Composite Ta–Cu powders prepared by high energy milling

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Received 30 November 2007; accepted 12 December 2007

Abstract

A mixture of Ta and 20 wt%Cu elemental powders were milled in a high energy mill under two conditions of milling intensity. Composite particles in both conditions were formed. The original Ta particles were firstly fragmented and then pierced in the deformed Cu particles. Cu hardens due to cold work and breaks. The final powder is finer than the initial powders. The final composite particles are homogeneous and consist of amorphous, separated Cu and Ta phases. The more intense milling condition produced composite particles with shorter milling time and amorphization of both phases after 50 h of milling. The less intense milling condition amorphized only the Cu phase. The composite particles can produce denser structures than mixed powders, if heated above the Cu melting point.

Keywords: Ta–Cu alloy; Amorphization; High energy milling; Composite particles

1. Introduction

High energy milling and mechanical alloying are terms utilized to name the synthesis of alloys and compounds by means of intensive milling that causes mixing at an intimate level and deformation of the materials’ microstructure [1,2]. Here, high energy milling (HEM) is used.

The Ta–Cu system can be compared to the W–Cu system. Ta and W are high melting point transition elements, which do not dissolve Cu nor are dissolved by it [3,4]. It is expected that liquid Cu wets poorly Ta. These characteristics make Ta–Cu a hard-to-sinter system. Depending on the Ta content, the Ta–Cu alloy can have different applications. If the Ta content exceeds 70 wt%, the alloy can be an alternative to W–Cu, WC–Cu, Mo–Cu as heat sink for semiconductor devices [5]. If the Ta content is lower than 10 at.%, Cu can be dispersion strengthened by fine Ta precipitates, as it occurs with Nb [6,7].

During HEM the following processes may happen: severe deformation that could lead to amorphization of the phases, formation of solid solutions (also with extended solubility), formation of composite particles, excellent dispersion of phases [1,2]. For the W–Cu system, literature [8,9] reports formation of composite particles, good dispersion, but does not mention amorphization of any phase. In the Nb–Cu system, the formation of a saturated solid solution of nanocrystalline Cu with up to 10 at.% Nb has been reported [6]. The absence of XRD and electron diffraction peaks, and SEM images that did not show any evidence of Nb particles supported this affirmation. According to the authors, Nb dissolves and diffuses in the Cu lattice along the dislocation lines. As the Ta–Cu system, Nb–Cu presents mutual insolubility.

Complete amorphization of both Ta and Cu by HEM of the elemental powders is reported [4] for milling times longer than 50 h in mixtures whose Cu content is in the 30–50 at.% range. Cu richer mixtures do not completely amorphize. On the other hand, Lee et al. [10] reported that in a Ta–30 at.%Cu mixture amorphization started after 30 h milling and had not finished after 100 h.

Systems such as W–Cu, Nb–Cu and Ta–Cu have positive enthalpy of mixture. Therefore formation of a solid solution of these elements is not expected. Nevertheless...
the introduction of strain and interfaces in the crystalline material can elevate its free energy to a value over that of a metastable solid solution (crystalline or amorphous) [4,10]. HEM is able to produce both effects.

This work focuses on the HEM milling of a Ta–20 wt%Cu mixture of elemental powders. The evolution of the structure of the particles and of the crystal lattice of the phases is followed by SEM and XRD.

2. Experimental procedure

Ta and Cu elemental powders were used in this work. The Ta powder had a mean particle size of 235 μm, and Cu 28 μm. Fig. 1a and b shows SEM micrographs of the as-supplied powders.

The Ta and Cu powders in a proportion of 20 wt%Cu were placed into a hardmetal lined vial together with hardmetal balls and cyclohexane for milling in a high energy planetary Fritsch Pulverisette 7 mill for 100 h, but samples were collected at shorter milling times (2, 10, 20, 50 and 75 h) so that the evolution of the powder during milling could be followed. Two different milling conditions that influenced the severity of milling were utilized. These conditions are described in Table 1. In all cases the milling velocity was set at 5 in a 1–10 scale range of the equipment.

For comparison, the elemental powders were mixed for 2 h in the vial without balls. This sample is called mixed powder.

The powder milled resulting from 100 h milling was characterized by SEM, EDX, XRD and laser scattering to measure the mean particle size. The powders collected at shorter milling times were characterized by SEM and XRD.

3. Results and discussion

Fig. 2 shows a SEM micrograph (BSE mode) of the mixed powder. The particles stand side by side without the formation of agglomerates. Due to the significant size and density difference, segregation is expected if such a powder is milled.

Fig. 3a–f shows SEM (BSE mode) of the powders milled 2, 20, 50, 75 and 100 h under condition 1. First, the flake-like Ta particles are fragmented (Fig. 3a). The Ta debris is smaller than the original Cu particles. The Cu particles are deformed but still Ta and Cu phases continue separate of each other (not welded together). After 20 h of milling, composite particles are already seen, but they are in an early stage of development (Fig. 3b). That is, the particles consist of Ta and Cu phases heterogeneously distributed. Longer milling times produce particle size refinement and homogeneity of the phase distribution (Fig. 3c–e). After 100 h of milling, the composite particles look very homogeneous. A nanometric rugosity is seen at the surface (Fig. 3f).

Literature describes the formation of composite particles [2]. During HEM, different powders will be strained and mixed at atomic level. Powders with some ductility are deformed into lamellae that cold weld together. In the milling sequence, the lamellae will increase in number and become thinner and harder. The hardened phase can be fractured. If any phase has low ductility, it tends to break instead of deforming. The hard debris pierces the

<table>
<thead>
<tr>
<th>Condition 1</th>
<th>Condition 2</th>
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<tr>
<td>- Mass of milling balls: 100 g</td>
<td>- Mass of milling balls: 150 g</td>
</tr>
<tr>
<td>- Ball diameter: 15 mm</td>
<td>- Ball diameters: 15 mm and 6 mm mixed</td>
</tr>
<tr>
<td>- Powder to ball weight ratio: 1:3</td>
<td>- Powder to ball weight ratio: 1:5</td>
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soft phase, forming the composite particles. Further milling will decrease the size of the particles of the hard phase that can be dissolved. In a last step, the phases can suffer amorphization.

In the present case, Ta is the hard phase, but has some ductility, since plates of Ta are seen in the milled powders as will be shown.

Fig. 4 shows the XRD patterns of the powders milled for 2, 20, 50, 75 and 100 h under condition 1. The intensity of the diffraction peaks decrease with increasing milling time and become wider. Both phases are crystalline, but the diffraction peaks of Cu became very wide and of low intensity. EDX (not shown) did not point out contamination. The mean particle size is 7.9 μm.

Fig. 5a–e shows SEM micrographs (BSE mode) of the powders milled for 2, 20, 50, 75 and 100 h under condition 2. It can be noticed that after two hours composite particles are well formed. Further milling increases homogeneity of the particles and decreases the mean size to 4.7 μm. This is a significant size reduction, compared to the original Ta and Cu particles. These composite particles are smaller than those produced under milling condition 1. EDX (not shown) indicates a small contamination by WC.

Fig. 6 shows the XRD patterns of the powders milled for 2, 20, 50, 75 and 100 h. It is observed that for milling times longer than 50 h both Ta and Cu become amorphous. Peaks of WC are visible in the pattern of the powder milled for 100 h. They are sign of contamination. The amorphization, the mean particle size difference and contamination of the powder are clear evidences of higher intensity under milling condition 2. This condition has a higher powder to ball weight ratio (PBWR) and balls of two different sizes. The higher the PBWR and the number
of balls, the higher the number of collisions per unit time. Consequently the milling intensity is increased. Therefore, the different characteristics of the powders produced by the two milling conditions are coherent with the fact that more intensive milling develops faster composite particles and damages more the crystal lattices of Ta and Cu.

Fig. 7a and b shows SEM micrographs (BSE mode) of a sample of the mixed powder and the powder milled under condition 2 for 100 h, after pressing and heating over the Cu melting temperature. A very heterogeneous structure results in the case of the mixed powder. Porous Ta agglomerates are surrounded by dense Cu. Cu does not infiltrate the Ta agglomerates.

The structure of the heated milled powder is very different. Composite particles are still present. They are surrounded by Cu, but the structure is dense. Small Ta particles are immersed in a Cu matrix in the former composite particles. Some of the Ta particles are elongated. It is expected that the Ta particles grow during heating, but
not into an elongated shape. The elongated Ta particles were formed during milling. Botcharova et al. [6,7] reported the amorphization of only Nb and the formation of a solid solution of Nb in Cu. Although they milled the powders for only 35 h, the PBWR is much higher (1:14). Other work [4] reported the amorphization of Ta and Cu after 50 h with a PBWR of 1:15. The results show that both Cu and Ta can be amorphized. This depends on the milling intensity, time and composition of the mixture. It seems that Cu richer mixtures are more difficult to amorphize.

This work also shows that amorphization is not a signal of solid solution formation. Separated amorphous Cu and Ta phases coexist. If the Ta and Cu milled particles are very small they are not discerned even under SEM.

4. Conclusions

HEM for 100 h of Ta and Cu with the composition Ta–20 wt.%Cu produces composite particles in which both phases are amorphous. Cu amorphizes earlier than Ta. Depending on the milling intensity Cu can amorphize after 20 h and Ta after 50 h. Ta is harder than Cu. The Ta particles are pierced in the deformed Cu particles and fracture, but they are also deformed. No signal of solid solution is found. Both phases can coexist separately in an amorphous state. The composite particles do not resemble the original particles in size and shape. As the final composite particles are smaller than the original Cu particles, they must have fragmented during milling. This is possible because the cold work caused by successive collisions hardens the Cu particles, making them fragile.

Acknowledgements

The authors are thankful to FAPERN and CNPq for financial support (Projects 35.0118/2005-1(NV)) and to the laboratories of NEPGN/UFRN through the Projects CTPETRO-INFRA and FINEP/LEM.

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