Microstructural, phase transformation and magnetic properties of Ni–Mn–Ga alloy fabricated by spark plasma sintering*

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The microstructural, phase transformation and magnetic properties of Ni–Mn–Ga alloy fabricated using the spark plasma sintering method have been investigated. The results show that both the as-sintered and annealed sintered specimens exhibit typical martensitic transformation behaviours. The martensite of the sintered specimen after annealing exhibits a ferromagnetic nature. Moreover, study of the fracture surface indicates that the transgranular fracture contributes to the higher ductility of sintered Ni–Mn–Ga alloy. In addition, the transformation strain in sintered Ni–Mn–Ga alloy is studied for the first time.

Keywords: ferromagnetic shape memory alloys, magnetic properties, martensitic transformations, spark plasma sintering

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1. Introduction

Ni–Mn–Ga ferromagnetic shape memory alloy has attracted a great deal of attention due to its large magnetic-field-induced strain (MFIS) and high response frequency.[1−4] The large MFIS was achieved through field-induced twin boundary motion and is affected by the crystal structure of the material.[5−8] Ni–Mn–Ga alloy exhibiting orthorhombic martensite has shown to have an up to 10% strain.[9] This makes it an ideal candidate for magnetically controlled shape memory applications. However, the extreme brittleness of Ni–Mn–Ga alloy prepared by a conventional melting techniques greatly limits its practical application. In order to improve the brittleness of the bulk alloy, there has been growing interest in the modification of Ni–Mn–Ga alloy by adding a fourth element. Recently, several rare earth elements[10−12] and Fe have separately been added to Ni–Mn–Ga alloys to improve their mechanical properties.[13,14] Therefore it is worthwhile investigating other fabrication processes for obtaining this alloy. Powder metallurgy is one of the most effective techniques for improving the ductility of bulk materials and 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 particularly effective at achieving fine grains and dense structures, which leads to high toughness and strength. So far, only a few investigations on sintered Ni–Mn–Ga ferromagnetic shape memory alloys fabricated by the SPS technique have been reported.[17,18] It has been found that such sintered Ni–Mn–Ga alloys indeed show a drastic enhancement in ductility compared to the alloys obtained by the conventional melting technique.[17] However, only a limited amount of information about the magnetic property in sintered Ni–Mn–Ga alloys has been found to date, despite its practical importance. Moreover, the martensitic transformation, microstructure and fracture surface of sintered Ni–Mn–Ga alloys needs further extensive study. Thus, the purpose of this paper is to investigate the microstructural, martensitic transformation and magnetic properties of Ni–Mn–Ga alloy fabricated by the SPS method. Furthermore, the transformation strain in sintered Ni–Mn–Ga alloy has been studied for the first time.

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2. Experiment

A polycrystalline $Ni_{48.8}Mn_{29.7}Ga_{21.5}$ 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 a 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 ball milled to achieve powder. Subsequently, the obtained powder was sintered by the SPS technique, sintering being performed at 1173 K for 10 min in a vacuum of 6 Pa under a pressure of 50 MPa in a graphite die. Part of the as-sintered alloys was then annealed at 1073 K for 12 h in a quartz tube under a vacuum. X-ray diffraction (XRD) measurements were performed to determine the crystal structure using a Rigaku D/max-rB with Cu K_α radiation. The microstructures and fracture surfaces of the specimens were studied using a MX2600FE scanning electron microscopy analysis system. The martensitic transformation temperatures were determined by Perkin–Elmer diamond differential scanning calorimetry (DSC) with a heating rate and cooling rate being both 20 K/min. The magnetic property was measured by a vibrating sample magnetometer. The thermal induced transformation strain was measured using a standard strain gauge technique.

3. Results and discussion

Figure 1 shows the DSC curve of the sintered Ni–Mn–Ga alloy annealed at 1073 K. The DSC curve is characterized by an exothermic peak on cooling and an endothermic peak during heating, corresponding to the martensitic and reverse transformations, respectively. This indicates that the sintered specimen after annealing exhibits the typical one-step thermoelastic martensitic transformation. Moreover, figure 1 also illustrates the DSC curve of the as-sintered Ni–Mn–Ga alloy. It can be obviously seen that the as-sintered Ni–Mn–Ga alloy also exhibits the martensitic transformation. Its transformation behaviour is basically similar to that of the sintered specimen after annealing, except for a slight shift of martensitic transformation temperature. However, a previous study[18] showed that martensitic transformation did not occur in as-sintered Ni–Mn–Ga alloy. This has been attributed to the fact that fast SPS process cannot thoroughly eliminate the stress effect in powder. Thus, stress leads to the inhibition of martensitic transformation behaviour. However, our results indicate that an as-sintered alloy fabricated by an appropriate SPS technique can exhibit martensitic transformation, which may benefit the application of this material. Therefore, since the annealing process encourages grain growth and improves the physical property of the alloy, we focus our attention on annealed sintered Ni–Mn–Ga alloy in the following.

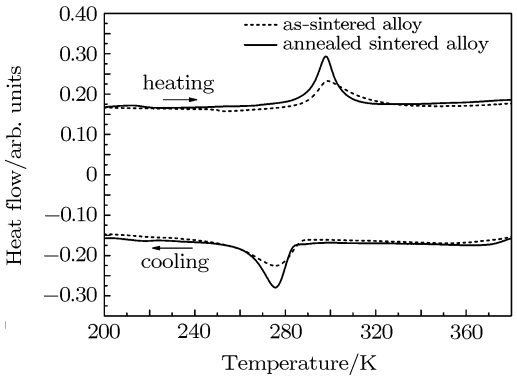


Fig. 1. DSC curves of as-sintered and annealed sintered Ni–Mn–Ga alloys.

Figure 2 illustrates the room temperature XRD patterns of the sintered Ni–Mn–Ga alloy annealed at 1073 K. The typical martensite peaks can be indexed in the studied alloys. The martensitic phase of this alloy is determined as the five-layer tetragonal martensite with the lattice parameters $a = b = 0.595$ nm and $c = 0.548$ nm. Narrower XRD peaks in our studied sintered specimen indicate that the annealing causes larger grain size and lower lattice strain.

Figure 3(a) shows the microstructure of the annealed sintered Ni–Mn–Ga alloy. It is apparent that the sintered specimen has a single-phase structure. There is no large second-phase region. Moreover, it can be seen that only a small number of fine pores are observed in the specimen sintered at 1173 K. This indicates that a sintering temperature of 1173 K is sufficient to obtain a dense structure. The average grain size of the sintered specimen is about 12 μm, which is smaller than that of the conventional melted alloy.[18] This is understandable because the SPS technique achieves refined grains. In addition, it is known that the ductility of an intermetallic compound is closely related to its fracture mode. Therefore, it is worthwhile investigating the fracture mode of sintered Ni–Mn–Ga alloy. Figure 3(b) shows the SEM image of the fracture surface of annealed sintered Ni–Mn–Ga alloy after compression testing. It is found that the fracture surface is indicative of transgranular fracture, while that for a conventional bulk alloy is mainly of intergranular fracture.[14] This difference in fracture mode

may be caused by the strengthening of grain boundaries and fine grains. However, it has been demonstrated that transgranular fracture may improve the mechanical property of an alloy.[14] Accordingly, it can be inferred that the transgranular fracture contributes to the higher ductility of the SPS-sintered Ni–Mn–Ga alloy compared with that of the alloy obtained by conventional melting technique.

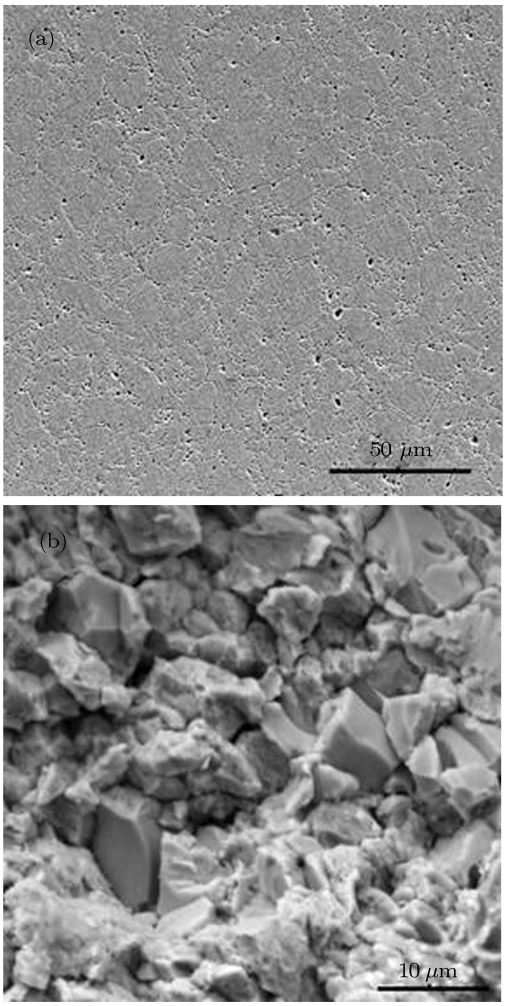


Fig. 2. (a) Microstructure of annealed sintered Ni–Mn–Ga alloy, (b) SEM image of the fracture surface of annealed sintered Ni–Mn–Ga alloy.

Figure 4 illustrates the magnetization curve of annealed sintered Ni–Mn–Ga alloy measured at room temperature. For the studied alloy, the magnetization curve quickly goes up until the saturation value for an applied magnetic field close to 7 kOe (1 Oe=79.5775 A/m). The saturation magnetization of the sintered specimen is 55 emu/g, which is comparable to that of the bulk alloy. The high saturation magnetization is favourable for MFIS. Moreover, the magnetization curve also indicates that the martensitic phase of sintered Ni–Mn–Ga alloy exhibits typical ferromagnetic behaviour, which is the basic condition for the observation of MFIS in ferromagnetic shape memory alloy. In addition, it can be inferred that for the sintered specimen, the Curie temperature is higher than the martensitic transformation temperature.

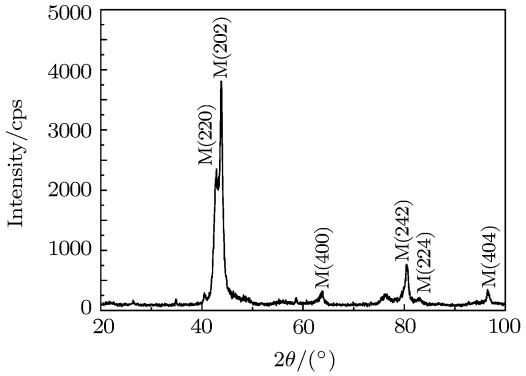


Fig. 3. XRD patterns of annealed sintered Ni–Mn–Ga alloy.

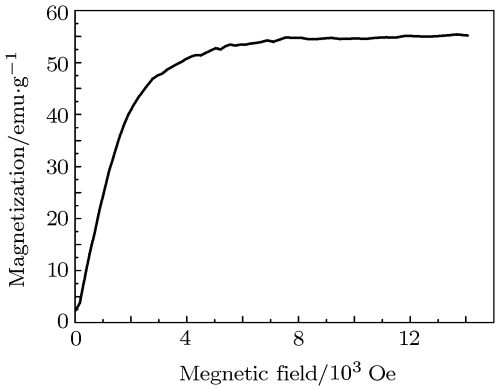


Fig. 4. Magnetization curve of annealed sintered Ni–Mn–Ga alloy.

Figure 5 shows the strain-temperature curve of annealed sintered Ni–Mn–Ga alloy. It is seen that the sintered specimen contracts for the austenite to martensite transformation and expands for the martensite to austenite transformation. The full transformation strain is 140 ppm, which is smaller than that of the Ni–Mn–Ga polycrystalline alloy.[19] In general, for the polycrystalline alloy, generating a transformation strain requires that the martensitic variant within the grain is not completely self-accommodated during martensitic transformation. For the present sintered specimen, a small transformation strain indicates that a degree of self-accommodation of the martensitic variant partially remains.

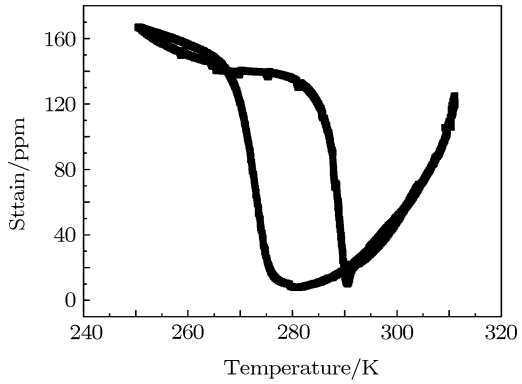


Fig. 5. Strain-temperature curve of annealed sintered Ni–Mn–Ga alloy.

4. Conclusions

For Ni–Mn–Ga alloy fabricated by the SPS method, the microstructure, martensitic transformation, magnetic property and the transformation strain have been investigated. The results show that both the as-sintered and annealed sintered specimens exhibit the characteristics of a typical one-step thermoelastic martensitic transformation. The martensite of the sintered specimen after annealing exhibits a ferromagnetic nature. Its saturation magnetization reaches 55 emu/g, which is comparable to that of the bulk alloy. Moreover, study of fracture surface indicates that the transgranular fracture contributes to the higher ductility of the SPS-sintered Ni–Mn–Ga alloy compared with that of the alloy obtained by the conventional melting technique. In addition, the transformation strain of 140 ppm in sintered Ni–Mn–Ga alloys has been obtained for the first time, which is smaller than that in the Ni–Mn–Ga polycrystalline alloy.

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