
Journal or publication title: *Applied Physics Letters*

Volume: 83

Number: 16

Page range: 3299-3301

Year: 2003

URL: http://hdl.handle.net/10097/51743

doi: 10.1063/1.1619220
Origin of nondetectable x-ray diffraction peaks in nanocomposite CuTiZr alloys

J. Z. Jiang

Department of Physics, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark and Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, People’s Republic of China

H. Kato, T. Ohsuna, J. Saida, and A. Inoue

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

K. Saksl and H. Franz

HASYLAB am DESY, Notkestrasse 85, D-22603 Hamburg, Germany

K. Ståhl

Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received 19 May 2003; accepted 20 August 2003

Microscopic structures of Cu60Ti10Zr30 (x = 0 and 10) alloys have been investigated by transmission electron microscopy, x-ray diffraction (XRD) and differential scanning calorimeter (DSC). In the Cu60Ti10Zr30 samples annealed at 708 K for times ranging from 0 to 130 min, where the enthalpy of the first exothermic peak decreases by 80%, the corresponding XRD patterns still look similar to that for the as-prepared sample. However, the simulated XRD patterns for the pure Cu51Zr49 phase, which is the crystalline phase formed during the first exothermic reaction, with small grain sizes and defects clearly show a broadened amorphous-like feature. This might be the reason that no diffraction peaks from the nanocrystalline component were detected in the XRD patterns recorded for the as-cast or as-spun Cu60Ti10+x,Zr30−x (x = 0 and 10) alloys and for the alloys annealed at lower temperatures, in which the enthalpy of the first exothermic peak has a significant reduction. The second exothermic peak found in DSC curves is due to the formation of another hexagonal phase, spacing group P63/mmc (194) and lattice parameters a = 5.105 Å and c = 8.231 Å. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619220]
Figure 1 shows DSC curves and the time dependence of the first and second exothermic peak areas for the as-cast Cu$_{60}$Ti$_{10}$Zr$_{30}$ rod and samples annealed at 708 K for various times.

(JEOL JEM-3000F). TEM specimens were prepared by low-energy ion milling at 2.5 kV and 5 mA with liquid nitrogen cooling.

Figure 1 shows DSC curves and the time dependence of the first and second exothermic peak areas for the as-cast and annealed Cu$_{60}$Ti$_{10}$Zr$_{30}$ rods. The DSC curve for the as-cast rod is in good agreement with data reported in the literature. With increasing annealing time, the enthalpy of the first exothermic peak monotonically decreases from 25 J/g for the as-cast rod to about 5 J/g for the sample annealed for 7.8 ks, while the second exothermic peak remains almost unchanged within experimental uncertainty. With further increasing annealing time, the second exothermic peak starts to decrease and its position shifts to lower temperatures. For 42.3 ks, the first exothermic peak disappears and the enthalpy of the second exothermic peak has a 35% reduction. Figure 2 shows TEM dark-field images of the as-cast Cu$_{60}$Ti$_{10}$Zr$_{30}$ rod and the sample annealed at 708 K for 7.8 ks. The nanocomposite microstructure for the as-cast rod is seen to consist of nanocrystals ranging 7–15 nm embedded in an amorphous matrix, which is consistent with the data reported in Refs. 9–11. Two striking features were detected from the image for the annealed sample: (1) the sample is dominated by nanocrystals and (2) the average size of nanocrystals of about 5 nm is smaller than that for the as-cast rod. The results strongly suggest that the first exothermic peak in Fig. 1 may be due to the primary nanocrystallization of the amorphous matrix of the as-cast sample. Figure 3 shows XRD patterns of as-cast Cu$_{60}$Ti$_{10}$Zr$_{30}$ rod and samples annealed at 708 K for various times. It is surprisingly found that samples annealed at 708 K for a time less than 8 ks have a similar XRD pattern with the as-cast rod although the enthalpy of the first exothermic peak drops by 80% as compared to the as-cast rod in Fig. 1. No crystalline diffraction peaks were detected in the sample annealed at 708 K for 7.8 ks. By fitting the broad peak located at 2\theta=40° using both Lorentz and Gauss line profiles, it is clear that the width at the half maximum (FWHM) in Fig. 3(b)(ii) decreases by a factor about 16% from as-cast to the sample annealed for 7.8 ks. The XRD pattern [Fig. 3(a)] recorded for the sample annealed for 42.3 ks shows diffraction peaks, which can be indexed to a hexagonal phase (hereafter marked H2), space group P6$_3$/mmc (194) and lattice parameters $a=5.105$ Å and $c=8.231$ Å. We believe that this crystalline phase corresponds to the reduction of the second exothermic peak in Fig. 1. In situ high temperature XRD measurements for both Cu$_{60}$Ti$_{10}$Zr$_{30}$ and Cu$_{60}$Ti$_{20}$Zr$_{20}$ ribbons were performed. Both alloys have similar DSC curves, indicating a similar crystallization process.

It found that the first detectable diffraction peaks for the Cu$_{60}$Ti$_{10}$Zr$_{30}$ glass are from the H2 phase. However, for the Cu$_{60}$Ti$_{20}$Zr$_{20}$ glass, the first detectable diffraction peaks are not from the H2 phase, as shown in Fig. 4. The peak recorded at 741 K looks very broad, similar to an amorphous-like pattern, but slight narrower than the pattern recorded at 295 K. The intensity at $2\theta=10°$ is higher than the pattern recorded at 295 K. Diffraction peaks, superimposed on the broadened amorphous peak, appear at 756 K, which can be indexed as a new hexagonal phase (hereafter marked H1), space group P6/m (175) and lattice parameters $a=11.235$ Å and $c=8.271$ Å. This phase is similar to a Cu$_{5}$Zr$_{14}$ phase. At temperatures above 790 K, the H2 phase appears. We further simulated the XRD patterns for the pure H1 phase with various grain sizes as shown in Fig. 4(b), in which we did not take into account defects and strain effects. For small grain sizes, diffraction peaks for the H1 phase strongly overlap. Consequently, the simulated patterns for grains less than 5 nm look indeed similar to an amorphous-like pattern as the pattern recorded at 741 K in Fig. 4(a). The peak width at around $2\theta=8.8°$ does get narrower as shown in Fig. 3(b) and the intensity at $2\theta=10°$ does increase as observed in Fig. 4(a). Note that defects, e.g., nonstoichiometric composition, interfaces, and microstrain, which most likely exist in the nanocomposite alloys, could further broaden diffraction peaks. Therefore, although the TEM results in Fig. 2 reveal that the average grain size of nanocrystals in the Cu$_{60}$Ti$_{10}$Zr$_{30}$ rod sample annealed at 708 K for 7.8 ks is about 5 nm, diffraction peaks from the H1 phase could still not be visible, as experimentally observed in Fig. 3. It also found that the average crystal size of the H1 phase in the Cu$_{50}$Ti$_{20}$Zr$_{30}$ alloy is larger than that in the Cu$_{60}$Ti$_{10}$Zr$_{30}$ alloy, which results in the appearance of diffraction peaks from the H1 phase prior to the H2 phase in the XRD patterns in the Cu$_{50}$Ti$_{20}$Zr$_{30}$ alloy.
observed a similar phenomenon in a nanostructured Zr$_{54.5}$Ti$_7$Cu$_{20}$Ni$_{3}$Al$_{10}$ alloy, in which they also suggested the particle size effect for the nondetectable X-ray diffraction peaks for quasicrystals.

In conclusion, microscopic structures of Cu$_{60}$Ti$_{10}$Zr$_{30}$ (x=0 and 10) alloys have been investigated by TEM, XRD, and DSC. The first crystalline phase formed during constant rate heating is a Cu$_{51}$Zr$_{14}$-like phase [space group P6$_3$/mmc (194) and lattice parameters $a=5.105$ Å and $c=8.231$ Å], which occurs at the second exothermic peak found in DSC curves. The puzzle in the CuZrTi system, i.e., that no diffraction peaks from the nanocrystalline component were detected in the XRD patterns recorded for the as-cast or as-spun Cu$_{60}$Ti$_{10+x}$Zr$_{30-x}$ (x=0 and 10) alloys and for the alloys annealed at lower temperatures, in which the enthalpy of the first exothermic peak has a significant reduction, has been solved.