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Formation of Cu–Zr–Ti amorphous powders with B and Si additions by mechanical alloying technique

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Abstract

Amorphous Cu-based alloys were successfully synthesized by mechanical alloying mixtures of pure crystalline Cu, Zr, Ti, B and Si powders with a SPEX high-energy ball mill. The structure and thermal stability of these alloys were analyzed by X-ray diffraction and differential scanning calorimeter. Several amorphous alloy samples were found to exhibit a wide supercooled liquid region before crystallization. The temperature interval of the supercooled liquid region defined by the difference between T_g and T_x, i.e. ΔT_x ($=T_x - T_g$), is 72 K for $Cu_{50}Zr_{27}Ti_{20}B_3$, 77 K for $Cu_{50}Zr_{25}Ti_{20}B_5$, 85 K for $Cu_{50}Zr_{24}Ti_{20}B_5Si_1$, and 89 K for $Cu_{50}Zr_{20}Ti_{20}B_5Si_5$. The results demonstrated that small addition of B and Si significantly improve the glass-forming ability of the Cu-based amorphous alloys.

Keywords: Amorphous phase; Mechanical alloying; Supercooled liquid region

1. Introduction

Recently, it has been reported that the Cu-based alloy produced by rapid quenching method exhibit a wide supercooled liquid region before crystallization and high tensile strength of 2000–2500 MPa [1–6]. Due to their high strength and promising application, it is important to develop the Cu-based bulk metallic glasses. An alternative way to prepare amorphous alloys is via solid-state amorphization reaction (SSAR processes) [7]. SSAR is a low temperature process and allows forming amorphous samples for compositions which cannot be amorphized by casting techniques. The techniques to synthesize amorphous alloys via SSAR include hydrogenation, multilayer interdiffusion, and mechanical alloying (MA). Amorphization by mechanical alloying has been observed for a variety of binary and ternary alloy systems [8–11]. The product material of mechanical alloying is in powder form and is suitable for compaction and densification into various shapes. Previous data show that the addition of a small amount of B or Si element to the basic ternary system increases the glass-forming ability (GFA) [12–15]. The objective of this paper is, therefore, to investigate the feasibility of preparing Cu–Zr–Ti–B–Si amorphous alloys by mechanical alloying. The formation and thermal stability of mechanically alloyed Cu-based powders is discussed.

2. Experimental procedure

Elemental powders of Cu (99.85%, <325 mesh), Zr (99.8%, <325 mesh), Ti (99.9%, <200 mesh), B (99%, <325 mesh) and Si (99.999%, <325 mesh) were accurately weighted to give the desired compositons. The pre-weighted powder mixtures were canned into an SKH 9 high-speed steel vial together with Cr steel balls under argon atmosphere within a glove box. The MA was performed in a SPEX 8000D shaker ball mill with a ball to powder weight ratio of 5:1. The overall MA process persisted for 5–10 h, which was interrupted every 15 min for the first hour and every 30 min after that. Each interruption was followed by an equal length of time (30 min) to cool down the vials, and then a suitable quantity of the mechanically alloyed powders was extracted to examine the progress of amorphization reaction. Techniques used to examine the status of amorphization include X-ray diffraction (XRD), scanning electron microscopy (SEM), and differential scanning calorimeter (DSC). The X-ray analysis was performed by a Rigaku diffractometer with Cu Kα radiation. The metallography and morphology of the mechanically alloyed powder were examined with a JSM 5600 SEM. Thermal stability of the as-milled powder was determined using a DuPont 2000 DSC, where the sample was heated from room temperature to 700 °C in purified argon atmosphere at a rate of 40 K/min.

3. Results and discussion

$Cu_{50}Zr_{30}Ti_{20}$ and $Cu_{50}Zr_{20}Ti_{30}$ were chosen to study the amorphization behavior of Cu–Zr–Ti system during MA. Fig. 1 displays the X-ray diffraction patterns of as-milled

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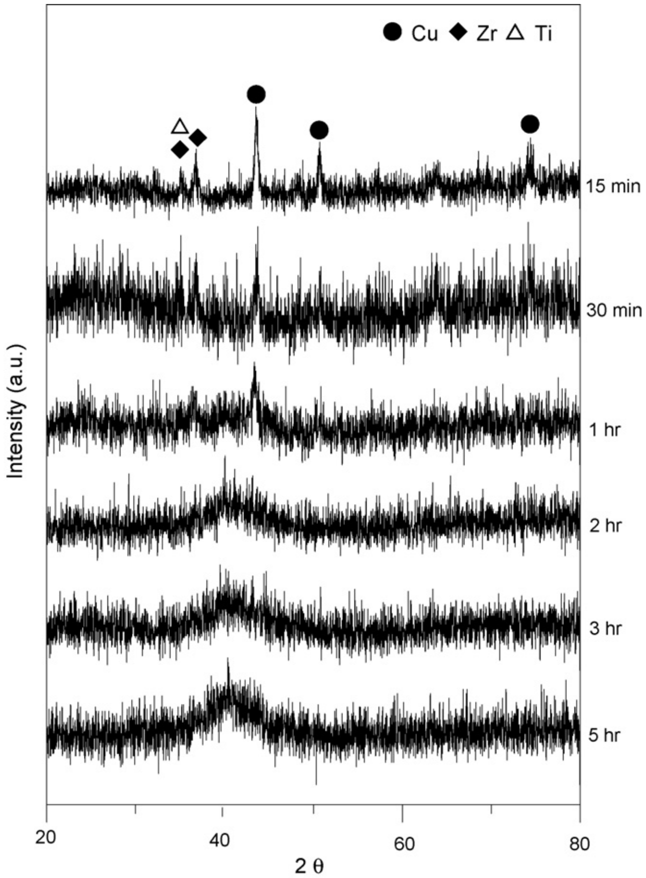

Fig. 1. XRD patterns of $Cu_{50}Zr_{20}Ti_{20}B_5Si_5$ as a function of milling time.

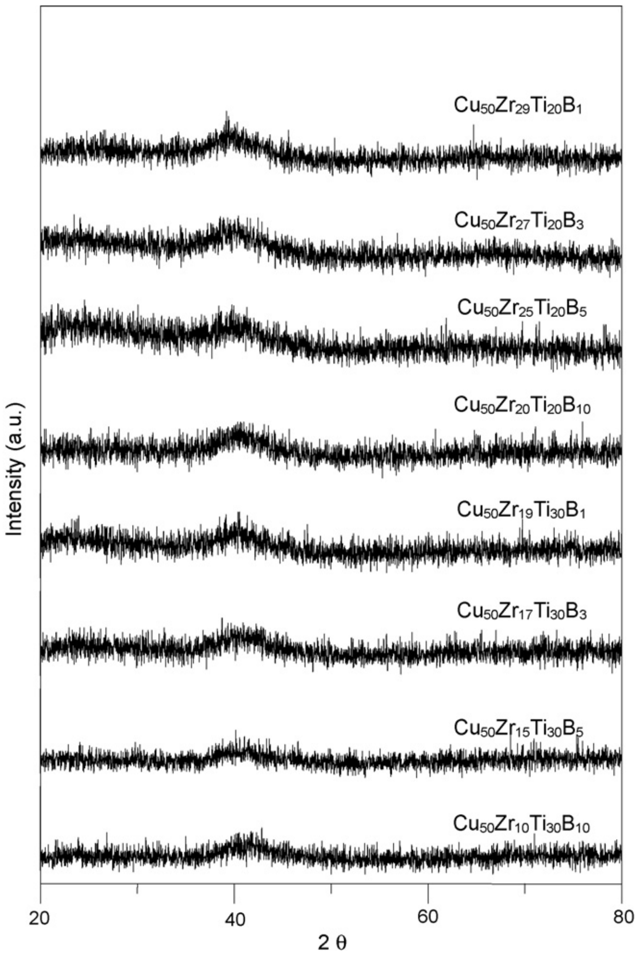

Fig. 2. XRD patterns of Cu–Zr–Ti–B powders after 5 h MA treatment.

$Cu_{50}Zr_{20}Ti_{20}B_5Si_5$ powders as function of milling time. After 1 h of ball milling, the peak intensities of Ti and Zr decreased rapidly, indicating a preferential alloying of these two elements. With further ball milling up to 3–5 h, all the crystalline peaks have disappeared; only a broad diffraction peak left, indicating that amorphization is complete within the resolution of X-ray diffraction. The gradual decrease of the elemental X-ray peaks during the early milling stages is similar to what is observed for amorphous phase formation by mechanical alloying in many binary alloy systems.

Figs. 2 and 3, respectively show XRD of Cu–Zr–Ti–B and Cu–Zr–Ti–B–Si alloy powders after 5 h MA treatment. The powders were amorphous for the $Cu_{50}Zr_{30-x}Ti_{20}B_x$ ($x = 1$, 3, 5, 10), $Cu_{50}Zr_{20-x}Ti_{30}B_x$ ($x = 1$, 3, 5, 10), $Cu_{50}Zr_{25-x}Ti_{20}B_5Si_x$ ($x = 1$, 5, 10), and $Cu_{50}Zr_{20-x}Ti_{30}B_5Si_x$ ($x = 1$, 5, 10). Many studies [16,17] have indicated two necessary conditions for the formation of binary amorphous alloys by the solid-state amorphization reaction (SSAR): (1) the system is an asymmetric diffusion couple; (2) the system possesses a large negative heat of mixing. The former ensures that the interdiffusion of the two metals will lead to the formation of a metastable amorphous alloy instead of a stable crystalline intermetallic compound, and the latter provides a large difference of free energy between the amorphous state and the crystalline state of the pure element. Therefore, from a thermodynamic point of view, it is expected that the formation of amorphous state should be much easier for compositions with a large negative heat of mixing (H_m) as reported by many researchers [16,17,18]. The values of $H_{m,}$ as calculated by the Miedema model [19] are for Cu–Ti (−9 kJ/mol), Cu–Zr (−23 kJ/mol), Ti–B (−43 kJ/mol), Zr–B (about −56 kJ/mol), Ti–Si (−49 kJ/mol), and Zr–Si (about −67 kJ/mol). This implies that amorphization should be easy for Cu–Zr–Ti–B and Cu–Zr–Ti–B–Si systems, as observed in this study. In addition, a marked asymmetry in diffusivity is the dynamic factor of glass-forming ability (GFA) for amorphous alloys, that is, one element diffusing much faster than the other. Since diffusional asymmetry is most likely associated with a size difference, it can be seen that the characteristics needed for the amorphization reaction have much in commmon with those favoring glass formation generally. In this study, the atomic sizes are as follows Zr (0.160 nm) > Ti (0.148 nm) > Cu (0.128 nm) > Si (0.118 nm) > B(0.097 nm) and the atomic size ratios are 1.08 for Zr/Ti, 1.25 for Zr/Cu, 1.16 for Ti/Cu, 1.08 for Cu/Si and 1.32 for Cu/B. These data on the atomic size ratios and heats of mixing imply that the present Cu-based alloys mostly satisfy the two necessary conditions.

The thermal stability of the present Cu-based amorphous powders was investigated by differential scanning calorimetry. Figs. 4 and 5, respectively show DSC scans for $Cu_{50}Zr_{30-x}Ti_{20}B_x$ ($x = 0$, 1, 3, 5, 10) and $Cu_{50}Zr_{30-5-x}$

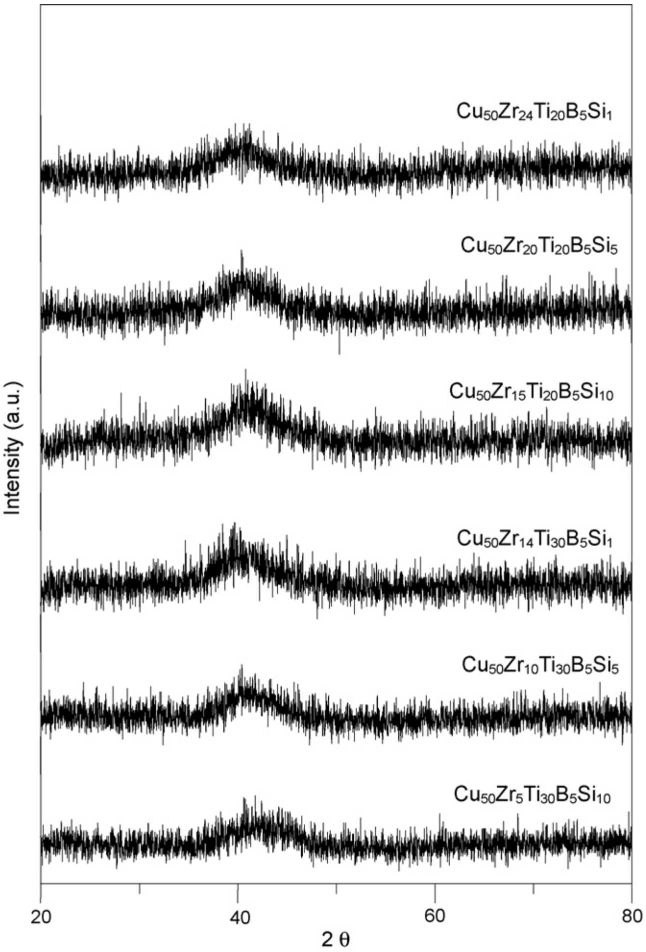

Fig. 3. XRD patterns of Cu–Zr–Ti–B–Si powders after 5 h MA treatment.

$Ti_{20}B_5Si_x$ ($x = 0$, 1, 5, 10) alloy powders after 5 h MA treatment. All the alloys, except $Cu_{50}Zr_{30-5-x}Ti_{20}B_5Si_x$ ($x = 10$), exhibit an endothermic heat event due to the glass transition followed by a sharp exothermic heat release events indicating the successive stepwise transformations from a glass to supercooled liquid state to crystalline phases. The glass transition temperature, T_g, and the crystallization temperature, T_x, were defined as the onset temperatures of the endothermic and exothermic DSC events, respectively. $\Delta T = T_x - T_g$ is referred to the supercooled liquid region. Table 1 summarizes the DSC results with respect to the T_g and T_x of these Cu-based amorphous alloys. A wide supercooled liquid region is found for most of present amorphous alloys. The ΔT are 72 K for $Cu_{50}Zr_{27}Ti_{20}B_3$, 77 K for $Cu_{50}Zr_{25}Ti_{20}B_5$, 85 K for $Cu_{50}Zr_{24}Ti_{20}B_5Si_1$, and 89 K for $Cu_{50}Zr_{20}Ti_{20}B_5Si_5$. As the results demonstrate small addition of B and Si significantly improved the glass-forming ability of the Cu-based amorphous alloys. It generally known that amorphous Cu–Ti and Cu–Zr alloys have been successfully prepared in a wide composition range by both rapid quenching and mechanical alloying process [20,21]. The Cu–Ti amorphous alloys exhibit only small supercooled liquid regions in a limited composition range, as showed in this study. However, the simultaneous presence of several elements was found to cause a significant extension of the supercooled region before crystallization. Many studies have reported

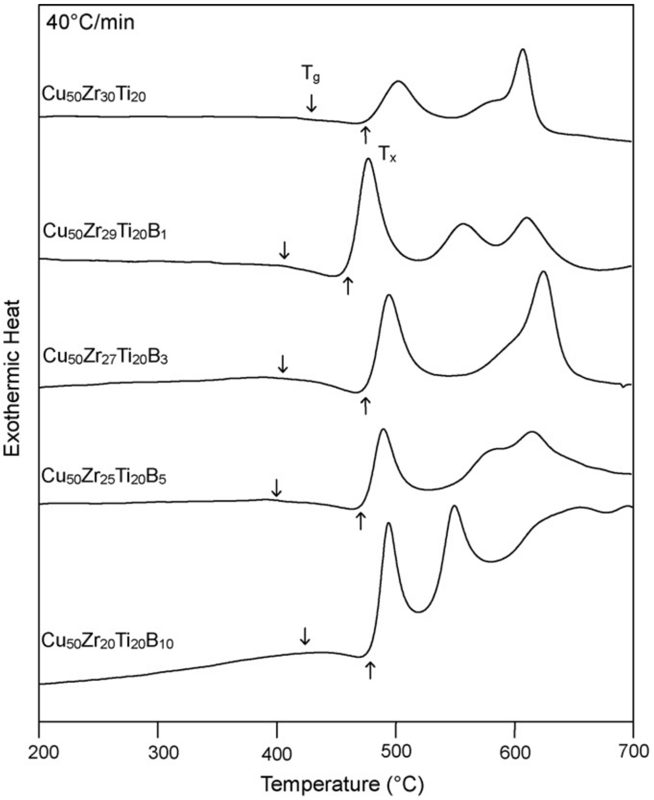

Fig. 4. DSC traces for the amorphous $Cu_{50}Zr_{30-x}Ti_{20}B_x$ ($x = 0$, 1, 3, 5, 10) alloys.

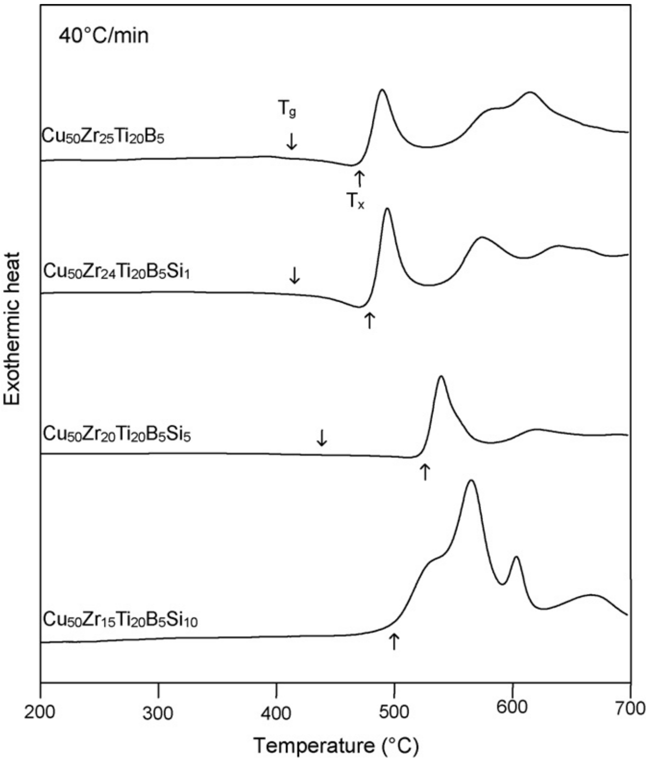

Fig. 5. DSC traces for the amorphous $Cu_{50}Zr_{25-x}Ti_{20}B_5Si_x$ ($x = 0$, 1, 5, 10) alloys.

Table 1
Thermal stability of Cu–Zr–Ti–B–Si amorphous alloys prepared by MA (heating rate of 40 °C/min)

Compositions	T_g (°C)	T_x (°C)	ΔT
$Cu_{50}Zr_{30}Ti_{20}$	420	476	56
$Cu_{50}Zr_{20}Ti_{30}$	390	450	60
$Cu_{50}Zr_{29}Ti_{20}B_1$	396	464	68
$Cu_{50}Zr_{27}Ti_{20}B_3$	404	476	72
$Cu_{50}Zr_{25}Ti_{20}B_5$	397	474	77
$Cu_{50}Zr_{20}Ti_{20}B_{10}$	423	481	58
$Cu_{50}Zr_{19}Ti_{30}B_1$	399	452	53
$Cu_{50}Zr_{17}Ti_{30}B_3$	401	459	58
$Cu_{50}Zr_{15}Ti_{30}B_5$	400	460	60
$Cu_{50}Zr_{10}Ti_{30}B_{10}$	431	467	36
$Cu_{50}Zr_{24}Ti_{20}B_5Si_1$	395	480	85
$Cu_{50}Zr_{20}Ti_{20}B_5Si_5$	436	525	89
$Cu_{50}Zr_{15}Ti_{20}B_5Si_{10}$	–	492	–
$Cu_{50}Zr_{14}Ti_{30}B_5Si_1$	414	472	58
$Cu_{50}Zr_{10}Ti_{30}B_5Si_5$	430	496	66
$Cu_{50}Zr_5Ti_{30}B_5Si_{10}$	–	470	–

that the addition of Si and B can enhance the glass formability of some alloy systems [22,23]. Inoue [24] have suggested that large atomic size ratio and attractive bonding nature between the constituent elements together with the difficulty of the redistribution of these elements for crystallization are dominant factors for the increase in glass-forming ability and the appearance of a wide supercooled liquid region. It can be seen that the difference in the atomic sizes of the five constituent elements exceeds 12%. It is believed that these atomic size differences lead to highly dense random packed structure in the amorphous phase, which enables the achievement of a large liquid/solid interfacial energy and makes the redistribution of atoms on a long range scale difficult.

4. Conclusion

1. Cu–Zr–Ti–B and Cu–Zr–Ti–B–Si amorphous alloys were successfully synthesized by MA process.
2. The temperature interval of the supercooled liquid region defined by the difference between T_g and T_x, i.e. ΔT_x (=$T_x - T_g$), is 72 K for $Cu_{50}Zr_{27}Ti_{20}B_3$, 77 K for $Cu_{50}Zr_{25}Ti_{20}B_5$, 85 K for $Cu_{50}Zr_{24}Ti_{20}B_5Si_1$, and 89 K for $Cu_{50}Zr_{20}Ti_{20}B_5Si_5$. Small addition of B and Si significantly improved the glass-forming ability of the Cu-based amorphous alloys.
3. The wide supercooled liquid region for the Cu-based amorphous alloys is attributed to the significantly different atomic sizes and large negative heats of mixing among the constituent elements.

Acknowledgements

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