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Amorphization in an immiscible Cu–Ta system by mechanical alloying

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Abstract

The amorphization of $Cu_{30}Ta_{70}$ powders by mechanical alloying has been studied. The structural changes in this material during mechanical alloying were monitored by X-ray diffraction and transmission electron microscopy. It was found that a nanocrystalline supersaturated solid solution of tantalum was formed in the initial stage of mechanical alloying. Amorphous transformation of alloyed powders began to take place when the milling time exceed 30 h and a single phase of an amorphous product was obtained after 100 h of milling. The crystallization reaction of the formed amorphous phase was studied by differential thermal analysis and the kinetics of the reaction has been examined as well. The present results suggest that the enhancement of the free energy due to the supersaturation of copper in tantalum and the introduction of a high density of defects by ball milling comprise the driving force for the amorphization of the Cu–Ta system.

1. Introduction

At present there is considerable interest in the basic mechanism of amorphization by mechanical alloying (MA) [1]. Generally, it has been observed that by MA it is possible to prepare glassy metals with hitherto unexplored composition ranges or even new systems not yet amorphized by rapid quenching techniques [2]. It is now known that amorphous phases can be synthesized by MA of either a mixture of elemental powders or intermetallic compound powders. For mixed elemental powders Johnson [3] argued that the parameters which control the crystal-to-glass transition are a large negative heat of mixing and an anomalously fast diffusion of one element in the host matrix of the other. In the case of amorphization of an intermetallic compound Koch *et al.* [4] suggested that the following mechanism might be responsible: the severe plastic deformation provided by MA generates lattice defects (point defects, dislocations, etc.) which cause the free energy of the crystalline phase to rise above that of the amorphous phase, resulting in vitrification of the compound phase.

The motivation of this work was to investigate the applicability of MA to the formation of an amorphous phase from a system where the heat of mixing is positive. Cu–Ta is a typical immiscible system with a positive heat of mixing [5]. In this paper we study the effect of ball milling on a mixture

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of copper and tantalum powders with nominal composition $Cu_{30}Ta_{70}$ by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential thermal analysis (DTA). The sequence of phase transformations for this material is clarified.

2. Experimental details

Mixtures of elemental powders of nominal composition $Cu_{30}Ta_{70}$ were prepared using 99.8% purity copper and 99.5% purity tantalum powders. The initial particle sizes were smaller than 75 μm for copper and 45 μm for tantalum. The ball milling was performed in a planetary ball mill with steel balls and vials. The mass ratio between the balls and the powders was 15:1. To avoid oxidation, the powders were sealed in the vials with the balls under an argon atmosphere. Samples for analysis were removed by interrupting the ball milling at various times. X-ray scans were carried out on a Philips PW 1700 diffractometer using Cu Kα radiation. TEM was performed in a Jeol 200 CX transmission electron microscope. In order to check the milling tool contaminations, an atomic absorption spectrophotometer was employed; this revealed an impurity of 1.2 at.% Fe in the sample milled for 100 h.

DTA (Perkin–Elmer DTA 1700) was used to determine the crystallization temperature; different heating rates were applied to evaluate the activation energy of crystallization of the amorphous phase by the Kissinger method.

3. Results and discussion

Changes in the XRD pattern of mixed $Cu_{30}Ta_{70}$ powders after different milling times are shown in Fig. 1. As the milling proceeded, the diffraction peaks of the crystalline phases broadened markedly, indicating a reduction in crystallite size and a build-up of internal strain. All the Bragg peaks related to the elements remained visible until the mixture has been subjected to 30 h milling, when the diffraction peaks indexing copper disappeared and the peaks due to tantalum shifted towards higher angles. This means most of the copper atoms have dissolved in the tantalum lattice. After 60 h of milling, a broad diffuse scattering maximum appeared together with a very weak Ta(110) diffraction peak. The broad diffuse scattering maximum indicates that an amorphous Cu–Ta phase has been formed. After 100 h of milling, no crystalline phase was detectable within the resolution of the XRD technique, which implies that the amorphization is almost complete. TEM examinations support these findings. Figure 2 shows a dark field TEM image and a selected area diffraction (SAD) pattern for $Cu_{30}Ta_{70}$ after 30 h of milling. The grain size of the sample as estimated from the micrograph is found to be approximately 10–20 nm. The SAD pattern shows that the powder is basically of the b.c.c. structure of tantalum. Further ball milling led to transformation of the tantalum supersaturated solution to glass, as indicated in Fig. 3 by

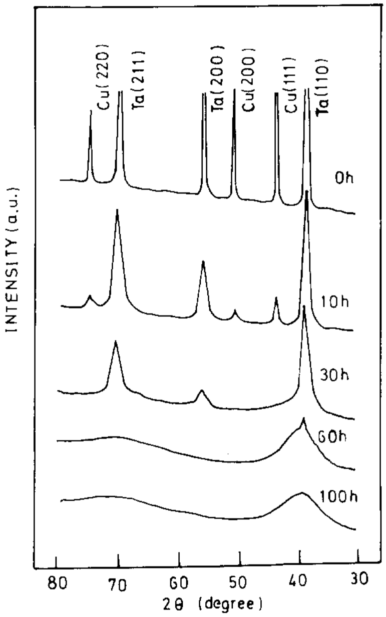


Fig. 1. X-ray diffraction patterns of $Cu_{30}Ta_{70}$ powders milled for various times.

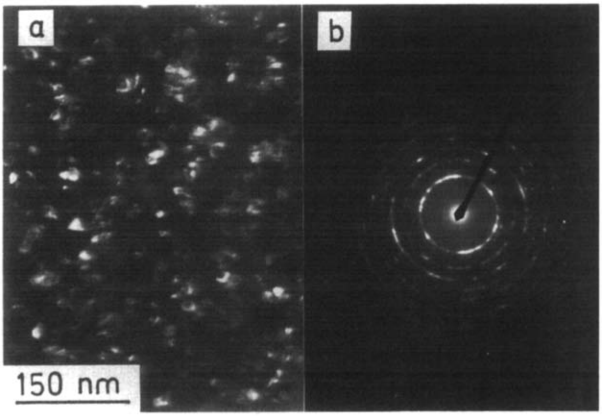
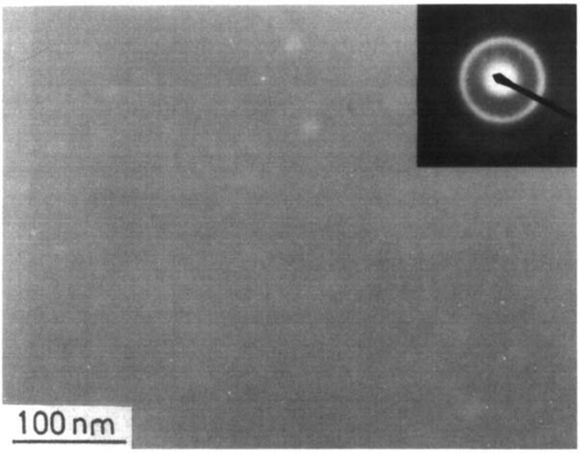


Fig. 2. (a) TEM dark field image of $Cu_{30}Ta_{70}$ after 30 h of milling. (b) Selected area diffraction pattern.

the featureless structure in the bright field image and diffuse halos in the electron diffraction pattern.

Figure 4 indicates the milling time dependence of the lattice parameter of tantalum. The reduction in the lattice parameter of tantalum with increasing milling time is attributed to an increase in solute content of copper. Although the solubility of copper in tantalum is almost zero in an equilibrium state, the solubility can be considerably extended by a non-equilibrium process such as MA. Previous works have proved that MA can greatly extend the



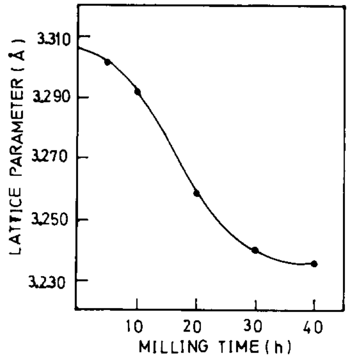
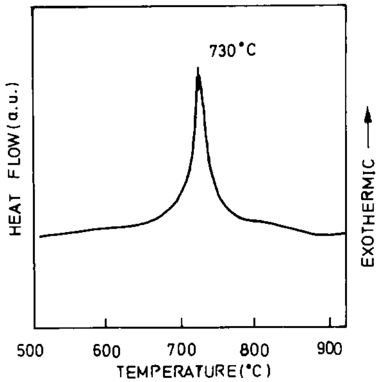


Fig. 3. TEM bright field image and corresponding diffraction pattern of amorphous $Cu_{30}Ta_{70}$ alloy formed after 100 h of milling.

Fig. 4. Milling time dependence of the lattice parameter of tantalum.



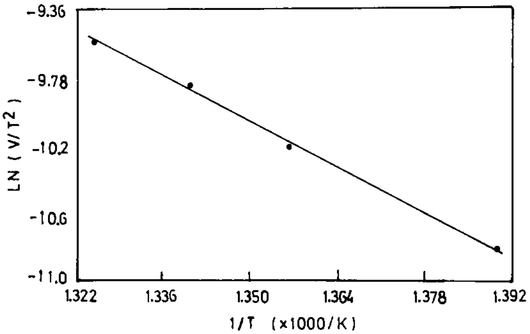


Fig. 5. DTA scan at 20 K min^{-1} of a $Cu_{30}Ta_{70}$ powder sample after 100 h of milling.

Fig. 6. Plot of $\ln(V/T^2)$ *vs.* $1/T$ as obtained from DTA scans for amorphous $Cu_{30}Ta_{70}$ alloy formed at different heating rates V. According to Kissinger's formula, an activation energy of 168 ± 5.3 kJ mol^{-1} is obtained.

solubility of various elements [6–8], even some which are immiscible [9–10]. Eckert *et al.* [11] suggested that the easy formation of supersaturated solid solution during MA is due to the small atomic size mismatch between the milled elements. Birringer *et al.* [12] demonstrated that the solute solubility of nanocrystalline materials may be several orders of magnitude larger than that of single crystals, which is also the case in the present study. Therefore we believe that the highly supersaturated solid solution together with the high density of structural defects (such as dislocations, grain boundaries, etc.) generated by intensive ball milling will evidently enhance the free energy of the alloy and eventually result in a destabilization of the crystal lattice, thus leading to the formation of an amorphous phase.

DTA allows monitoring of the heat release during crystallization of the amorphous phase. Figure 5 shows a heating scan (at rate of 20 K min^{-1}) of the formed amorphous $Cu_{30}Ta_{70}$ alloy, indicating crystallization of glass with a relatively broad temperature range around 730 °C. The kinetics of this crystallization reaction can be examined by a Kissinger analysis based on the peak position changes for the DTA curves with different scanning rates V (varied between 10 and 40 K min^{-1}). By plotting $\ln(V/T^2)$ *vs.* $1/T$, the Kissinger analysis yields an activation energy of 168 ± 5.3 kJ mol^{-1} (Fig. 6).

4. Conclusions

The present study clearly shows, on the basis of X-ray diffraction, transmission electron microscopy and differential thermal analysis results, that an amorphous $Cu_{30}Ta_{70}$ alloy can be synthesized by mechanical alloying of copper and tantalum elemental powders, even though they have a positive heat of mixing. The amorphization process of $Cu_{30}Ta_{70}$ may be divided into two stages: (1) formation of a nanocrystalline supersaturated solid solution of tantalum; (2) transformation of the tantalum solid solution to glass. The supersaturated solution of tantalum with high copper content and the high density of defects introduced by ball milling appear to be responsible for the crystal-to-glass transformation.

Acknowledgment

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