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# Structural transition of Ni-Mn-Ga ferromagnetic shape memory alloy particles prepared by ball milling

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**Abstract:** The size, crystal structure and phase transformation of $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ alloy particles prepared by planetary ball milling (PBM) and vibration ball milling (VBM) were investigated by SEM, XRD and DSC. The results show that the particles milled by PBM for 4 h exhibit irregular polyhedron, with the size distribution between 5 μm and 40 μm. These particles present disordered fct structure with no phase transformation behaviour. When annealed at 600 ℃ for 1 h, the crystal structure of the particles evolves from disordered fct to Heusler completely. The particles milled by VBM for 4 h exhibit flaky shape, with the size distribution from 3 μm to 30 μm. The particles present disordered fcc structure with no phase transformation behaviour. However the crystal structure of these particles doesn't transform from disordered fcc to Heusler completely after annealing at 600 ℃ for 1 h, for the severe lattice distortion induced in the VBM process is not eliminated entirely.

**Key words**: Ni-Mn-Ga alloy particles; structural transition; phase transformation; ball milling

## 1 Introduction

Ni-Mn-Ga ferromagnetic shape memory alloys have drawn much attention for their large magnetic field induced strain up to 10 % and high response speed in magnetic field[1−3]. The magnetic shape memory behavior, martensitic transformation, magnetic properties, and so on, have been extensively studied[4−6]. Though so many properties of the bulk Ni-Mn-Ga alloys have been studied systematically, as we know, the brittleness of polycrystalline and single crystalline bulk alloys strongly limit the practical use for Ni-Mn-Ga alloys. To overcome this problem, the thin films, melt-spun ribbons and particles/polymer composite materials have been studied widely[7−10]. The particles/polymer composite approach is a very simple and effective method for reducing brittleness and achieving the shape we desired. However, the fabrication of Ni-Mn-Ga particles is seldom reported, except that the magnetic properties[11−12] and magnetocaloric effect[13] of Ni-Mn-Ga fine particles prepared by spark erosion method have been studied.

Ball milling method is more cost-effective than spark erosion method for preparing alloy particles. In this study, two types of $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ micro-particles were prepared by planetary and vibration ball milling methods, respectively, and their structural transition was studied.

## 2 Experimental

A polycrystalline ingot of $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ alloy was prepared by arc-melting furnace under argon atmosphere using high purity elements of 99.8% Ni, 99.7% Mn and 99.9% Ga. After annealing at 850 ℃ for 10 h, the ingot was mechanically crushed into particles with size less than 3 mm. These particles mixed with acetone were sealed in a vial. Ball milling was performed in the QM-1SP4 planetary ball mill and the QM-3A vibration ball mill, respectively. The hardened steel balls were used and the ball-to-powder mass ratio was about 10∶1. After milling for 0.5 h, 1 h and 4 h, respectively, the particles were taken out from the vial followed by drying. The 4 h milling particles were annealed at 600 ℃ for 1 h. Then, the phase transformation temperatures of as-milled and annealed particles were measured by Perkin-Elmer Diamond DSC at a cooling/heating rate of 20 ℃/min. X-ray diffraction (XRD) was carried out for phase identification at room temperature using a Panalytical X-pert PRO diffractometer with Cu $K_\alpha$

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radiation. The morphology of all particles was determined with Cambridge-S240 scanning electron microscope (SEM), and the particle-size distribution was measured using Rise-2002 particle-size analyzer.

## 3 Results and discussion

### 3.1 Observation for morphology of as-milled particles

Fig.1 shows the surface morphologies of 4 h as-milled particles by PBM (4 h-PBM-particles) and VBM (4 h-VBM-particles), observed by SEM. From Fig.1(a), the shape of particles is polyhedron with size distribution from 5 μm to 40 μm. In Fig.1(b), it can be seen that the particles is in flaky shape mainly with size distribution between 3 μm and 30 μm. The energy of VBM is much higher than that of PBM, so the particles ball milled by VBM should be destroyed more seriously in contrast to PBM process during the same ball milling time. Therefore, the different particle shape can be obtained by these two ball milling process.

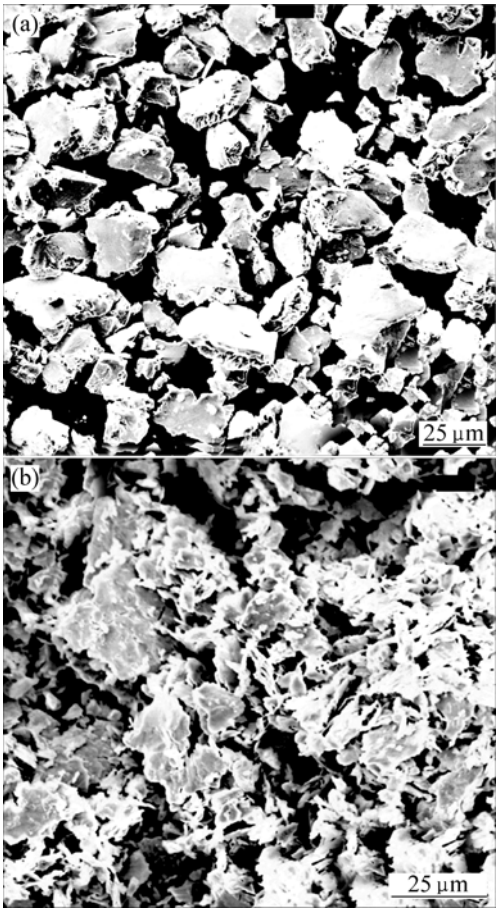


**Fig.1** SEM images for $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ alloy particles prepared by PBM(a) and VBM(b) for 4 h

### 3.2 Structural transition of particles during ball milling

The room temperature XRD patterns for particles after different ball milling times using PBM and VBM are shown in Fig.2. By referring to Ref.[5], the bulk alloy could be indexed as 5M tetragonal martensite. After ball milling for 0.5 h and 1 h by PBM, the diffraction peaks of martensite become weak gradually such as (202), (400) or (004) peaks. When up to 4 h, the martensite peaks almost disappear completely, and other new diffraction peaks appear. These new peaks can be indexed as phase with fct structure, which has also been found by WANG et al[14] in $Ni_2MnGa$ ball-milled particles. In Ref.[14], the fct structure phase is considered to be a nonmodulated martensite with $M_s$ (about 343 K) close to Currie temperature $T_c$ (about 375 K). But according to DSC result shown in Fig.3(a), the ball milled $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ alloy particles do not undergo a martensitic transformation when the temperature range extends from −20 ℃ to 120 ℃. Hereby, this fct structure phase should not be a martensite phase, but a disordered fct structure phase. So the structure evolves from tetragonal structure to disordered fct structure after 4 h PBM process. However, the different structure evolution result in VBM process has been obtained in contrast to PBM process. The result can be seen in Fig.2(b), the martensite peaks have disappeared completely in the particles ball milled for 0.5 h owing to the severe lattice deformation, which is different from the result of 0.5 h PBM process. With ball milling time increasing to 4 h,

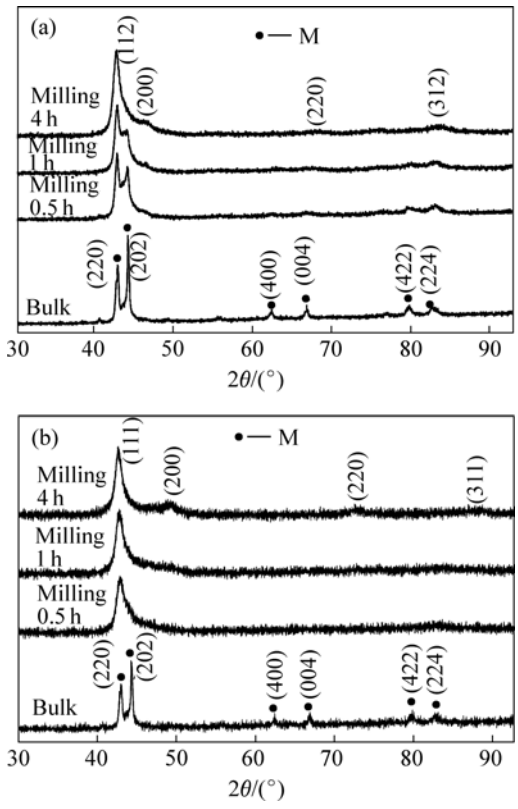


**Fig.2** XRD patterns of bulk samples and ball milled $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ particles by PBM(a) and VBM(b) for different times

some other diffraction peaks have also been found, which can be indexed as disordered fcc structure according to the Ref.[14]. So the structure of particles evolves from 5M tetragonal structure to disordered fcc structure after 4 h VBM. This structural transition from the lower crystal symmetry (tetragonal structure) to the higher crystal symmetry (cubic structure) should be attributed to the severe lattice distortion generated in the VBM process.

It is known that the particles are crushed predominantly under shearing stress in PBM process and under compressing stress in VBM process. The energy of VBM is also larger than PBM. So these two different ball milling conditions may lead to the two structural transition during the ball milling process.

### 3.3 Influence of annealing on structure of as-milled particles

The eligible particles used in smart composites should have the same physical properties as the bulk alloy, so the ball-milled particles are annealed at 600 ℃ for 1 h. The DSC results of bulk, ball-milled particles and annealed particles are shown in Fig.3. As shown in Fig.3(a), the phase transformation peaks of 4 h-PBM-particles disappear in contrast to the bulk materials, and then reappear after annealing at 600 ℃. By calculation the martensitic transformation latent heat of annealed particles is slightly smaller than that of the bulk alloy. The martensitic and reverse transformation temperatures are also very similar to the bulk material. The XRD result for the annealed particles is shown in Fig.4(a), it is evident the diffraction peaks can be indexed to the same crystal structure phase as the bulk, 5M tetragonal martensite phase. So the physical properties of 4 h-PBM-particles can be resumed to the state of bulk material after annealing at 600 ℃ for 1 h. Therefore, these annealed particles are suitable to be used in smart composites.

From Fig.3(b), the phase transformation behavior can not be seen in 4 h-VBM-particles. Moreover, it also doesn't occur when these particles are annealed at 600 ℃ for 1 h, which is different from the result in the annealed 4 h-PBM-particles. The XRD pattern for annealed 4 h-VBM-particles is shown in Fig.4(b). By indexing, the cubic austenite phase exists predominantly in these particles. There are two small peaks which can not be indexed appearing in the two sides of austenite (220) peak. The high energy of VBM has led to the very large deformation of crystal lattice for the alloy. During annealing process, the atoms will gradually adjust to the configuration of Heusler structure by diffusion. But the atom configuration from disordered fcc to Heusler is not complete in the process, annealing at 600 ℃ for 1 h, due to the severe lattice distortion. So the space of some

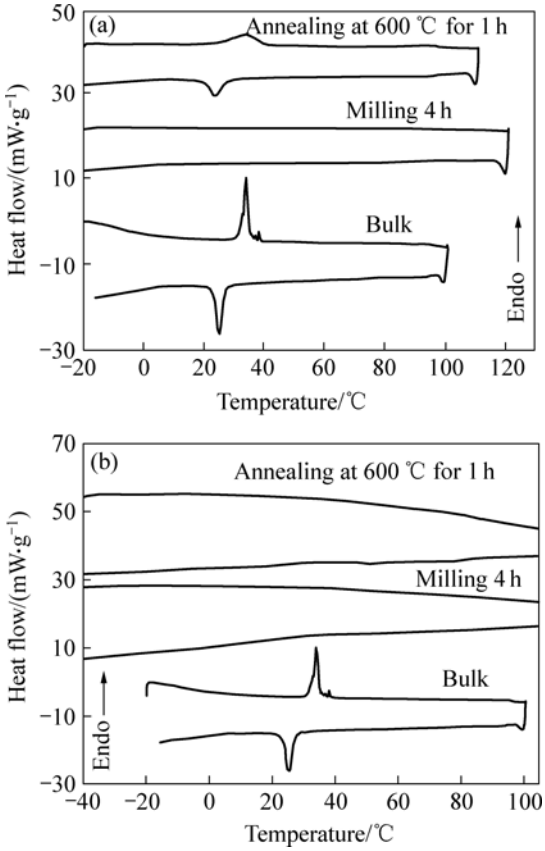


**Fig.3** DSC curves of bulk samples, 4 h as-milled and then annealed at 600 ℃ for 1 h $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ particles prepared by PBM(a) and VBM(b)

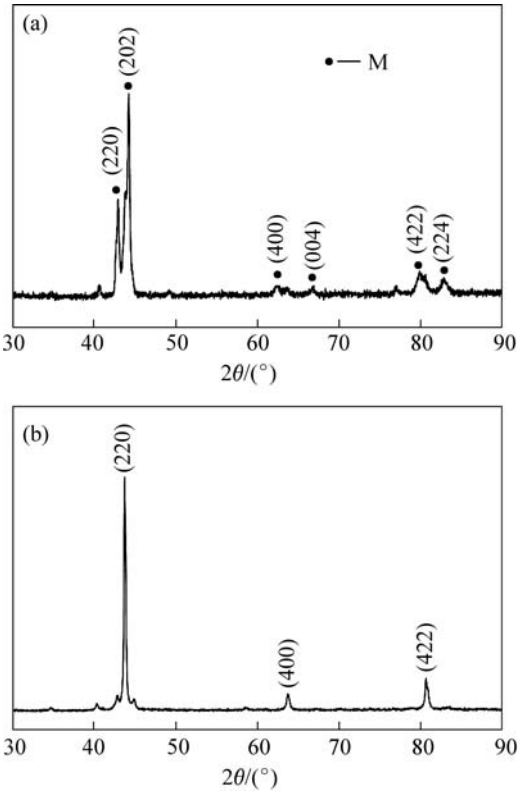


**Fig.4** XRD patterns of annealed $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ particles at 600 ℃ for 1 h prepared by PBM(a) and VBM(b)

crystal faces may be smaller or larger than that of Heusler structure austenite phase (220) crystal face. Hereby, these two corresponding small diffraction peaks can be seen in the two sides of austenite (220) peak. The internal stress will be induced owing to the lattice distortion still existing in the annealed particles, which will influence the martensitic transformation. The result of internal stress inhibiting the intermartensitic transformation has been reported by WANG et al[15]. So the disappearance of martensitic transformation in the annealed 4 h-VBM-particles should be attributed to the internal stress effect. The complete atom configuration of these 4 h-VBM-particles from disordered fcc to Heusler structure should need higher temperature annealing above 600 ℃, or longer annealing time than 1 h at 600 ℃.

According to the above results, it is found that the disordered fct structure in the 4 h-PBM-particles will completely evolve to the Heusler structure after annealing 600 ℃ for 1 h. However, the disordered fcc structure in the 4 h-VBM-particles don't transform to the Heusler structure completely after annealing at 600 ℃ for 1 h. This result is due to the higher severe distortion for the alloy particles caused in VBM than in PBM process.

## 4 Conclusions

1) The polygon $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ alloy particles and flaky shape $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ alloy particles have been fabricated by 4 h PBM process and 4 h VBM process, respectively.

2) The structural transition of the particles from 5M tetragonal to disordered fct structure and from 5M tetragonal to disordered fcc structure have been found during the PBM and VBM processes, respectively.

3) After annealing at 600 ℃ for 1 h, both the disordered fct and disordered fcc structure of the ball milled particles evolve to the Heusler structure.

4) The physical property of ball milled Ni-Mn-Ga particles may retrieve to the bulk state after appropriate temperature annealing. This indicates that these annealed Ni-Mn-Ga particles would be suitable to be used in smart composites.

## References


[1] MURRY S J, MARIONI M A, KUKLA A M, ROBINSON J, O'HANDLEY R C, ALLEN S M. Large field induced strain in single crystalline Ni-Mn-Ga ferromagnetic shape memory alloy [J]. J Appl Phys, 2000, 87(9): 5774−5776.

[2] ULLAKKO K, HUANG J K, KANTNER C, KOKORIN V V, O'HANDLEY R C. Large magnetic-field-induced strains in Ni2MnGa single crystals[J]. Appl Phys Lett, 1996, 69: 1966−1968.

[3] SOZINOV A, LIKHACHEV A A, LANSKA N, ULLAKKO K. Giant magnetic-field-induced strain in NiMnGa seven-layered martensitic phase[J]. Appl Phys Lett, 2002, 80(10): 1746−1748.

[4] MARIONI M A, O'HANDLEY R C, ALLEN S M, HALL S R, PAUL D I, RICHARD M L, FEUCHTWANGER J, PETERSON B W, CHAMBERS J M, TECHAPIESANCHAROENKIJ R. The ferromagnetic shape memory effect in Ni-Mn-Ga[J]. J Magn Magn Mater, 2005: 290/291: 35−41.

[5] JIANG C B, MUHAMMAD Y, DENG L F, WU W, XU H B. Composition dependence on the martensitic structures of the Mn-rich NiMnGa alloys[J]. Acta Materialia, 2004, 52: 2779−2785.

[6] STRAKA L, HECZKO O, LANSKA N. Magnetic properties of various martensitic phases in Ni-Mn-Ga alloy[J]. IEEE Trans Magn 2002, 38(5): 2835−2837.

[7] DONG J W, XIE J Q, LU J, ADELMANN C, PALMSTRøM C J, CUI J, PAN Q, SHIELD T W, JAMES R D, MCKERNAN S. Shape memory and ferromagnetic shape memory effects in single-crystal Ni2MnGa thin films[J]. J Appl Phys, 2004, 95(5): 2593−2660.

[8] PONS J, SEGUI C, CHERNENKO V A, CESARI E, OCHIN P, PORTIER R. Transformation and ageing behaviour of melt-spun Ni-Mn-Ga shape memory alloys[J]. Mater Sci Eng A, 1999: 273/275: 315−319.

[9] FEUCHTWANGER J, MICHAEL S, JUANG J, BONO D, O'HANDLEY R C, ALLEN S M, JENKIS C, GOLDIE J, BERKOWITZ A. Energy absorption in Ni-Mn-Ga-polymer composites[J]. J Appl Phys, 2003, 93(10): 8528−8530.

[10] SCHEERBAUM N, HINZ D, GUTFLEISCH O, MÜLLER K H, SCHULTZ L. Textured polymer bonded composites with Ni-Mn-Ga magnetic shape memory particles[J]. Acta Materialia, 2007, 55: 2707−2713.

[11] SOLOMON V C, MCCARTNEY M R, SMITH D J, TANG Y J, BERKOWITZ A E, O'HANDLEY R C. Magnetic domain configurations in spark-eroded ferromagnetic shape memory Ni-Mn-Ga particles[J]. Appl Phys Lett, 2005, 86: 192503.

[12] TANG Y J, SMITH D J, HU H, SPADA F E, HARPER H, BERKOWITZ A E. Structure and phase transformation of ferromagnetic shape memory alloy Ni49Mn30Ga21 fine particles prepared by spard erosion[J]. IEEE Trans Magn, 2003, 39(5): 3405−3407.

[13] TANG Y J, SOLOMON V C, SMITH D J, HARPER H, BERKOWITZ A E. Magnetocaloric effect in NiMnGa particles produced by spark erosion[J]. J Appl Phys, 2005, 97: 10M309.

[14] WANG Y D, REN Y, NIE Z H, LIU D M, ZUO L, CHOO H, LI H, LIAW P K, YAN J Q, MCQUEENEY R J, RICHARDSON J W, HUQ A. Structural transition of ferromagnetic Ni2MnGa nanoparticles[J]. J Appl Phys, 2007, 101: 063530.

[15] WANG W H, LIU Z H, ZHANG J, CHEN J L, WU G H, ZHAN W S. Thermoelastic intermartensitic transformation and its internal stress dependency in Ni52Mn24Ga24 single crystals[J]. Phys Rev B, 2002, 66: 052411.


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