Microstructure evolution of Cu – 22 % In alloy subjected to the high pressure torsion

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Abstract. Microstructure studies of Cu – 22 wt. % In alloy after annealing and severe plastic deformation were carried out by means of scanning and transmission electron microscopy. Two samples of the alloy were annealed at 350 ºC and 520 ºC for 553 hours and then subjected to high pressure torsion at room temperature under a pressure of 5 GPa in a Bridgman anvil-type unit. The sample annealed at 350 ºC exhibited duplex microstructure: copper matrix with embedded plates of δ phase (Cu_7In_3) and δ phase with lamellar precipitates of copper. The microstructure of the sample annealed at 520 ºC consisted of copper matrix with spherical precipitates of δ phase. The subsequent severe plastic deformation resulted in a substantial grain refinement in copper matrix to nanoscale size. However, the morphology and size of δ phase precipitates did not change. The measurements of microhardness and calorimetric studies were also performed in order to study the specific properties of δ phase.

1. Introduction

In last decades, the Cu-In alloys cause broad interest because they are included in some different ternary alloys (eg. Ag-Cu-In [1], Cu-In-Pb [2], Cu-In-Sn [3]) which are widely used in the electronics industry as solder materials. The Cu–In alloys have attracted interest also as materials for production of semiconductors [4] as well as thin-film solar cells [5, 6]. However, several intermetallic phases such as Cu_7In_3, Cu_2In, $Cu_{11}In_9$ present in the Cu–In equilibrium phase diagram [7] hinder the formation of films with uniform structure [4]. The use of severe plastic deformation (SPD) which can induce dissolution of phases, formation or decomposition of a supersaturated solid solution [8], disordering of ordered phases [9], amorphization of crystalline phases [10] etc. among with substantial grain refinement [11-12] can help to overcome such obstacles. In the present paper the influence of high pressure torsion (HPT) deformation on the microstructure of the Cu – 22 wt. % In alloy pre-annealed in the two-phase region (α + δ) at temperatures of 350 and 520 ºC for 553 hours, is examined.

2. Experimental

The Cu – 22 wt. % In alloy has been prepared from high-purity 5N Cu and 5N In by vacuum induction melting in the form of cylindrical ingots. For HPT processing, the 0.6 mm thick discs were cut from the as-cast ingots, then ground and chemically etched. They were sealed into evacuated silica ampoules with a residual pressure of approximately 4×10^{-4} Pa at

room temperature. Samples were annealed at 350 and 520 °C for 553 h, and then quenched in water. The annealed samples were processed by HPT for five full rotations at a constant rotation speed of 2π per minute and a pressure of 5 GPa using a custom built computer controlled HPT device (W. Klement GmbH, Lang, Austria). Samples for microstructural investigations were cut from the HPT-processed discs at a distance of 3 mm from the sample center. For the metallographic investigations the samples were ground with SiC grinding paper, and sequentially polished with 6, 3, and 1 µm diamond pastes. The prior inspection of obtained material was carried out on a Philips XL30 scanning electron microscope (SEM) equipped with a LINK ISIS an energy-dispersive X-ray spectrometer (EDS) produced by Oxford Instruments. The details of the phases, especially in nanoscale, were revealed using a TECNAI G2 FEG super TWIN (200 kV) transmission electron microscope (TEM) equipped with an energy dispersive X-ray (EDX) spectrometer manufactured by EDAX. X-ray diffractograms were obtained using Bragg–Brentano geometry in a powder diffractometer (Philips X'Pert) with CuKa radiation. The peak profile parameters (peak intensity, full width at half maximum and integral breadth) were determined by fitting a Pearson VII function to the measured peaks. The volume averaged crystallite size and the microstrain were estimated from the XRD peak broadening using a modified Williamson–Hall method correcting for systematic errors as described in Ref. [13]. All reflections with Miller indices up to (420) were used for the grain size and microstrains estimates. A LaB_6 standard was used to determine the correction for instrumental broadening. The samples after annealing and HPT deformation were studied with the aid of differential scanning calorimetry (DSC) using DSC 404 F1 Pegasus, Netzsch calorimeter in argon atmosphere, Al_2O_3 crucibles, at the cooling and heating rates of 10 °C /min. In order to record the DSC curves, the samples were heated from 50 to 950 °C. The microhardness was measured with the Vickers method at the load of 100 µN using the CSM Instrument.

3. Results and discussion

The microstructure of two samples of Cu - 22wt. % In alloy annealed at 350 and 520 °C is shown in Fig.1. The sample annealed at 350 °C has the eutectoid microstructure consisting of two phases. One of them is the α solid solution (Cu) with precipitates of intermetallic δ phase (Cu_7In_3), and the second one is the δ phase with precipitates of α phase (Fig. 1a,b). The volume fraction of δ phase reached about 50%. Increasing the annealing temperature to 520 °C resulted in a partial dissolution of δ phase and its volume fraction reached now about 20%. The microstructure of so annealed sample has large (about 10 µm) rounded or slightly faceted precipitates of δ phase, uniformly contains in a copper matrix (Fig. 1c).

The results of XRD analysis (Fig. 2) of annealed samples showed a slight and significant shift of the copper peaks (as compared to pure copper) to the lower diffraction angles in the sample annealed at 350 and 520 °C respectively. Significant shift of the copper peaks to the lower diffraction angles points is attributed to the dissolution of In atoms from δ phase in the copper matrix during long period of annealing at high temperature. The XRD peaks from δ phase are clearly visible in the XRD spectra of the sample annealed at 350 °C, while they are almost invisible (located at the level of background) in the sample annealed at 520 °C due to the low volume fraction of δ-phase.
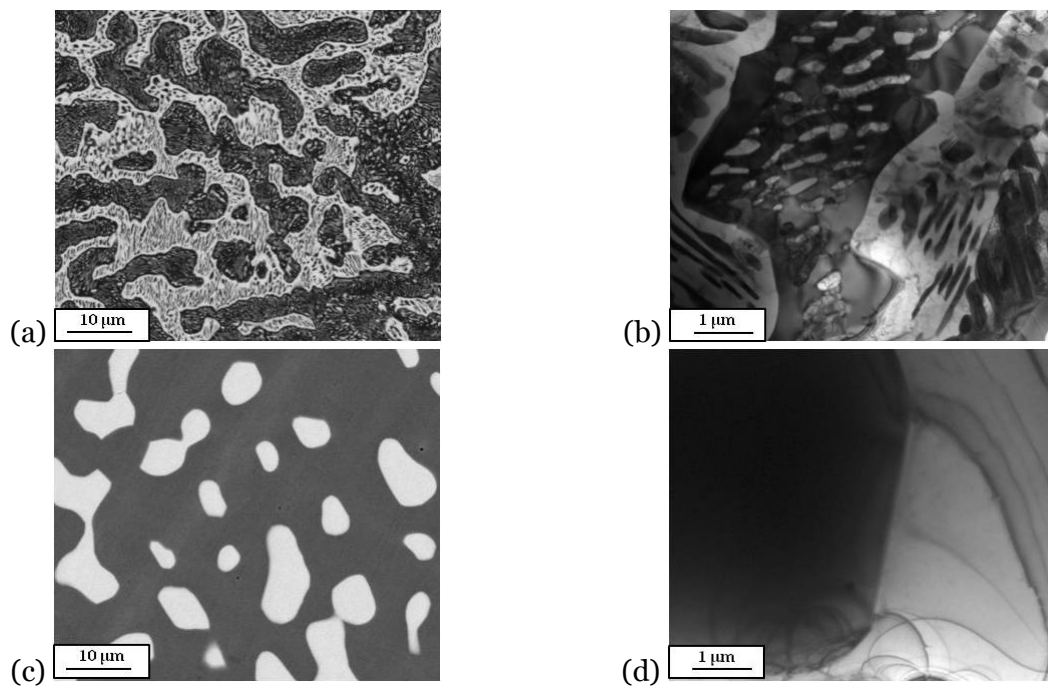
Figure 1. SEM/BSE (a, c) and TEM (b, d) images of Cu − 22 wt. % In alloy after annealing at 350 °C (a, b) and 520 °C (c, d) for 553 h. The δ phase has a bright contrast in comparison with a dark α phase in SEM images and has a dark contrast in comparison with a bright α phase in TEM images.
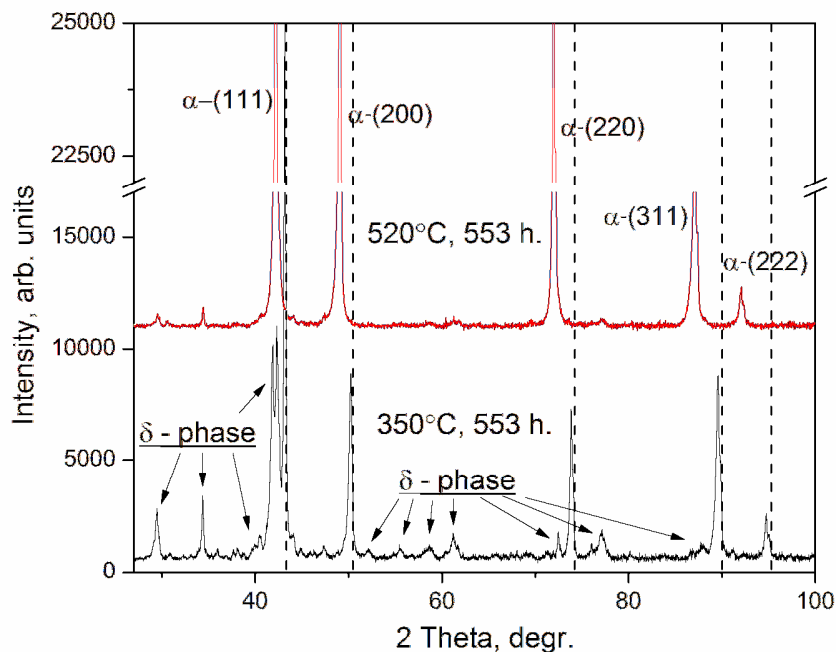

Figure 2. X-ray diffraction pattern of the samples of Cu − 22 wt. % In alloy annealed at 350 °C (bottom curve) and 520 °C (top curve) for 553 h. Peak positions attributed to pure Cu are indicated by vertical dashed lines.

        The EDX analyze of chemical composition of α solid solution and δ phase precipitates confirm that indium dissolves in the copper matrix during annealing at a high temperature.

For example, α solid solution at 350 °C contained about 1% at. In, while at 520 °C - about 5% at. In (Table 1).

Table 1. The Cu:In ratio (% at.) of α and δ phases in the samples annealed at 350 and 520 °C.

phase	ratio Cu:In, % at.	
	Annealing at 350 °C	Annealing at 520 °C
α	99:1	95:5
δ	74:26	75:25

The SEM microstructure investigation of samples after HPT deformation showed an unexpected phenomenon: the δ phase appeared intact, i.e. it neither dissolved nor became refined in the α phase (Fig. 3), and its volume fraction did not change.
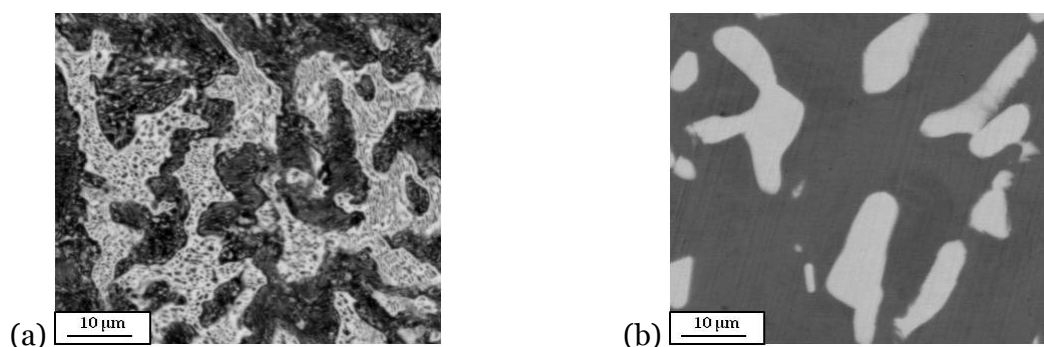

(a)   10 μm   (b)   10 μm

Figure 3. SEM/BSE micrographs of Cu – 22 wt. % In alloy after HPT deformation, previously annealed at 350 (a) and 520 °C (b) for 553 h.

Detailed study of the microstructure of deformed samples in TEM showed strong grain refinement of α phase down to the nanometer range. Due to complex diffraction contrast, separate grains of α phase cannot be resolved in the bright field images (Fig. 4b). The δ phase in the sample pre-annealed at 350 °C, appears elongated and its boundaries are poorly visible (Fig. 4a). The content of In in the δ phase in both samples after HPT deformation is unchanged as compared to as-annealed state and is equal to about 25% at.

XRD of the deformed samples showed a significant decrease in intensity and increase in width of the copper peaks. Widening of the peaks is mainly due to the strong grain refinement and internal stresses caused by HPT deformation. The calculated α grain size in the sample, pre-annealed at 350 °C, was found to be 24±3 nm and in the sample, pre-annealed at 520 °C, was 6±1 nm. Intensity of the δ phase peaks also significantly decreased and became almost equal to the background.
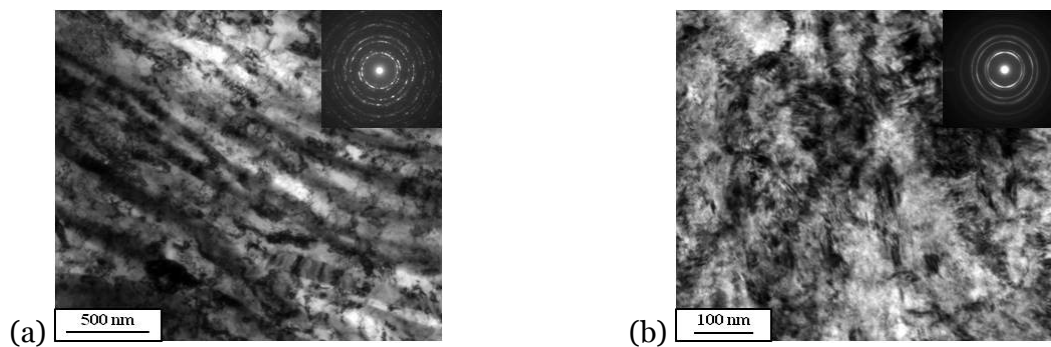
Figure 4. Bright field TEM micrographs of Cu – 22 wt. % In alloy after HPT deformation, previously annealed at 350 (a) and 520 °C (b) for 553 h. Micrograph a) showing (α+δ) microstructure; micrograph b) showing the strongly deformed α phase. Selected area of electron diffraction patterns taken from the area of about 0,27 μm² are also inserted.
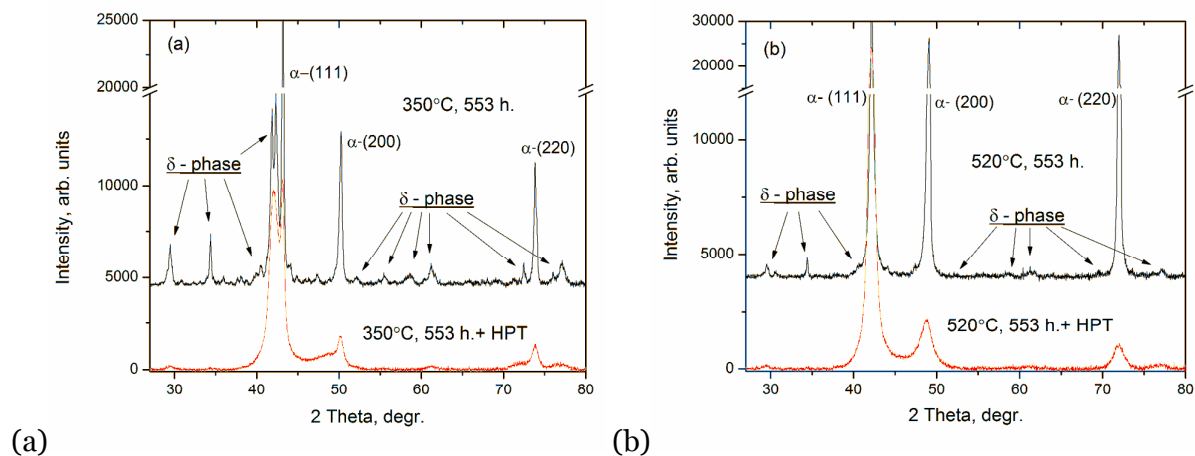

Figure 5. X-ray diffraction patterns of the samples before (top curves) and after HPT deformation (bottom curves), previously annealed at 350 (a) and 520 °C (b) for 553 h.

The DSC curves for the sample annealed at 350 °C and for the HPT deformed one (Fig. 6) look very similar and show a sequence of four endothermic reactions. The first one in the temperature range 430-540 °C could be associated with dissolution of α grains contained small amount of In. Onset temperature of the second reaction, 573 °C is equal to the temperature of the eutectoid transformation ß → α + δ. Thus, this peak is associated with the dissolution of δ phase. Onset temperature of the third peak, 709 °C, coincides with the temperature of peritectic transformation L + α → ß. Therefore this peak corresponds to the dissolution of ß phase. The fourth broad peak around 900 °C, is associated with the melting of α crystals. It should be noted that the values of integrated enthalpy absorption corresponding to the dissolution of δ phase before and after deformation are similar (14 and 12 J/g respectively). A similar situation is observed in calorimetric investigation of the sample annealed at 520 °C and subjected to HPT deformation, where the enthalpy absorption of the second peak is about 11 J/g in both samples (thermograms are not shown). Close values of the enthalpy absorption before and after HPT deformation additionally confirms the presence of δ phase after deformation.
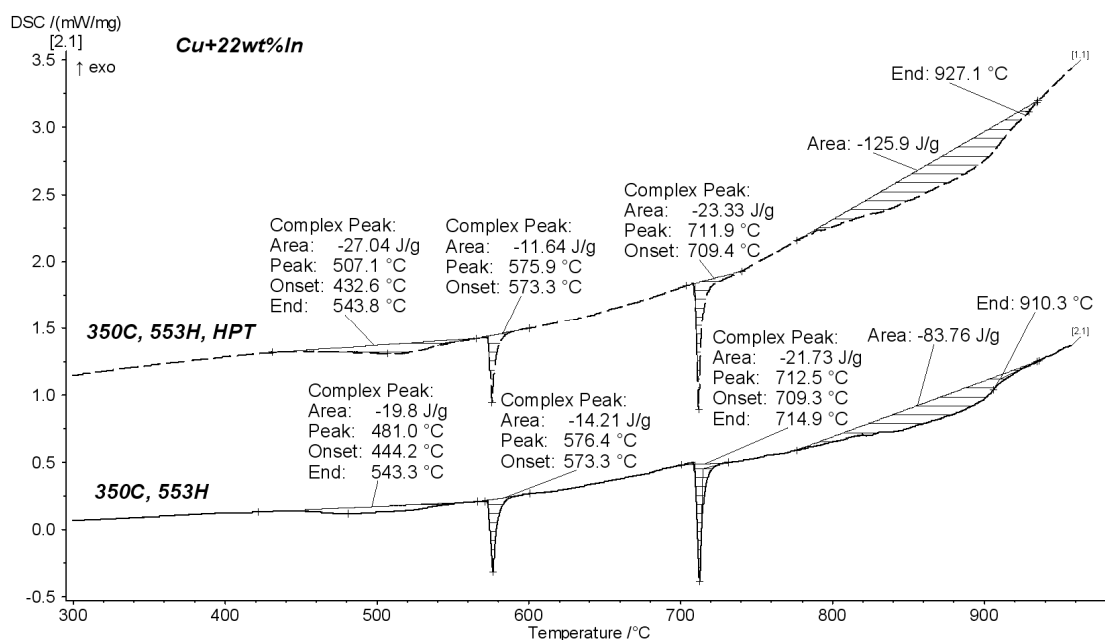
Figure 6. DSC heating curves of the samples annealed at 350 °C and subjected to HPT deformation.

Unfortunately, due to small sizes of α and δ phase it was not possible to resolve the microchardness of these two phases in the sample annealed at 350 °C. The measurements for the α solid solution in the sample annealed at 520 °C showed that the microhardness before and after deformation was about 106 and 202 HV, respectively, while microhardness of δ phase before and after deformation reached about 200 and 275 HV respectively. This implies that δ phase is much harder than α phase (almost two times in the annealed state). As a result of HPT, the hardness of δ phase increased by about 38%, and hardness of the α phase became greater by about 90%. It is, therefore, possible that δ phase neither dissolved nor became refined after deformation due to its high hardness (about 200 HV in initial state).

4. Conclusions

Annealing at 350 and 520 °C for 553 h of the alloy Cu – 22 wt. % In resulted in the formation of two different microstructures. The formation of eutectoids consisting of two phases are observed at the low temperature annealing: the first phase is the α solid solution based on Cu with precipitates of intermetallic δ phase (Cu_7In_3), and the second one is the δ phase with precipitates of α phase. The volume fraction of δ-phase in this sample is about 50%. Large (about 10 μm) rounded or slightly faceted precipitates of δ phase, uniformly distributed in a copper matrix, are formed in the microstructure of the alloy Cu – 22 wt. % In after annealing at 520 °C. The volume fracture of δ phase reaches here about 20%.The severe plastic deformation by HPT method resulted in strong grain refinement of Cu matrix (down to the nanometer range), while there was no refinement or dissolution of δ phase. The volume fraction of δ phase after deformation was almost the same to that in the initial state (before HPT). It is possible that this unusual behavior of the δ phase is related to its significant hardness, which reached about 200 HV before deformation.

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