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Ion polishing as a method of imaging the magnetic structures in CoNiGa monocrystal

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ABSTRACT

Magnetic domain structure of magnetic shape memory alloy was observed using backscattered electron detector in scanning electron microscope and using Fresnel imaging in transmission electron microscope. The sample subjected to additional ion polishing allowed observation of the contrast associated with the magnetic structure of the material under conditions that exclude the use of Foucault or Fresnel transmission electron microscopy imaging. The additional research conducted using atomic force microscopy showed a significant relationship between the method of preparation and the magnetic shape memory alloy sample surface.

Introduction

Magnetic shape memory alloys (MSMAs) are currently under intensive development. Alloys of this type feature a martensitic or austenitic state, where the temperature of the phase transformation is independent and can be different from the temperature of the ferromagnetic to paramagnetic transition. Simultaneous magnetic and microstructural imaging can be thus a powerful tool to shed light on the underlying phenomena and their interaction.

Most popular techniques for imaging the magnetic domain structures are electron holography [1] and Fresnel imaging [2]. Electron holography offers the largest research capabilities, but requires a highly specialized transmission electron microscope [3]. The second method is relatively easy to perform in any transmission microscope, by switching off the objective lens and focusing the image using intermediate lens in a field-free conditions of the sample. This technique required the manual control of lens current and unfortunately provide low resolution images. Only instruments equipped with special low-field objective pole pieces or additional mini-lenses outside the conventional pole piece can provide magnetic observations in true nano scale.

MSMAs have been repeatedly the subject of transmission electron microscopy (TEM) research, but the process of sample preparation in numerous publications has not been sufficiently described – including CoNiGa [4], NiMnGa [5–7] as well as in NiFeGa alloy [8]. Most authors decided to finish the preparation process using electrolytic polishing [9–13]. Some of the researchers decided to conduct finishing ion polishing [14,15] and one team decided to base their preparation only on mechanical and ion polishing [16]. When it comes to conventional metallic materials, ion polishing improves sample surface quality and allows widening the available TEM observation area. Preliminary studies carried out by the author showed that the observed microstructure of the CoNiGa single crystal varies significantly considering different methods of preparation.

Magnetic domain structure of CoNiGa alloys is not as well described in literature as the structure of other types of shape memory alloys, such as CoNiAl [12] or NiMnGa [5,17]. The aim of this article is to reveal the domain structure of $Co_{49}Ni_{21}Ga_{30}$ single crystal in room temperature and to determine the influence of specimen preparation on the TEM images.

Materials and methods

The $Co_{49}Ni_{21}Ga_{30}$ alloy was prepared from pure elements: Co, Ni and Ga by melting in a high frequency induction furnace under high vacuum conditions. Single crystals were subsequently obtained using the Bridgman method and observed in [0 0 1] zone axis.

Scanning electron microscopy (SEM) observations were performed on TEM sample, for confirmation of the presence of magnetic microstructure. The observations were made on tungsten filament JEOL JSM-6610A scanning electron microscope, using backscattered electron detector [18]. The accelerating voltage was experimentally set to 15 kV in case of minimizing the amount of the transmitted beam with still

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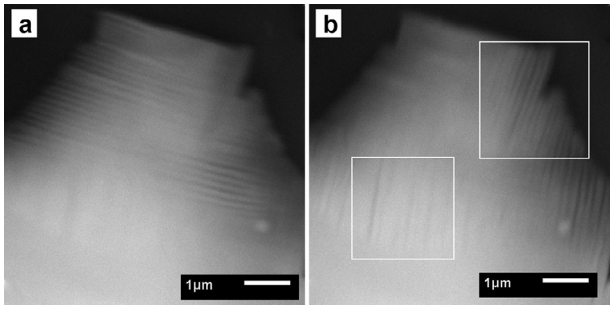

Fig. 1. SEM backscattered electron image of magnetic domain structure of $Co_{49}Ni_{21}Ga_{30}$ single crystal, with the focus plane on the top (a) and bottom (b) surface of thin foil. Frames mark places observed during TEM investigation.

observable magnetic contrast. Emission current was set to 50 μA.

Samples for TEM observations were prepared using mechanical thinning down to 100 μm, followed by electrolytic polishing (Struers Tenupol 5). Additional ion milling (GATAN DuoMill) with 5 kV was applied to investigate the differences in the microstructure. The samples were observed using tungsten filament Hitachi H-800 transmission electron microscope operated at an accelerating voltage of 150 kV and emission current of 160 μA. Observations of magnetic domain structure were conducted in Fresnel mode, which involved objective lens switched off, with manual control of the lens current. Maximum magnetic field in the pole piece gap was measured using Asonik SMS 102 Hall probe magnetometer and amounted to 6 mT. Further observations were performed with objective lens switched on. Observations were also confirmed on the JEOL JEM-100C transmission electron microscope.

Bulk samples for AFM observations were prepared with three different methods. The first sample was prepared using final polishing with 0.5 μm diamond paste, the second one was additionally electropolished in a reagent containing 10% perchloric acid in butoxyethanol, and the last one was subjected to finishing ion polishing using 5 kV and 5 mA in GATAN DuoMill device.

The AFM investigation was conducted on Park System XE-100 atomic force microscope in contact mode. Measurements were carried out in a wide range of scan areas from 40 μm × 40 μm to 500 nm × 500 nm, with the same scanning frequency of 0.5 Hz. All obtained images displayed scanning errors below 2 Å. Further image processing included basic flattening compensating the eventual slopes generated during previously described sample preparation processes.

Results and discussion

$Co_{49}Ni_{21}Ga_{30}$ in the austenitic state (B2 lattice [13]) after mechanical and electrolytic polishing was observed in SEM on the edge of the thin foil allowing the later TEM observations in the same place. Backscattered electron detector in composition mode shows the presence of two domain families. Focusing on the top (Fig. 1a) and bottom (Fig. 1b) part of thin foil shows, that domains exist in two orientations, rotated by an angle of approximately 90°. Distance between dark and bright fringes is approximately 100 nm.

For the purpose of verifying and ascertaining the presence of magnetic structure in the investigated sample, the Fresnel imaging was performed in field-free conditions on the sample prepared in the same way – mechanically and electrolytic polished (Fig. 2). The first intermediate lens of the microscope was used for focusing, which resulted in maximum available magnification level of 1000×. Because of the usage of high-resolution bottom-mounted camera, image can be digitally magnified to the level of 10,000×. Due to thickness of the sample, there was no possibility to extinguish the magnetic contrast in the entire field of view. It was decided to illustrate domain structure from the top layer of the sample (according to Fig. 1b). Under and over focusing from in-focus position showed appearing alternating light and dark fringes (marked with frames on Fig. 2). Their color changes negatively depending on the focus position, which suggests that their position corresponds to the alternating boundaries of magnetic domains. The spacing between dark and white fringes is 100 nm, which corresponds to the value of magnetic domain width. The measured value is in accordance with the previous SEM observations. Domains located on the both sides of the thin foil visually intersect in some regions.

Further TEM observations were performed after additional ion milling, in classical bright field mode, with objective lens turned on. According to the theory of contrast in the Fresnel type, in the strong magnetic field of the objective pole piece domains should be reoriented and invisible. Despite this, the magnetic domain boundaries are visible as dark lines that intersect at an angle of 90° (Fig. 3a). At the intersections regions an unusual contrast with curved contours was observed. Magnetic domains are arranged along {0 0 2} family planes and cross at 90°. Contrast of the magnetic domains has no direct similarities to the Fresnel or Foucault contrast and was not associated with focus position, but is changing as a function of the sample tilt.

The selected area diffraction pattern taken in the place of Fig. 3a shows wide, elongated spots, characteristic to patterns distorted with the internal magnetic field of the sample [2]. The (0 0 2) reflections are deviated outside the central spot and (0 2 0) reflections are shifted inside the pattern (Fig. 3b). Dark field image obtained in the (0 0 2) and spots of SAED pattern do not show any relationship with the domain structure (Fig. 3c) but highlights the curved lines, arranged along the magnetic domains. The dark field images observed in every spot gave similar effect. With the objective lens pole turned on, we managed to register an image qualitatively similar to the domain microstructure of the sample. It leads to the conclusion, that contrast observed in conventional TEM mode cannot be directly associated with the magnetic structure, but with the shape of the sample. The relationship between the tilt of the sample and observed contrast indicates that we are seeing

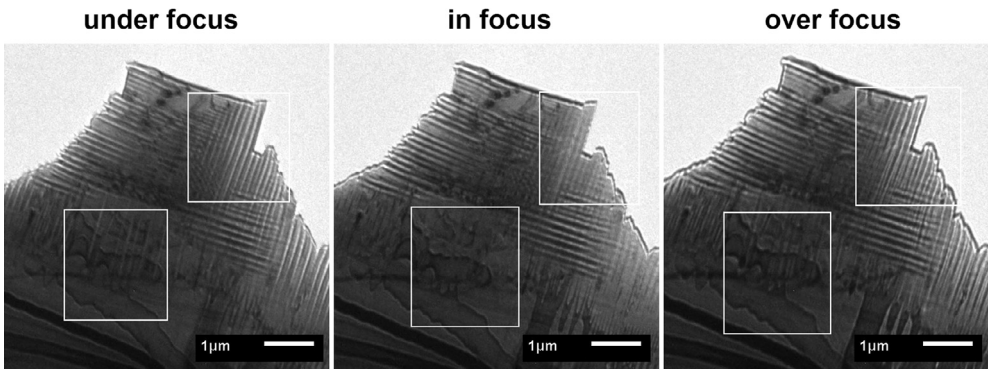

Fig. 2. Fresnel TEM image of magnetic domain structure of $Co_{49}Ni_{21}Ga_{30}$ single crystal in [0 0 1] zone axis. Frames marks places from Fig. 1, showing no contrast in focus position.

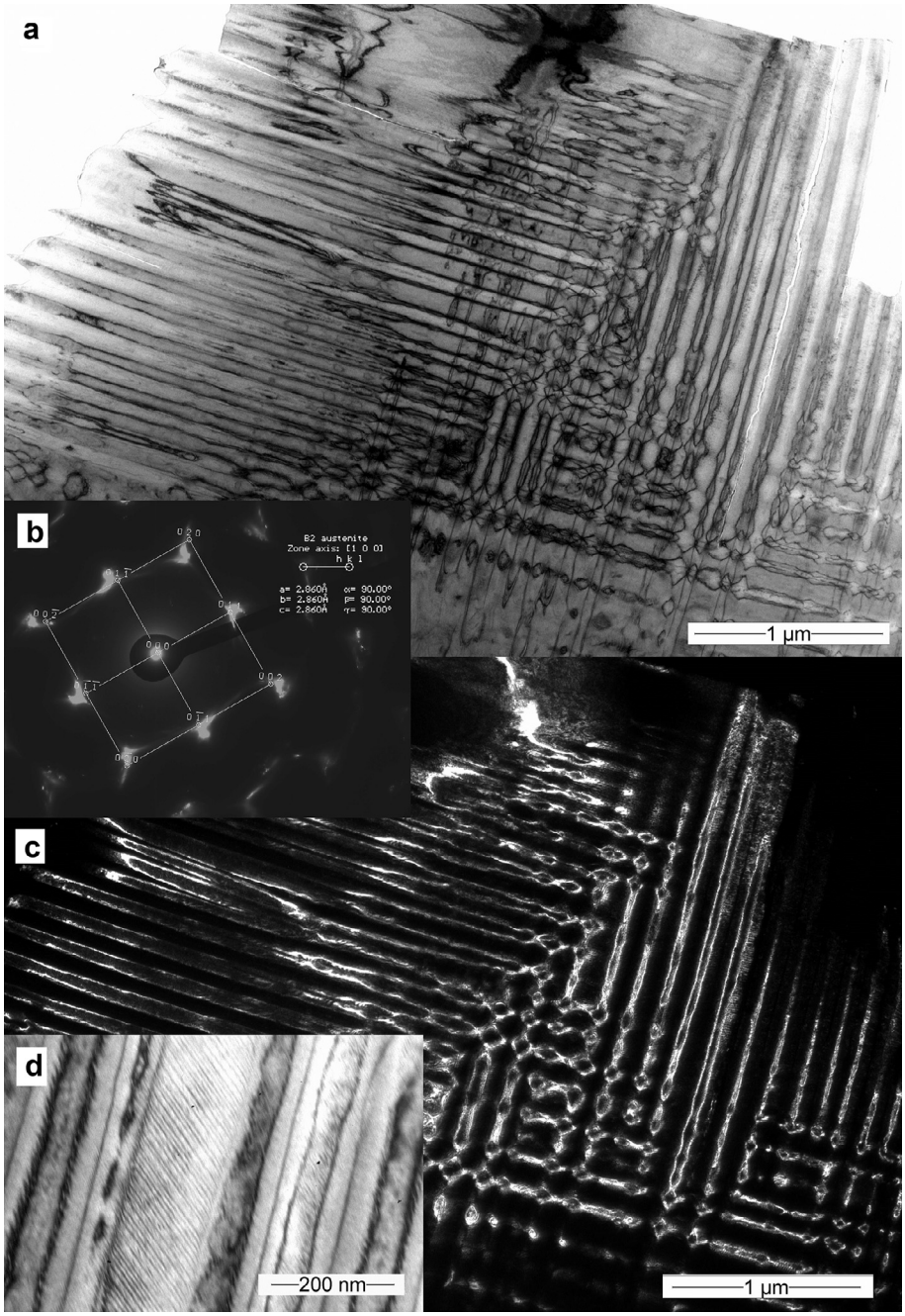

Fig. 3. (a) Bright-field image of $Co_{49}Ni_{21}Ga_{30}$ single crystal in [0 0 1] zone axis after additional ion polishing (b) corresponding SAED pattern and (c) dark-field image in (0 2 0) reflection (d) magnified view of Fig. 3a, showing presence of nanotwinning inside martensite phase.

simple extinction contours, formed in the sample after the ion polishing process. Larger magnification of the image bright-field image shows the presence of the nanotwinning inside the material (Fig. 3d), arranged at an angle of 51° to the parallel magnetic domains boundaries. The new observation method gives the possibility of associating the domain structure with high magnification observations in TEM.

The AFM observations was performed to confirm the surface morphology change after performing additional ion polishing and to justify the visibility of the magnetic contrast in the conventional, non-Lorenz TEM. Bulk $Co_{49}Ni_{21}Ga_{30}$ single crystal surface after mechanical, electrolytic and ion polishing showed significant differences. The mechanically polished sample shows shallow traces of diamond grains, and the maximum deviation from the mean value was $-18/+11$ nm for the scan area of 2.5 μm × 2.5 μm. For the electrolytic polished sample the measurements depict any oriented structures with the slight height deviation value of $-2/+3$ nm. Ion milled sample showed significant change of surface morphology, with the highest height deviation value of $-70/+80$ nm. Furthermore, the investigated surface shows a clear directionality and predominant distance of about 100 nm between elongated slopes. The broadest observed features were 200–300 nm wide. It distinctly corresponds with contrast observed in TEM images, but without previously described unequivocal, orthogonal arrangement. A probable explanation for this fact is that the sample for the AFM was polished on one side when the TEM sample was polished on both sides (Fig. 4).

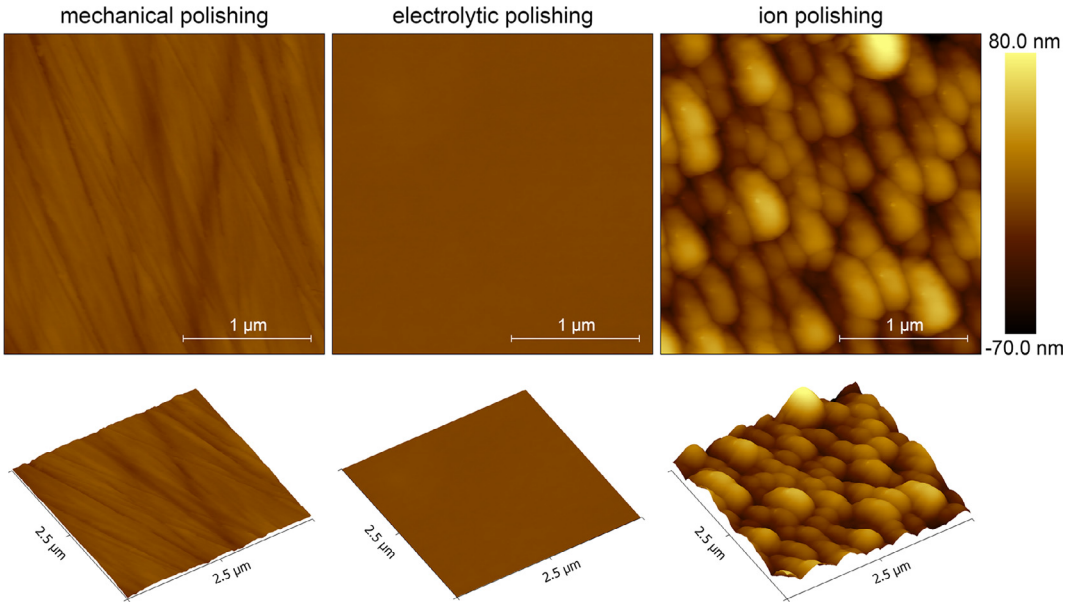

Fig. 4. AFM profiles of bulk $Co_{49}Ni_{21}Ga_{30}$ single crystal after mechanical, electrolytic and ion polishing. All samples are presented in the same physical scale. Visible significant surface development after ion polishing.

Conclusions

Combining SEM and TEM observations, it has been proven that the magnetic structure of the $Co_{49}Ni_{21}Ga_{30}$ single crystal consists of domains about 100 nm wide, arranged along a {0 0 2} planes family. The sample subjected to additional ion polishing allowed observation of the contrast associated with the magnetic structure of the material with the objective pole piece turned on. Additional AFM observations clearly confirmed that ion polishing can significantly affect the MSMA's surface morphology. The exact explanation of this phenomenon has not yet been described, but researchers should be aware of this effect and the consequences of the preparation methods on TEM observations. Due to the fact that the exact mechanism of creating the image in the new method is not yet described, we suggest to confirm the obtained results by observing in Foucault or Fresnel mode.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.rinp.2018.06.020.

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