JOURNAL OF MATERIALS SCIENCE **39** (2004) 2557–2559

# New approach to preparing unidirectional NiMnFeGa magnetic shape memory alloy

H. X. ZHENG, W. Z. MA, Y. Y. LU, M. X. XIA, J. G. LI*
*School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China*
*E-mail: lijg@sjtu.edu.cn*

$Ni_2MnGa$ has attracted a great deal of attention for application in actuators [1]. Magnetic-field-controlled strains as large as 6% in the single crystal $Ni_2MnGa$ have been reported [2]. Webster [3] reported that the cubic structure of the high temperature phase had no magnetic anisotropy and the tetragonal low temperature phase had magnetic anisotropy. Magnetic shape memory alloys are smart materials which can undergo large reversible deformations in an applied magnetic field [4]. For some time, active materials have been studied and developed for applications such as actuators, sensors, vibration dampers, underwater sound projectors, and surface control systems. However, the most common actuator materials currently in use have several drawbacks. Shape memory materials capable of giving high strains are actuated by heating or cooling, a relatively slow and inefficient process that produces little work [5]. Terfenol-D gives a strain of about 0.2% in a magnetic field of a few thousand Oe, but rare earth metals are expensive [6]. PZT gives a strain of about 0.1% in an electric field of several hundred V/cm. While this material is an insulator that can be used at higher frequencies than metallic Terfenol-D, PZT is an oxide and thus brittle [7]. Features similar to the one observed in $Ni_2MnGa$ have been reported in other alloys, such as Ni-Mn-Al, Fe-Pd and $Fe_3Pt$. However, practical applications of these alloys are limited because of several problems, such as their extreme brittleness in the polycrystalline state and the high cost of constituent elements [8–10].

Recently, some new groups of magnetic shape memory alloys in Co-Ni-Al, Co-Ni-Ga, Ni-Fe-Ga and Ni-Mn-Fe-Ga system have been developed [11–14]. The present studies concentrated on the basic magnetic properties, martensitic transformation of single crystal or as-cast alloys, and few reports on how to prepare bulk practical engineering alloys were found. Unidirectional solidification technique is a promising crystal growth method to prepare new materials and improve the performance of traditional materials [15]. In the article, we report on an experiment in the unidirectional growth of $Ni_{51.2}Mn_{20.0}Fe_{13.0}Ga_{15.8}$ magnetic shape memory alloy using a self-design super-high temperature gradient unidirectional solidification apparatus, and the orientation of martensitic variants along the crystal growth direction is investigated.

$Ni_{51.2}Mn_{20.0}Fe_{13.0}Ga_{15.8}$ master rods with the dimensions of $\phi 7$ mm $\times$ 120 mm were prepared by the induction melting method using high purity elements in argon atmosphere, the method has been described elsewhere [16]. The master rod is then contained in a high purity and thin wall $Al_2O_3$ crucible, of internal diameter 7.1 mm and length 150 mm, and fixed in the middle of a pancake induction coil. High purity argon gas was backfilled into the chamber three times after the vacuum system was evacuated to $2 \times 10^{-3}$ Pa, and the high purity argon atmosphere in the chamber was 0.08 MPa. An approximately 5 mm long molten zone was formed by heating with the pancake coil driven by a 175 KHz current. After the zone melted fully, the $Al_2O_3$ crucible was lowered with a velocity of 6.0 $\mu$m/s. The temperature gradient of liquid/solid interface was maintained at about 800 K/cm, the temperature of the molten zone was monitored by an infrared pyrometer. The sample was quenched into Ga-In-Sn liquid metal. The Schematic diagram of this super-high temperature gradient unidirectional solidification apparatus is given in Fig. 1. The unidirectional sample obtained was sealed in a

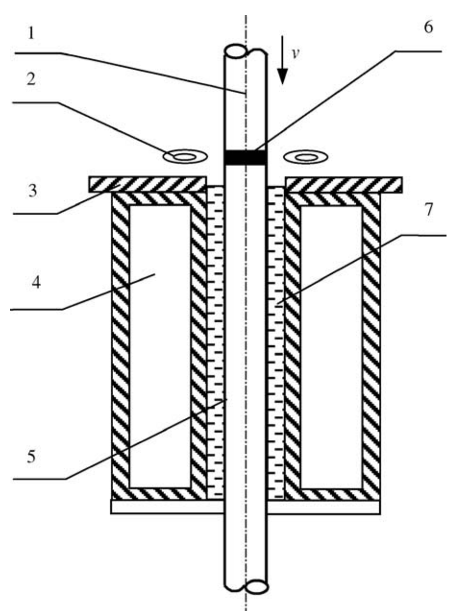


*Figure 1* Schematic diagram of super-high temperature gradient unidirectional solidification apparatus. 1-specimen 2-induction coil 3-insulator 4-cooling water 5-crucible 6-melting zone 7-liquid metal.

*Author to whom all correspondence should be addressed.


*Figure 2* Macrostructure of unidirectional NiMnFeGa alloy.

vacuum quartz capsule and heat treated at 1073 K for 96 h in order to homogenize and produce the ordered crystal structure. After heat treatment, the capsule was quenched into ice water.

Specimens were cut along the crystal growth direction and microstructure observation was carried out using a Neoplot-1 optical microscope. Specimens were etched with 4% nitric acid solution. The phase transformation temperatures were measured by a Perkin-Elmer differential scanning calorimeter with heating and cooling rates of 20 K/min.

Fig. 2 is the macrostructure of a unidirectional sample and Fig. 3 is the microstructures of the NiMnFeGa alloy. For solidification in normal conditions, we observed equiaxed grains with randomly aligned martensitic variants, with the $\gamma$ phase distributed in the matrix (Fig. 3a). For solidification under unidirectional conditions, along the crystal growth direction the microstructure exhibited an obvious columnar grain structure with axially aligned martensitic variants, and the $\gamma$ phase also changed into discontinuous ribbons (Fig. 3b). When the crystal grew into the steady growth zone, the microstructure consisted of columnar grains completely (Fig. 3c and d) and martensitic variants inside the grains were parallel to the crystal growth direction. The $\gamma$ phase was refined and distributed homogeneously (Fig. 3e). The microstructural characteristics of cross section resembled that of longitudinal section (Fig. 3f).

Solidification in a magnetic field is a novel process which can produce oriented materials. Due to the magnetocrystalline anisotropy, grains orient during

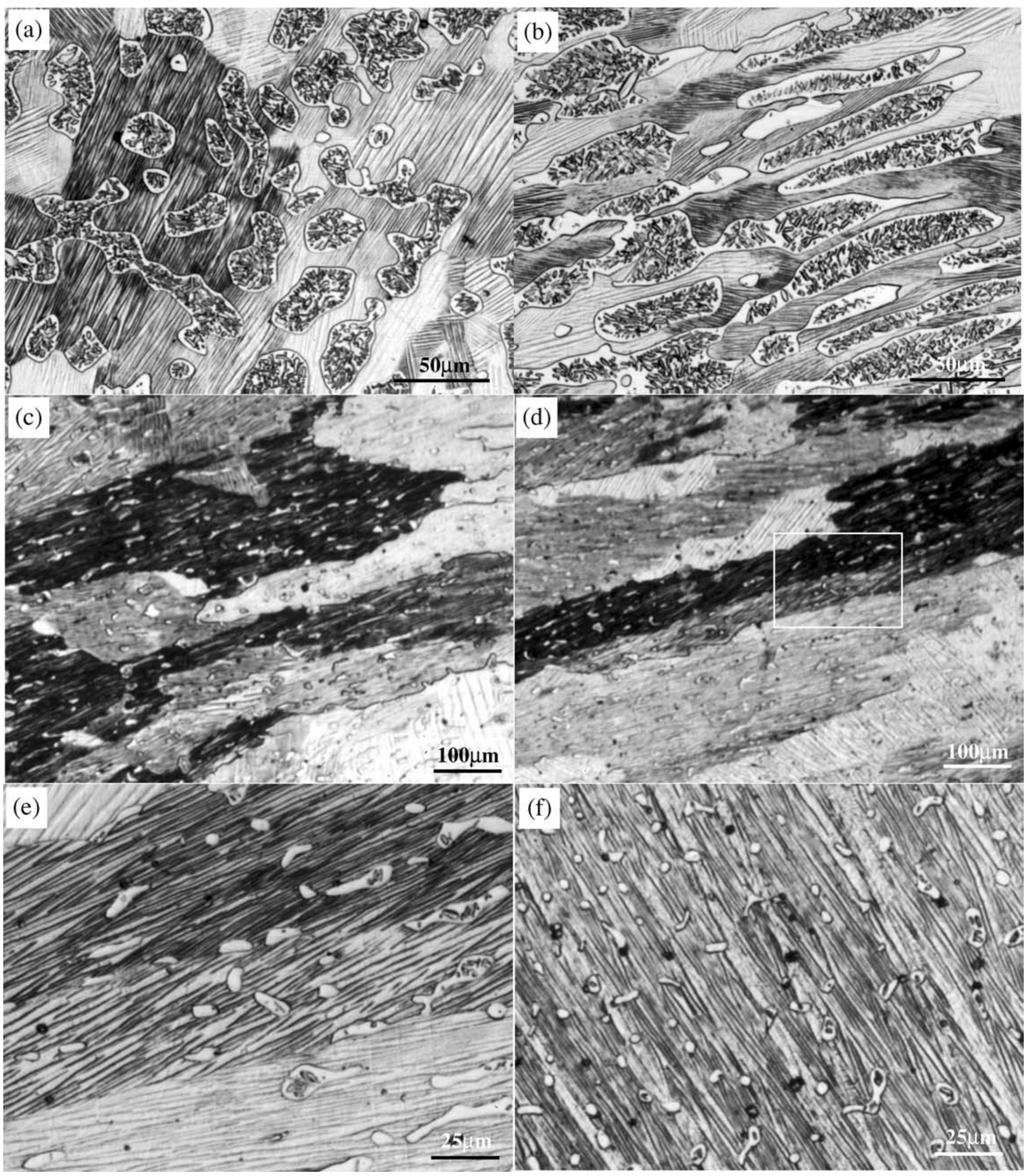


*Figure 3* Microstructures of NiMnFeGa alloy along the crystal growth direction: (a), (b), (c) and (d) are the longitudinal microstructures of A, B, C and D marked in Fig. 2e is the enlarged view of rectangle frame marked in Fig. 3d, f is the microstructure of cross section D.

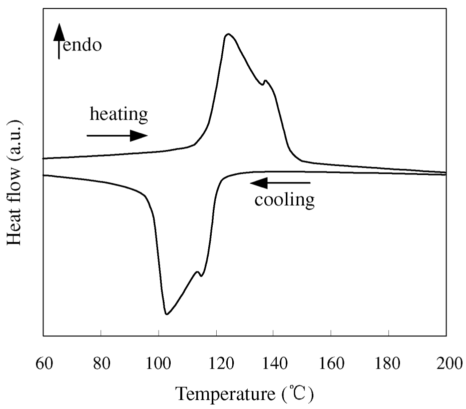


*Figure 4* DSC curve of NiMnFeGa alloy.

solidification with their easy magnetization axis along the direction of the applied magnetic field [17]. Legrand [18] proposed the solidification of molten alloys in a static magnetic field as a new way of orienting polycrystalline materials and prepared $Sm_2Co_{17}$ compound with easy magnetization axis parallel to the direction of the magnetic field successfully. In this work, when the pancake induction coil heated the alloy, it is worth of nothing that a dynamic high-frequency AC magnetic field parallel to the crystal growth direction was produced. The temperature gradient of the solid/liquid interface was as high as 800 K/cm and the axial magnetic field strengthened the vertical convective motion of the melt, promoting a tendency to form columnar grains. On the other hand, the temperature of liquid metal near the solid/liquid interface was approximately 280 K, the axial magnetic filed strongly affected the orientation of the easy magnetization axis of martensitic variants inside the columnar grains, even the orientation of $\gamma$ phase in the primary growth stage (Fig. 3b). However, the interpretation of the orientation of martensitic variants under high-frequency AC magnetic field remains open and more experiments and theoretical considerations are needed.

Fig. 4 shows DSC curve of the NiMnFeGa alloy. During cooling, an exothermic peak was observed in the DSC curve originating from a thermoelastic martensitic transformation, the martensite starting temperature $M_s$ and finishing temperature $M_f$ are 394.3 and 372.3 K. Inversely, during heating, an endothermic peak was observed in the DSC curve originating from the retransformation and the austensite starting temperature $A_s$ and finishing temperature $A_f$ are 391 and 420 K, respectively.

## Acknowledgments
The authors express their appreciation for the financial support of the National Natural Science Foundation of China and the National Science Fund for Distinguished Scholars of China.

## References
1. K. ULLAKKO, J. K. HUANG, C. KANTNER *et al.*, *Appl. Phys. Lett.* **69** (1996) 1966.
2. S. J. MURRAY, M. MARIONI, S. M. ALLEN *et al.*, *ibid.* **77** (2000) 886.
3. P. J. WEBSTER, K. R. A. ZIEBECK, S. L. TOWN and M. S. PEAK, *Philos. Mag.* B **49** (1984) 295.
4. K. ULLAKKO, *J. Mater. Eng. Perf.* **5** (1996) 405.
5. Y. LI, L. CUI, Y. ZHENG and D. J. YANG, *Mater. Sci. Lett.* **20** (2001) 1685.
6. W. MEI, T. OKANE, T. UMEDA and S. ZHOU, *J. Alloy. Comp.* **248** (1997) 151.
7. RABINDRA N. DAS, RANJAN K. PATI and PANCHANAN PRAMANIK, *Mater. Lett.* **45** (2000) 350.
8. H. SHIRAISHI, Y. IGUCHI, K. OHOYAMA *et al.*, *J. Magn. Magn. Mater.* (226–230) (2001) 1081.
9. A. LIKHACHEV and K. ULLAKKO, *ibid.* (226–230) (2001) 1541.
10. V. V. KOKORINA and M. WUTTIG, *ibid.* **234** (2001) 25.
11. Z. H. LIU, M. ZHANG, W. Q. WANG *et al.*, *J. Appl. Phys.* **92** (2002) 5006.
12. Y. LI, C. B. JIANG, T. LIANG, Y. Q. MA and H. B. XU, *Scri. Mater.* **48** (2003) 1255.
13. K. OIKAWA, T. OTA, F. GEJIMA, *et al.*, *Mater. Trans.* **42** (2001) 2472.
14. K. OIKAWA, T. OTA, Y. SUTOU *et al.*, *ibid.* **43** (2002) 2360.
15. H. MINAGAWA, K. KAMADA and H. NAGAI *et al.*, *J. Magn. Magn. Mater.* **248** (2002) 230.
16. C. C. JI, W. Z. MA, J. G. LI and Y. H. ZHOU, *J. Alloy. Comp.* **327**(1/2) (2001) 220.
17. A. E. MIKELSON and Y. K. KARKLIN, *J. Cryst. Growth* **52** (1981) 524.
18. B. A. LEGRAND, D. CHATEIGNER, R. P. DE LA BATHIE and R. TOURNIER, *J. Magn. Magn. Mater.* **173** (1997) 20.

*Received 1 July*
*and accepted 24 October 2003*