Giant magnetic-field-induced strain in NiMnGaSi magnetic shape memory alloy prepared by diffusion-reduction

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Abstract: NiMnGaSi alloys were prepared by diffusion-reduction reacting which is a new and simple method. The effect of small mount of Si addition on the martensitic transformation temperature ($T_m$) and strain was investigated. It was found that the addition of Si caused a stronger magnetic exchange interaction leading to higher Curie temperature and giant magnetic field-induced strain. The typical Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy shows high martensitic transformation temperature ($T_m$) of 300K and a 0.56% giant strain measure at a magnetic field of 0.7 T.

1. Introduction

In recent years ferromagnetic shape memory alloys (FSMAS) have attracted increasing attention due to their large magnetic-field-induced strains (up to 10%) and the possibility of using these materials as actuators and sensors[1-4]. FSMAS show magnetic-field-induced strains at room temperature greater than any magnetostrictive, piezoelectric or electrostrictive material, and faster frequency response than temperature-driven shape memory alloys. Some alloy systems have developed up to now, such as Ni-Mn-Ga, Fe-Pd, Fe-Pt, Co-Ni-Ga and Co-Ni-Al alloys. Heusler alloy Ni$_2$MnGa is one of the most promising candidates for magnetically actuated devices due to its low hysteresis, large strains and adjustable transition temperature by composition variation.

The ferromagnetic shape memory alloy NiMnGa has been intensively investigated in recent years as a potential actuator material due to its unique giant magnetic field induced strain, based on the magnetic-field-induce rearrangement of martensitic variants. Because of the promising prospect in the design of a different kind of actuators or sensors, great effort has been devoted to giant magnetostrain in Ni-Mn-Ga Single crystals. NiMnGa alloy is quite limited in application due to a low transformation temperature and high brittles, many ways to improve combination properties of this alloy have been studied.

In general, the Ni$_2$MnGa alloys were prepared by a series of complicated methods such as smelting, directional solidification method[5-7]. But, it is difficult to prepared samples with big size for such as smelting, directional solidification method. Furthermore, in the case of high-frequency alternating applied field, it is a question for the energy loss caused by eddy current. In this paper, A new method is exploited to fabricate Ni-Mn-Ga alloys. NiMnGaSi alloy powder were prepared by diffusion-reduction, then the NiMnGaSi alloy power was bonded and shaped a rod. The structure and magnetic properties of the sample were measured, the effect of little Si addition on the martensitic transformation temperature ($T_m$) and strain was investigated.
2. Experiment

NiMnGaSi alloys were prepared by diffusion-reduction which is a new and simple method. NiO powder, MnO₂ powder, Ga₂O₃ powder, SiO₂ powder and Ca powder were mixed in vacuum according a certain proportion and the mixture was heated in a vacuum stove. In the process of heating, the diffusion-reduction reaction was performed between NiO, MnO₂, Ga₂O₃, SiO₂ and the Ca powder, then Mn, Ga and Si atoms which has been reduced from the oxides diffused immediately to the reduced Ni, then the NiMnGaSi alloy powder was prepared, the powder was flushed with water so that the CaO powder can be eliminated. After a series of heat treatment process, the NiMnGaSi alloy powder was bonded and shaped a rod. The crystal structure of samples at room temperature was confirmed by power X-Ray diffraction using Cu-Kα radiation. The field dependence of magnetization and the temperature dependence of low-field ac magnetic susceptibility were measured by a PPMS measurement system.

3. Results and discussion

Crystal structure of Ni₄₃.₀₃Mn₃₂.₀₇Ga₁₈.₄₈Si₆.₄₃ powder was studied by X-ray diffraction(XRD) using Cu Ka radiation. Figure 1 is the X-ray diffraction pattern of NiMnGaSi alloy, showing the strong peaks of (022), (004) and (224) of the martensitic structure, it is suggested that the martensitic transformation temperature ($T_M$) of the NiMnGaSi alloy is above the room temperature. In general, NiMnGa alloy was limited in application because the martensitic transformation temperature ($T_M$) of the NiMnGa alloy was much lower than the room temperature, while, as shown in figure 1, the addition of Si element into NiMnGa alloy was effective for elevating martensitic transformation point. The mechanism is not clear, the possible explanation is that the smaller Si atoms diffuse into the NiMnGa crystal lattice, as a result, the crystal lattice has a small distortion, thus, the activation energy of martensitic/austenitic transformation would be increased.

![X-ray diffraction pattern of Ni₄₃.₀₃Mn₃₂.₀₇Ga₁₈.₄₈Si₆.₄₃ alloy](image)

**Figure 1.** X-ray diffraction pattern of Ni₄₃.₀₃Mn₃₂.₀₇Ga₁₈.₄₈Si₆.₄₃ alloy

In general, the martensitic transformation temperature ($T_M$) and the Curie temperature ($T_C$) of Ni₂MnGa alloys are much low than room temperature, the low martensitic transformation temperature ($T_M$) and the Curie temperature ($T_C$) is a drawback for potentional applications because the material can not be used at high temperature environment. Temperature dependence of ac susceptibility has been measured over the temperature range from 4K to 300K for Ni₄₃.₀₃Mn₃₂.₀₇Ga₁₈.₄₈Si₆.₄₃ alloy, as shown in figure 2. It is apparent that the martensitic transformation
temperature ($T_m$) is near 300K. For some reason, the temperature dependence of ac susceptibility has not been measured at high temperature exceeds 300 K, but it is obvious that the Curie temperature ($T_c$) is much high than room temperature. This is consistent with XRD result.

![Temperature dependence of low-field magnetic susceptibility measured during heating](image1)

**Figure 2.** Temperature dependence of low-field magnetic susceptibility measured during heating

Powder samples were used for magnetization at 4K, 77K and 300K with a high applied field up to 2T by using the quantum design SQUID magnetometer. Magnetization Curves of the Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy powder measured at 300K was shown in figure 3. Very low hysteresis of magnetization curves and very low magnetic moments were observed. It is well known that the magnetic moments are substantially associated with Mn. The ferromagnetism mainly origiantes from the localized moments of Mn atom, about 4.0 $\mu_B$ per Mn ion, and the moment of Ni is less than 0.3 $\mu_B$, the contribution of Ni atoms is neglected. For the Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy sample, the Mn atoms are superfluous, the excess Mn atoms change the outer electronic structure of the unsubstituted Mn atoms, resulting in a greater decrease of the magnetic moment of the unsubstituted Mn atoms with the increase of Mn content[8].

![Magnetization Curves of the Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy powder measured at different temperature](image2)

**Figure 3.** Magnetization Curves of the Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy powder measured at different temperature
The bonded Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy rod was prepared for magnetic-field-induced-strain (MFIS) measurements. Fig. 4 shows the MFIS measured in the longness direction of the rod as a function of magnetic fields at room temperature. As shown in figure 4, the MFIS of Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy comes to 0.56% at a magnetic field of 0.7T, room temperature. More recently, Murray et. al report a 6% MFIS in Ni$_{47.2}$Mn$_{32.1}$Ga$_{20.5}$ with a compressive stress of 2 Mpa applied orthogonal to the magnetic field$^9$. However, Our MFIS is completely stress-free, and nearly three times as large as that of the typical magnetostriction materials Terfenol-D. In general, a large proportion of martensite variants is reoriented toward one and the same direction in the single crystal, while the grain boundaries obstruct the reorientation in the polycrystal. The improved MFIS in our sample can be attributed to the number of the grain boundaries.

![Figure 4. MFIS of the bonded Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy rod as a function of the magnetic field](image)

Figure 5 shows the scanning electron microscopy photograph of the bonded Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy. As shown in figure 5, the grain size was not symmetrical and many pores were observed. The Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy which has a high porosity due to a wash process leading to CaO grains removal and NiMnGaSi alloy dissolution by the water, exhibits coral-like structure with many pores on the surface of the NiMnGaSi alloy grains. Inside of the bonded Ni$_{43.03}$Mn$_{32.07}$Ga$_{18.48}$Si$_{6.43}$ alloy rod, NiMnGaSi alloy grains were accumulated closely due to the dissymmetrical and porous structure, which results in a large MFIS of the sample. Similar results were reported by several papers$^{10,11}$. 

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4. Summary
Si additive is very effective to elevate martensitic transformation temperatures and improve the magnetic-field-induced strains of the NiMnGa alloy. The magnetic-field-induced strain up to 0.56% with a bias magnetic field of 0.7 T has been obtained in Ni_{43.03}Mn_{32.07}Ga_{18.48}Si_{6.43} alloy.

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Figure. 5 the scanning electron microscopy photograph of the the bonded NiMnGaSi alloy