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Rapid Communication

Binary Ni–P bulk amorphous glass prepared by electrodeposition method

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Abstract

Compact and uniform bulk Ni–P binary amorphous alloys (BAAs) with thickness of up to 1 mm were prepared using electrodeposition method. This is the first finding that amorphous alloy can be obtained up to 'bulk' size not by rapid solidification but by electrochemical method. By improving the electrodeposition techniques, selecting proper plating solution, electrodeposition is probably a new method for preparing bulk amorphous alloys. The formation mechanism of the bulk amorphous was discussed within the concept of 'disorder solid'.

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Keywords: Alloys; Indentation; Microindentation

1. Introduction

The development of amorphous alloys strongly depends on their preparation methods. Amorphous alloy was firstly produced by Kramer [1] with deposition method in 1937, and until 1960, deposition remained the main way to prepare amorphous films. Obtaining amorphous Au–Si ribbon by rapid quenching [2] makes liquid–solid transformation the first selective way to produce amorphous alloys. Because of the limited sizes either by deposition or quenching method, the development of amorphous materials was slow in the last sixty years. The rules for formation of bulk amorphous alloys (BAAs) mentioned by Inoue and Johnson et al. [3,4] and the discovery of binary BAAs recently, makes BAAs develop rapidly both in theory and application [5–7].

In fact, early in 1946, Brenner et al. [8] used electrochemical method to produce Ni–P amorphous alloys, and it was the first application in the amorphous alloys industry. Ni–P alloys are of great commercial interest [9], when applied over various substrates, take diamond particles and aluminium alloys for example, the corrosion resistance, tribological properties and hardness can be improved [10,11]. Recently, much more attention has been paid to the characteristics of amorphous Ni–P alloys as catalysts and potential materials for making ohmic contact with III–V devices [12–14]. Till now, many transition elements-metalloid can be co-deposited to obtain amorphous films but with the increase of plating time, the main defect in the deposited-layer is splitting, separating from the substrate and falling off, therefore, by traditional electrochemical method, the thickness of non-crystalline layer is less than 100 μm. Finding a new electrochemical technique in which amorphous alloys with bulk sizes are obtained by electrochemical method is important for synthesizing a new BAAs system and further understanding the mechanism of glass transformation. In this paper, we report that compact bulk Ni–P amorphous alloys with uniform compositions can be prepared up to thickness of 1 mm by an improved deposition technique.

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2. Experimental

Impurities diffusing into the inner deposited-layer will lead to strain defect. Therefore, an activated nickel plate (8 cm × 12 cm × 1 cm) of 99.99% purity is used as a soluble anticathode to provide Ni^{+}, and a quenched-tempered 45 steel disk (∅4 cm × 0.4 cm), being a cathode, is used for depositing Ni–P alloy. Sulfurous acid mainly supplies phosphorus, and the role of nickel chloride is to prevent anodic passivation. By adding multi-times-distilled water and sulfurous acid solution of 10 wt% to make the solution stable, 0.5 wt% saccharin is used to eliminate strain, and the pH value is adjusted by boracic acid. The optimal bath composition and plating bath conditions will be shown later in Table 1. To obtain an electroplating layer with uniform and large thickness, adding rare earth elements and mechanical force-holding sample are introduced to improve the deposition technique. The rare earth element does not deposit in the Ni–P amorphous alloy because its ions are adsorbed on the surface of electrode, which leads to the increase of the cathode polarization [15]. A special mould is designed: A steel disk (a cathode), placed between two pieces of transparent polymethy methacrylate (PMMA), is electrically connected to the cathode of a direct current supply by a lead-wrapped steel sheet whose extended part is covered with insulated plastic to reduce plating solution consummation. Fig. 1 shows the diagram of the electrodeposition and the improved set-up of deposited sample. By controlling the plating parameters, the composition of the $Ni_{100-X}P_X$ ($X = 19$–23) amorphous alloys can be deposited. In this paper, $Ni_{80}P_{20}$ was used for discussion. The amorphous character is measured by X-ray diffraction (XRD) with CuKα radiation in D/MAX-Rb diffractometer and transmission electron microscopy (TEM) with an accelerating voltage of 200 kV (JEM2010). The uniform quality of deposited sample is analyzed along the cross section by scanning electron microscopy (SEM) with an accelerating voltage of 30 kV (KYKY-2800).

The DSC measurements were carried out under a purified argon atmosphere in a Nestzsch STA449C at the heating rates, φ, ranging from 5 K/min to 80 K/min. Nanoindentation experiments were performed at room temperature (300 K) using a TriboIndenter® (Nanomechanical Test Instrument, HYSITRON) with Berkovich indenter.

Table 1
Basic bath composition and plating conditions

Composition	$NiSO_4 \cdot 6H_2O$	$NiCl_2 \cdot 6H_2O$	H_3PO_3	$B_2O_3 \cdot 3H_2O$
Content (g/L)	240	45	15	30
Current density		pH value	Saccharin	Bath temperature
3 A/dm^2		1.25	0.5 wt%	330 K

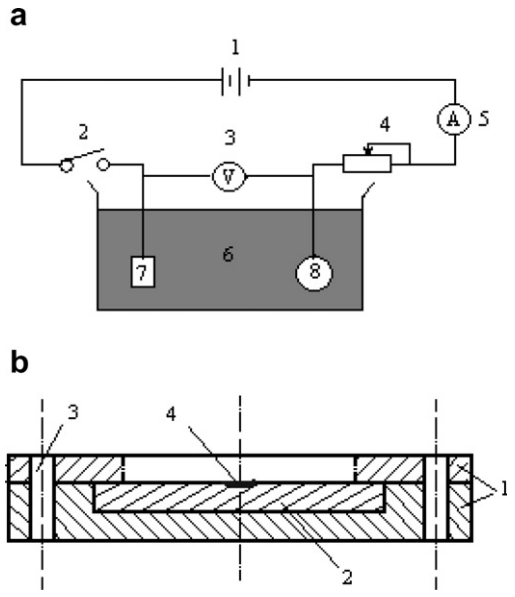

Fig. 1. Set-up of the improved electrodeposition technique: (a) diagram of the electrodeposition; 1, power supply; 2, switch; 3, voltmeter; 4, resistor; 5, ammeter; 6, plating solution; 7, activated nickel plate (anticathode); 8, steel disk (a cathode). (b) Details of part 8; 1, polymethy methacrylate (PMMA); 2, steel disk; 3, bolt; 4, steel sheet.

3. Results and discussion

The morphology and its XRD pattern for the deposited specimen are shown in Fig. 2. We can see that the surface of the Ni–P BAA is smooth and its thickness is up to 1 mm. A broad peak near 43° followed by another broad peak of lesser intensity is characteristic of the amorphous structure, and the diffused ring in the selected-area electron micrograph also confirms the X-ray result. No crystalline phase can be detected. Compared with its surface quality, longitudinal layer quality is much more difficult to control. In order to investigate the quality of this Ni–P BAA, SEM and line-scanning are employed along its cross section; the result is shown in Fig. 3. From the cross-sectional morphology, a typical layer structure can be found, which is characteristic of amorphous Ni–P, a similar result can also be found in amorphous Ni-20P film [16]. No abrupt up-low distribution in both Ni and P spectra indicates that the amorphous layer is uniform.

The density of the electrodeposited Ni–P BAA and its crystallized state was measured by Archimedes' principle; the data show that compared with the density 7.9 g/cm^3 of the binary Ni–P BAA, there is only an increase of ~1.1% in density upon crystallization, while the density difference between crystalline and amorphous state in BAAs produced by rapid solidification is about ~0.6% [4]. According to Ma [17], BSAP type with Voronoi index $\langle 0,2,8,0\rangle$ is the main short-range-ordered unit in $Ni_{80}P_{20}$ amorphous alloy, therefore, the theory density is calculated to be 7.8 g/cm^3. Nigam once reported that various organic additives (such as saccharin) added to the plating solution can produce bright, leveled and compact deposits; some