Investigation on ferromagnetic shape memory alloys

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Abstract

Ferromagnetic shape memory alloys, exhibiting large recoverable strain and rapid frequency response, appear to be promising shape memory actuator material. These materials exhibit large shape memory effect associating with martensitic transformation, and magnetic-field-induced strain in the martensite state. The recent development in researches on NiMnGa, NiFeGa, and CoNiGa in our group is briefly reviewed. The perspectives of the ferromagnetic shape memory alloy are also described.

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1. Introduction

In conventional shape memory alloys, which are paramagnetic, the martensitic transformation underlying the shape memory effect is induced by changes in temperature or stress or both. The same transformation in ferromagnetic shape memory alloys (FSMAs) can be triggered not only by changes in temperature and stress, but also by changes in the applied magnetic field. Therefore, it has attracted much attention as high performance solid-state actuator materials. Many FSMAs systems have been developed from Heusler alloy system, such as Ni$_2$MnGa [1–3], Ni$_2$MnAl [4], Co–Ni–Ga (Al) [5,6], and Ni–Fe–Ga [7,8]. There have been many reports on their structure, magnetic properties, martensitic transformation, magnetically controlled shape memory effect, superelasticity and magnetic-field-induced strains (MFIS). In this paper, we review some specific contributions carried out by Institute of Physics, CAS to this field since 1999.

2. Field controlled-shape memory and magnetostrain

The typical FSMA is Heusler alloy Ni$_2$MnGa with cubic L2$_1$ structure as the parent phase. It is ferromagnetic and exhibits a thermoelastic martensitic transformation at lower temperature, which indicates that the shape memory behavior is possible to be affected by an external field [1]. However, it lasts too long time for people to concern the shape memory behavior in an applied magnetic field. The earliest related observation was reported by Ullakko et al. at MTI in 1996 [2]. After their work, we modified the composition to adjust the operating temperature of the shape memory close to the room temperature and used cold crucible technique to grow single crystals with high performance. Based on these studies, two functional behaviors, the external field-controllable shape memory and the large magnetostrain in NiMnGa FSMA were clearly revealed by our research work in 1999–2001, respectively [3,9,10], as shown in Fig. 1.

3. Dynamics of martensitic transformation

Generally, it is believed that the free samples only exhibit a little strain upon martensitic transformation due to the intrinsic self-accommodation, and the large strain and the magnetostrain are attributed to the preferential orientation of the martensitic variants. But why was a large strain
observed in our free single crystal? Our work revealed that the residual stress caused by the directional solidification during the growth worked as an extrinsic factor imposed on the sample and reduced the intrinsic self-accommodation and establishing a preferential orientation of the variants [9]. The systematical research further indicated that the martensitic transformation is very sensitive to the internal stress. Based on our calculations and modeling, an average internal stress of 13.8 MPa purposely induced in the distorted lattice will force the parent phase to take a totally different martensitic transformation path: which results in the entire suppression of seven-layer modulation (7M) and lead the transition going to the five-layer modulation (5M) directly [11]. The related observations were shown in Fig. 2.

For the thermodynamics of NiMnGa alloy, we calculated the energy consumed for phase boundary motion in a Ni$_{52}$Mn$_{23}$Ga$_{25}$ single-crystalline sample during martensitic transformation using a boundary friction phenomenological theory. It was found that the energy consumed for phase boundary motion is 13.14 J/mol, only a small part of the latent heat of martensitic transformation. Furthermore, the results of transformation loops measured by ac magnetic susceptibility proved that the thermal hysteresis of martensitic transformation is in direct proportion to the volume fraction of martensite. It was also indicated that the thermal hysteresis of martensitic transformation originates from the friction of phase boundary motion [12].

![strain-field curve](image1.png)

**Fig. 1.** Single crystal with modified composition of Ni$_{52}$Mn$_{23}$Ga$_{25}$ exhibited a field controlled-shape memory behavior (left): the magnitude and the sign of the shape memory sample can be controlled by an external magnetic field. The single crystals also showed a large magnetostrain up to 1.2% with 100% free recoverability (right).

![temperature dependence of magnetic susceptibility](image2.png)

**Fig. 2.** Temperature dependence of ac magnetic susceptibility (left). The intermartensitic transformation disappeared when the internal stress was induced in ground powder sample with varying particle size $D$. Inset: the 7M martensite recovered in the powder sample with $D<50$ µm after annealing at 500 °C for eliminating the stress. Right: the different martensitic transforming path examined by XRD for stressed powder (a) and annealed powder (b).
4. New FSMAs

Although large MFIS and transformation strain has been obtained in Ni–Mn–Ga single crystal, the alloys are very brittle, which might restrict their application. In order to improve the magnetic and mechanical properties for the practical application, single crystals of Ni50.5Mn28Fe9Ga24 have been grown. The substitution of Fe for Mn strengthens the magnetic exchange interactions, increasing the Curie temperature to 381 K. The shape memory strain in this pseudoquaternary Heusler alloy increased to 2.4% in zero field and can be enhanced to 4.2% by a field of 1.2 T. A field-induced strain of 1.15% was obtained which only decreased to 0.73% as the temperature was lowered to 170 K. This temperature dependence of the magnetostain is much better than that in undoped samples where a dramatic decrease of MFIS from 1.2 to 0.36% just occurred only as the temperature was lowered from 280 to 250 K. This is a quite successful attempt to improve the material properties by dopant for FSMAs [13]. Further, systematical investigation on quaternary Heusler alloy of Ni50.5Mn28–xFe9Ga24 and Ni50.4Mn28–xFe9Ga24 focused on the structure, martensitic transformation, and magnetic properties. It was found that, substituting Fe for Mn up to about 70%, the pure L21 phase and the thermoelastic martensitic transformation still can be observed in these quaternary systems. Fe dopant dropped the martensitic transformation temperature from 220 to 140 K, increased the Curie temperature from 351 to 429 K, and broadened the thermal hysteresis from about 7 to 18 K. Magnetic analysis revealed that Fe atoms contribute to the net magnetization of the material with a moment lower than that of Mn. The temperature dependence of magnetic-field-induced strains has been improved by this doping method [14].

In 2003, we reported a class of new promising FSMAs of Ni–Fe–Ga synthesized by using the melt-spinning technique [8]. It was verified that the new alloys have a high chemical ordering L21 structure for parent phase at high-temperature and exhibit a thermoelastic martensitic transformation from cubic to orthorhombic structure at low temperature. The stoichiometric Ni3FeGa alloy has a martensitic transformation temperature of 142 K, a relatively high Curie temperature of 430 K, a magnetization of 73 A m2/kg, and a low saturated field of 0.6 T. The textured samples with preferentially oriented grains show a completely recoverable two-way shape memory effect with a strain of 0.3% upon the thermoelastic martensitic transformation. It should be noted the stoichiometric Heusler alloy Ni3FeGa can only be synthesized by melt-spin method, otherwise, the second γ phase would be formed if a normal solidifying way was used. Comparably, the B2 phase of Ni–Fe–Ga can only be obtained when the composition seriously deviates the Heusler compound, as reported by Okawa et al. [7].

This work indicates that the fast-solidifying is an effective way to synthesize some chemical formula of X2YZ in Heusler alloy and avoid forming the fcc disordered structure (γ phase) in the alloys. Some new ferromagnetic Heusler alloys, such as Cu5FeAl and NiFeSb have been successfully synthesized by this way and the characterization was confirmed [15,16].

For the purpose to deeply understand the magnetism and martensitic transformation, we calculated the electronic structures of the Heusler alloy Ni3FeGa for both the cubic and the orthorhombic structures by self-consistent full-potential linearized-augmented plane-wave method. The localized moment of Fe atom is interpreted based on the electronic structure and the popular explanation of the localized moment of Mn in Heusler alloy X2MnY. Comparing the density of states of cubic and orthorhombic structures, we observed that a Ni peak near the density of states of d band for the cubic structure splits for the orthorhombic structure, indicating a band Jahn-Teller mechanism responsible for the structural transition. Accompanied by this transformation, an increase of Ni moment and magnetization redistribution occurred. Temperature-dependence anisotropy field shows an evidence of martensitic transformation between 125 and 190 K. The magnetic behavior seems to contain a transition from Heisenberg-like at temperature below 70 K to itinerant magnetism at temperature higher than 160 K upon martensitic transformation. Temperature dependence of saturation magnetization reveals the spontaneous magnetization at martensite and parent phase are 3.170 and 3.035 μB, respectively. The calculated magnetic moment at martensite is 3.171 μB, which is quite consistent with the experimental value. The magnetic moment of Fe and Ni atom in Heusler alloy Ni3FeGa is analyzed based on the computational results and the experimental magnetization curves. It is found that the magnetic moment of Fe atoms is about 10–43% larger than that of z-Fe [17].

For other FSMAs, we studied the field-controlled shape memory [18] in single crystals of CoNiGa. We obtained that two-way shape memory with 22.3% strain has been obtained in free samples. By applying a bias field of up to 2 T, the shape memory strain can be continuously controlled from negative 2.3% to positive 2.2% giving it a total strain of 4.5%. This work proved that CoNiGa is a good shape memory material working at relatively high-temperature of up to 450 K and has a lower magnetic anisotropy than NiMnGa.

Other workers have reported that CoNiGa alloys have a good superelastic property. In order to develop it for the practical application, we doped Fe in the single crystal of Co50Ni2Ga28: Fe (x = 0, 1.5, 2, 2.5) single crystals. It resulted in that the samples showed strong anisotropic superelasticity behaviors, including the varied strains, superelastic parameters and even transformation path related to the different crystalline orientations under compression. A large superelastic strain up to 11% has been obtained in tension test. The iron-doped materials also displayed perfect superelasticity under bending and torsion [19].
5. Micromagnetism of Ni–Mn–Ga Heusler alloys

In view of micromagnetism, we studied the first in situ observation of temperature-dependent micromagnetic and twin structure in oriented single crystals of Ni–Mn–Ga Heusler alloys. Micromagnetic measurements were made over a temperature interval of 50 to −35 °C covering both forward and reverse martensitic transformation. Magnetic domains in the martensite phase were found to be uniformly spaced (25–30 μm); the direction of the domain walls conforms to the changing direction of the magnetic easy axis as they traverse from one twin to another. The martensite twins could be reoriented in applied fields as low as 1300 Oe [20].

6. Half metallic materials

In Heusler alloy X₂MnZ, the separation of the Mn ions (> 4 Å) is too large for direct d–d coupling. Thus, the magnetic interaction is thought to arise from an indirect interaction that takes place by means of the polarization of the conduction electrons. Electronic band-structure calculations have predicted the existence of half metals, with a perfectly spin-polarization (~ i.e. P = 100%). Notable among the half metallic candidates are a number of the Heusler alloys [21]. We investigated on structural, magnetic, transport, and spin-polarization measurements of the Heusler alloys Co₂MnSi and NiMnSb. Room temperature transport measurements showed a negative magnetoresistance in NiMnSb. Point-contact Andreev reflection measurements of the spin polarization yield polarization values for Co₂MnSi and NiMnSb of 56 and 45%, respectively. Temperature dependence of resistivity for Co₂MnSi reveals a relatively large residual resistivity ratio (r293 K/r5 K) typical of single-crystal Heusler alloys. In NiMnSb, resistivity and magnetization as a function of temperature show evidence of a magnetic phase transition near 90 K [22].

7. Magnetostrictive materials

As mentioned above, we found the high chemical ordering could be achieved by a fast-cooling solidifying method. This method was also used for other magnetostrictive materials. Magnetostriction of Fe–Al alloys has been largely improved by using melt-spun method. The large magnetostriction up to −700 ppm obtained in Fe₇₅Al₁₅ sample is about five times as large as that in conventional bulk samples of Fe–Al composition [23]. It has been ascribed to the high concentration of Al–Al atom pairs created by melting–spinning method and their strongly preferential orientation in [100] textured ribbon plane. The remarkable anisotropic magnetostriction reflects the magnetoelastic competition occurring in those strong textured and thin ribbon samples. For Fe₆₅Ga₁₅ alloys, large magnetostrictions up to −1300 and +1100 ppm related in the different directions were obtained in our stacked Fe₆₅Ga₁₅ ribbon samples, as shown in Fig. 3 [24]. In the case of non-180° domain magnetization in the high anisotropic samples, the magnetostriction was mainly attributed to the existence of Ga clusters which preferentially orient with the ribbon normal due to the ribbon grain texturing. Forming the modified DO₃ structure, the Ga–Ga atom pairs distribute in the matrix and cause the X-ray diffraction peak split in melt-spun ribbons. As a special micromorphology, Ga clusters highly condensed in some nanoscale dots have also been experimentally observed for the first time, as shown in Fig. 4 [24].

8. Large magnetoresistance in quaternary Heusler alloy Ni–Mn–Fe–Ga

Quaternary Heusler alloy Ni₅₀Mn₃₀Fe₁₀Ga₂₅ ribbons have been prepared by melt-spun method. The ribbons exhibit large negative magnetoresistance up to 9% over a wide temperature region, particularly in the region during the martensitic phase transformation. MR decreases significantly after annealing. The large MR is isotropic and is mainly attributed to the local magnetic disorders, magnetic clusters and heterogeneity. The maximum MR at martensitic transformation may be due to the redistribution of electrons and the increase of phase

![Fig. 3. Magnetostriction measured from the stacked sample along the ribbon length direction (a) and thickness direction (b).](image-url)
9. Conclusions

Investigation on ferromagnetic shape memory alloys has been carried out by our research group since 1999. Some interesting results on the magnetostrain, field-controlled shape memory, superelasticity, magnetostriction and magnetoresistance have been obtained. It was found the fast-solidifying is an effective way to synthesize some Heusler alloy. By this way, some new Heusler alloys with ferromagnetic shape memory effect have been successfully synthesized. These studies indicate that FSMAs is a very useful functional materials and a potential source for farther research in the fields of physics and material science. We will keep hunting for new candidates for actuator materials in this field and promise to report new FSMA in very close future.

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