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Stress-free two-way thermoelastic shape memory and field-enhanced strain in $Ni_{52}Mn_{24}Ga_{24}$ single crystals

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Stress-free and two-way thermoelastic shape memory, with 1.2% strain and 6 K temperature hysteresis, has been found in single crystalline $Ni_{52}Mn_{24}Ga_{24}$. The deformation can be enhanced more than three times, up to 4.0% shrinkage with a bias field 1.2 T applied along the measurement direction, or changed to 1.5% expansion by the 1.2 T applied perpendicular to the measurement direction. For achieving a large deformation, the magnetic field exhibits a more evident contribution than an external stress on this material. These characteristics can be attributed to the low level of internal stress and the preferential orientation of the martensitic variants. © *2000 American Institute of Physics.* [S0003-6951(00)02246-4]

Ferromagnetic Heusler alloy Ni_2MnGa has been attracting interest as potential actuator material. This material exhibits shape memory effect associating with the martensitic transformation,[1] superelasticity,[2,3] and magnetic field-induced strain[4–6] in the martensitic state. Various micromagnetic models have been established based on the experimental observation,[7,8] which indicated that the preferential orientation of martensitic variants plays an important role in the field-induced macroscopic strain. In the previous work, external stress was usually used to promote this preferential orientation and to obtain a large transformation strain for shape memory.[9] In this letter, we report a completely *stress-free* two-way thermoelastic shape memory behavior in $Ni_{52}Mn_{24}Ga_{24}$. The results indicated that an approximately treated single crystal sample would provide a good material exhibiting magnetic-field tuned strain. Thus, a field-enhanced or field-controlled shape memory material is attained.

The composition of $Ni_{52}Mn_{24}Ga_{24}$ was slightly deviated from a stoichiometric Heusler alloy, Ni_2MnGa, in order to raise the martensitic transformation temperature to room temperature.[9,10] The single crystals were grown in [001] direction of the cubic parent phase by the Czochralski method.[5] A two-step postgrowth treatment was adopted: as-grown crystals were annealed at about 800 °C for 24 h for high chemical ordering,[11] then cooled to 500 °C quickly by compressed air and annealed at this temperature again for 24 h for eliminating disordering residual stress caused by the quick cooling. A sample was cut having thickness in the [100], [010] and [001] (growth) directions of 9, 2, and 12 mm, respectively. The metal strain gauges with maximum measurement of 5% and the highly elastic epoxy resin were utilized to ensure measurement reliability and avoid the gauge debonding.

Figure 1 shows the strain-versus-temperature curve in the [001] and [100] directions, respectively, without an applied field or a stress. In the cooling run, the martensitic transformation occurs at about 286 K and shrinks the sample about 1.2% in the longitudinal [001] direction, while the sample expands about 0.6% in its lateral [100] direction. In the heating run, the reverse martensitic transformation occurred at about 292 K and the deformation is completely recovered by transformation strains with the same magnitude. One can see that the Heusler alloy $Ni_{52}Mn_{24}Ga_{24}$ exhibited a complete two-way shape memory effect with quite a large strain of 1.2% and a narrow temperature hysteresis of 6 K, notably without the assistance of external stress or a magnetic field. This complete shape memory was reproduced in many circles. For the comparison, Fig. 1 also shows the strain-versus-temperature curve from a polycrystalline

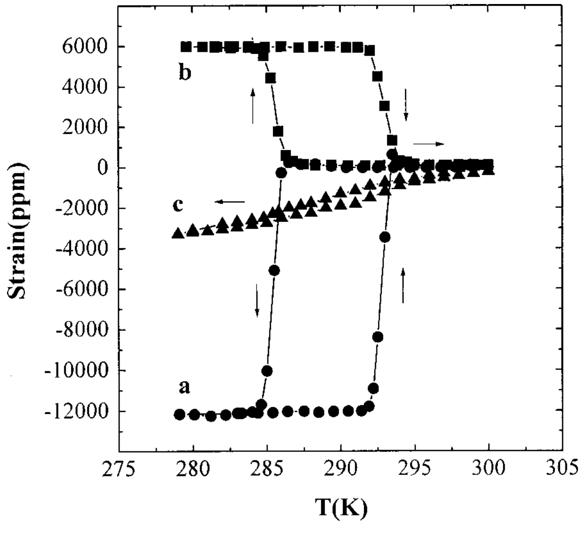

FIG. 1. Strains-vs-temperature curves of $Ni_{52}Mn_{24}Ga_{24}$ free sample measured in [001] (a) and [100] (b) directions of single crystal and polycrystal (c).

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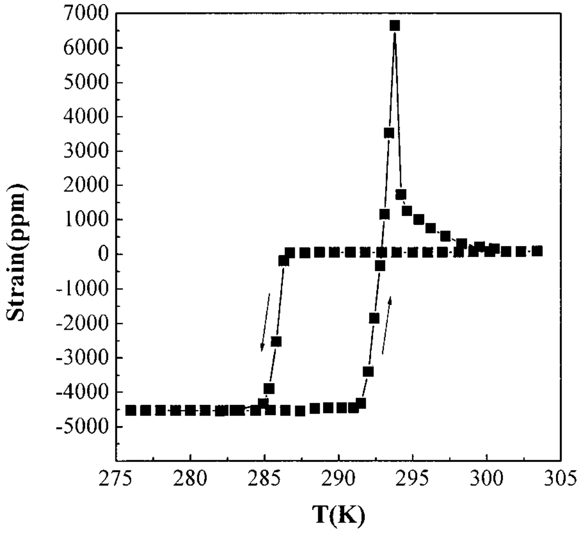

FIG. 2. Strain-vs-temperature curve measured in a single crystal sample which was directly quenched from 800 °C in ice water without a further annealing at 500 °C.

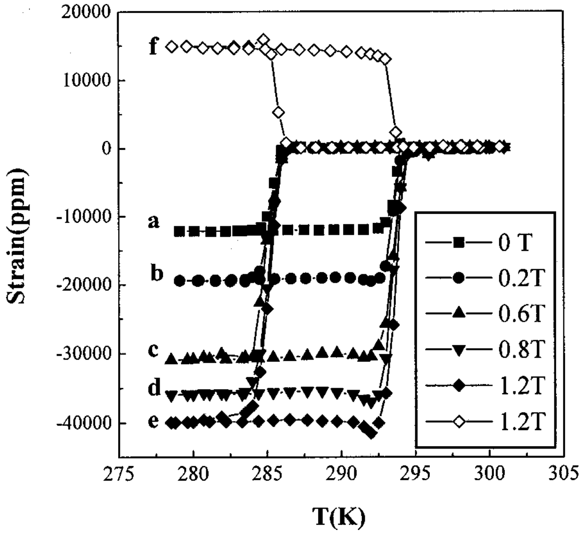

FIG. 3. Strain-vs-temperature curves measured without a field bias (a), and with various field biases applied in [001] direction [(b)–(e)] and in [100] direction (f), respectively.

sample [curve (c)]. No sign of a large strain can be found during the phase transition. The polycrystalline sample cannot achieve a preferential orientation of the martensitic variants related to the geometric shape of the sample.

The longitudinal [001] and lateral [100] directions in our single crystalline samples are crystallographically equivalent for martensitic variants. As mentioned above, no shape memory treatment, such as cold drawing or hot rolling, was deliberately adopted for the samples. As shown in Fig. 1, however, the shape deformation behaviors in these two directions are quite different. It implies that an extrinsic or technical factor might have been imposed on the sample, which worked as a shape memory treatment for reducing the intrinsic self-accommodation and establishing a preferential orientation of the variants. Furthermore, we have found that the direction in which the shape memory has the largest strain is invariantly the [001], the growth direction of crystals, as shown by the curve (a) in Fig. 1. Therefore, it is reasonable to believe that the residual stress caused by the directional solidification during the growth is the origin for the preferential orientation of the variants in our crystals. It is analogous to some mechanical treatments to induce some directionally internal defects or stresses in some shape memory alloys.[12]

In order to explore the influence of the internal stresses, a special sample was treated by directly quenching into ice water after 24 h annealing at 800 °C and without further annealing at 500 °C, to induce disordering (nondirectionally) internal stress in the sample on purpose. As shown in Fig. 2, the strain is dramatically decreased to only 0.4%, implying that the preferential orientation of the variants has been potentially reduced by the disordering internal stresses. It is interesting that the strain appears as an instantaneous rebound with a net value about 1.2% during the reverse transformation. This asymmetrical shape deformation implies that, with the sample under disordering internal stress condition, the phase transition might take different paths in the whole temperature cycle.

The strain-versus-temperature curves were also taken *in the [001] direction* of the sample with a biasing magnetic field applied along [001], the strain-measuring direction. It has been found that the two-way shape deformation can be enhanced up to three times by the biasing magnetic field. As shown in Fig. 3, the strain in the [001] direction increases from 1.2% to 4.0% with the bias field from 0 to 1.2 T [curves (a), (b), (c), (d), and (e)]. At about 1.2 T, the strain saturates. The net strain enhanced by the field of 1.2 T is $4.0\% - 1.2\% = 2.8\%$, which is much larger than the maximum strain 1.2% from the free sample without a bias field [curve (a)]. This result indicates that the magnetic field can drive more variants to further orient in the field direction. Therefore, an opposite shape deformation with a strain of 1.5% [curve (f)] can be obtained by changing the field *laterally*, to the [100] direction of the sample. In this way, a four-stroke shape-memory device may become possible by using a multi-pole electromagnet.

Based on Kokorin and Martynov's work,[3] an initial prestress about 40 MPa was needed to initiate the twin boundary motion and then 6.5 MPa more external stress was required to create a strain of 2.3%. The later is corresponding to a mechanical energy in the order of 2.3×10^6 erg/cm^3. However, magnetic anisotropy energy density,[4] $M_s H_a/2 \approx 1.17 \times 10^6$ erg/cm^3, is just enough to obtain the same net strain in this work [Fig. 3, curve (d)]. It is apparent that the magnetic field is more effective to achieve a large strain shape memory than an external stress in our sample, due to the large difference in magnetic anisotropy energy between two phases of this material.[4,13,14] It is possible that part of external stress was used to overcome the internal stress or induce a phase transition simultaneously. As shown in Fig. 3, however, even the largest field of 1.2 T does not have a significant influence on the phase transition temperature and the temperature hysteresis. This indicates that the mechanism of field-enhanced strain in this material is the twin boundary motion.[8] The field energy, at the magnitude used in this study, is not involved in the free energy of phase.

In summary, the stress-free and complete two-way thermoelastic shape memory behavior, with a large strain 1.2% and a temperature hysteresis of only 6 K, has been found in single crystal $Ni_{52}Mn_{24}Ga_{24}$. The shape deformation can be enhanced by a bias magnetic field of 1.2 T, to shrink the sample 4% with the applied field parallel to the [001] direction, or to expand the sample 1.5% with the applied field perpendicular to the [001] direction. These results originate from the low level of disordering internal stress within the single crystal and the magnetic characteristic of Heusler alloy $Ni_{52}Mn_{24}Ga_{24}$. The magnetic field works more effectively to achieve a large strain shape memory than an applied external stress in this material. Under application of an external stress of 102 MPa, the mature shape memory material of Ti 50.2 at. % Ni cold-drawn and annealed wire can provide a two-way shape memory with the same strain based on B2-R-B19′ transformation with a much larger temperature hysteresis about 40 K.[15] By comparison, $Ni_{52}Mn_{24}Ga_{24}$ may become a shape memory material to design a shape memory device with more actuation freedom controlled by an electromagnet.

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