Journal of Alloys and Compounds 514 (2012) 210–213

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Grain size effect on martensitic transformation, mechanical and magnetic properties of Ni–Mn–Ga alloy fabricated by spark plasma sintering

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A R T I C L E I N F O

Article history:
Received 31 October 2011
Received in revised form
13 November 2011
Accepted 15 November 2011
Available online 23 November 2011

Keywords:
Ferromagnetic shape memory alloys
Phase transitions
Mechanical property
Sintering

A B S T R A C T

The sintered Ni–Mn–Ga alloys with various grain sizes have been fabricated by using the spark plasma sintering method. The effect of grain size on martensitic transformation, mechanical and magnetic properties of Ni–Mn–Ga alloys have been investigated for the first time. The results show that martensitic transformation and transformation hysteresis are significantly affected by the grain size. All as-sintered Ni–Mn–Ga alloys exhibit high saturation magnetization despite their different grain sizes. Moreover, it is found that the grain size plays important roles on mechanical properties. The sintered specimen with appropriate grain size exhibits the highest fracture strain reported so far.

1. Introduction

Ni–Mn–Ga ferromagnetic shape memory alloy has been widely investigated due to its ability to exhibit large magnetic-field-induced strain (MFIS) and high response frequency [1–4]. The MFIS is based on the rearrangement of martensite twin variants by the twin boundary motion under an applied magnetic field. A MFIS of up to 10% has been reported in a single crystal Ni–Mn–Ga alloy [5]. This makes it an ideal candidate for magnetically controlled shape memory application. However, the extreme brittleness of Ni–Mn–Ga alloys prepared by conventional melting technique greatly limits their practical application. In order to improve the brittleness of the bulk alloy, there has been growing interest in the modification of Ni–Mn–Ga alloys by adding a fourth element. Recently, several rare earth elements [6–8] and Fe have been added to Ni–Mn–Ga alloys to improve the mechanical properties [9,10]. Moreover, several other forms based on the alloy have been developed, including ribbons and thin films [11–14]. However, although the ductility is expected to be improved by these methods, the shape of specimens is limited and the fabrication of bulk specimens with a relatively large size is difficult.

On the other hand, it is worth investigating other fabrication process to obtain this alloy. Powder metallurgy is one of the most effective techniques for improving the ductility of bulk materials, which has been successfully utilized for a number of brittle shape memory alloys [15,16]. In particular, the spark plasma sintering (SPS) technique is designed to sinter metal powder in a short time to achieve dense materials. High speed sintering is of particular advantage to achieve fine grains and dense structures, which leads to high toughness and strength. So far, only few investigations on sintered Ni–Mn–Ga ferromagnetic shape memory alloys fabricated by the SPS technique have been reported [17,18]. Very recently, we have investigated the mechanical and magnetic properties of sintered Ni–Mn–Ga alloys fabricated by the SPS method [19]. We reported that such sintered Ni–Mn–Ga alloys show a drastic enhancement in ductility compared to the alloys obtained by conventional melting technique. Moreover, the MFIS has also been confirmed [19]. Furthermore, it is well known that the grain size is closely related to the microstructure and martensitic transformation behaviors of shape memory alloy, and significantly influences its mechanical and magnetic properties [20]. However, up to now, the effect of grain size on the martensitic transformation, mechanical and magnetic properties of sintered Ni–Mn–Ga alloys has not been reported despite its practical importance. Therefore, the purpose of this paper is to investigate the effect of grain size on the martensitic transformation, mechanical and magnetic properties of sintered Ni–Mn–Ga alloys fabricated by the SPS technique. The results show that the martensitic transformation and transformation hysteresis are significantly affected by the grain size. Furthermore, it is found that the sintered Ni–Mn–Ga alloy with appropriate grain size exhibits the highest fracture strain reported so far.

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doi:10.1016/j.jallcom.2011.11.077

2. Experimental

A $Ni_{50}Mn_{29}Ga_{21}$ (at.%) alloy was prepared with high-purity elements melted four times in an arc-melting furnace under an argon atmosphere. The arc-melted alloy was sealed in quartz tube under a vacuum, then annealed at 1073 K for 24 h and quenched into iced water for homogeneity. The annealed arc-melted alloy was mechanically crushed and followed by ball milling to achieve powder. In order to produce microstructures with various grain sizes, three different ball milling times were employed. Subsequently, the obtained powder was sintered by the SPS technique, sintering being performed at 1073 K for 8 min in a vacuum of 6 Pa under a pressure of 40 MPa in a graphite die. Three kinds of as-sintered specimens obtained by varying ball milling time have average grain sizes of 15, 34 and 50 μm, respectively. X-ray diffraction (XRD) measurements were performed to determine the crystal structure using a Rigaku D/max-rB with Cu Kα radiation. Microstructures of the specimens were studied in a MX2600FE scanning electron microscopy analysis system. The martensitic transformation temperatures were determined by differential scanning calorimetry (DSC) with a heating and cooling rate of 20 K/min. Compression testing was conducted at ambient temperature on an Instron-1186 machine at a strain rate of 0.05 mm min^{-1} using the sintered specimens with a rectangular shape of about 3 mm × 3 mm × 5 mm. The magnetic property was measured by the vibrating sample magnetometer.

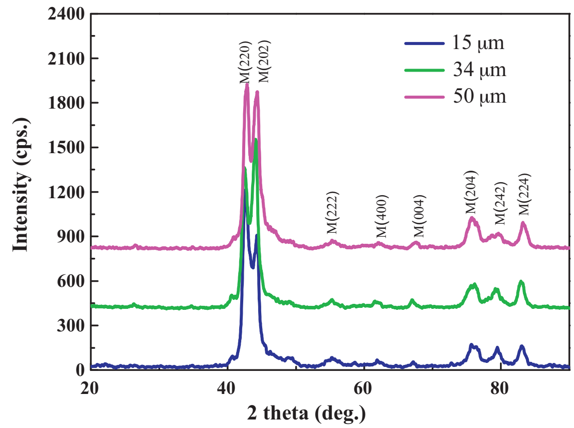

Fig. 1. XRD patterns of the as-sintered Ni–Mn–Ga alloys with grain sizes of 15, 34 and 50 μm, respectively.

3. Results and discussion

Fig. 1 illustrates the room temperature XRD patterns of the as-sintered Ni–Mn–Ga alloys with grain sizes of 15, 34 and 50 μm, respectively. The XRD patterns of all sintered specimens maintain the same crystal structure. The typical martensite peaks can be obviously seen in studied alloys. This indicates that grain size has little effect on the crystal structure. According to the XRD results, the crystal structures can be indexed by the five-layer tetragonal martensite with the lattice parameters $a = b = 0.596$ nm and $c = 0.557$ nm. Previous studies [17] show that the as-sintered Ni–Mn–Ga alloys exhibit the broadened XRD peaks. Such broadening arises from the simultaneous variation of lattice strain and grain size, which is due to the grinding-induced stress. Compared to previous results, the narrower XRD peaks in our studied sintered specimens show that lower lattice strain has been produced in the SPS process.

Fig. 2 shows the microstructure of the sintered Ni–Mn–Ga alloys. It is apparent that all sintered specimens have a single-phase structure without any large second-phase regions. Moreover, it can be seen that only a small amount of fine pores is observed in the specimen sintered at 1073 K. This indicates that the sintering

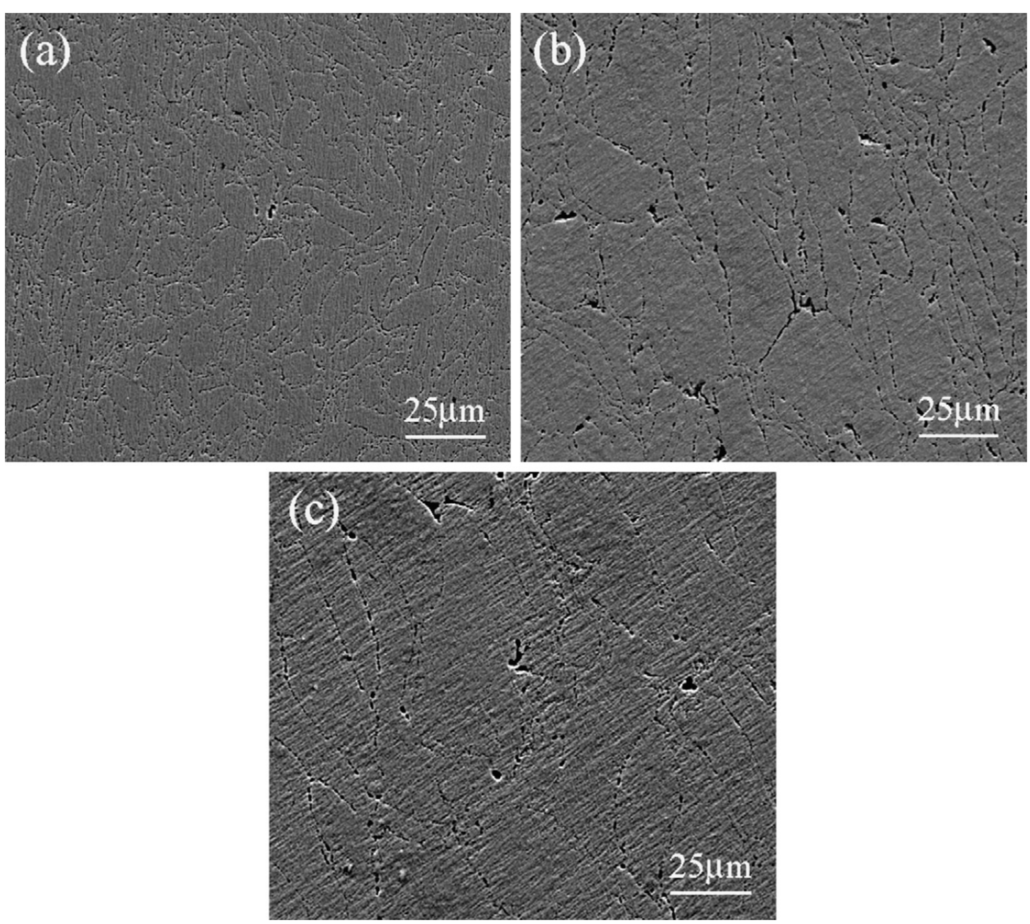

Fig. 2. Microstructure of sintered Ni–Mn–Ga alloys with grain sizes of (a) 15 μm, (b) 34 μm and (c) 50 μm.

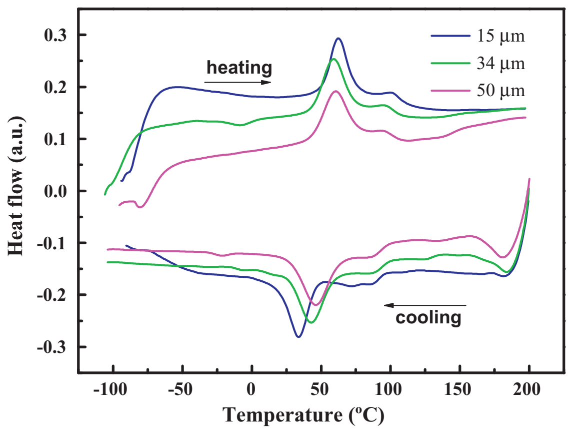

Fig. 3. DSC curves of as-sintered Ni–Mn–Ga alloys.

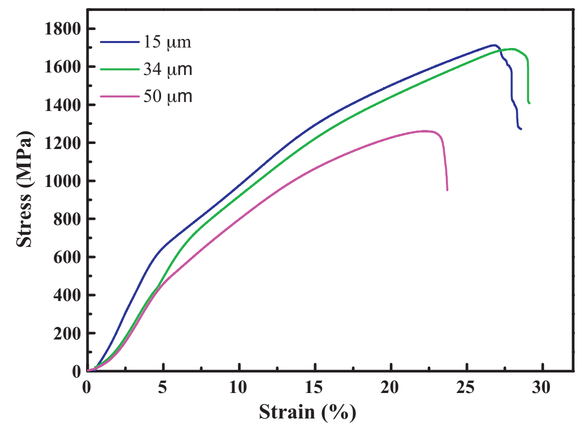

Fig. 4. Compressive stress–strain curves of sintered Ni–Mn–Ga alloys at room temperature with various grain sizes.

temperature of 1073 K is sufficient to obtain a high density. The average grain size of the sintered specimen is lower than 50 μm, which is smaller than that of the conventional melted alloy [17]. This is understandable because the SPS technique achieves refined grains.

Fig. 3 shows the DSC curves of the as-sintered Ni–Mn–Ga alloys with various grain sizes during heating and cooling. It is found that there are clear exothermic and endothermic peaks appear in the cooling and heating curves, corresponding to the martensitic transformation. This indicates that as-sintered specimens maintain the characteristics of the typical one-step thermoelastic martensitic transformation of the arc-melted Ni–Mn–Ga alloy. It is worthy noting that in the case of ball milled Ni–Mn–Ga powder, previous studies [21] show that the thermal peaks due to the martensitic transformation became lower during the grinding process. When the grain size of the powder is less than a certain value, the thermal peaks disappear in the DSC curves. The martensitic transformation even does not occur after sintering, and recovers only after annealing. The reason for these phenomena is the fact that the stress-induced lattice distortion has lead to the inhibition of the martensitic transformation. However, in this study, the martensitic transformation could be observed in as-sintered state. This indicates that the appropriate SPS process can eliminate the stress effect in powder thoroughly, which benefit the practical application of this material. Moreover, it can be seen that the martensitic transformation temperatures of the sintered specimens decrease with decreasing the grain size. This obviously shows that martensitic transformation temperatures of sintered Ni–Mn–Ga alloys are sensitive to the grain size. Small grain size would result in the decrease of martensitic transformation temperature in ferromagnetic shape memory alloys. In addition, it is found that the transformation hysteresis increases with decreasing grain size. This is because the specimen with smaller grain size contains more grain boundaries. The grain boundaries can act as barriers to the martensitic reverse transformation as a result of extra energy required during transformation. Thus, fine-grain specimens which have lots of grain boundaries would be expected to have larger transformation hysteresis, as shown in Fig. 3.

In order to investigate the effect of grain size on the mechanical properties of the sintered specimens, compression tests were carried out at room temperature. All specimens were compressed to fracture. Fig. 4 shows the compressive stress–strain curves at room temperature obtained from the sintered specimens with various grain sizes. It can be seen that both the compressive strength and fracture strain of all sintered specimens are significantly higher than those of the arc-melted specimen. This clearly demonstrates that the ductility of Ni–Mn–Ga alloys is significantly enhanced by powder metallurgy using the SPS technique. The enhancement of the ductility for the sintered specimen may be attributed to the strengthening of grain boundaries and reduction of the grain size, which has been reported in Cu–Al–Ni alloys [16]. Furthermore, it is found that the grain size significantly affects the compressive strength and fracture strain. The compressive strength increases with decreasing grain size and stays almost constant of 1712 MPa for grain size of 15 μm. In particular, for the sintered specimen with grain size of 34 μm, the fracture occurred at a strain of about 29%. This is higher than that of other sintered specimens with larger or smaller grain sizes and is the highest fracture strain reported to date in the Ni–Mn–Ga alloy system. Therefore, our results obviously indicate that the sintered Ni–Mn–Ga alloy with appropriate grain size exhibits the best ductility. In these studies, the sintered Ni–Mn–Ga with a grain size of about 34 μm has the highest fracture strain.

Fig. 5 illustrates the magnetization curves of sintered Ni–Mn–Ga alloys with different grain sizes measured at room temperature. It is found that all magnetization curves quickly increase until saturation for an applied magnetic field close to 7 kOe. Moreover, it can be seen that grain size has little effect on the saturation magnetization. The saturation magnetization of the sintered specimens is about 59 emu/g, which is comparable to that of the bulk alloy. It is expected that high saturation magnetization is favorable to the MFIS. However, it has been reported that in contrast to the sintered specimen, the ball milled Ni–Mn–Ga powders exhibit ferromagnetic behavior with much reduced saturation magnetization [22]. The saturation magnetization of the

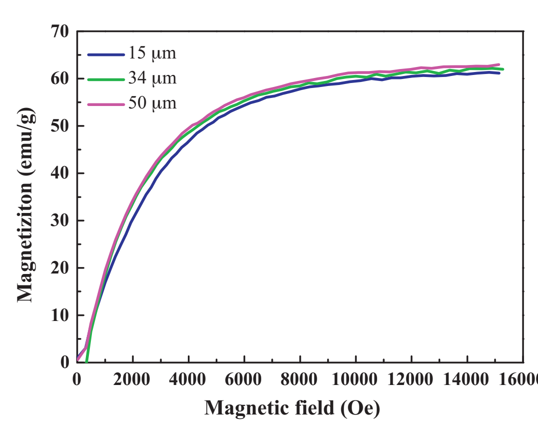

Fig. 5. Magnetization curves of sintered Ni–Mn–Ga alloys with different grain sizes measured at room temperature.

milled specimen at 50 kOe is 14 emu/g, which is approximately 23% of our studied specimens. This is caused by the destruction of Mn–Mn ferromagnetic exchange induced by ball milling. Based on our results, it can be demonstrated that sintering at 1073 K is effective in restoring the ferromagnetism of the material. Moreover, the magnetization curves also indicate that the martensitic phase of sintered Ni–Mn–Ga alloy exhibits the typical ferromagnetic behavior. In addition, it can be inferred that for the sintered specimen, the Curie temperature is higher than the martensitic transformation temperature. This implies that MFIS is expected to be observed in sintered Ni–Mn–Ga ferromagnetic shape memory alloys.

4. Conclusions

In summary, for Ni–Mn–Ga alloys fabricated by the SPS method, the effect of grain size on martensitic transformation, mechanical and magnetic properties has been investigated for the first time. The results show that all as-sintered specimens maintain the characteristics of the typical one-step thermoelastic martensitic transformation of the arc-melted Ni–Mn–Ga alloy, while their martensitic transformation temperatures decrease with decreasing grain size. In addition, the transformation hysteresis increases with the reduction of grain size owing to increase of grain boundaries. All as-sintered Ni–Mn–Ga alloys exhibit high saturation magnetization regardless of different grain sizes. Moreover, it is found that the grain size plays important roles on mechanical properties. The sintered specimen with grain size of 34 μm exhibits the highest fracture strain of 29% reported so far.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (grant nos. 50971052, 50801018 and 51071059), and the Fundamental Research Funds for the Central Universities (no. HIT.KLOF.2010005).

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