New \textit{V}_{45}\textit{Zr}_{20}\textit{Ni}_{10}\textit{Cu}_{10}\textit{Al}_{2.5}\textit{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 \textit{V}_{45}\textit{Zr}_{20}\textit{Ni}_{10}\textit{Cu}_{10}\textit{Al}_{2.5}\textit{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 ($\Delta H_k$) is $-1.78 \text{kJ/mol}$. The supercooled liquid region before crystallization, $\Delta T_x$ of the synthesized glass 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.

(Received January 30, 2002; Accepted February 20, 2002)

Keywords: ball milling, mechanical alloying, solid-state reaction; multicomponent metallic glassy material, X-ray diffraction, transmission electron microscope, scanning electron microscope, thermal stability

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 a 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)$^3$ 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 metallurgy. The difficulties of using the liquid phase of \textit{V}_{45}\textit{Zr}_{20}\textit{Ni}_{10}\textit{Cu}_{10}\textit{Al}_{2.5}\textit{Pd}_{2.5} powder 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 \textit{V} (<300 \text{µm}), \textit{Zr} (50 \text{µm}), \textit{Ni} (25 \text{µm}), \textit{Cu} (10 \text{µm}), \textit{Al} (10 \text{µm}) and \textit{Pd} (10 \text{µm}) were balanced to give the desired nominal composition of \textit{V}_{45}\textit{Zr}_{20}\textit{Ni}_{10}\textit{Cu}_{10}\textit{Al}_{2.5}\textit{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 \text{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 CuK$\alpha$ 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 \textit{V}_{45}\textit{Zr}_{20}\textit{Ni}_{10}\textit{Cu}_{10}\textit{Al}_{2.5}\textit{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 \textit{V}_{45}\textit{Zr}_{20}\textit{Ni}_{10}\textit{Cu}_{10}\textit{Al}_{2.5}\textit{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
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The XRD patterns of ball milled V_{45}Zr_{20}Ni_{20}Cu_{10}Al_{2.5}Pd_{2.5} powder after MA time. The XRD patterns of the final-product are displayed after heating to (a) 920 K and (b) 993 K.

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_{2}Cu, -Zr_{2}Pd and -Zr_{2}Ni 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 $-1.34 \text{ kJ/mol}$. The second exothermic reaction in which its enthalpy change of crystallization has a smaller value ($-0.44 \text{ kJ/mol}$) takes place 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 the 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 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).

<table>
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<th>Ni</th>
<th>Cu</th>
<th>Al</th>
<th>Pd</th>
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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).
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 ($\Delta H_{cr}$) is $-1.78 \text{ kJ/mol}$. The supercooled liquid region before crystalization, $\Delta T_{cr}$ and the reduced glass transition temperature of the synthesized glassy powder were 98 K and 0.52, respectively.

REFERENCES