relative densities of sintered Cu-Ta alloys investigated.

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Theoretical Density (g/cm³)</th>
<th>Measured Density (g/cm³)</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuTa15/1</td>
<td>8.71</td>
<td>5.50</td>
<td>63.1</td>
</tr>
<tr>
<td>CuTa10/1</td>
<td>8.71</td>
<td>6.67</td>
<td>76.6</td>
</tr>
<tr>
<td>CuTa5/1</td>
<td>8.71</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuTa10/1-Met</td>
<td>8.71</td>
<td>4.30</td>
<td>49.4</td>
</tr>
<tr>
<td>CuTa10/1-Hex</td>
<td>8.71</td>
<td>4.77</td>
<td>54.8</td>
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</tbody>
</table>

References


