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Effect of post annealing on phase transformation of Ni-Mn-Ga ferromagnetic shape memory alloy particles prepared by ball milling

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Abstract: The effect of post annealing on the phase transformation of $Ni_{52}Mn_{24}Ga_{24}$ ferromagnetic shape memory alloy particles prepared by ball milling was studied. $Ni_{52}Mn_{24}Ga_{24}$ alloy particles at micron scale were prepared successfully by ball milling the crushed bulk alloy. SEM observation reveals that the shape of the as-milled particle is regular polygon and a lot of cracks can be seen at the surface of the particles. For as-milled particles, the widening of characteristic peak can be found in the XRD pattern, and no transformation characterization can be detected by DSC. Post annealing at the elevated temperature will recover the transformation behavior of milled particles to the same level as that of bulk sample. It is shown that with increasing annealing temperature above 400 ℃, M_s decreases and A_s increases, while the magnetic transition temperature keeps constant. XRD results indicate that the change of grain size of the particles results in such an effect of post annealing.

Key words: NiMnGa particle; phase transformation; ball milling; ferromagnetic shape memory alloy

1 Introduction

Since its single crystal with a specified composition is found to possess a large magnetic field induced strain in 1996[1], NiMnGa ferromagnetic shape memory alloys (FSMA) have been widely investigated. It is believed that this material can be applied to micro-actuator and sensor for its unique properties including high response speed[2−4]. To extend its application, FSMA composite consisting of fine NiMnGa particles becomes a subject of interest[5−7]. It is thought that using NiMnGa particles to reinforce polymer matrix can improve the ductility of NiMnGa alloy[8]. For preparing the composite, the first step is to obtain the NiMnGa particles with optimum properties. Therefore, it is necessary to investigate the fabrication, transformation behavior and other properties of NiMnGa particles. The microstructure and magnetic properties of fine particles fabricated by spark erosion were investigated[9−11]. WANG et al[12] also studied the intermartensitic transformation of NiMnGa particles by grinding a single crystal. However, the conventional ball milling is seldom reported to prepare NiMnGa particles up to date. Compared with the spark erosion, the ball milling is thought to be more convenient and cheaper, moreover it is more suitable for industrial production. In present work, the unique phenomenon of $Ni_{52}Mn_{24}Ga_{24}$ ferromagnetic shape memory alloy particles prepared by ball milling and the effect of post annealing on the phase transformation were studied.

2 Experimental

A button-like polycrystalline ingot of $Ni_{52}Mn_{24}Ga_{24}$ alloy was prepared by arc-melting under argon atmosphere using high purity elements of 99.99% Ni, 99.7% Mn and 99.99% Ga. Then the ingot was annealed at 1 073 K for 10 h in a vacuum quartz tube for homogeneity, and quenched in water. The ingot was mechanically crushed and followed by ball milling to achieve the particles with the size in micrometer scale. The ball milling was performed with a rotation speed of 500 r/min and mixed with acetone. Sealed in the vacuum quartz tube, these particles were annealed at 400, 500, 600 and 800 ℃ for 2 h, respectively, and then cooled in air. The phase transformation temperatures of the samples were measured by Perkin-Elmer DSC with a cooling/heating rate of 20 ℃/min. The crystal structure at room temperature was measured by powder X-ray diffractometry with Panalytical X'pert PRO X-ray

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diffractometer using Cu K_α radiation. The Particles morphology was observed by Cambridge-S240 scanning electron microscope (SEM).

3 Results and discussion

3.1 Micro-morphology of particles

Fig.1 shows the micro-morphologies of the $Ni_{52}Mn_{24}Ga_{24}$ particles after milling for 2 h and 14 h, respectively. When the milling time is 2 h, the particles exhibit the irregular polygon with a lot of cracks on the surface. For the particles obtained after 14 h milling, it can be seen that each particle consists of many thin flakes. It is suggested that a lot of plastic deformation induced by the ball milling causes such a shape change. Furthermore, no obvious difference can be seen for the size of these two samples.

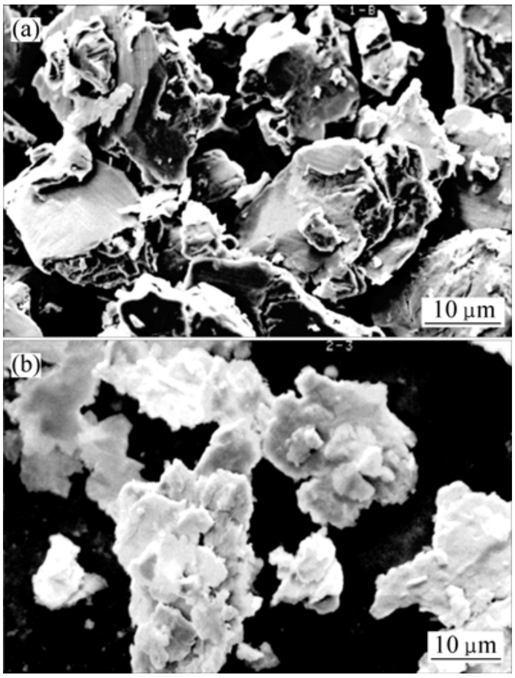

Fig.1 SEM images of $Ni_{52}Mn_{24}Ga_{24}$ particles after milling for different time: (a) 2 h; (b) 14 h

3.2 Phase transformation of particles

Fig.2 illustrates the DSC curves for $Ni_{52}Mn_{24}Ga_{24}$ alloy samples under different conditions. As known in a DSC curve, one obvious peak stands for the first order transformation process. Here the tangent rule is used to determine martensitic transformation starting temperature (M_s) and its reverse transformation starting temperature (A_s). A stagger, appearing at about 85 ℃, represents the second order transformation, which corresponds to ferromagnetic transition of the parent phase[9]. And the transition temperature is denoted as T_c.

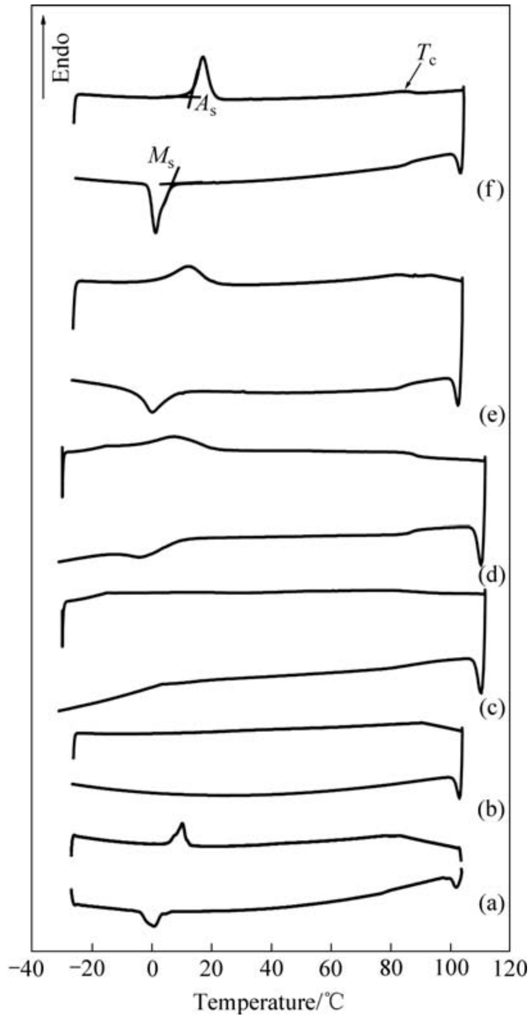

Fig.2 DSC curves for $Ni_{52}Mn_{24}Ga_{24}$ samples: (a) Bulk alloy; (b) As-milled particles; (c) Particles annealed at 400 ℃; (d) Particles annealed at 500 ℃; (e) Particles annealed at 600 ℃; (f) Particles annealed at 800 ℃

It can be seen that $Ni_{52}Mn_{24}Ga_{24}$ bulk alloy annealed at 850 ℃ for 2 h exhibits one step thermal elastic martensitic transformation and reverse transformation, as depicted in Fig.2(a). M_s, A_s and T_c are 3.7 ℃, 5.7 ℃ and 83 ℃, respectively. In contrast, no martensitic transformation peaks from −20 ℃ to 100 ℃ can be found for the particles after milling for even 2 h. The ferromagnetic transition can still be found by DSC, which is shown in Fig.2(b). Such a phenomenon as the disappearance of martensitic transformation of the NiMnGa particles after ball milling has not been reported ever before. SOLOMON et al[9] just reported the transformation behavior of the annealed sample by spark erosion. However, they did not investigate the as-prepared particles. Figs.2(c)−(d) show the DSC curves for the particles annealed at 400, 500, 600 and 800 ℃, respectively. Except for the particles annealed at 400 ℃, the remaining three samples undergo one step martensitic and its reverse transformation. It should be noted that all the samples (original and annealed particles) exhibit ferromagnetic transition and have similar T_c. The detailed martensitic transformation and magnetic transition temperatures of the samples are summarized in Table 1. With the increase of annealing temperature, the transformation peaks become sharper and sharper gradually. The rise of A_s and the decrease of M_s can also be found, which indicates that the stability of parent phase of NiMnGa particles is improved by annealing. The conclusions can be drawn as follows: 1) high energy ball milling inhibits martensitic transformation of NiMnGa alloys; 2) ball milling does not destroy ferromagnetic transition of NiMnGa alloys; 3) appropriate heat treatments will recover the martensitic transformation of as-milled particles; 4) T_c is not affected by the milling and the post annealing.

Table 1 Characteristic temperatures of martensitic and magnetic transformation of $Ni_{52}Mn_{24}Ga_{24}$ samples

Sample	M_s/℃	A_s/℃	T_c/℃
Bulk	3.7	5.7	83
As-milled particles	−	−	89
Particles after 400 ℃ annealing	−	−	82.4
Particles after 500 ℃ annealing	9	−2.4	83.6
Particles after 600 ℃ annealing	8.1	3.7	83
Particles after 800 ℃ annealing	6.5	13.1	85

3.3 Structure of particles

To explain the effect of milling and post annealing on martensitic transformation of $Ni_{52}Mn_{24}Ga_{24}$ particles prepared by ball milling, the microstructure change is analyzed by XRD method. Fig.3 shows the XRD patterns of different $Ni_{52}Mn_{24}Ga_{24}$ samples at room temperature. For the bulk sample, three typical diffraction peaks of BCC structure can be found. While after 2 h milling, only one wide diffraction peak of (220) remains in the XRD pattern. It is known that, three main reasons will cause the widening of the characteristic peak of XRD pattern, i.e. the refining of grain size, the transition from crystalline state to amorphous one and the micro-strain caused by the lattice distortion. As discussed in DSC analysis, all the particles, not only the as-milled but also the annealed ones, undergo the ferromagnetic transition and T_c shows no change. If the milled particles are amorphous, it is impossible to find the ferromagnetic transition by DSC curve. So the second reason is excluded. By comparing Fig.3(a) with Fig.3(f), different 2θ of (220) peak can be seen. It is suggested that the ball milling process introduces micro-strain into the particles. WAITZ et al [13] has reported that the martensitic transformation doesn’t happen when the grain size is below about 50 nm in a nanocrystalline NiTi alloy. The grain size of the present as-milled particles is calculated to be about 50 nm by using Scherrer equation. Therefore, it can be inferred that the combination of grain refining and the micro-strain caused by ball milling results in the disappearance of martensitic transformation. After annealing at 400 ℃ for 2 h, although the XRD pattern indicates that the particles are at parent phase state (bcc), no martensitic transformation appears. The reasonable explanation has not been obtained. It is assumed that the grain size is still below the critical value although the micro-strain has been erased. When the annealing temperature is above 500 ℃, the characteristic peaks of $L2_1$ phase can be found and become much shaper. So the grain size becomes large enough to overcome the barrier of martensitic transformation. That is, annealing at a certain temperature will change the grain size of the NiMnGa particles, resulting in the appearance of martensitic transformation.

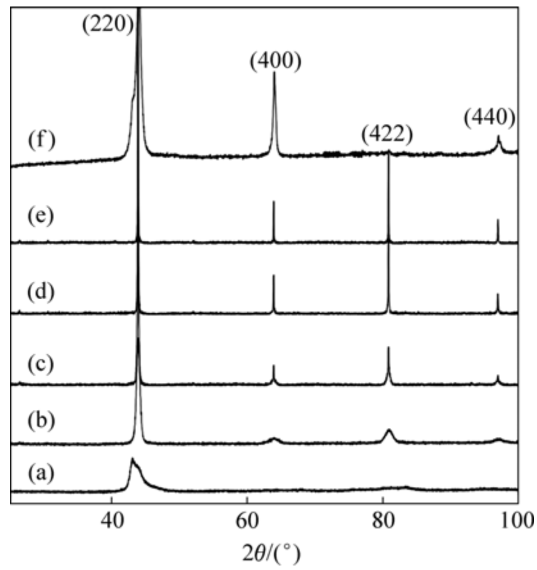

Fig.3 XRD patterns of $Ni_{52}Mn_{24}Ga_{24}$ samples: (a) As-milled particles; (b) Particles annealed at 400 ℃; (c) Particles annealed at 500 ℃; (d) Particles annealed at 600 ℃; (e) Particles annealed at 800 ℃; (f) Bulk alloy

4 Conclusions

1) Ball milling can obtain the NiMnGa particles with the micro-size.

2) The combination of grain refining and micro-strain leads to the disappearance of martensitic transformation after ball milling.

3) Post annealing at an appropriate temperature can resume the martensitic transformation.

4) T_c is almost not affected by ball milling and post annealing, indicating that it is not associated with the grain size.

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