Journal of Alloys and Compounds 577S (2013) S179–S183

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Crystallization and grain refinement of Ti—30Ni—20Cu (at%) alloy ribbons prepared by melt spinning

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ARTICLE INFO

Article history:
Received 19 September 2011
Received in revised form 31 October 2011
Accepted 29 December 2011
Available online 5 January 2012

Keywords:
Shape memory alloys (SMA)
Grain refining
Crystallization
Melt spinning
Two-step annealing

ABSTRACT

Crystallization behavior of amorphous Ti—30Ni—20Cu (at%) alloy ribbons and martensitic transformation behavior, shape memory effect and superelasticity of crystallized ribbons were investigated by means of X-ray diffraction, differential scanning calorimetry, scanning electron microscopy, thermal cycling tests under constant load and tensile tests. Crystallization occurred in the sequence of amorphous–B2–Ti(Ni,Cu)$_2$ and the activation energy for crystallization of the B2 phase was 198.8 kJ/mol. Average grain size of the sample annealed in two-step, i.e., annealing at 773 K for 40 s followed by annealing at 748 K for 3.6 ks was 0.25 μm, which was very small comparing with the sample annealed in one-step, i.e., annealing at 823 K for 3.6 ks (1.20 μm). Grain refinement reduced the heat of transformation (ΔH) associated with the B2–B19 transformation and increased the critical stress for slip deformation causing the perfect shape memory recovery under the applied stress of 400 MPa.

1. Introduction

Grain size refinement of Ti—Ni based shape memory alloys has been studied extensively because grain size affects both martensitic transformation behavior and mechanical properties such as the shape memory effect and superelasticity. Martensitic transformation start temperature (Ms) decreases with decreasing grain size because grain boundaries serve to stabilize the parent phase [1,2]. Transformation hysteresis decreases with decreasing grain size [3–5], which was attributed to a specific arrangement of martensitic variants (single pair of variants) in small grains [4].

Many attempts for grain refinement of Ti—Ni based shape memory alloys have been made in order to investigate an effect of grain size on transformation behavior and mechanical properties [1–7]. Severe cold working and subsequent annealing, i.e., thermo-mechanical treatment (TMT) is the most frequently used for grain refinement. From TMT, very fine grains with an average size of 50–200 nm were obtained depending on the amount of cold working and annealing temperature [1,5,6]. Introduction of dislocations, however, always occurs by TMT. Since dislocations also affect both martensitic transformation behavior and mechanical properties of Ti—Ni based alloys [8,9], TMT is not suitable for investigating an effect of grain size solely on transformation behavior and mechanical properties transformation.

Crystallization of amorphous ribbons is known to be effective to control grain size by varying crystallization condition such as annealing temperature and time. An advantage of crystallization from amorphous ribbons is that it can exclude introduction of dislocations. In fact, from crystallization of amorphous ribbons, grains with an average size of 0.5–5.0 μm were obtained depending on annealing temperature and time [2,7]. Recently, the present authors report that a novel two-step annealing builds up very fine grains with an average grain size of 0.25 μm from amorphous Ti—30Ni—20Cu (at%) alloy ribbons prepared by melt spinning [10]. The two-step annealing is designed based on experimental results that activation energy required for the crystal growth is lower than that for the nucleation in Ti—Ni alloys [11,12]. The first step annealing is made at a high temperature enough for supplying thermal energy for nucleation for short time with minimizing grain growth. The second step annealing is made at a low temperature enough for supplying thermal energy for growth of the crystals nucleated in the first step annealing. However, martensitic transformation behavior, shape memory effect and superelasticity of the two-step annealed ribbons are not reported yet.

In the present study, amorphous Ti—30Ni—20Cu (at%) ribbons were prepared by melt spinning and then they were crystallized by two-step annealing for obtaining fine grains. Transformation behavior and mechanical properties such as shape memory effect

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2011.12.163

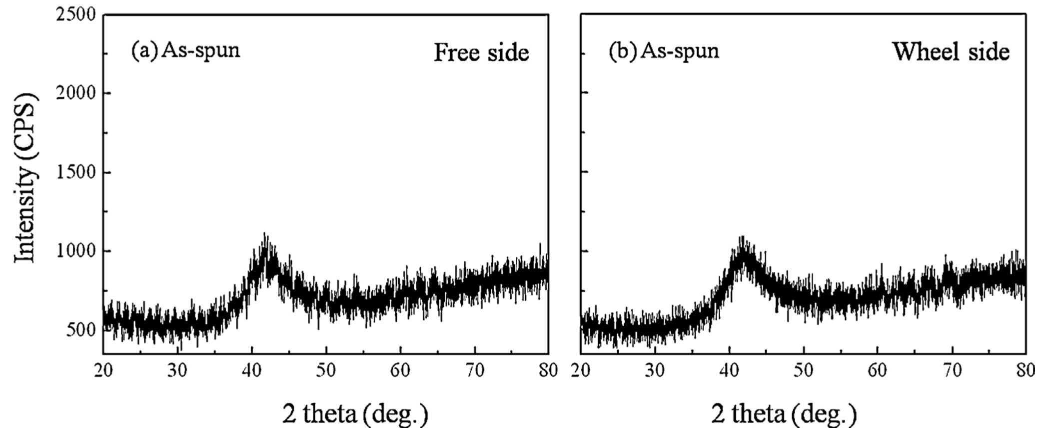

Fig. 1. XRD patterns obtained from free side (a) and wheel side (b) of as-spun Ti—30Ni—20Cu alloy ribbons.

and superelasticity of the two-step annealed ribbons were investigated and results obtained were compared with the ribbons crystallized at a specific temperature (one-step annealing).

2. Experimental procedure

A Ti—30Ni—20Cu (at%) pre-alloy was prepared by high frequency vacuum induction melting. Billet charges of about 15 g cut from the pre-alloys were placed into quartz crucibles and the chamber of the melt spinning system had been pumped down to less than 1×10^{-3} Pa before re-melting. After re-melting, it was ejected through the nozzle on the outer surface of the rotating quenching wheel made of copper. Melt spinning temperature and the linear velocity were 1873 K and 40 m/s, respectively. Average width and thickness of the ribbons obtained were found to be 3.1 mm and 21.3 μm, respectively. Two-step annealing for crystallization was made by annealing (the first step) at 773 K for 40 s followed by annealing (the second step) at 748 K for 3.6 ks. For comparison, some ribbons were annealed at 823 K for 3.6 ks (one-step annealing).

Microstructures of the alloy ribbons were examined by field emission scanning electron microscopy (FE-SEM) after etching in a solution of H_2O:HCl:H_2O_2 (3:2:1). The crystal structures of the ribbons were investigated by X-ray diffraction (XRD) using Cu Kα radiation with successively changing experimental temperatures. For the study of crystallization behavior and martensitic transformation behaviors of the ribbons, differential scanning calorimetry (DSC) measurements were made at heating and cooling rate of 0.17 K/s using TA Instrument DSC-2010. Thermal cycling tests under the various applied stress with a cooling and heating rate of 0.017 K/s and tensile tests were made for investigating the shape memory effect and deformation behavior of the crystallized ribbons, respectively. Average sample size was 3.0 mm (width) × 19.5 μm (thickness) × 50.0 mm (length) and gage length was 30.0 mm.

3. Results and discussion

Fig. 1(a) and (b) are XRD patterns obtained from free side and wheel side of as-spun Ti—30Ni—20Cu alloy ribbons, respectively. Any significant diffraction peaks corresponding to crystals are not observed in both patterns, indicating that the as-spun ribbons are amorphous. In order to investigate crystallization behavior of amorphous Ti—30Ni—20Cu alloy ribbons, DSC measurements were made on the ribbons at various heating rates ranging from 0.08 K/s to 0.42 K/s and then DSC curves obtained are shown in Fig. 2(a). Two exothermic DSC peaks are observed in the curves. From the Ti—Ni—Cu alloy phase diagram [13] and Ref. [14], the DSC peak designated by single headed arrow is considered to be due to crystallization of the B2 phase from amorphous and that designated by double headed arrow is attributed to formation of Ti(Ni,Cu)$_2$. Measuring the peak shifts of the DSC curves with varying in heating rate in Fig. 2(a), the apparent activation energy for crystallization of the B2 phase from amorphous is obtained from the Kissinger plots. The Kissinger equation is as follows:

$$\ln\left(\frac{B}{T^2}\right) = -\frac{E}{RT} + \text{constant}$$

where B is the heating rate, E is the apparent activation energy, R is the gas constant and T is a specific absolute temperature such as peak temperature measured at selected heating rates B. By plotting $\ln(B/T^2)$ vs. $1/(RT)$, as shown in Fig. 2(b), the activation energy is obtained from the slope of a straight line. The activation energy obtained is found to be 198.8 kJ/mol, which is very small comparing with 350–450 kJ/mol in Ti—Ni alloy thin films [15,16]. Relatively small activation energy for crystallization comparing with Ti—Ni alloys was also observed in Ti—25Ni—25Cu (at%) alloy ribbons [17].

Amorphous as-spun ribbons were annealed at various temperatures, as shown in DSC curves of Fig. 2(a), for crystallization. Annealing for crystallization was made in two ways; one-step annealing and two-step annealing. The one-step annealing is done

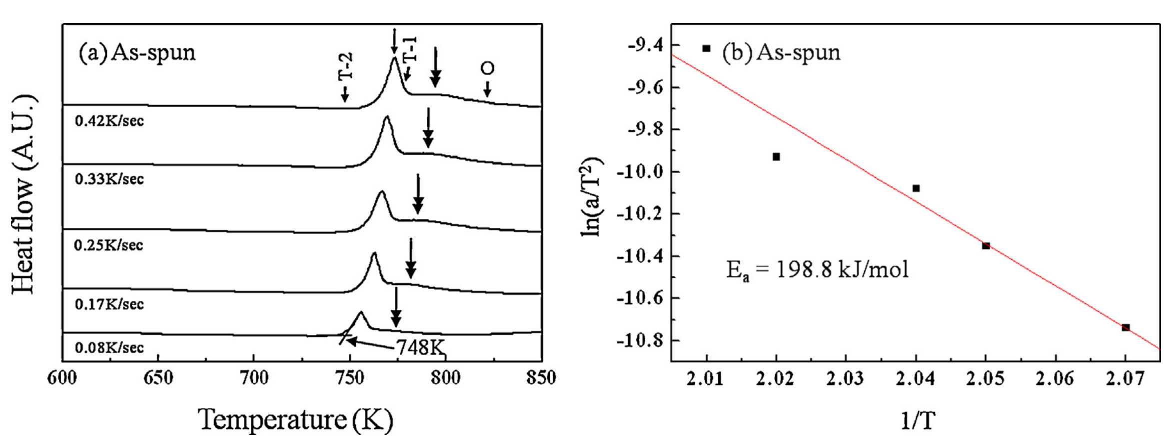

Fig. 2. (a) DSC curves of as-spun Ti—30Ni—20Cu alloy ribbons obtained at various heating rates (b) Kissinger plot obtained from (a).