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Origin of nondetectable x-ray diffraction peaks in nanocomposite CuTiZr alloys

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Microscopic structures of Cu_{60-\delta}Ti_{10+\delta}Zr_{30-\delta} (x=0 and 10) alloys have been investigated by transmission electron microscopy, x-ray diffraction (XRD) and differential scanning calorimeter (DSC). In the Cu_{60-\delta}Ti_{10+\delta}Zr_{30} 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 Cu_{51}Zr_{14} 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 Cu_{60-\delta}Ti_{10+\delta}Zr_{30-\delta} (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 P6_{3}/mmc (194) and lattice parameters a = 5.105 Å and c = 8.231 Å. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619220]

In 1995, the Cu–Ti–Zr–Ni system, the first Cu-rich bulk metallic glass forming alloys, was discovered and then Cu–Ti–Zr–Ni–Si and Cu–Ti–Zr–Ni–Sn systems were reported. Very recently, the report of ternary Cu_{60} Ti_{10} Zr_{30} and Cu_{60} Ti_{20} Zr_{20} systems, exhibiting excellent mechanical properties, has triggered considerable research activity in this area, especially in the microstructure of the ternary systems. Inoue et al., reported that bulk glassy alloys with a rod diameter of 4 mm can be formed in the ternary Cu_{60} Ti_{10} Zr_{30} and Cu_{60} Ti_{15} Hf_{25} systems. However, only the x-ray diffraction (XRD) technique was applied to characterize the samples. Louzguine and Inoue further studied the microstructures of the samples annealed at various stages using transmission electron microscopy (TEM). Formation of nanocrystals in annealed samples was observed. Electron microscopic studies on both as-cast and as-spun Cu_{60} Ti_{10} Zr_{30} samples clearly demonstrated that as-prepared samples contain significant volume fraction (about 5%–10%) of nanocrystals with diameters ranging from 5 to 15 nm. It is concluded that the as-prepared ternary samples are classified as a nanocomposite: nanocrystals embedded in an amorphous matrix. However, one experimental fact reported in the literature still remains a puzzle for the community, i.e., 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} Zr_{30} samples. In this letter, we uncover the origin of the puzzle by performing TEM, XRD and differential scanning calorimeter (DSC) measurements of as-prepared and annealed Cu_{60} Ti_{10} Zr_{30} and Cu_{60} Ti_{20} Zr_{20} alloys.

Alloy ingots with the composition of Cu_{60} Ti_{10} Zr_{30} and Cu_{60} Ti_{20} Zr_{20} were prepared by arc melting pure metals of 99.99% copper, 99.99% zirconium, and 99.9% titanium in a purified argon atmosphere. Cylindrical Cu_{60} Ti_{10} Zr_{30} and Cu_{60} Ti_{20} Zr_{20} samples of 2.5 mm in diameter were prepared by a copper mold casting method. Ribbons of Cu_{60} Ti_{10} Zr_{30} and Cu_{60} Ti_{20} Zr_{20} samples were prepared by the melt-spinning method. Heating treatments of the as-cast rod was carried out in a vacuum of 10^{-5} mbar at 708 K for various times from 0 to 42.3 ks. Room-temperature XRD measurements were carried out with Cu K_{\alpha} radiation and in situ high-temperature XRD measurements were carried out at beamline Petra1, HASYLAB in Hamburg, Germany, using a wavelength of 0.3542 Å and an image plate detector. Samples in capillary tubes with a vacuum of 10^{-5} mbar were heated with a heating rate of 3 K/min. Thermal analyses were performed in a Seiko DSC6300 DSC at a heating rate of 0.33 K/s under a flow of purified argon. Both Cu_{60} Ti_{10} Zr_{30} and Cu_{60} Ti_{20} Zr_{20} ribbon samples show a similar thermal behavior. The microstructures of the alloy were examined by using field-emission gun high-resolution transmission electron microscopy with an accelerating voltage of 300 kV.
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(c)] 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.\footnote{11,12} 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 $2\theta=10^\circ$ 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$_{91}$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 $2\theta=8.8^\circ$ does get narrower as shown in Fig. 3(b) and the intensity at $2\theta=10^\circ$ 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$_{51}$Zr$_{14}$ phase is larger than that in the Cu$_{60}$Ti$_{20}$Zr$_{20}$ 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$_{60}$Ti$_{20}$Zr$_{20}$ alloy. In addition, Xing et al.\footnote{17} studied the high temperature XRD measurements for both Cu$_{60}$Ti$_{10}$Zr$_{30}$ and Cu$_{60}$Ti$_{20}$Zr$_{20}$ ribbons. Both alloys have similar DSC curves, indicating a similar crystallization process.\footnote{11,12}
observed a similar phenomenon in a nanostructured Zr_{54.5}Ti_{17.5}Cu_{20}Ni_{10}Al_{10} alloy, in which they also suggested the particle size effect for the non-detectable 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 [spacing group \(P6_3/mmc\) (194) and lattice parameters \(a=5.105 \text{ Å}\) and \(c=8.231 \text{ Å}\)] with nanometer-sized grains. The first exothermic peak found in DSC curves corresponds to the amorphous-to-nanocrystalline Cu_{51}Zr_{14}-like phase transition. Due to overlapping of the diffraction peaks, XRD is unable to distinguish a single amorphous phase from the nanocomposite of Cu_{51}Zr_{14}-like nanocrystals (with small grain sizes and defects) embedded in an amorphous matrix. The second crystalline phase is also a hexagonal phase, space group \(P6_3/mmc\) (194) and lattice parameters \(a=5.105 \text{ Å}\) and \(c=8.231 \text{ Å}\), 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+}Zr_{10-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.