Thermally Enhanced Glass Formation in Multilayered $\text{Cu}_{33}\text{Zr}_{67}$ Composite Particles

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A single phase of glassy $\text{Cu}_{33}\text{Zr}_{67}$ powders has been synthesized by post-annealing the mechanically alloyed $\text{Cu}_{33}\text{Zr}_{67}$ composite powders at 685 K for 1.8 ks. The heat of glassy phase formation was measured directly and found to be -2.59 kJ/mol. The glassy powders transform to big-cube CuZr_2 metastable phase (E9 structure) upon heating to 760 K. This metastable phase does not withstand against the temperature increasing during the DSC analysis and therefore transforms completely into the most stable phase of tetragonal CuZr_2 (C16 structure) at 918 K.

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Solid amorphous materials can be fabricated by a wide variety of techniques.¹⁾ Of these, solid-state amorphization reaction (SSAR)²⁾ and mechanical alloying (MA)³⁾ where the reaction between the diffusion couples takes place at low temperatures. For a successful SSAR, in which thin layers of polycrystalline elements react at temperatures far below the liquids to form a solid amorphous, strong interactions between the diffusion are necessary.⁴⁾ However, the formations of amorphous alloys via isothermal annealing of the multilayered materials have been studied in some binary systems,^{5–10)} they are novel in metallic glassy materials. Hereon, we report the first novel technique for formation of a single glassy phase via post-annealing the mechanically alloyed multilayered $\text{Cu}_{33}\text{Zr}_{67}$ powders in a DSC under Ar gas flow.

Elemental powders (99.9%) of Cu (20 μm) and Zr (50 μm) were balanced to give the nominal composition of $\text{Cu}_{33}\text{Zr}_{67}$ (at%), mixed and sealed into a tempered chrome steel vial (250 mL in volume) together with fifty tempered chrome steel balls (10 mm in diameter), in a glove box under a purified argon atmosphere. The ball-to-powder weight ratio was maintained as 14:1. The MA process was performed in a planetary ball mill (Fritsch P5) at a rotation speed of 2.1 s^{-1} . The multilayered composite powders were annealed at 685 K in a differential scanning calorimeter (DSC) under purified (99.999 mass%) argon flow for 1.8 ks. As soon as the annealing procedure is achieved, the DSC was rapidly cooled and the sample was subsequently removed from the DSC heating chamber. The annealing experiments were performed three times under the same experimental conditions to confirm the reproducibility of the results. A reference sample of glassy $\text{Cu}_{33}\text{Zr}_{67}$ powders was prepared by milling the starting materials for 360 ks. The as-milled and as-annealed samples were characterized by means of X-ray diffraction (XRD) employing $\text{CuK}\alpha$ radiation, transmission electron microscopy (TEM), using a 300 kV field emission microscope, DSC at a constant heating rate of 0.67 K/s and under flow of a purified

argon gas, and optical microscopy. Energy Dispersive Spectroscopy (EDS), using an electron beam of 5 nm has been used for analyzing the concentration of the alloying elements for Cu and Zr, and the degree of Fe contamination in the milled powders. In addition, the oxygen content was determined by the helium carrier fusion-thermal conductivity method.

The XRD pattern of 22 ks MA $\text{Cu}_{33}\text{Zr}_{67}$ powders is displayed in Fig. 1(a). Obviously, the powders are polycrystalline mixture of unprocessed fcc-Cu and hcp-Zr particles. The bright field image (BFI) and the corresponding selected area diffraction pattern (SADP) of the powders at this stage of milling, are presented in Figs. 2(a) and (b), respectively. The powders contain many intimate thin layers (~ 10 nm) of the diffusion couples (Figs. 2(a) and (b)). When these Cu/Zr multi-layered composite particles are subjected to a DSC heating run in the range between 298 K and 993 K, three exothermic reactions are taking place (Fig. 3(a)). Whereas the second and third peaks are somewhat overlapped, the first peak is separated. The XRD pattern of the sample that heated up to 685 K (just above the first exothermic peak) is shown in Fig. 1(b). In contrast to the initial mixture of polycrystalline Cu and Zr (Fig. 1(a)), a broad diffuse halo coexisting with unreacted crystalline Cu and Zr peaks appears, implying the formation of an amorphous phase.

In order to enhance the solid-state reaction between the diffusion couples of Cu and Zr, the mechanically alloyed composite powders were annealed in a DSC at 685 K under an Ar gas flow for 1.8 ks. The as-annealed sample appears homogeneous and fine in structure (Fig. 2(c)), indicating the completion of the solid-state reaction and the formation of a single phase. Moreover, the corresponding SADP (Fig. 2(d)) shows a typical halo-pattern of an amorphous phase. To assess the distribution of the alloying elements (Cu and Zr) in the annealed powders, the local composition and the degree of homogeneity of the sample have been examined by the TEM/EDS technique. Some selected examined regions for this sample are indexed in Fig. 2(a). The corresponding EDS

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Fig. 1 The XRD patterns of Cu₃₃Zr₆₇ powders as (a) MA for 22 ks, (b) MA for 22 ks and then heated to 685 K, (c) 22 ks MA + annealing at 685 K for 1.8 ks + heating to 760 K and (d) 22 ks MA + annealing at 685 K for 1.8 ks + heating to 993 K.

Table 1 The local compositional EDS analyses of 22 ks mechanically alloyed powders that were annealed at 685 K (Fig. 2(a)) and then at 760 K (Fig. 4(a)).

As-MA for 22 ks + annealing at 685 K for 1.8 ks				
Region	1	2	3	4
Cu	32.87	32.43	33.23	33.76
Zr	67.13	67.57	66.77	66.24
As-MA for 22 ks + annealing at 685 K for 1.8 ks + heating to 760 K				
Region	1	2	3	4
Cu	32.18	33.13	32.41	31.54
Zr	67.82	66.87	67.59	68.46

analyses for the selected regions are listed in Table 1. The compositions are essentially the same from region to region and the constituent elements of Cu and Zr are very uniformly distributed in the powders, being very closed to the starting nominal composition of Cu₃₃Zr₆₇.

The thermal characteristics of the glassy phase that obtained upon annealing the milled powders are examined by the DSC (see Fig. 3(b)). The absence of the low temperature peak and the appearance of an endothermic reaction at 696 K correlated to the glass transition (T_g), indicating the completion of the thermally enhanced glass formation reaction (TEGFR) and the formation of a single glassy phase. The T_g was confirmed by heating the samples to a temperature just above the T_g (710 K) and then cooled down to about 320 K.

Fig. 2 BFIs and the corresponding SADPs of Cu₃₃Zr₆₇ powders as (a and b) MA for 22 ks and (c and d) MA for 22 ks and then annealed at 685 K for 1.8 ks.

Then, a second heating/cooling run was performed to confirm the reproducibility of the T_g and to establish a base line. The T_g always appears at the same temperature (731 K) for all of the three heating runs. The heat of glassy phase formation (ΔH^{TEGFR}), which is directly measured from the area under the first exothermic peak of Fig. 3(a), is found to be -2.59 kJ/mol. Therefore, it can be concluded that when pure multilayered Cu/Zr composite particles are subjected to post-annealing at 685 K for 1.8 ks, a solid-state diffusion reaction is taking place and a glassy phase is yielded.

In order to explore the origin of the fully separated exothermic reactions that are taking place at onset temperatures of 731 K and 918 K, two independent glassy samples were heated just above each reaction for XRD and TEM/EDS investigations. The XRD pattern of the sample that was taken after the completion of the first exothermic reaction (Fig. 1(c)) reveals a new structure of big-cube ($E9_3$ structure) metastable CuZr₂ phase, with a lattice parameter of 1.22631 nm. It is worth noting that the precipitation of such metastable phase has been previously reported for some Zr-based glassy materials (see for example ref. 11)) but never, so far as we know reported for CuZr₂ glassy material, nor its oxide. The oxygen and iron contamination contents in the as-milled and as-annealed powders are the same being, 0.08 mass% and 0.03 mass%, respectively. Aside from the rather low levels of impurities, their levels remained constant whereas the phase transformation takes place. This strongly suggests that they do not play any role in the formation of such reported new

Fig. 3 DSC thermograms of $\text{Cu}_{33}\text{Zr}_{67}$ powders as (a) MA for 22 ks, (b) MA for 22 ks and then annealed at 685 K for 1.8 ks and (c) as MA for 360 ks.

Fig. 4 (a) DFI and (b) the correlated SADP of the 22 ks MA $\text{Cu}_{33}\text{Zr}_{67}$ powders that were annealed at 685 K for 1.8 ks and then heated to 760 K.

metastable phase. We have also examined the local compositions of this sample, using TEM/EDS technique, and the results of the analysis are summarized in Table 1. The analyses have not shown any significant compositional fluctuation between this sample and that annealed at 685 K, indicating that both the glassy and metastable phases are similar in composition and homogeneous at the atomic scale. Thus, the glassy-big cube phase transformation takes place without any compositional changes, implying a polymorphic reaction.

Figure 4(a) shows the dark field image (DFI) and the cor-

responding indexed SADP (Fig. 4(b)) of the sample that was obtained after the first exothermic reaction. The powders consist of nanocrystalline grains with less than 30 nm in diameter (Fig. 4(a)) of metastable CuZr_2 , as indicated by the Debye-Scherrer rings (Fig. 4(b)).

The XRD pattern of the sample that was taken upon annealing the powders at 993 K (above the second exothermic reaction in Fig. 3(b)) reveals tetragonal- CuZr_2 (ordered phases) with no indication of any residual big cube metastable phase (Fig. 1(d)), suggesting the completion of metastable-ordered phase transformation. The enthalpy changes of crystallizations of the first (ΔH_{x1}) and second (ΔH_{x2}) exothermic peaks are -4.48 kJ/mol and -2.08 kJ/mol, respectively. We should emphasize that the glassy $\text{Cu}_{33}\text{Zr}_{67}$ powders, which are obtained after long term of milling time (360 ks), transforms to tetragonal- CuZr_2 (ordered phase) through a single crystallization step, characterized by the sharp exothermic reaction in Fig. 3(c) with $\Delta H_x = -6.67$ kJ/mol. This difference in the thermal stabilities, indexed by T_g , T_x and ΔH_x would be attributed to the difference in the mechanism between the TEGFR and MA processes. Long-term of milling always offers homogenization opportunity and overcomes the possibility of the nucleation in the glassy powders.¹²⁾

In conclusion, we have demonstrated a novel process for formation of a single $\text{Cu}_{33}\text{Zr}_{67}$ glassy phase via isothermal annealing the mechanically alloyed multilayered composite powders at 685 K for 1.8 ks. Our results have shown that the glassy powders transforms into nanocrystalline metastable phase of big-cubic CuZr_2 upon annealing at 760 K. The lattice parameter of this new metastable phase was calculated to be 1.22631 nm. It, however, transforms to the stable tetragonal- CuZr_2 phase at rather high temperature (918 K). For a successful thermally enhanced glass forming, the binary system must exhibit a large negative heat of formation. Such large heat of mixing provides the necessary chemical driving force for the solid-state reaction.²⁾ Correlation between the layer thickness and the enthalpy of glass formation of multilayered $\text{Cu}_{33}\text{Zr}_{67}$ composite particles will be reported elsewhere.

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