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Phase Transformation and Magnetic Property of Ni-Mn-Ga Powders Prepared by Dry Ball Milling

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This study investigated the phase transformations and magnetic properties of Ni-Mn-Ga alloy powders prepared by dry ball milling in argon atmosphere. The Fe and Cr elements were found to be introduced in the alloy after ball milling, which should result from the severe collision and friction among the particles, balls, and vial. The x-ray diffraction result indicated that the Fe and Cr elements should have alloyed with the Ni-Mn-Ga matrix. The martensitic transformation temperature and Curie temperature of the 800 °C annealed powders decreased by ~33 °C and increased by ~28 °C, respectively, as compared to that of the bulk alloy. The comprehensive effect of the changing of valence electron concentration of the alloy due to the introduction of Fe and Cr and the grain refinement of the alloy caused by ball milling should be responsible for the reduction of martensitic transformation temperature. The saturation magnetization of the 800 °C annealed powders became larger (~5 emu/g) than that of the bulk alloy. The enhancement of magnetic properties, such as the increase of Curie temperature and enhancement of saturation magnetization of the annealed Ni-Mn-Ga powders, should be attributed to the increase of magnetic exchange caused by introduction of Fe in the alloy. The contaminations of Fe and Cr elements emerging from the dry ball milling process changed the phase transformation and magnetic properties of the Ni-Mn-Ga alloy. Therefore, the dry ball milling process is difficult to control the contamination from the milling medium and not suitable to prepare Ni-Mn-Ga powders. On the contrary, the wet ball milling method under liquid medium should be a better method to prevent the contamination and fabricate pure Ni-Mn-Ga ferromagnetic shape memory alloy powders.

Keywords ferromagnetic shape memory alloy, magnetic property, martensitic transformation, Ni-Mn-Ga powder

1. Introduction

The research of Ni-Mn-Ga ferromagnetic shape memory alloy (FSMA) has drawn much interest over the past few years because of the large magnetic-field-induced strain (MFIS) (Ref 1, 2). The MFIS originates from the motion of martensitic twin boundaries under a proper magnetic field. The martensitic transformation, magnetic property, and magnetotransport property have been widely investigated (Ref 3-5). However, as is well known, Ni-Mn-Ga is an intermetallic compound, and its intrinsic brittleness has hindered its practical applications. To conquer the disadvantage of the alloy, the composite consisting of ductile polymer matrix and Ni-Mn-Ga particles has been proposed and developed (Ref 6-11), in which the polymer provides integrity of the composite, and the Ni-Mn-Ga particles satisfy the requirement of functionality. It was found that the phase transformation strain of Ni-Mn-Ga particle-epoxy composite increased with decreasing the particle size (Ref 11). The energy absorption capacity of the epoxy composite became larger with the addition of Ni-Mn-Ga particles because of the twin boundary movement of the particles (Ref 8). Therefore, the properties of Ni-Mn-Ga particles are crucial for the performance of the composite. In addition, the Ni-Mn-Ga particles can also be used in the field of magnetic recording, magnetic refrigeration, and micromagnetic actuation because of the small size.

In our previous studies (Ref 12-14), the Ni-Mn-Ga particles were prepared by the ball milling method because of the advantages of simplicity, high productivity, and cost-effectiveness of the ball milling in fabricating metallic particles compared with spark erosion approach (Ref 15). It has been reported that the ball milling energy imposing on the alloy played an important role for the structural transition of the Ni-Mn-Ga particles (Ref 12). The low milling energy (planetary ball milling) leads to a face centered tetragonal (fct) structure after ball milling, and the martensitic transformation behavior of the powder particles after annealing at above 500 °C can recover to the bulk alloy state. On the other hand, the powder particles after high-energy milling (vibration ball milling) exhibit a face centered cubic (fcc) structure, and the martensitic transformation behavior of the particles after annealing even at 800 °C is still weak and cannot retrieve to the bulk alloy state. For these two ball milling processes, we performed them by using an acetone as the wet milling medium to cool the milling

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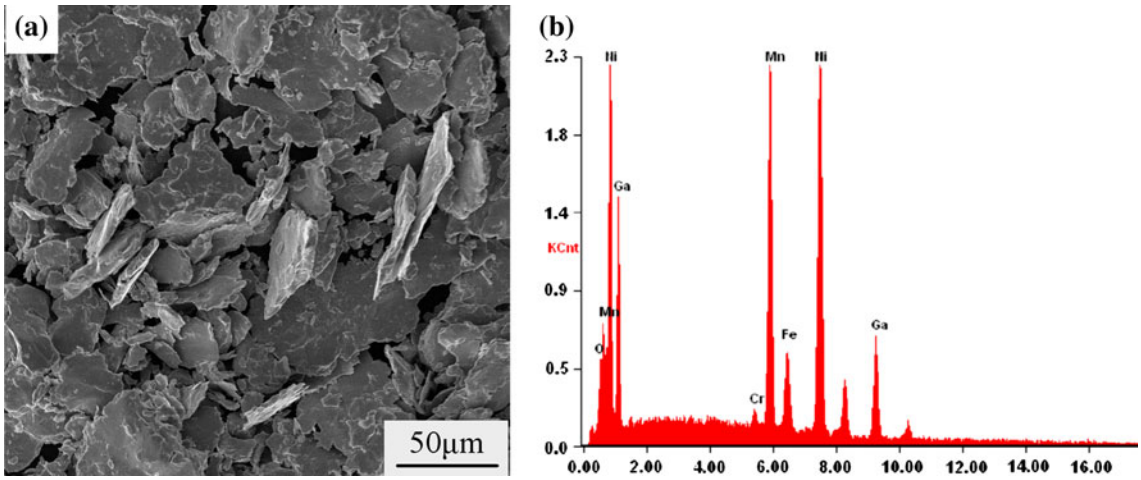

Fig. 1 SEM image (a) and EDS result (b) of as-milled Ni-Mn-Ga powder particles

system for avoiding overheating in the local area of the milling vial and therefore preventing oxidation of the alloy. Except for adding the liquid milling medium in the vial, another effective way to protect the alloy from oxidation is filling inert gases in the milling vial. Meanwhile, the dry milling under inert gases will provide a higher milling energy than the wet milling process in the liquid medium because of the rapid rising of temperature in the dry milling process without coolant when the other milling parameters are kept similar.

In this article, the Ni-Mn-Ga particles were prepared by the dry ball milling method under the argon gas atmosphere. The microstructure, phase transformation, and magnetic property of the Ni-Mn-Ga particles depending on the annealing temperatures were investigated and discussed.

2. Experimental Procedures

A polycrystalline alloy ingot with a nominal composition of $Ni_{52}Mn_{24}Ga_{24}$ (at.%) was prepared by arc melting high purity elements of Ni, Mn, and Ga in an argon atmosphere. The ingot was heat treated at 850 °C for 10 h in a vacuum followed by water quenching for chemical homogenization. The homogenized ingot was mechanically crushed into small particles with a size of ~3 mm and then milled for 4 h continuously in a QM-1SP4 planetary ball mill (Nanjing University Instrument Plant, China) with the hardened steel balls with a ball-to-powder weight ratio of 10:1. The milling speed was 500 rpm. The milling vial was vacuumed and then filled with the argon gas during ball milling to prevent oxidation. Finally, the as-milled powder particles were sealed in the quartz tubes under high vacuum and annealed at different temperatures for 2 h.

The microstructure observation of the powders was performed using a FEI Quanta200 scanning electron microscope (SEM) equipped with an energy dispersive spectrometry (EDS) analyzer. The martensitic transformation was investigated using a Perkin-Elmer Diamond differential scanning calorimeter (DSC). The low-field ac magnetic susceptibility was also measured as a function of temperature to determine the martensitic transformation and Curie transition. x-ray diffraction (XRD) analysis was carried out at room temperature to investigate the crystal structure using a Panalytical X-pert PRO diffractometer with Cu Kα radiation. Magnetic properties were measured using a Physics Property Measurement System (PPMS) manufactured by Quantum Corporation.

3. Results and Discussions

Figure 1(a) shows the SEM image of the as-milled Ni-Mn-Ga particles. It is seen that the particles are flaky shape with sizes of 5-50 μm. Figure 1(b) shows the EDS result of the as-milled particles, which shows that O, Fe, and Cr elements were introduced into the particles. The introduction of O should be caused by the minor oxidation of Mn on the surface of particles. Fe and Cr elements may come from the steel milling balls and vial because of the severe mutual collision and wear among the alloy particles, steel balls, and vial. On the contrary, the Fe and Cr elements were not found in the particles produced by wet milling processes in our previous studies (Ref 12-14). It might be attributed to the fact that the liquid medium (acetone) can cool the milling system and also act as a lubricant to decrease the mutual collision and friction of the particles, balls, and vial, thereby preventing the contaminations of Fe and Cr elements during the wet milling process.

Figure 2(a) shows the DSC curves of the bulk alloy, as-milled powder, and 800 °C annealed powder. It is seen that the original bulk alloy exhibits a one-step martensitic transformation upon cooling, the martensitic transformation peak temperature (M_p) being 5.2 °C. The small step at 86.5 °C during cooling corresponds to the Curie transition (T_c) from paramagnetic to ferromagnetic austenite. Upon heating, the martensite transforms to austenite phase at 12.8 °C (austenitic transformation peak temperature, A_p), as shown in the figure. When the temperature is up to 87.5 °C, the step corresponding to the Curie transition from ferromagnetic austenite to paramagnetic austenite appears. After ball milling, it can be seen that no transformation peaks or any other signals are detected on the curve, indicating the martensitic transformation, and Curie transition disappeared after ball milling, which is attributed to the atomic disordering caused by ball milling (Ref 13, 14). Post-annealing process after ball milling is effective to restore the martensitic transformation behavior of

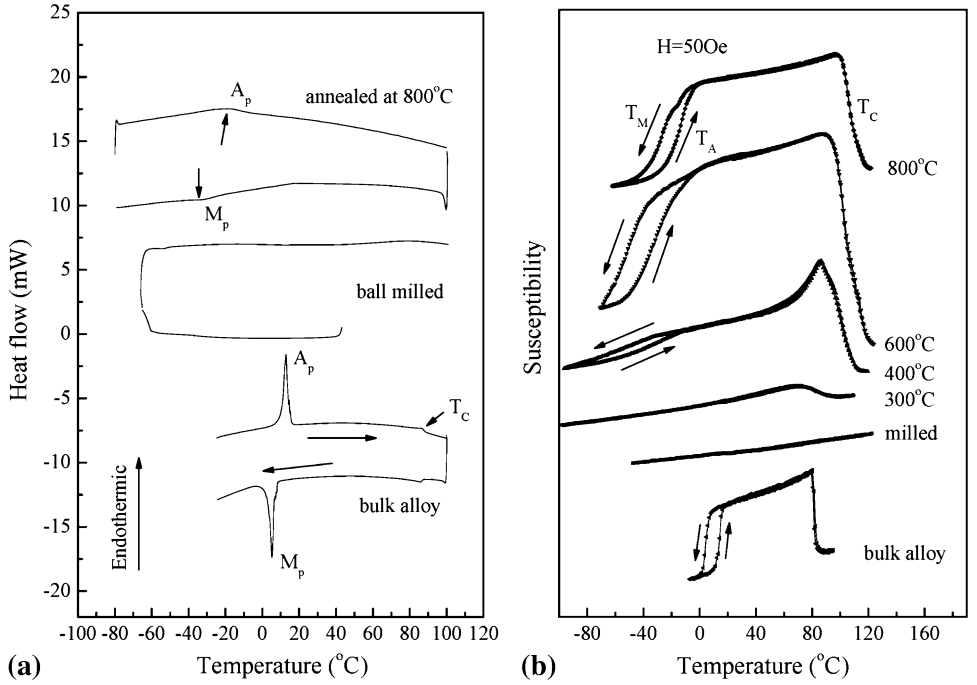

Fig. 2 (a) DSC curves for Ni-Mn-Ga bulk alloy, as-milled powder, and powder after annealing at 800 °C for 2 h; (b) ac-susceptibility vs. temperature curves for Ni-Mn-Ga bulk alloy, as-milled powder, and powders after annealing at 300, 400, 600, and 800 °C for 2 h. The field was 50 Oe

the Ni-Mn-Ga powders. However, the DSC measurement indicates that the martensitic transformation of the powders after annealing at 300, 400, and 600 °C still cannot recover. The DSC curves of 300, 400, and 600 °C annealed powders are not shown in the figure. After annealing at 800 °C, a very weak transformation peak can be observed on the curve with remarkably reduced transformation temperatures (M_p: −31 °C, A_p: −17 °C) compared to that of the original bulk alloy (M_p: 5.2 °C, A_p: 12.8 °C). It is also noted that the Curie transition step cannot be detected on the DSC curve of the annealed sample.

Figure 2(b) shows the ac susceptibilities of different samples with the variation of temperature. For the bulk alloy, an abrupt increase of susceptibility at 80 °C upon cooling indicates the Curie transition of the alloy. Continue cooling, a sudden drop of the susceptibility at 5 °C means the occurrence of martensitic transformation (T_M). An increase of susceptibility at 14 °C on heating stands for the austenitic transformation (T_A). After ball milling, it is clearly seen that the martensitic transformation of the alloy disappeared. The martensitic transformation of the milled powders does not recover after 300 °C annealing. After 400 °C annealing, a very weak martensitic transformation appears with reduced transformation temperature, as compared with the bulk alloy. The martensitic transformation behavior becomes very clear after 600 °C annealing, and the forward and reverse transformation temperatures are −52 and −32 °C, respectively, which are much lower than the transformation temperatures of the bulk alloy. For the sample annealed at 800 °C, the forward and reverse transformation temperatures increase a little compared with 600 °C annealed sample, which are characterized at −28 and −14 °C, respectively. It is surprising to note that the martensitic transformation for the 400 and 600 °C annealed samples was not found in the DSC measurement but detected in the ac-susceptibility test, the reason for which is still not clear at present. In addition, the Curie transition of the 800 °C annealed sample can be found apparently by ac-susceptibility measurement, but it was also not detected on the DSC test, as shown in Fig. 2(a).

Unlike the martensitic transformation which appeared at greater than 400 °C annealing, the Curie transition occurred at a relatively low annealing temperature (300 °C), as shown in Fig. 2(b). This is because the first-order martensitic transformation needs higher atomic order than the second-order Curie transition (Ref 13). The Curie temperature (∼107 °C) of the powders annealed at above 400 °C is higher than that of the bulk alloy (80 °C).

Figure 3 shows the XRD patterns of the different samples measured at room temperature. For the bulk alloy, the pattern can be indexed as a cubic austenite phase, which is consistent with the DSC measurement result that the austenite phase exists at room temperature. After ball milling, it is seen that the characteristic diffraction peaks belonging to the cubic austenite phase disappeared, and other new diffraction peaks occurred. These new peaks can be indexed as a disordered fcc phase (Ref 12), as shown in the inset of Fig. 3. For the samples annealed at 300, 400, 600, and 800 °C, clearly, the diffraction peaks of the austenite phase recovered gradually with the increase of annealing temperature. It is noted that, for the samples annealed at 600 and 800 °C, the superlattice diffraction peak (111) standing for the high atomic ordering state of the alloy occurred, indicating the almost full recovery of Heusler structure in the alloy. No diffraction peaks belonging to the elemental Fe or Cr were found in the diffraction pattern, which indicates that these two elements have been alloyed with the Ni-Mn-Ga matrix.

It has been reported that the addition of Fe in the Ni-Mn-Ga alloy can increase the Curie transition temperature and decrease the martensitic transformation temperature of the alloy (Ref 16-18). The

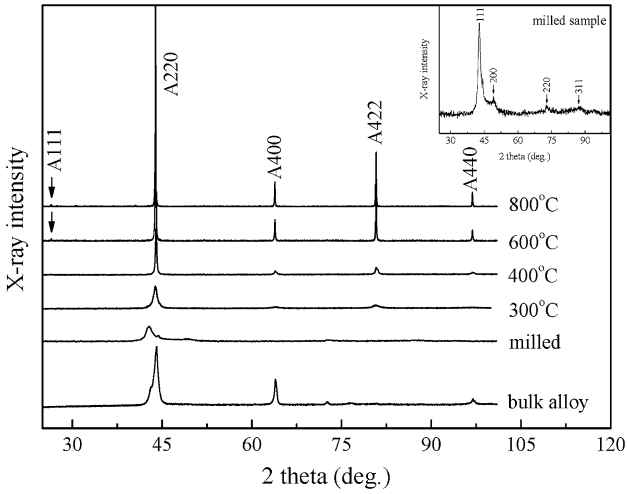

Fig. 3 The room temperature XRD patterns for Ni-Mn-Ga bulk alloy, as-milled powder, and powders after annealing at 300, 400, 600, and 800 °C for 2 h. The inset shows the locally enlarged pattern of the milled sample

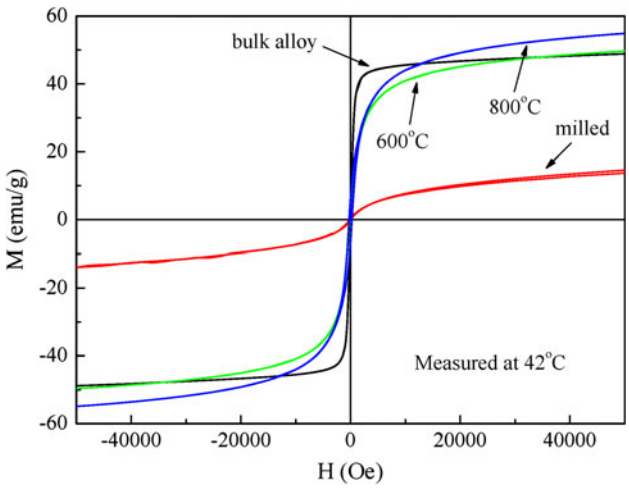

Fig. 4 The magnetic hysteresis loops measured at 42 °C for Ni-Mn-Ga bulk alloy, as-milled powder and powders after annealing at 600 and 800 °C for 2 h

decrease of martensitic transformation temperature is thought to be related to the increase of valence electron concentration (e/a) of the alloy after the addition of Fe (Ref 16, 17) and the increase of Curie temperature is caused by the enhancement of magnetic exchange of the alloy due to the addition of Fe (Ref 17, 18). In addition, the reduction of grain size also results in the decrease of martensitic transformation temperature in the Ni-Mn-Ga alloy (Ref 9). Thus, in the present Ni-Mn-Ga powders, the grain refinement caused by ball milling (Ref 12) and the alloying of Fe and Cr with the Ni-Mn-Ga matrix resulting in the variation of e/a might be responsible for the decrease of martensitic transformation temperature, and the increase of Curie temperature may be caused by the introduction of Fe which enhances the magnetic exchange of the alloy.

Figure 4 shows the magnetic hysteresis loops of the different samples measured at 42 °C. It is inferred that the samples should be at austenite phase at this measurement temperature based on the susceptibility-temperature testing results shown in Fig. 2. It can be seen that the bulk alloy exhibited a typical ferromagnetic behavior with saturation magnetization of 45 emu/g when external magnetic field reaches ~4500 Oe. After ball milling, the sample still exhibited the ferromagnetic behavior but with much reduced saturation magnetization. The magnetization at 30000 Oe is about 12 emu/g, being 26% that of the bulk alloy, which is caused by atomic disordering of the alloy after ball milling, similar to the result reported in Ref 13. After annealing at 600 and 800 °C, it is seen that the magnetic property of the powders was recovered to the bulk alloy state because of the enhancement of atomic ordering level (Ref 13). For the sample annealed at 600 °C, the saturation magnetization of the powder is nearly equal to that of the bulk alloy. The magnetization for the powder is saturated at a higher magnetic filed (~12000 Oe) than that for the bulk alloy (~4500 Oe), indicating the annealed powder is more difficult to be magnetized than the bulk alloy. For the sample annealed at 800 °C, the powder shows ~5 emu/g higher saturation magnetization than the bulk alloy at the magnetic field of 40000 Oe. The increase of the magnetization for the 800 °C annealed sample should be caused by the enhancement of magnetic exchange of the alloy due to the introduction of Fe. The 800 °C annealed sample exhibits a little higher saturation magnetization than the 600 °C annealed sample, which might be because the atomic ordering level in the 600 °C annealed sample is relatively lower than that in the 800 °C annealed sample (Ref 13).

4. Conclusions

The Ni-Mn-Ga alloy particles with flaky shape have been prepared by ball milling under the argon atmosphere. The Fe and Cr elements were introduced in the Ni-Mn-Ga alloy because of the severe collision and friction among the alloy, milling balls, and vial. The martensitic transformation and Curie transition of the alloy disappeared after ball milling because of the atomic disordering and were recovered after appropriate temperature annealing. The decrease of martensitic transformation temperature of the annealed powders should be related to the change of valence electron concentration and grain refinement of the alloy. The increase of Curie temperature and enhancement of saturation magnetization of the annealed powders should result from the introduction of Fe, which enhances the magnetic exchange of the alloy.

Acknowledgments

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