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Effect of minor Cu content on microstructure and mechanical property of NiTiCu bulk alloys fabricated by crystallization of metallic glass powder

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ABSTRACT

Ultrafine-grained $Ni_{50.2-x}Ti_{49.8}Cu_x$ ($x = 0$, 2.5, 5, and 7.5) bulk shape memory alloys were fabricated by sintering of metallic glass (MG) powder and crystallization of amorphous phase. Non-isothermal crystallization kinetic analysis reveals that the crystallization mechanism of the synthesized $x = 5$ MG powder is typical interface-controlled two dimensional growth of nuclei followed by volume diffusion-controlled three dimensional growth of nuclei. In contrast, the crystallization mechanism of the synthesized $x = 7.5$ MG powder is typical volume diffusion-controlled three dimensional growth of nuclei in whole crystallization process. Correspondingly to different crystallization mechanisms, the two sintered and crystallized (SCed) bulk alloys have the same crystallized phases of bcc B2, fcc $NiTi_2$ phases, and monoclinic B19′, but these phases display different morphologies and distributions. The SCed $x = 5$ bulk alloy has a microstructure of bcc B2 matrix surrounding fcc $NiTi_2$ phase region, while the SCed $x = 7.5$ bulk alloy possesses discontinuous bcc B2 phase region. Consequently, the different crystallization mechanisms and microstructures causes extreme high yield strength and large plasticity for the SCed $x = 5$ bulk alloy and low strength and no plasticity for the SCed $x = 7.5$ bulk alloy. Especially, the yield strength of the SCed $x = 5$ bulk alloy is at least two times of that of the counterpart alloy prepared by melt solidification. The results provide a method fabricating high performance bulk alloys by tailoring crystallization mechanism using powder metallurgy.

1. Introduction

As advanced functional materials, NiTi shape memory alloys have been widely used in aerospace and biomedical fields because of their superior shape memory effect and high super-elasticity [1–3]. Recently, fabrication of Cu-containing NiTi shape memory alloys has attracted much attention. The advantages of Cu substitution for Ni are resulting in narrowing the transformation hysteresis, reducing the chemical composition dependency of transformation temperatures, and improving the ability to respond and corrosion resistance, etc., when compared to a binary Cu-free NiTi alloy [4–7]. Besides, it is well accepted that high size precision and tolerance is a significant prerequisite to shape memory alloys parts under some specific usable conditions. This put forward a necessary requirement for property index of shape memory alloys parts. In other words, only by obtaining satisfied mechanical properties, i.e., high yield strength along with high fracture strength and moderate plasticity, combined with superior shape memory effect, can guarantee shape memory effect under wider range of loaded stress for shape memory alloys parts under some extreme engineering application.

Generally, NiTi shape memory alloys are prepared by melt solidification [8–10]. However, limitation of cooling rate causes coarse grain ranging from several tens to several hundreds micrometers for these solidified alloys [11,12]. This decides unsatisfied mechanical properties of relative low yield and fracture strength. Recently, nano-sized TiNi powder with an average size of 50 nm was used as precursor to produce bulk alloy by powder consolidation [13]. More recently, a material forming method by coupling sintering of metallic glass (MG) powder with crystallization of sintered bulk MG was introduced to prepared ultrafine-grained titanium alloys with composite structure [14–20]. Ultrafine-grained composite structure leads to excellent combination of high strength and large plasticity for the prepared titanium alloys.

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The advantages using MG powder as precursor in this material forming method is that only after experiencing crystallization of MG powder at high temperature, nucleated grains begins to grow and thus have shorter grain growth time relative to using nanocrystalline powder as precursor. This is certainly helpful for fabricating titanium alloys with finer grain. Unfortunately, involved relationship between crystallization mechanism of sintered bulk MG (or synthesized MG powder) and microstructure and mechanical property of sintered and crystallized (SCed) bulk alloys in this method is unclear.

In the present work, ultrafine-grained NiTiCu bulk shape memory alloys were fabricated by tailoring crystallization mechanism of synthesized MG powder during powder sintering process. The fabricated bulk alloy has extreme high yield strength, at least two times of that of the counterpart alloy prepared by melt solidification. The involved effect of crystallization mechanism of MG powder on microstructure and mechanical property of SCed bulk alloys was elucidated. The results provide a method fabricating high performance bulk alloys by tailoring crystallization mechanism using powder metallurgy.

2. Experiment methods

High-purity elemental powders of Ti, Ni, and Cu with a stoichiometry of $Ni_{50.2-x}Ti_{49.8}Cu_x$ (x = 0, 2.5, 5, and 7.5) were used. The purity of the used element powders is above 99.5 wt.%. Their particle sizes are about 50 μm. The uniform mixture powders with four compositions were put into four stainless steel vials together with stainless steel balls, the diameters of which were 15, 10, and 6 mm with a weight ratio of 1:3:1. The ball to powder weight ratio was 7:1. Mechanical alloying was performed in a planetary ball mill at the speed of 4 s^{-1} under a protection argon atmosphere (99.999%, 0.5 MPa). A small amount of powders would be removed out for further examinations every 10 h in the Vacuum Glove Box under a protection argon atmosphere, until the alloy powders have the maximum volume fraction of MG phase. Subsequently, in order to investigate the effect of different content of Cu alloying substitution on microstructure and mechanical property of SCed bulk alloys, spark plasma sintering (SPS) system was used to sinter and crystallize the milled alloy powders with maximum volume fraction of MG phase. The sintering conditions were set up as several stages of first heating to 353 K at 20 K/min, to 1253 K at 100 K/min, then to 1273 K at 20 K/min, and holding for 10 min at 1273 K, respectively. Sintering pressure in the whole process is hold at 40 MPa. The SCed bulk alloys had the cylindrical shape of Φ20 × 7 mm. For comparison with the SCed bulk alloys, the counterpart alloys with the same compositions were prepared by suction casting of chemically homogeneous alloy melts after four times smelting of alloy ingots.

The thermal behavior of the milled alloy powders was measured by differential scanning calorimetry (DSC) under a high-purity argon atmosphere at different heating rates. The structure evolution of the milled alloy powders for different milling times were confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The phase constitution, microstructure and mechanical property of the SCed bulk alloys were characterized by XRD, SEM, TEM, and testing system. The density of the SCed bulk alloys was obtained using a technique based on Archimedes' principle. The detailed experimental procedures can be found in Refs. [21,22]. In addition, the O and Fe pick-ups for the milled glassy powders were determined by colorimetry and TC600 Nitrogen/Oxygen Determinator (LECO Co., US) with an uncertainty of 0.025 ppm, respectively.

3. Results

The XRD patterns of the milled powders with different milling times are present in Fig. 1(a). Obviously, for the initial powder, XRD pattern exhibits all sharp diffraction peaks of Ti, Ni and Cu elements. After 10 h milling, the diffraction peaks of Cu disappeared. This means that the Cu atoms dissolved in Ti and Ni atoms, and the diffraction peaks intensity of the Ni and Ti decreased gradually. Meanwhile, the diffraction peaks was broadened simultaneously. This is due to a decrease in crystallite size and an increase in lattice distortion because of a high stresses evolved during milling balls impacts. After 20 h milling, the broad diffraction peak appears, meaning the formation of MG phase. When the milling time exceeds 40 h, the diffraction peak of Ti vanished, and a broad and weak diffraction peak appears, implying the formation of body center cubic (bcc) NiTiCu (B2) phase. Prolonging the milling time to 60 h, no further structure changes are found in the milled alloy powder. This means that the milled alloy powders possess the maximum volume fraction of MG phase. Notice that the O and Fe contents are 0.275 ± 0.005 wt.% and 0.280 ± 0.005 wt.% for the milled MG powders, respectively. These minor pick-ups can't cause formation of any oxide and compound as shown in Fig. 7 and thus exert no effects on crystallization behaviors of the milled MG powders and mechanical properties of the sintered bulk alloys. Fig. 1(b) shows the XRD patterns of the milled $Ti_{49.8}Ni_{50.2-x}Cu_x$ powders with the maximum volume fraction of MG phase after different milling times. It can be seen that the four milled alloy powders have nearly complete glassy structure.

Thermal properties of the milled $Ti_{49.8}Ni_{50.2-x}Cu_x$ (x = 0, 2.5, 5, and 7.5) powders after different milling times are measured

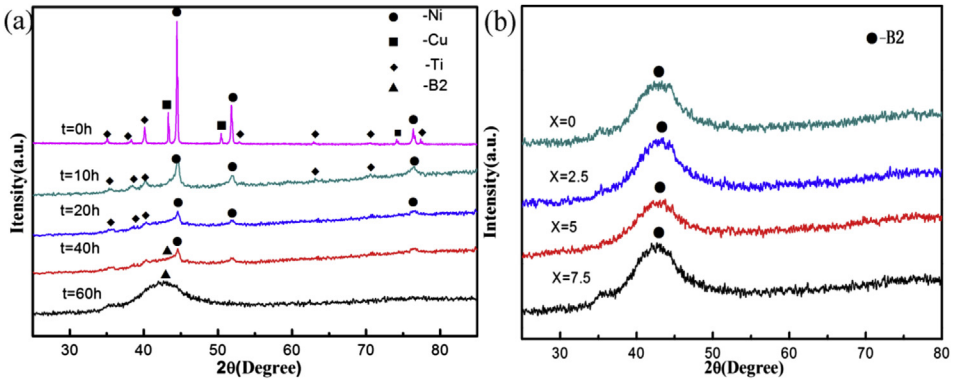

Fig. 1. (a) XRD patterns of the milled $Ti_{49.8}Ni_{42.5}Cu_{7.5}$ powders after different milling times. (b) XRD patterns of the milled $Ti_{49.8}Ni_{50.2-x}Cu_x$ powders after different milling times: (I) x = 0 after 80 h milling, (II) x = 2.5 after 80 h milling, (III) x = 5.0 after 60 h milling, (IV) x = 7.5 after 60 h milling.