ELSEVIER

Journal of Alloys and Compounds 453 (2008) 108–114

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Effects of consolidation temperature and pressure on microstructures and mechanical properties of Cu-based bulk amorphous alloys consolidated by spark plasma sintering

Chang Kyu Kim [a], Sunghak Lee [a,*], Seung Yong Shin [b], Do Hyang Kim [c]

[a] *Center for Advanced Aerospace Materials, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea*
[b] *Production Technology Center, Korea Institute of Industrial Technology, Cheonan 330-825, Republic of Korea*
[c] *Center for Non-crystalline Materials, Yonsei University, Seoul 120-749, Republic of Korea*

Received 4 October 2005; received in revised form 14 November 2006; accepted 14 November 2006
Available online 12 December 2006

Abstract

This study aims at fabricating Cu-based bulk amorphous alloys by a spark plasma sintering (SPS) method. Consolidation temperature, consolidation pressure, and holding time were established to obtain good microstructures and compressive properties of consolidated amorphous alloys. Bulk amorphous alloys having a few micropores and nanocrystalline phases could be obtained with a consolidation pressure of 80 MPa, but were fractured in an intergranular mode along prior powder boundaries. Microstructures and compressive properties of the alloys consolidated with a pressure of 300 MPa were significantly modified as prior amorphous powders were sufficiently bonded without micropores. Fractographic investigation of these alloys indicated that vein patterns appeared on fracture surfaces as amorphous powders were strongly bonded during the high-pressure consolidation. These findings suggested that the high-pressure consolidation was effective in suppressing the crystallization of amorphous phases and in strongly bonding amorphous powders.

Keywords: Bulk amorphous alloy; Spark plasma sintering; Consolidation; Crystallization

1. Introduction

Because atoms in amorphous alloys are aligned like in liquid, unlike in crystallized alloys, they show excellent properties such as stiffness, strength, magnetism, and corrosion resistance [1–8]. Most of bulk amorphous alloys are fabricated by casting methods, and their shape and size are seriously limited in the case of the alloys having relatively low amorphous forming ability, which also limits the wide range of their applications [9–11]. Powder metallurgy methods can produce good amorphous microstructures, and has an advantage of fabricating larger bulk amorphous alloy products than those fabricated by casting methods, although its process is somewhat complicated [12,13].

The powder metallurgy process for fabricating bulk amorphous alloys is generally composed of fabrication of amorphous alloy powders and high-temperature consolidation [10–15]. The high-temperature consolidation is conventionally conducted by the vacuum hot pressing in the supercooled liquid temperature region (ΔT_x) between T_g (glass transition temperature) and T_x (crystallization onset temperature) to obtain the large decrease in effective viscosity of amorphous alloys. In the vacuum hot pressing, degassing and high-temperature consolidation processes are combined into one process, and powders are pressed in a vacuum chamber. Thus, the gas remained in powders and the gas generated during the consolidation can be effectively eliminated. This method is appropriate for consolidating high-quality amorphous alloy products because it can effectively prevent the formation of crystalline phases due to exposure to air and can produce consolidated alloys in which retained pores are minimized. Recently, a spark plasma sintering (SPS) method where spark plasma is used for instantaneous heating by a dc pulse has been drawing attentions [16]. Since heating rate of 400 °C/min and cooling rate of 50 °C/min are available in the SPS, the SPS is more advantageous over the conventional vacuum hot pressing in terms of heating, holding, and cooling of amorphous alloy powders, particularly those in which crystalline phases are easily formed

* Corresponding author. Tel.: +82 54 279 2140; fax: +82 54 279 5887.
E-mail address: shlee@postech.ac.kr (S. Lee).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.11.054

when the temperature moves away from the appropriate ΔT_x region or when the holding time increases. This is because the SPS expedites the consolidation process, and thus prevents or minimizes the formation of crystalline phases.

In the present study, the SPS was attempted for the high-temperature consolidation of Cu-based bulk amorphous alloys having lower amorphous forming ability than that of Zr-based amorphous alloys. Their microstructures and mechanical properties were investigated in order to establish consolidation parameters such as consolidation temperature, pressure, and holding time since the consolidation in the ΔT_x temperature region can easily produce micropores, crystalline phases, or nanocrystalline phases which can deteriorate mechanical properties. Comparative analysis was also made to a cast amorphous alloy having the same composition.

2. Experimental

The material used in the present study was a Cu-based amorphous alloy having excellent hardness, strength, and corrosion resistance [17], and its chemical composition was $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$ (at.%). A master alloy ingot was made by melting in a vacuum induction furnace of 30 kg capacity. It was molten at 1240 °C in an argon atmosphere, and then the N_2 gas atomization was performed on this melt at a pressure of 14 bar to fabricate amorphous alloy powders. The chemical composition of the atomized powders was $Cu_{47.6}Ti_{32.7}Zr_{10.5}Ni_{6.1}Sn_{2.1}Si_1$ (at.%), which was similar to the target composition. The shape of atomized powders was spherical, and their average size was about 30 μm. Coarse powders larger than 100 μm were hardly present. Powder sizes were classified, and X-ray diffraction analysis was conducted on the powders of each size range. The results are shown in Fig. 1. Broad halo patterns which are typical in amorphous alloys are observed in all the powder size ranges, indicating that crystalline phases are not present even in the largest powders.

Because the crystallization of alloys during consolidation is largely dependent on the consolidation temperature and holding time, a differential scanning calorimetry (DSC) analysis was conducted on amorphous alloy powders. Fig. 2 shows a thermogram of amorphous alloy powders of 26–45 μm in size at a heating rate of 40 °C/min. From this thermogram, T_g and T_x were measured to be 449 °C and 486 °C, respectively. Thus, amorphous alloys were consolidated in the temperature range from 450 °C to 480 °C by an SPS equipment (model; Dr. Sinter, Sumitomo Coal Mining Co., press capacity; 10 tonnes). Amorphous powders were charged into a tungsten carbide mold of 20 mm in diameter, which was then inserted into a vacuum chamber for degassing up to 5×10^{-2} Torr at

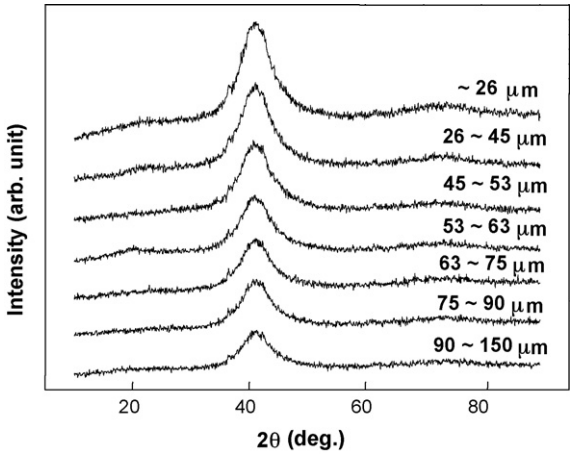

Fig. 1. X-ray diffraction patterns of Cu-based amorphous alloy powders having different powder sizes. Note broad halo patterns which are typical in amorphous alloys.

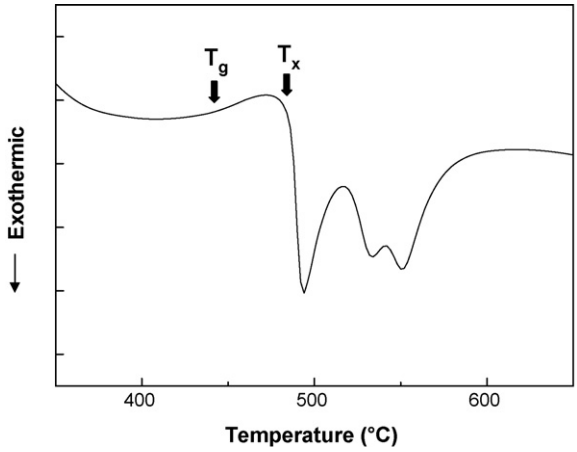

Fig. 2. DSC (differential scanning calorimetry) thermogram of amorphous alloy powders of 26–45 μm in size at a heating rate of 40 °C/min. From the thermogram, T_g and T_x are measured to be 449 °C and 486 °C, respectively.

room temperature for 5 min. After the degassing, powders in the mold were pressed up to 80 MPa and 300 MPa, while the temperature rose to the consolidation temperature (450–480 °C) at a heating rate of 40 °C/min, and then were held for 0.5–5 min to achieve thermal equilibrium. After the consolidation pressure was released, the consolidated alloy was cooled at a rate of 50 °C/min.

Consolidated alloys were sectioned perpendicular to the flat surface, polished, and observed by an optical microscope. Hardness of the alloys was measured by a Vickers hardness tester under a 1 kg load. Phases present in the alloys were analyzed by an X-ray diffraction, and the formation process of crystalline phases was also investigated by the cooling experiment of the alloys by a differential thermal analyzer (DTA). The consolidated alloys were machined into cylindrical specimens of $2\varphi \times 4$ mm in size, and room-temperature compression tests were conducted on these specimens at a strain rate of 2×10^{-4} sec^{-1}. After the test, fracture surfaces were examined by a scanning electron microscope (SEM) to observe fracture modes.

3. Results and discussion

3.1. Microstructures and compressive properties of amorphous alloys consolidated under 80 MPa

X-ray diffraction patterns of the alloys consolidated at 450–480 °C under a pressure of 80 MPa and an injection-cast Cu-based amorphous alloy are provided in Fig. 3. The cast alloy

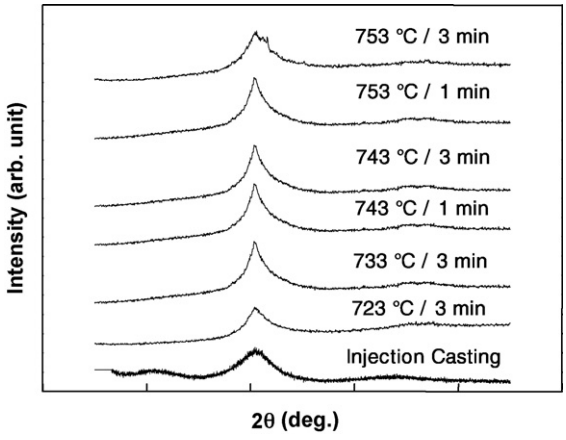

Fig. 3. X-ray diffraction patterns of Cu-based amorphous alloys consolidated at 450–480 °C for 1–3 min under 80 MPa.