Structural Order, Martensitic Transformation and Magnetic Domains in Ni–Fe–Ga Shape Memory Microwire

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We investigate $Ni_{50}Fe_{27}Ga_{23}$ prepared as glass-coated microwires by the Taylor–Ulitovsky method. Temperature-induced martensitic transformation was observed by cooling in liquid nitrogen using optical microscope. From cubic austenite the wire transformed to heavily twinned martensitic phase. The magnetic domain structure (domain size and orientation) and its evolution were observed by magnetic force microscope at the same place after the sample was magnetized in three perpendicular directions. Surprisingly, after various magnetizing the domain structure stayed similar, and changes were minor. This probably happened due to presence of antiphase boundaries on which the domain walls are pinned. The Mössbauer spectroscopy determines the ratio between ten percent of Fe atoms in non-magnetic state and the magnetically ordered phase with $L2_1$ order which is typical for austenite.

1. Introduction

Shape memory alloys are a unique class of materials, which can be readily deformed by applying an external force. Deformation is accompanied by structural transformation leading to the changes of material shape and size (strain). Temperature, stress, or magnetic field can be external stimuli leading to transformation. Shape memory effect is accompanied by existence of two phases that are structurally different. High-temperature phase, called austenite, has usually cubic structure, and low-temperature phase, called martensite, has a crystal structure with lower symmetry. The transformation between these two phases is called thermoelastic martensitic transformation [1]. On the other hand, magnetic field-induced structural transformations are referred to as magnetically induced martensite and magnetically induced austenite depending on the phase that is stabilized in the magnetic field [2]. This group includes the Heusler alloys based on Ni–Fe–Ga. A lot of attention has been paid to this alloy lately, which is shown in published results [3]. The main obstacle is the preparation of single crystalline material with well-defined crystallographic orientation. One of the possible ways to produce high quality samples in a suitable form which provides single crystalline character is the Taylor–Ulitovsky method [4]. This method provides effective quenching of the melt, setting, and checking parameters as: melt temperature, moving speeds of the glass tube and rod precursor, coolant speed, and temperature.

In our previous work we have investigated temperature-induced phase transformation in the Heusler microwire based on $Ni_{50}Fe_{25}Ga_{25}$. Ferromagnetic shape memory alloy $Ni_{50}Fe_{25}Ga_{25}$ is manifested by a structural transition from cubic austenite to monoclinic martensite, as was reported in [5]. Hysteresis loops indicate a different magnetocrystalline anisotropy of both phases. A large change in anisotropy manifests itself in a change in permeability as an inverted function. Here we present the direct observation of martensitic transformation in the single wire and the field-induced changes of magnetic domains at austenitic state and we probe the alloy structural ordering using the Mössbauer spectroscopy.

2. Experimental

The master alloy with chemical composition $Ni_{50}Fe_{25}Ga_{25}$ was prepared using arc-melting of pure elements under argon atmosphere. Glass-coated microwire was fabricated by the Taylor–Ulitovsky method. The experimental analysis was performed on microwire without glass. The glass cover was removed mechanically. The microwire was embedded into the thermosetting resin and then the surface of sample was ground and polished.

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The microstructure and chemical composition of microwire was characterized by scanning electron microscope (SEM) Tescan FERA 3 equipped with an energy dispersive X-ray spectrometer (EDX) EDAX Octane Super 60 mm^2 at room temperature. Optical micrographs were taken using optical microscope ZEISS Axio Imager Z1.m. The twinning in martensitic phase was visualized by differential interference contrast — DIC (known also as the Nomarski contrast). The liquid nitrogen was used to achieve low temperatures ($T < M_S$).

In order to visualize magnetic domains, the magnetic force microscopy (MFM) measurements were used and it was performed on Bruker Dimension Icon ambient AFM microscope using MESP tips (with magnetic CoCr coating).

The images were taken from several areas. In order to obtain well-defined initial magnetic state the magnetic domain pattern was achieved by applying strong local magnetic field ($B^\perp \approx 1.5$ T and $B^\parallel \approx 1$ T) produced by permanent magnet.

The ^{57}Fe Mössbauer spectrum of the sample, consisting of a few hair-thick microwires in a lead shielding, was acquired in a transmission geometry using a constant-acceleration spectrometer equipped with a ^{57}Co/Rh source. The isomer shifts are given with respect to α-iron Mössbauer spectrum at room temperature. The spectra were evaluated using MossWinn® [6] fitting program.

3. Result and discussion

The prepared microwire is austenitic phase at the room temperature and has a strong texture with $[\bar{1}1\bar{2}]$ orientation along the main axis of microwire, obtained from electron backscatter diffraction (EBSD) analysis (Fig. 1). The grinded and polished surface of the sample is smooth and grain boundaries were not observed. The average chemical composition of the microwire is confirmed by EDX analysis to be $Ni_{50}Fe_{27}Ga_{23}$ ($\pm 1\%$).

As indicated by magnetic susceptibility, microwire with similar chemical composition ($Ni_{50}Fe_{25}Ga_{25}$) shows the transformation from austenite to martensite well below the room temperature [5]. To make the transformation visible, we used liquid nitrogen mixed with ethanol to cool the sample. In a short time, the sample was placed under the microscope, and a martensitic transformation from martensite to austenite was observed during heating (Fig. 2). In Fig. 2, it can be seen that austenite is initiated already at the temperature below 208 K ($A_s \approx 208$ K) for $Ni_{50}Fe_{27}Ga_{23}$ microwire.

The size and shape of magnetic domains in austenite has been analyzed using MFM. Figure 3 shows the magnetic domain structure of the same place (area with 70×70 μm^2) of $Ni_{50}Fe_{27}Ga_{23}$ microwire. The microwire embedded in the resin was exposed to a magnetic field in three directions. The first MFM micrograph shows the orientation of magnetic domain on the surface without magnetic field action (Fig. 3a). Here, the magnetic domains are seen as a strongly contrasting maze pattern
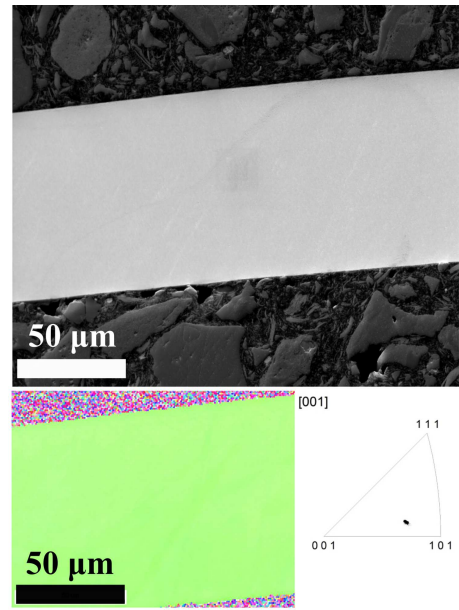

Fig. 1. (Top) SEM micrograph of $Ni_{50}Fe_{27}Ga_{23}$ microwire in the austenitic phase using SE signal, (down) EBSD analysis of $Ni_{50}Fe_{27}Ga_{23}$ microwire showing a single-crystal structure (green belt is sample, whereas spotted areas on the top and bottom represents noise from areas without EBSD signal).
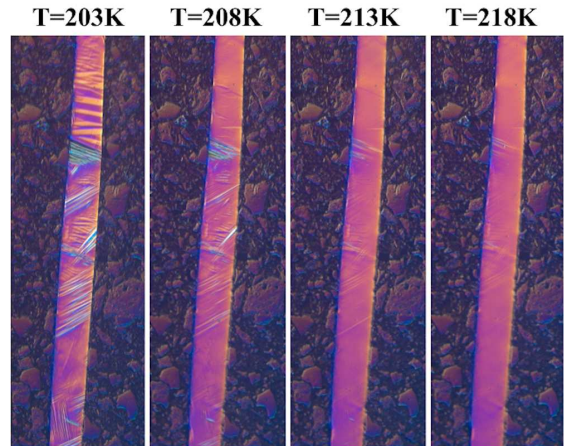

Fig. 2. Optical images of phase transformation from martensite to austenite. The different colors of optical image are due to the Nomarski contrast and indicate the different tilt of the surface in martensitic microwire due to twinning.

which suggests that the magnetization is perpendicular to surface of sample. The other three pictures show how the magnetic domains structure was influenced by the application of relatively strong (saturating) magnetic field (the direction and size of the magnetic field are indicated in Fig. 3) prior to observation. Applying a magnetic field of 1 T parallel to the main microwire axis has led to a slight change in magnetic domains (Fig. 3b). The domain structure are slightly re-oriented in the direction of the
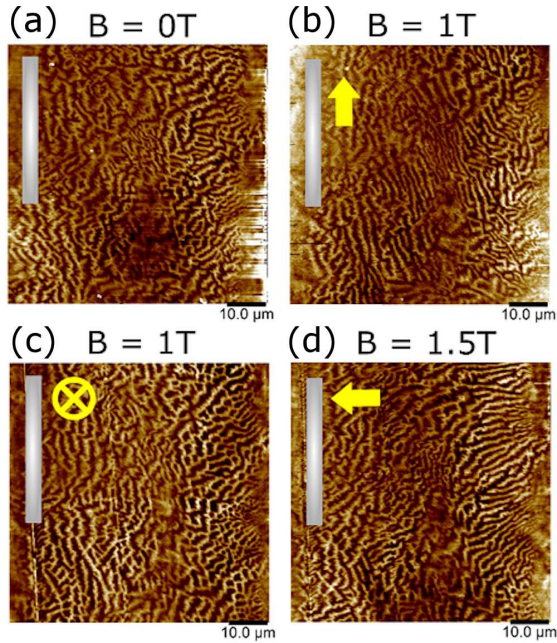
Fig. 3. Micrographs of magnetic domains captured by MFM. Images show the same place of $Ni_{50}Fe_{27}Ga_{23}$ microwire after applying external magnetic field in three orthogonal directions (marked with yellow color) prior measurement.

Fig. 4. The ^{57}Fe Mössbauer spectrum of the microwires acquired at room temperature.

magnetic field application and an average length of domain is 25 μm. Similar slight reorientation occurred when magnetizing in plane but perpendicularly to the wire axis (Fig. 3d). Here the magnetic domains are oriented in the magnetic field direction with average length of 20 μm.

An MFM micrograph of an out-of-plane magnetized sample (Fig. 3c) show maze pattern without any apparent direction. In all cases the magnetization is perpendicular to surface of microwire. The presented observation is puzzling. The austenite has very low cubic magnetic anisotropy and one would expect that owing to demagnetization the magnetization would be in plane and along the wire axis. However, the magnetic domains structure indicates perpendicular orientation of magnetization and moreover, the magnetic domains structure is not affected by external magnetic field applied prior observation. The perpendicular arrangement suggests the presence of strong internal stress in austenite and relative stability of domain structure suggests that the domain walls are pinned on antiphase boundaries. The antiphase boundaries are common in ordered structures as $L2_1$. The pinning on the domain walls on APBs was demonstrated recently for Ni–Mn–Ga [7].

The ^{57}Fe Mössbauer spectrum of the Ni–Fe–Ga microwire is shown in Fig. 4. It has rather unfortunately poor quality owing to the small fraction of the active area of the sample (many microwires pieces lied next to each other). The room temperature Mössbauer spectrum of austenite was fitted with a distributed sextet S1 ascribed to the magnetically-ordered phase $L2_1$ and
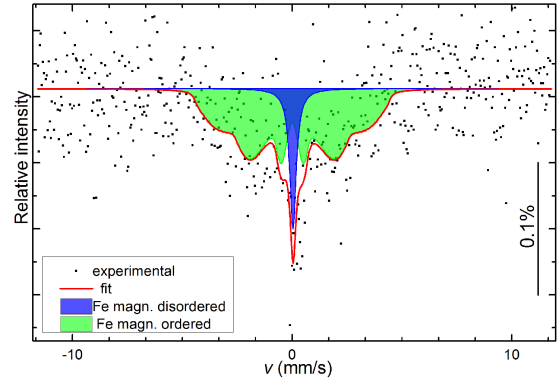
a singlet L1 ascribed to the magnetically non-ordered phase. Assuming the quadrupole splitting QS equals 0, which is well justified for a highly symmetric environment of Fe atoms in such alloy, the sextet S1 with isomer shift $IS = 0$ mm/s and mean hyperfine magnetic field $B_{hf} = 16.9(2)$ T makes approximately 85% percent of the spectrum intensity. The singlet L1 with isomer shift $IS = 0.03(2)$ mm/s is ascribed to the rest of the iron atoms. The presence of the singlet and thus non-magnetic iron is surprising. Fe atoms are probably misplaced from proper $L2_1$ positions, atoms close to surface and atoms sitting within antiphase boundaries. In any case the Mössbauer spectroscopy seems to be suitable tool to probe internal structure of Ni–Fe–Ga Heusler alloy and further investigation is planned.

4. Conclusions

In this work, the Heusler alloy with chemical composition $Ni_{50}Fe_{27}Ga_{23}$ was investigated as a promising candidate of ferromagnetic shape memory alloy. The observation of martensitic transformation was achieved by cooling in liquid nitrogen and ethanol. Optical micrographs show transformation from martensite to austenite phase at the temperature $A_s \approx 208$ K by disappearance of twinning. The prepared microwire is in the austenite phase at room temperature and has strong texture with $[\bar{1}1\bar{2}]$ orientation along the main axis of microwire. A large number of magnetic domains are associated with large austenite permeability. The application of the magnetic field affects the orientation and size of the magnetic domains only slightly. The orientation of magnetic domains on the surface of microwire without magnetic field action and with an out-of-plane magnetized sample shows a maze pattern. Magnetization parallel to the main axis and in-plane of microwire leads to weak re-orientation in the direction of external magnetic field. The Mössbauer spectrum indicate that the environment of Fe atoms in such alloy is highly symmetric as expected for $L2_1$ ordered structure and surprisingly, more than 10% of Fe atoms are non-ferromagnetic.

Acknowledgments

References

[1] J.M. Jani, M. Leary, A. Subic, M.A. Gibson, *Mater. Des.* **56**, 1078 (2014).

[2] O. Heczko, N. Scheerbaum, O. Gutfleisch, in: *Magnetic Shape Memory Phenomena*, Eds. J.P. Liu et al., Springer, New York 2009, p. 399.

[3] Y. Zhu, G. Dui, *Mech. Mater.* **42**, 429 (2010).

[4] L. Galdun, T. Ryba, V.M. Prida, V. Zhukova, A. Zhukov, P. Diko, V. Kavečanský, Z. Vargova, R. Varga, *J. Magn. Magn. Mater.* **453**, 96 (2018).

[5] L. Frolova, J. Mino, T. Ryba, et al., *J. Alloys Compd.* **747**, 21 (2018).

[6] Z. Klencsár, E. Kuzmann, A. Vértes, *J. Radioanal. Nucl. Chem.* **210**, 105 (1996).

[7] L. Straka, L. Fekete, M. Rames, E. Belas, O. Heczko, *Acta Mater.* **169**, 109 (2019).