Materials Science and Engineering A 396 (2005) 166–171

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Synthesis of amorphous/crystalline composite using electroless copper plated amorphous powder

Yoon B. Kim [a,*], H.M. Park [b]

[a] *Advanced Metal Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea*
[b] *Department of Advanced Materials Engineering, Korea University, Seoul 136-701, Republic of Korea*

Received 30 August 2004; received in revised form 6 January 2005; accepted 24 January 2005

Abstract

An amorphous/crystalline composite was synthesized by warm extrusion of copper-deposited $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder. Electroless plating method was applied to deposit crystalline copper on $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder after fabricating $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder by gas-atomization technique. Fully amorphous $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ powder with a supercooled liquid region of 58 K could be obtained in the particle size range below 75 μm. Uniform deposition of crystalline copper on the $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powders was successfully performed by electroless plating. The optimum processing conditions for extrusion were obtained from the time–temperature-transformation curve determined by isothermal annealing of $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder. The extruded amorphous/crystalline composite shows plasticity after yielding and exhibits a strength level of 1.3 GPa and plastic stain of about 3% under compressive condition. While monolithic bulk $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous alloy fabricated under same extrusion condition shows no plastic deformation.

Keywords: Amorphous powder; Composite; Electroless plating; Copper; Gas-atomization; Bulk amorphous alloy

1. Introduction

Amorphous alloys exhibit several superior properties that cannot be obtained in crystalline materials. In most cases, high cooling rates are required for the formation of an amorphous phase from the liquid state. Consequently, the amorphous alloys have been fabricated in the form of powders, ribbons and wires with small thickness or diameter. Therefore, the application of amorphous alloys as a structural material has been limited. Recently, it has been reported that many bulk amorphous alloys with a wide supercooled liquid region are successfully produced in several alloy systems [1–5]. The existence of wide supercooled liquid region enables the fabrication of bulk metallic glass by consolidation process utilizing the significant viscous flow of the supercooled liquid state. Therefore, the consolidation process using an amorphous powder is known as a promising technique to overcome the size limitation of bulk amorphous alloys. This process has been successfully attempted in the fabrication of bulk amorphous alloys with large supercooled liquid region (above 100 K) such as Zr-based amorphous alloys [6,7]. However, bulk amorphous alloys typically show catastrophic failure due to the lack of plastic deformation. Much effort has been devoted to improve the mechanical properties of the bulk amorphous alloy. The preparation of composite by introducing ductile second phase in amorphous matrix can be one of the effective ways to increase the ductility and toughness of bulk amorphous alloys.

Electroless plating has attracted considerable attention in depositing metal coating on any kind of powders and shown a possibility to fabricate composite powders. Therefore, electroless plating can be an alternative method to introduce the second phase into the amorphous matrix. Up to now, many metal coatings have been successfully prepared on various kinds of powders such as metals, ceramics and polymers [8–19]. However, no results have been reported on the

* Corresponding author. Present address: Advanced Metal Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Republic of Korea. Tel.: +82 2 958 5426; fax: +82 2 958 5409.
E-mail address: ybkim@kist.re.kr (Y.B. Kim).

0921-5093/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2005.01.035

metal coating on amorphous powder by electroless plating method.

In this study, electroless plating was applied to deposit crystalline copper on $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder after fabricating the $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder by gas-atomization technique. And then the feasibility of preparing amorphous/crystalline composite by warm extrusion of the copper-deposited $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder was investigated.

2. Experimental procedure

$Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder used in this study was fabricated by gas-atomization method. The $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ alloy was remelted in the atomization furnace under an Ar atmosphere and the temperature of alloy melt maintained at about 1673 K before starting the atomization process. The $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder was produced at an argon pressure of 40 bars using a guide tube with a hole diameter of 2.5 mm. The formation of amorphous phase of the gas-atomized powder was verified by a X-ray diffractometer (XRD) using Cu Kα-radiation. Thermal stability and crystallization behaviour of the amorphous powder were examined by differential scanning calorimetry (DSC). The powder morphology was observed by means of scanning electron microscope (SEM). Fully amorphous $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ powder was used for subsequent electroless plating of copper.

Before starting electroless plating, the $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powders were ultrasonically cleaned at room temperature in a methyl-alcohol. And then, sensitisation was carried out by dispersing the amorphous powders in an aqueous solution containing 40 ml/l hydrochloric acid (HCl) and 10 g/l stannous chloride ($SnCl_2$) for 2 min at room temperature. The amorphous powders were than activated by immersing them into an aqueous solution containing 10 ml/l hydrochloric acid and 0.5 g/l palladium chloride ($PdCl_2$) for 2 min at room temperature. After pre-treatments mentioned above, electroless plating was carried out by introducing the $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powders into a copper electroless plating bath. The bath was composed of 29 g/l $CuSO_4$, 40 g/l NaOH and small amount of stabilizer. An amount of 20 ml/l of 37% formaldehyde solution was used as a reductant. The pH value of the electroless plating bath was 11.5. The electroless plating was performed on a hot plate with a magnetic stirrer at 313 K and the electroless plating time was varied to control the amount of copper deposited on the $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder. After electroless plating, the powders were cleaned with de-ionized water and methyl-alcohol for several times, and finally dried in air. The coating characteristics of the copper-deposited $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder were analysed by scanning electron microscope (SEM) and X-ray diffraction.

The copper-deposited $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powders were cold pressed into a cylindrical form with a diameter of 10 mm and length of 15 mm. The relative density of the pre-compacted from was 60%. Subsequently, the pre-compacted form was located in the extrusion die and heated up to the extrusion temperature of 843 K and then extruded at an extrusion ratio (ratio of cross-section-area before and after extrusion) of 4. The load applied for extrusion was 600 MPa and was applied when the temperature of extrusion die reached at 843 K. For comparison, $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powders without copper deposition (monolithic) was extruded at the same extrusion condition after preparing the pre-compacted form by hot pressing at 833 K. The phases present of the extruded samples were verified by a X-ray diffractometer. The uniaxial compression test of the extruded samples was performed at room temperature at a strain rate of $1 \times 10^{-4}\ s^{-1}$.

3. Results and discussion

In this study, we have chosen an amorphous alloy composition of $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$. The amorphous $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ alloy is found to exhibit a glass transition temperature (T_g) of 829 K, an onset crystallization temperature (T_x) of 896 K and a supercooled liquid region (ΔT) of 67 K [20]. The large supercooled liquid region of the $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ alloy makes it possible to synthesize a bulk amorphous alloy by consolidation of $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amorphous powder.

The XRD patterns of the gas-atomized powder with different particle size range are shown in Fig. 1. As can be seen in Fig. 1, fully amorphous phase of the gas-atomized powder without any crystallinity formed in the particle size range smaller than 75 μm. Further increase in the particle size of the gas-atomized powder exhibits sharp diffraction peaks superimposed on a weak Halo pattern, which results in the coexistence of amorphous and crystalline phase ($Ni_{10}Zr_7$). The XRD pattern of gas-atomized powders larger than 125 μm shows clearly sharp diffraction peaks for crystalline $Ni_{10}Zr_7$ phase. Most of the gas-atomized $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ amor-

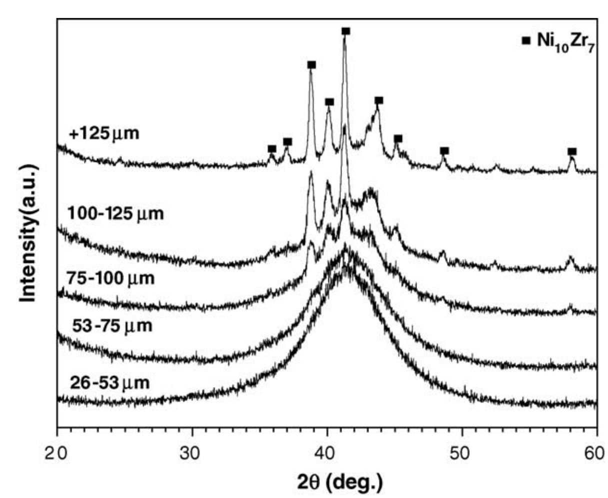

Fig. 1. XRD patterns of gas-atomized $Ni_{57}Zr_{20}Ti_{18}Si_3Sn_2$ powder with different particle size ranges.