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MICROSTRUCTURE EVALUATION OF Ni-Mn-Ga ALLOY

SUMMARY

This paper summarises the applications of MSMA materials, outlines the mechanism of magnetic shape memory effect and provides the procedure for microstructure evaluation of samples as well as the results of microstructure analysis using the example of the Ni-Mn-Ga alloy.

Keywords: *MSMA, Ni-Mn-Ga alloy*

MIKROSTRUKTURA STOPU Ni-Mn-Ga

W artykule scharakteryzowano zastosowania materiałów z magnetyczną pamięcią kształtu (MSMA). Opisano mechanizm działania magnetycznej pamięci kształtu. Przedstawiono procedurę mikroskopowej oceny próbki i jej wyniki na przykładzie stopu Ni-Mn-Ga.

Słowa kluczowe: *MSMA, stop Ni-Mn-Ga*

1. INTRODUCTION

Shape memory materials are popularly described as elements capable of assuming most intricate, previously memorised shapes or at least capable of dimensional changes under the influence of external factors, such as:

- electric field, affecting piezoelectric, electrostrictive and electrorheological (ER) materials and electrorheological composites;
- magnetic field, affecting magnetorheological (MR) fluids, magnetostrictive materials, MSMA (Magnetic Shape Memory Alloys) alloys otherwise referred to as FSMA alloys (Ferromagnetic Shape Memory Alloys) based on the magnetic shape memory effect;
- temperature, affecting SMA alloys, and shape memory polymers and composites.

Literature on the subject still lacks reports on industrial applications of MSMA materials and alloys. Magnetic properties of the Ni-Mn-Ga alloy (Nickel- Manganese-Gallium) were first observed by Ullako in 1996 (Ullako, 1997). The key feature of such alloys is their ability to change their shape comparable to SMA alloys at operating frequencies higher by about two orders of magnitude, about 1 Hz when compared to several Hz for SMA alloys. A great deal of attention has been given mostly to Heusler- type alloys, their general composition being given as Ni-Mn-Ga. Their main drawbacks include relatively low levels of admissible compression strength, ranging from 4 to 10 MPa and high price, amounting to 40 euro for 1 mm^3. The most characteristic parameter of MSMA materials is the blocking stress σ_b, when it is exceeded, the shape memory effect ceases to operate. Nevertheless, the Finnish company "AdaptaMat" started the production of vibration generators based on the Ni-Mn-Ga alloy, which they manufacture, too. Vibration generators are mostly intended for diagnostics in laboratory tests. Research is now underway on MSMA alloys containing the admixtures of iron. Their shape memory features are supposed to be most favourable, approaching 10% and the admissible compressive strength is about 40 MPa, so their parameters are similar to those of the most popular SMA alloy – NiTinol, containing nickel and titanium.

Research work on potential applications of materials to the control of motion in mechanical systems continued in the Department of Process Control AGH University of Science and Technology (AGH-UST) at the Faculty of Mechanical Engineering and Robotics is focused chiefly on MR fluids and magnetostrictive materials. To extend the scope of the research program, an attempt was made to build the test rig for macroscopic testing of MSM alloys. Since MSM materials are available in the limited extent only, and their manufacturing technology is most complicated and stringent, microstructure evaluation of samples is applied before they are used for testing, to ensure the reliability of the test results. Tests were run on a sample of the NiMnGa alloy obtained from the "AdaptaMat" Company.

This paper summarises the applications of MSMA materials, outlines the mechanism of magnetic shape memory effect and provides the procedure for microstructure evaluation of samples as well as the results of microstructure analysis using the example of the Ni-Mn-Ga alloy.

2. MAGNETO-ACTIVE MATERIALS IN TECHNICAL APPLICATIONS

The search of new smart materials is aimed to allow the synthesis of self-repairing materials to facilitate the assembly technologies, materials for bio-engineering purposes

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and those generating linear displacements. On account of their capability of dimensional change, smart materials help simplify the design and structure of various types of actuators and manipulators in many fields of application. Moreover, due to the interaction of external fields, the physical properties of smart materials change too, which opens up new possibilities.

Various devices based on MR fluids are now in more widespread use, such as MR dampers that have a wide range of applications, from vibration isolation of drums in automatic washing machines to vibration suppression of cables suspending bridge structures. Similar to piezoelectric devices, those utilising MR fluids have now moved beyond the laboratory applications and are now manufactured on a commercial scale.

Apart from MR fluids, widely known materials sensitive to magnetic field fluctuations include those based on the magnetostriction effect, which was first observed by Joule in 1842. In the case of typical ferromagnetic elements, such as Fe, Ni, we are able to achieve the relative strain of the order of $10^{-4}\%$ of the sample length. With special magnetostrictive alloys, such as Terfenol-D (Tb-Dy-Fe), the relative strain approaches 0.1% of the sample length, encompassed by the magnetic field lines. Magnetostrictive materials are used for manufacturing supersonic heads, vibration generators, high-quality amplifiers and sensors.

The search for smart materials whose geometric parameters should be controlled by the application of an external magnetic field has so far resulted in the synthesis of Ni-Mn-Ga alloys, which are now best identified and tested, which prompted further efforts to formulate models. In literature on the subject we encounter the terms MSMA or FSMA alloys. The latter name implies that these materials are ferromagnetic. In order to eliminate certain shortcomings of Ni-Mn-Ga alloys, particularly limited resistance features and large energy demand required to trigger the conversion of martensite structure, research work is now focused on alloys with different composition, such as Co-Ni-Ga (Liu J, 2006), Fe-Mn-Si-Cr-Ni (Wen, 2007), Ni-Fe-Ga-Co (Liu J, 2008), Co-Ni-Al (Liu Z, 2008), Ni-Mn-Co-In (Karaca, 2008).

3. PROPERTIES AND OPERATION MECHANISM OF MSM ALLOYS

Manufacturing of MSM alloys on the industrial scale by the currently used technology is rather difficult. Apart from most precise control of its chemical composition, it requires a specialised heat treatment combined with mechanical working. At first in the high-temperature stage, a MSM element is the phase of non-transformed austenite structure (high-temperature) characterised by regular forms of unit cells with the side length A0 (Fig. 1a). During the cooling stage, the sample is subjected to constant compression stress σ_{xx} (Fig. 2), whilst the condition is retained that $\sigma_{sv} < \sigma_{xx} < \sigma_b$, where σ_{sv} – compressive stress triggering the formation of variant 1 of the martensitic structure; σ_b – blocking stress. Exceeding the critical value of σ_b causes the shape memory effect to disappear whilst maintaining the stresses below σ_{sv} causes that martensitic structure will not be formed in a variant 1. Following the strict regime during the synthesis of the Ni-Mn-Ga alloy will finally yield a sample comprising the martensitic structure in its entire volume in variant 1 (Fig. 1b). During the cooling stage, apart from the martensitic transformation, magnetic domains are formed with the directions of magnetic polarisation ***M*** coinciding with that of acting compressive stress σ_{xx}.

In the neighbouring magnetic domains separated by magnetic walls, the direction of the magnetisation vector ***M*** is reversed (Fig. 2) to balance magnetic polarisation of the domains.

In the low–temperature martensitic phase three variants of martensite are available (Fig. 1b, c, d). The crystalline direction of variants, referred to as the free magnetic axis, shall coincide with the direction determined by shorter edges of unit cells.

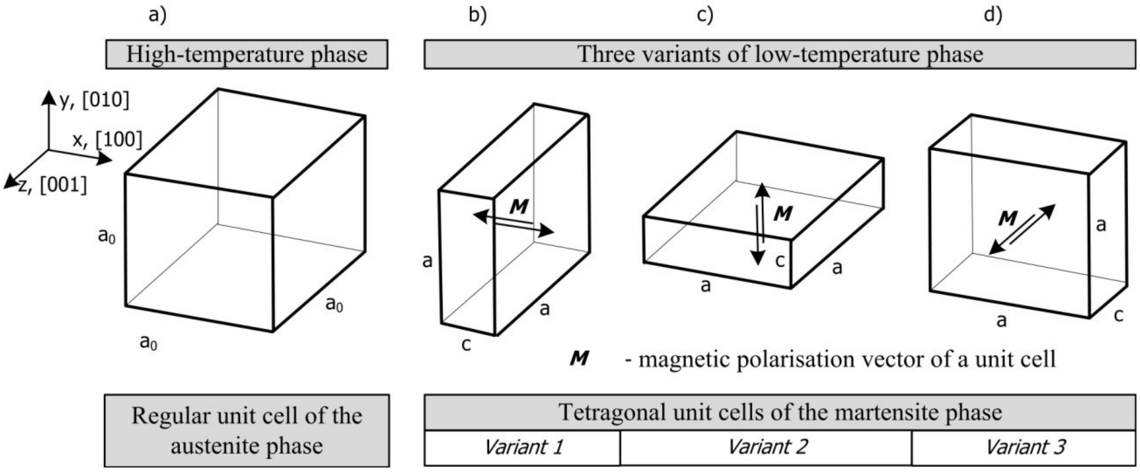

Fig. 1. Structure of a unit cell of Ni-Mn-Ga alloy: a) austenite phase – high temperature; b) variant 1 of the martensitic phase; c) variant 2 of the martensitic phase; d) variant 3 of the martensitic phase

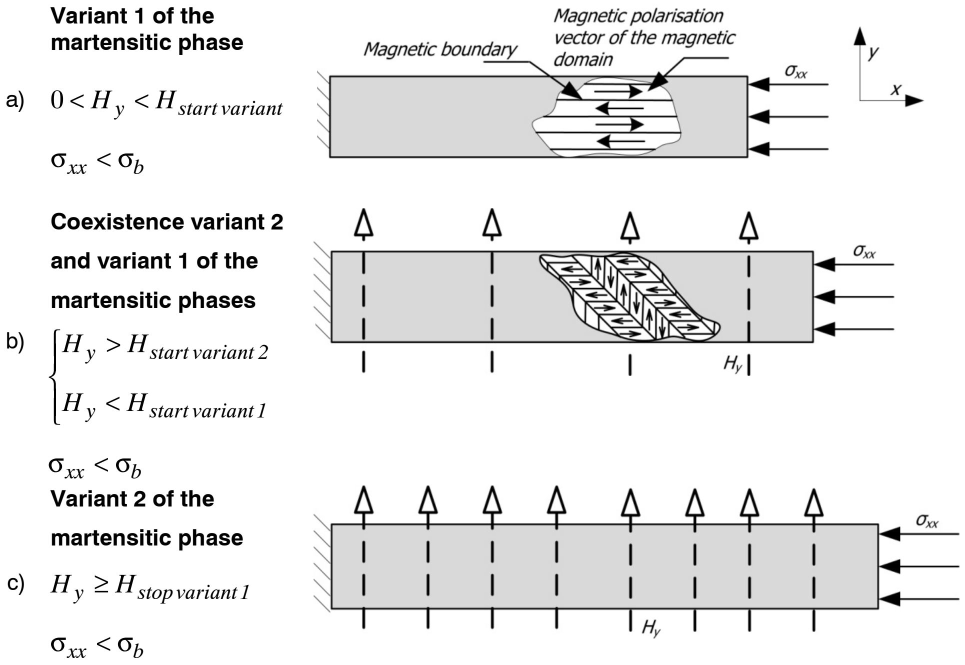

Fig. 2. Mechanism of magnetic shape memory: a) loaded sample with no external magnetic field H_y; b) loaded sample under the external magnetic field with the field strength H_y causing the martensite formation in variant 2; c) sample with load applied, under the external magnetic field with the field strength H_y causing martensite to disappear in variant 1; further elongation of the sample will be impossible

Subjecting the MSM alloy to an external magnetic field with the strength H_y (Fig. 2b, c) and placing it orthogonally to the applied compressive stress σ_{xx} axis causes an increase of the variant 2 of martensite, in micro-scale. Domain walls are re-located and reoriented, accompanied by twin migrations (Fig. 2b). Variants 1 and 2 coexist whilst an increase of magnetic field strength causes variant 2 to enhance at the cost of variant 1. Thus formed deformations of macroscale reorientation lead to sample elongation. The entire process then is based on magnetically induced reorientation of martensite variants.

4. EXPERIMENTAL PROCEDURE

Tests were run on polycrystalline alloy sample obtained from the "AdaptaMat" Company. The sample is shaped like a rectangular prism, having the mass 0.003 kg; its dimensions are: length – 15.0 mm; width – 2.0 mm and thickness – 0.8 mm. The sample was first polished to make its surface sufficiently smooth for microscope tests. The quantitative analysis of the elemental composition and topography observations were taken using a scanning electron microscope FEI E-SEM (Phillips), incorporating an X-ray spectrometer EDAX Genesis 4000. Microscope observations were taken using an electron beam 25 keV, under the zoom 1000× and 2000×.

The phase composition of the alloy was established by the X-ray diffraction method and measurements were taken with an X'Pert Pro (PANanalytical) diffraction meter in the Bragg-Brentano configuration, applying monochromatic radiation CuKa in the angle range 2θ from 10 to 90 deg. The goniometer was operated in the continuous mode, with the predetermined step 0.00816 deg and the whole measurement procedure took 2 hours. The device incorporates a semi-conductor bar counter X'Celerator. The sample for measurements was in the powered form, made by milling the polycrystalline alloy to obtain the grain size below 100 µm in order to minimise the negative interactions of the sample's texture with the X-ray measurement procedure.

5. RESULTS AND DISCUSSION

The elemental analysis of the alloy was performed at five most representative points in the crystal and the results were very similar, which implies that the alloy Ni-Mn-Ga is homogeneous in its entire volume. Besides, the alloy's homogeneity is further confirmed by the maps of elemental distribution obtained from X-ray tests. Selected results are shown in Figure 3.

At the level of X-ray micro-probe detection, no contaminants were found in the form of other alloy components except some trace amounts of carbon contaminant and oxygen remaining on the surface.

The quantitative analysis revealed that the alloy's actual composition can be approximated by the formula $Ni_5Mn_3Ga_2$. It was followed by measurements of the phase composition of the powdered sample, using the X–ray diffraction method. Results are shown in Figure 4.

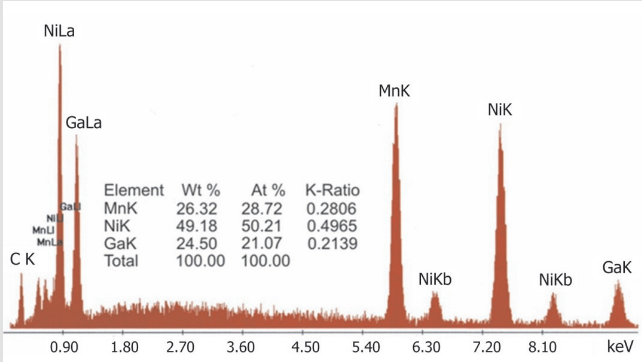

Fig. 3. Elemental analysis and quantitative data

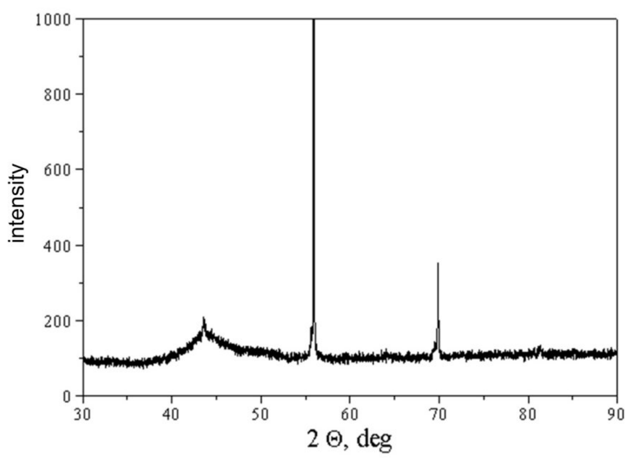

Fig. 4. X-ray diffraction image of the alloy $Ni_5Mn_3Ga_2$

Comparing the diffraction image with the reference standards, we come to the conclusion that the structure of the tested alloy corresponds to that of nickel- revealing a face-centred cubic lattice with the group symbol Fm-3m (Bojarski 2001). Differences between the registered and referenced peak intensities might be attributable to substitution of several nickel planes by the atoms of the remaining alloy components, leading to the deformation of a unit cell, which in consequence causes the peaks to be shifted with respect to their reference positions.

The microstructure of the tested material observed under the scanning electron microscope is shown in Figure 5.

Microscope images reveal the striped structure with variable topography. Two types of striped features are registered: the first identified as convex or concave features, the latter as parallel strips with variable contrast. Recalling the homogeneous distribution of elements in the entire volume, confirmed by the spectral analysis of X-ray energy dispersion (Fig. 4), it is reasonable to suppose that strips of the first kind are associated with changes of crystallographic orientation. These changes might occur during the SEM microscope observations, when the sample is subjected to the action of an electromagnetic field. As a result, the field can trigger a reversible crystalline transformation within the alloy Ni-Mn-Ga. Strips of the second kind might be attributable to magnetic domains, which is borne out by their shape and location. More extensive study of these strips shall be undertaken in the course of further research work.

6. CONCLUSIONS

FSMA materials belong to a group of new magneto-active materials, their history going back only to 13 years ago. Applications of these materials are still extensively tested in laboratory conditions. Despite their limited mechanical resistance, their operation frequency at full elongation renders it fully reasonable to expect a range of industrial applications in the nearest future. High precision required for synthesis of these materials demands their evaluation before use in testing applications. Test results presented in this study provide a solid basis for future evaluation efforts.

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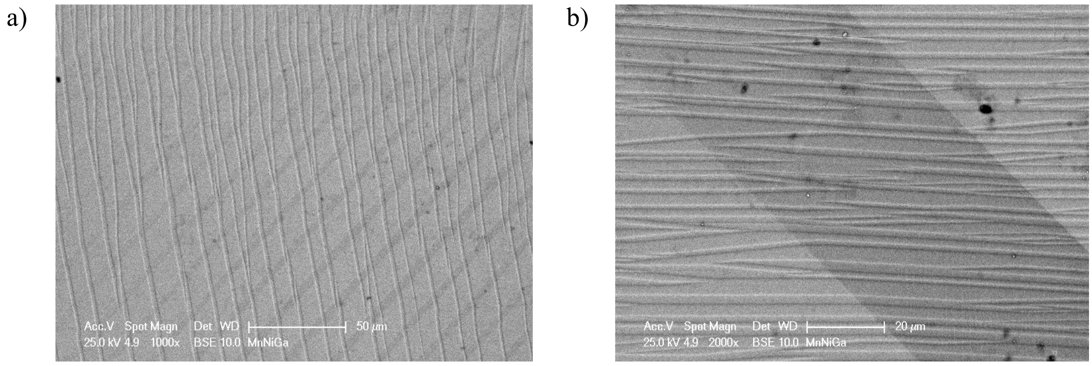

Fig. 5. Microstructure of the alloy $Ni_5Mn_3Ga_2$ observed under the scanning microscope using back-scattered electrons (BSE): a) zoom 1000×, revealing convex or concave irregular strips and parallel strips with variable contrast; b) zoom 2000× – revealing morphological details of the two strips

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