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New $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ Glassy Alloy Powder with Wide Supercooled Liquid Region

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New multicomponent V-based glassy alloy powder has been synthesized by mechanical alloying a mixture of elemental $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder at room temperature, using a low energy ball mill. The glassy powder of the end-product (720 ks) in which its glass transition temperature (T_g) lies at a rather high temperature (745 K), crystallizes through two sharp exothermic reactions at 843 K and 919 K, respectively. The total enthalpy change of crystallization (ΔH_x) is -1.78 kJ/mol. The supercooled liquid region before crystallization, ΔT_x of the synthesized glassy powder shows a high value (98 K) for a metallic glassy system. The reduced glass transition temperature (ratio between T_g and liquidus temperatures, T_l (T_g/T_l)) was found to be 0.52.

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1. Introduction

Metallic glasses possess unique and attractive properties that cannot be found in their more stable crystalline states.[1)] High hardness, excellent corrosion resistance, soft magnetic properties with low hysteresis losses under cyclic magnetic excitation are some of these properties[2–6)] that have added new dimension to the world of materials science and metallurgy. Such advanced materials can be fabricated by a wide variety of techniques.[2)] Of these, mechanical alloying (MA)[7)] has the feature that the reaction between the diffusion couples takes place at low temperatures. In fact, the term MA is becoming increasingly common in both materials science and glass science due to the capability of MA to produce wide varieties of materials[8–13)] that cannot be fabricated by the traditional melting and casting techniques.

Hereon we report the first study on the formation of a glassy V-based alloy, which has been obtained by ball milling a mixture of $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder. This glassy alloy in which has a large atomic-size mismatches, exhibits a wide supercooled region. The difficulties of using the liquid metallurgy may restrict the fabrication of such alloy that may find a wide range of engineering applications as hydrogen absorbing material.

2. Experimental Procedure

Pure elemental powders (99.9% or better) of V (<300 μm), Zr (50 μm), Ni (25 μm), Cu (10 μm), Al (10 μm) and Pd (10 μm) were balanced to give the desired nominal composition of $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ and mixed in a glove box under a pure argon atmosphere. The mixed powder of the starting reactant materials was then sealed into tempered chrome steel vials (1000 mL in volume) together with fifty tempered chrome steel balls (14 mm in diameter) in the glove box. A ball-to-powder weight ratio of 25:1 was chosen. The MA process was performed in a tumbling mill at a rotation speed of 1.1 s^{-1}. The milling process was interrupted after selected MA times and the powder was completely discharged from the vials in the glove box. Hence, new reactant elemental powder was charged again into the vial for further milling runs. The structural changes with the milling time of the powder were followed by X-ray diffraction (XRD) with CuKα radiation and transmission electron microscopy (TEM) using a 300 kV field emission microscope. Whereas, the metallographical and morphological examinations of the milled powder were performed by means of light microscopy and scanning electron microscopy (SEM/EDS), using a 15 kV field emission microscope. The samples were thermally analyzed with a differential scanning calorimeter (DSC) and a differential thermal analyzer (DTA), using heating rates of 0.67 K/s. Energy Dispersive Spectroscopy (EDS) measurements, using an electron beam of 5 nm have been used to analyze the concentration of the constituent elements and to detect the degree of Fe contamination in the milled powder. The oxygen contamination content was determined by the helium carrier fusion-thermal conductivity method. The iron and oxygen contamination contents for the powder at the end-product (720 ks of MA time) are 0.137 and 0.063 mass%, respectively.

3. Results and Discussion

The XRD patterns of ball-milled $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder after 173 ks and 720 ks of MA time are shown in Figs. 1(b) and (c), respectively. In contrast to the initial mixture of polycrystalline powder (Fig. 1(a)), a broad diffuse halo coexisting with unreacted crystalline powder appears after 173 ks of MA time (Fig. 1(b)), indicating the formation of an amorphous phase. After 720 ks, all the Bragg-peaks corresponding to starting materials disappear and more pronounced smooth haloes appear, implying a single amorphous phase of $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ with no indication of any residual crystalline phases (Fig. 1(c)). The powder of this end-product (720 ks) appear homogeneous (Fig. 2(a)) with a

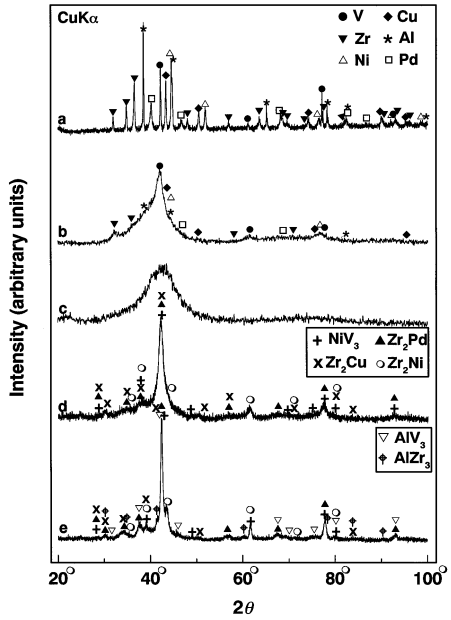

Fig. 1 The XRD patterns of ball milled $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder after (a) 0 ks, (b) 173 ks and (c) 720 ks (final-product) of MA time. The XRD patterns of the final-product are displayed after heating to (a) 920 K and (b) 993 K.

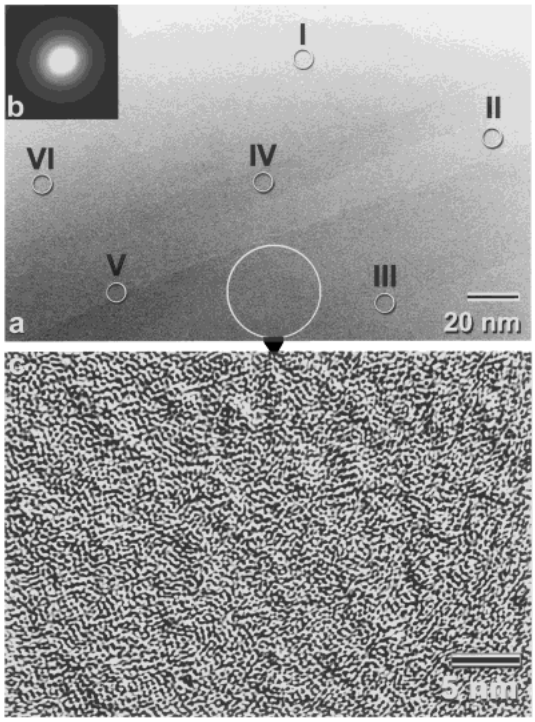

Fig. 2 (a) BFI and (b) the corresponding SADP of ball milled $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder after 720 ks of MA time. The indexed numbered circles refer to the regions that were selected for EDS compositional analysis (see Table 1). The HRTEM image of a selected region is shown in Fig. 2(c).

typical halo-pattern of an amorphous phase (Fig. 2(b)). The image of a high-resolution transmission electron microscope (HRTEM) of a selected zone of this sample (the large circle in Fig. 2(a)) shows a maze pattern contrast of an amorphous (Fig. 2(c)).

In order to assess the distribution of the alloying elements in the powder of the final-product (720 ks), the local composition and the degree of homogeneity of the ball-milled sample have been examined by the TEM/EDS technique. Some selected examined regions for this sample are indexed in Fig. 2(a) and the corresponding EDS analyses are listed in Table 1. Obviously, the compositions do not fluctuated drastically from region to region and the constituent elements of V, Zr, Ni, Cu, Al and Pd are almost uniformly distributed in the powder, being very closed to the starting nominal composition of $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$.

Table 1 The local compositional EDS analyses of mechanically alloyed $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder after ball milling for 720 ks. The analyzed regions are indexed in Fig. 2(a).

Region	V	Zr	Ni	Cu	Al	Pd
I	44.8	19.7	20.1	10.2	2.4	2.8
II	44.9	20.2	19.9	10.0	2.1	2.9
III	45.2	19.9	20.1	9.8	2.6	2.4
IV	45.1	19.8	20.2	9.9	2.4	2.6
V	45.2	19.7	19.7	9.7	2.8	2.9
VI	45.0	19.9	20	9.9	2.5	2.7

Figure 3(a) displays the typical DSC scan of the ball-milled powder at the final stage of MA (720 ks). The scan reveals three separated reactions that lie at 745 K (endothermic reaction), 843 K and 919 K. The endothermic reaction that is corresponding to the glass transition temperature (T_g) was confirmed by heating the samples to a temperature just above T_g and then cooled down to about 320 K–400 K. Then, second and third heating runs were performed to confirm the reproducibility of the T_g and to establish a base line. The T_g always appears at the same temperature (745 to 746 K) for all the three heating runs. It is worth mentioned that the supercooled liquid region before crystallization, ΔT_x ($\Delta T_x = T_x - T_g$) of the end-product (720 ks) exhibits a wide value (98 K) for a metallic glassy alloy.

The X-ray examinations of the two samples, which were separately heated to above the temperature of each exothermic reaction, are displayed in Figs. 1(d) and (e), respectively. The results of these examinations indicate that glassy $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder crystallize through two stages. The first crystallization stage is taking place due to the formation of ordered cubic-NiV_3 and tetragonal-Zr_2Cu, -Zr_2Pd and -Zr_2Ni phases, as indicated by the XRD pattern (Fig. 1(d)) of the sample which was heated to 915 K (just above the first exothermic reaction in Fig. 3(a)). The enthalpy change of crystallization of the first exothermic reaction was found to be -1.34 kJ/mol. The second exothermic reaction in which its enthalpy change of crystallization has a smaller value (-0.44 kJ/mol) takes places due to the formation of ordered cubic-AlV_3 and tetragonal-$AlZr_3$, as shown in the XRD pattern of the sample which was heated to 993 K (Fig. 1(e)).

The DTA technique was employed to determine the melting (T_m) and liquidus (T_l) temperatures of the final-product of glassy $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ alloy powder (Fig. 3(b)). The typical DTA curve of this sample shows two endothermic reactions, which have onset-starting temperature (melting temperature, T_m) of 1379 K and 1455 K, respectively. The onset-liquidus temperatures (T_l) of the first and second reactions are 1428 K and 1516 K. These value are very close with

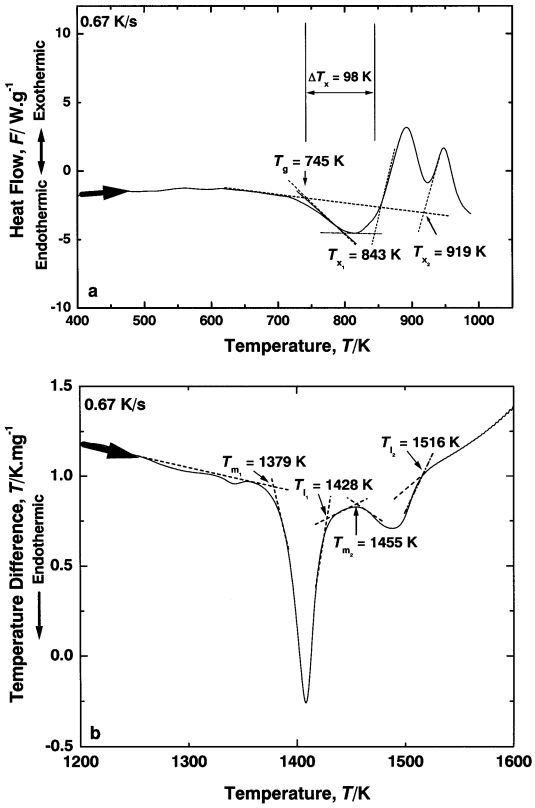

Fig. 3 The (a) DSC and (b) DTA curves of ball milled $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ powder after 720 ks of MA time.

those of the final-product 1431 K and 1476 K, respectively. The reduced glass transition temperature (ratio between T_g and liquidus temperatures, T_l (T_g/T_l)) was found to be 0.52.

4. Conclusions

Mechanical alloying method, using a ball milling technique has been employed to prepare new multicomponent glassy $V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5}$ alloy powder. The powder that was obtained after 720 ks in which its glass transition temperature (T_g) lies at 745 K, crystallizes through two crystallization steps at 843 K and 919 K, respectively. The total enthalpy change of crystallization (ΔH_x) is -1.78 kJ/mol. The supercooled liquid region before crystallization, ΔT_x and the reduced glass transition temperature of the synthesized glassy powder were 98 K and 0.52, respectively.

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