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Effect of ball milling on structure and thermal stability of $Al_{84}Gd_6Ni_7Co_3$ glassy powders

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ABSTRACT

The influence of ball milling on microstructure and thermal stability of the gas-atomized $Al_{84}Gd_6Ni_7Co_3$ glassy powder has been investigated as a function of the milling time. The results show that the traces of crystalline phases present in the as-atomized powder decrease gradually with increasing the milling time. The thermal stability of the fcc-Al primary phase increases while the thermal stability of the intermetallic phases decreases with increasing milling. Moreover, significant improvement in hardness occurs after milling, which is attributed to the amorphization of the residual crystalline phases present in the as-atomized powder. These results demonstrate that milling is an effective way for amorphizing the residual crystalline present in the amorphous matrix and to control the thermal stability of the material.

1. Introduction

Nanostructured/amorphous Al-based alloys have attracted significant interest owing to their promising properties, such as high strength combined with low density [1–5]. The tensile strength of Al-based glassy ribbons can reach 1000 MPa, which is nearly two times higher than the conventional high-strength Al-based alloys [6–8]. The strength can be further enhanced in Al-based alloys with microstructures consisting of nano-crystalline fcc-Al particles homogeneously dispersed in an amorphous matrix, which can reach tensile strength up to 1560 MPa [9]. Despite the remarkable mechanical behavior of these alloys, their use for structural applications is severely hindered by their limited dimensions of bulk Al-based amorphous or nanocrystalline samples produced by solidification methods [6]. Most of Al based metallic glasses produced by rapid solidification are in the form of ribbons and powders, which are not suitable for immediate engineering applications. As a result, consolidation of Al-based glassy/nanostructured ribbons and powders into bulk specimens becomes technologically important.

It has been found out that during consolidation, the thermal stability of the glassy powders or ribbons has a direct influence on the microstructure and related properties of the final bulk consolidated material [4,10–15]. In other words, the microstructural state of the starting powders or ribbons is critical for controlling the consolidation parameters and to obtain bulk samples with the desired properties. As a result, the control of the initial structural state of powders (or ribbons) and the corresponding thermal stability and phase evolution during heating is a crucial aspect for the consolidation process.

Quenched-in nuclei or nanocrystals are frequently present in Al-based glassy alloys even in samples produced by rapid quenching, such as gas-atomized powders or melt-spun ribbons, due to the poor glass formability of these alloys [16–19]. The high density of quenched-in nuclei has a significant influence on the microstructure and thermal stability of the glassy ribbons or powders during heating. The crystallization mechanism of Al-based amorphous alloys containing quenched-in nuclei usually includes the growth of the quenched-in nuclei at temperatures below the crystallization of the glassy phase and results in relatively low activation energies for the primary crystallization [12–14]. For example, it has been observed in the $Al_{88}Gd_6La_2Ni_4$ metallic glass that quenched-in Al nuclei grow well below the glass transition temperature before the

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onset of primary crystallization, where a high density of Al nanocrystals nucleates from the residual glassy matrix [20]. It is therefore important the ability to accurately control the volume fraction of the quenched-in nuclei or nanocrystals in the amorphous matrix through amorphization/crystallization methods to achieve the desired microstructure and properties of the consolidated bulk material.

Among the different processing routes, ball milling (BM) has been extensively used for the formation of amorphous powders from crystalline precursors (elemental powders or mixtures of intermetallic compounds [21]) through the microstructural breakdown followed by inter-diffusion of elements or mechanically driven atomic mixing among previously formed nanocrystals multilayer [21–26]. Alternatively, glassy powders can be produced directly by mechanical pulverization of amorphous ribbons [27]. However, depending on the system and on the milling parameters, BM of amorphous precursors can also lead to mechanically-induced crystallization of the glassy phase [28,29]. Therefore, ball milling represents the ideal tool for controlling microstructure and thermal stability of amorphous powders.

Accordingly, in this work the effect of ball milling on microstructure and thermal stability of gas-atomized $Al_{84}Gd_6Ni_7Co_3$ glassy powder has been investigated in detail. Particle size and morphology, which are of significant importance for any sintering process, have been analyzed as a function of the milling time. Finally, structure evolution of the milled powders during heating has been studied by in-situ high-energy X-ray diffraction in order to correlate the observed changes of the thermal stability induced by milling with any phase modification.

2. Experimental

Glassy powders with nominal composition $Al_{84}Gd_7Ni_6Co_3$ (at.%) were produced by gas atomization (for details on preparation see Ref. [30]). Milling experiments were carried out at room temperature under protective argon atmosphere using a Retsch PM400 planetary ball mill equipped with hardened steel vials. The powders (particle size < 100 μm) were blended with hardened steel balls to give a ball-to-powder mass ratio of 10:1 and milled for different times (0, 5, 15, 30, 50, 80 and 100 h) at a rotational speed of 150 rpm. To avoid strong temperature rise, 15 min interval was taken after each 15 min milling. The structure of the as-milled powders was studied by scanning electron microscopy (SEM), using a Gemini 1530 microscope equipped with an energy dispersive X-ray spectroscopy (EDX) and by X-ray diffraction (XRD) using a D3290 PANalytical X'pert PRO diffractometer (Co-Kα radiation, $\lambda = 0.17889$ nm). The thermal stability of the powders was in constant-rate heating mode (20 K/min) investigated by differential scanning calorimetry (DSC) using a Perkin–Elmer Diamond DSC under a continuous flow of purified argon. The activation energy for the first crystallization event was calculated using the Kissinger method [31,32] through the variation of the peak temperature with the heating rate. For this, the DSC experiments were performed at different heating rates (5, 10, 20, 40 and 60 K/min). The structure evolution of the powders during heating was studied *in-situ* by XRD in transmission using a high-intensity high-energy monochromatic synchrotron beam ($\lambda = 0.01249$ nm) at the ID11 beamline of the European Synchrotron Radiation Facilities (ESRF). The samples were induction-heated to about 873 K and X-ray patterns were recorded *in-situ* every 20 s. Diffraction data were collected at a constant heating rate of 20 K/min to compare the structural evolution with the thermal stability investigated by DSC. The effect of milling on the mechanical behavior of the as-milled powders was investigated by Vickers microhardness using a Shimadzu HMV-2000 hardness testing machine. The device is equipped with a typical diamond indenter in the form of a square based pyramid with an angle of 136° between the opposite faces. The powders were embedded in a Struers Specific-20 (room temperature curing) epoxy resin and then indented using an applied load of 0.01 kgf (0.098 N) for 10 s, which gives a characteristic indentation length of about 7 μm. The hardness was measured on particles with size exceeding 20 μm. The small indentation length with respect to the particle size permits to perform the indentation at the center of the particles and at a reasonable distance from the resin, thus avoiding potential artifacts (e.g. non-symmetric indentations) due to the proximity of the embedding material. At least 30 readings were taken to calculate the mean hardness value. Impurity content in the milled powder was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).

3. Results

3.1. Phase analysis and thermal stability of the as-milled powders

Fig. 1(a) shows the XRD patterns of the $Al_{84}Gd_7Ni_6Co_3$ powder as a function of the milling time. The as-atomized powder (BM 0 h) displays the broad diffraction maxima typical of amorphous materials along with a few crystalline peaks belonging to fcc Al and orthorhombic $Al_{19}Gd_3Ni_5$ (space group *Cmcm*). The intensity of the peaks from Al and $Al_{19}Gd_3Ni_5$ is rather weak, which indicates that only small amounts of crystalline phases are present. The presence of the crystalline phases can be ascribed to the cooling rate achieved during gas atomization [33]. Large particles (Fig. 1(b)), which experience a relatively slow cooling rate, display crystalline precipitates, whereas the more rapidly cooled small particles (Fig. 1(c)) show a featureless amorphous appearance. The intensity of the crystalline peaks in Fig. 1(a) decreases with increasing the milling time and, after milling for 80 h, the peaks are no longer visible. This indicates that ball milling is effective for reducing the amount of crystalline phases in the glass. Finally, the pattern of the sample milled for 100 h displays the double diffraction broad maxima in the range between 20 and 35 nm^{-1} (marked by arrows in Fig. 1(a)) frequently observed for Al-based glasses with high Al content [12].

The effect of ball milling on the thermal stability of the powders is shown in Fig. 1(d). The isochronal DSC curve (heating rate 20 K/min) of the as-atomized powder is characterized by an endothermic event at about 555 K due to the glass transition (T_g), followed by two main exothermic peaks T_1 and T_3 with peak temperatures at 583 and 650 K along with two minor exothermic peaks (T_2 and T_4) at 607 and 735 K. Milling drastically changes the thermal stability of the powders. The T_1 peak decreases its intensity and shifts to higher temperatures with increasing milling, whereas the intensity of T_2 significantly increases in the same milling period. The changes of T_3 are even more drastic: the peak splits into two distinct peaks for milling times longer than 15 h with position and intensity continuously varying with milling. In contrast, T_4 does not show appreciable variations resulting from the mechanical treatment. These results suggest that change of the glass composition occurs during milling as a result of the amorphization of the residual Al and $Al_{19}Gd_3Ni_5$ phases and corroborates that mechanically-induced amorphization takes place in the present system.

3.2. Phase evolution during heating

The remarkable variation of the thermal stability of the $Al_{84}Gd_7Ni_6Co_3$ powder shown in Fig. 1(d) indicates that the phase evolution during crystallization of the as-atomized glass may be drastically changed by the milling process. In order to clarify this aspect, the structure evolution during heating of the as-atomized material and of the powders milled for 30 and 100 h was studied