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CRYSTALLOGRAPHIC AND MICROSTRUCTURAL PROPERTIES OF THE $NI_{2,14}MN_{0,86}GA$ ALLOY

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Key words: shape memory alloys, magnetic shape memory, Heusler alloys, Ni-Mn-Ga.

Abstract

The paper presents the results of experimental investigations into the structure of the $Ni_{2,14}Mn_{0,86}Ga$ alloy immediately after casting. The study was performed using an atomic force microscope (AFM), an optical microscope and an X-ray diffractometer (XRD). The results of microscopic analyses (AFM + OM) indicate that grain structure is non-homogenous. Twin structure was not observed immediately after casting. However, the columnar structure of alloy grains suggests that twin structure can be obtained after heat treatment.

During XRD investigations the $Ni_{2,14}Mn_{0,86}Ga$ alloy was exposed to the effects of an external magnetic field whose intensity varied from 130÷250 mT. The results were analyzed assuming an ideal arrangement of atoms in the crystal lattice in the austenitic phase. The crystallographic R factor of structure divergence was determined for particular magnetic intensities.

KRYSTALOGRAFICZNE I MIKROSTRUKTURALNE WŁAŚCIWOŚCI STOPU $Ni_{2,14}Mn_{0,86}Ga$

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Słowa kluczowe: stopy z pamięcią kształtu, magnetyczna pamięć kształtu, stopy Heuslera, Ni-Mn-Ga.

Streszczenie

Praca przedstawia eksperymentalne wyniki badań struktury stopu $Ni_{2,14}Mn_{0,86}Ga$ w stanie bezpośrednio po odlaniu. Badania przeprowadzono na mikroskopie sił atomowych, (AFM), mikroskopie optycznym oraz dyfraktometrze rentgenowskim. Badania przeprowadzone zarówno na mikroskopie sił atomowych, jak i mikroskopie optycznym wskazują na niejednorodną budowę ziarn. W stanie bezpośrednio po odlaniu nie stwierdzono wyraźnej struktury bliźniakowej, ale kolumnowa budowa ziarn umożliwia uzyskanie struktury bliźniakowej z wyraźnymi granicami przez zastosowanie obróbki cieplnej.

Podczas badań dyfraktometrycznych stop $Ni_{2,14}Mn_{0,86}Ga$ poddano oddziaływaniu zewnętrznego pola magnetycznego o natężeniu od 130 do 250 mT. Badania przeanalizowano przy założeniu występowania stanu austenitycznego oraz idealnego uporządkowania atomów w sieci krystalicznej. Dla poszczególnych obciążeń magnetycznych wyznaczono wskaźnik R rozbieżności struktury.

Introduction

Alloys of the Ni-Mn-Ga type having non-stoichiometric composition close to Ni_2MnGa are characterized by regular structure *fcc* $L2_1$ with the space group *Fm3m* (no 225) at room temperature and in a stress-free state (Fig. 1a). Such alloys are classified into the group of the so called intelligent materials, showing a two-directional shape memory effect *SME*. In the Ni_2MnGa phase subjected to cooling below a characteristic temperature (Ms≈220K) the crystal lattice undergoes homogenous strain and transformation into a tetragonal (Fig. 1b), orthorhombic or monoclinic lattice (ZHELUDV et al. 1996). A distinguishing feature of alloys of the Ni-Mn-Ga type representing shape memory materials is their ability to undergo considerable strains (reaching even 20%) in the martensitic state, caused by the effects of an external magnetic field (AYUELA et al. 1999). This phenomenon is referred to as the magnetic shape memory (*MSM*) effect. The phenomenon of magnetic shape memory occurs mostly in materials with homogenous structures, containing a phase characterized by a high degree of atom ordering in the crystal lattice (austenite), which undergoes non-diffusive homogenous

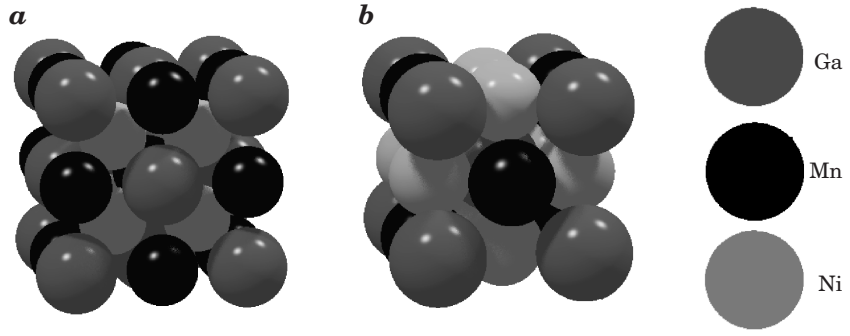

Fig. 1. Unit cell of the Ni_2MnGa phase: a – regular lattice *fcc Fm3m*, b – tetragonal lattice *bct*

strain when affected by temperature. The austenitic phase is then transformed into a phase characterized by a lower degree of ordering (*martensite*). The passage from a higher to lower symmetry (*austenite to martensite*) may take various courses in different parts of the material, leading to the formation of the so called twin structure (ENKOVAARA, 2003). As mentioned before, an advantage of this change is its reversible nature. The influence of an external magnetic field on the martensitic phase leads to boundary displacement, resulting in strain.

Alloys having non-stoichiometric composition, close to Ni_2MnGa, have been the subject of numerous studies, aimed at receiving the optimum (martensitic) structure at room temperature, allowing to obtain a high strain rate even with an insignificant effect of a magnetic field.

Experimental

The study was performed on the $Ni_{2,14}Mn_{0,86}Ga$ alloy with non-stoichiometric composition, immediately after casting. To determine its structure, diffractometric analyses were made at room temperature, with the use of $CuK\alpha$ radiation. Figure 2 presents the results of the experiment in the form of a X-ray diffraction pattern. The results obtained show that the material examined is characterized by a two-phase structure, and contains both an austenitic and martensitic phase (*M*).

At the next stage of the study changes in the alloy structure following its exposure to an external magnetic field of intensity 130÷250 mT were analyzed, assuming an ideal arrangement of atoms in the crystal lattice in

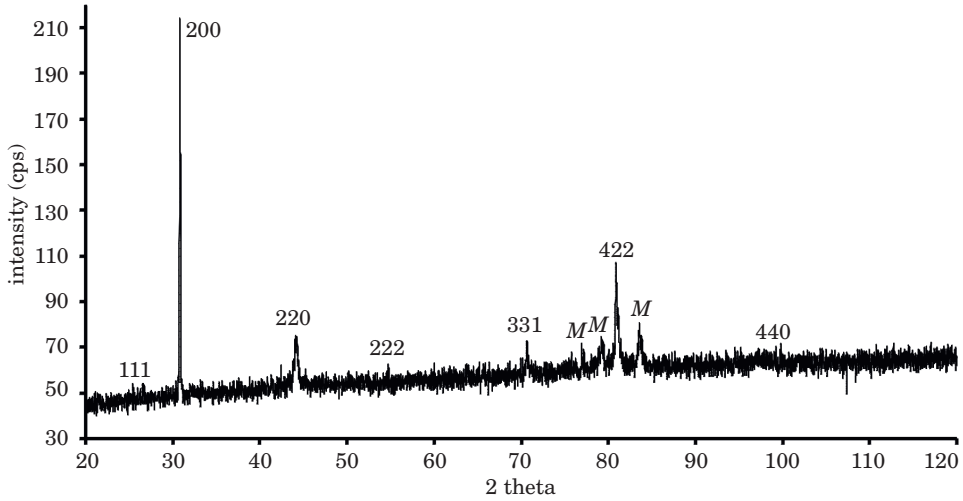

Fig. 2. XRD pattern of the $Ni_{2,14}Mn_{0,86}Ga$ alloy

the austenitic phase. To estimate the degree of atom ordering in the crystal lattice, the structure factor $|F_{hkl}|$ was determined. This factor is defined as a ratio between the amplitude of a wave scattered by all unit cell atoms and the amplitude of a wave scattered by a single electron. Its value has a significant effect on the value of a diffracted X-ray beam, because the intensity of a diffracted beam on all atoms of a unit cell is directly proportional to $|F_{\{hkl\}}|^2$. According to equation (1), the structure factor is dependent upon the type of atoms and the phase angle φ_n between radiation scattered by the n-th atom and radiation scattered by the atom located at the origin of the lattice (CULLITY 1964).

$$F_{\{hkl\}} = \sum_{n=1}^{N} f_n \cdot \exp(i\varphi_n) \tag{1}$$

where:

f_n – atomic scattering factor, defined as a ratio between the amplitude of a wave scattered by a single atom and the amplitude of a wave scattered by a single electron,

i – imaginary unit,

$\varphi_n = 2\pi(hu_n + kv_n + lw_n)$ – phase angle between radiation scattered by the n-th atom and radiation scattered by the atom located at the orogin of the lattice,

khl – Miller indices,

u_n, v_n, w_n – positions of atoms in a unit cell,

N – number of atoms in a unit cell.

The results of the computations show that reflections with mixed Miller indices (hkl) become extinguished (F_{hkl}=0), whereas for all unmixed indices (i.e. even or odd) the structure factor is as follows:

- $F_{\{h\ k\ l\}} = 4 \cdot (f_{Ga} - f_{Mn})$ – for the odd sum $n=h+k+l$,
- $F_{\{h\ k\ l\}} = 4 \cdot (f_{Ga} + f_{Mn} + 2f_{Ni})$ – for the even sum $n=h+k+l$, where n is an even multiple of 2,
- $F_{\{h\ k\ l\}} = 4 \cdot (f_{Ga} + f_{Mn} - 2f_{Ni})$ – for the even sum $n=h+k+l$, where n is an odd multiple of 2.

The above values of the structure factor were determined for an ideally ordered structure. It is a well-known fact that in reality all phases (except superlattices) are characterized by a certain degree of disorder as regards atom arrangement in the crystal lattice.

Determining theoretical $|F_{hkl}^{obl.}|$ and experimental $|F_{hkl}^{eksp.}|$ values, we also determined the crystallographic R factor of structure divergence, according to equation (2) (WALLWORK 2001).

Table 1

Results of XRD investigations

hkl	*A*(*θ*)	*LP*	*p*	$\left\|F_{hkl}^{obl.}\right\|$	$\left\|F_{hkl}^{eksp.}\right\|$	$\left\|F_{hkl}^{e.-s.o.}\right\|$	$I_{eksp.}$	*k*	*R*
B=0 mT									
200	0.9990	25.4808	6	18.28	0.3617	179.3715	19.98	495.91	0.8260
220	0.9990	11.5675	12	284.35	0.2363	117.2061	7.75		
331	0.9990	4.0627	24	12.72	0.1493	74.0253	2.17		
422	0.9990	3.1953	24	223.10	0.3385	167.8535	8.78		
B=130 mT									
200	0.9990	25.4189	6	18.2787	0.3612	130.3917	19.8776	360.9969	0.6390
220	0.9990	11.5875	12	284.3537	0.1725	62.2874	4.1355		
422	0.9990	3.1853	24	206.4952	0.7386	266.637	41.6643		
620	0.9990	3.0497	24	185.8632	0.6528	235.6747	31.1642		
B=170 mT									
200	0.9990	25.4057	6	18.2787	0.3449	59.9216	18.1126	173.7465	0.7353
220	0.9924	11.5084	12	284.0383	0.1528	26.5410	3.1980		
422	0.9407	3.1864	24	206.5333	1.2252	212.8686	107.9836		
600	0.9004	2.7956	6	21.6291	0.7096	123.2940	7.6052		
620	0.8880	3.0467	24	169.9248	1.5988	277.7790	165.9694		
B=250 mT									
111	0.9990	34.3743	8	17.4261	0.0687	14.6503	1.2966	213.2484	0.0229
200	0.9975	25.3965	6	18.8311	0.0883	18.8366	1.186		
422	0.9145	3.1865	24	205.9809	0.9789	208.7513	67.0187		

$$R = \frac{\sum_{hkl} \left\| F_{hkl}^{eksp.} \right| - \left| F_{hkl}^{obl.} \right\|}{\sum_{hkl} \left| F_{hkl}^{eksp.} \right|} \tag{2}$$

The values $\left|F_{hkl}^{eksp.}\right|$ were determined from equation (3), describing the intensity of a diffracted X-ray beam (CULLITY 1964).

$$I = \left|F_{hkl}\right|^2 \cdot LP \cdot p \cdot A(\theta) \tag{3}$$

where:

$LP = \frac{1+\cos^2\theta}{\sin^2\theta\cos\theta}$ – Lorenz-Thomson polarization factor,

p – diffraction plane multiplication factor.

$A(\theta) = 1 - \exp\left(-\frac{2\mu t}{\sin\theta}\right)$ – absorption factor,

μ – linear absorption factor,

t – depth of X-ray penetration.

In order to compare the experimental and theoretical structure factors, they were expressed on the same scale, applying the conversion factor $k = \frac{\sum\left|F_{hkl}^{obl.}\right|}{\sum\left|F_{hkl}^{eksp.}\right|}$. The results of XRD investigations are summarized in Table 1.

The external magnetic field caused changes in the intensity of diffraction reflections. Their occurrence also depended on field strength, which is connected with changes in the symmetry of the crystallographic structure. Figure 3 shows changes in the intensity of diffraction lines. It was found that for the criteria assumed, an increase in the magnetic field strength from 130 to 250 mT was accompanied by a decrease in the crystallographic R factor of structure divergence from 0.8260 to 0.0229, which indicates a higher degree of atom ordering in the crystal lattice.

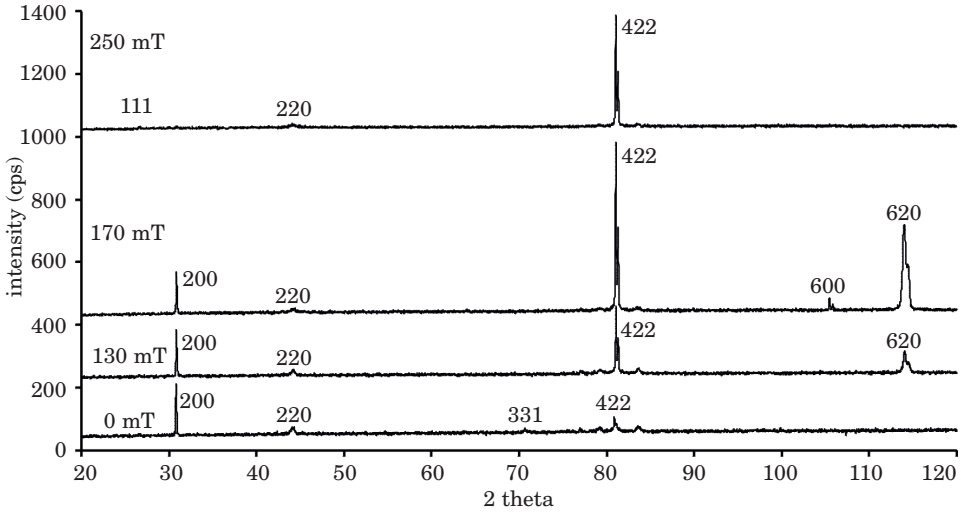

Fig. 3. Changes in the intensity of XRD diffraction lines of the $Ni_{2,14}Mn_{0,86}Ga$ alloy in a magnetic field

As already mentioned, XRD investigations showed that the alloy examined was characterized by a two-phase structure, which was also confirmed by atomic force microscopy (NT-MDT, Russia) with phase contrast imaging. Two-phase structure of the $Ni_{2,14}Mn_{0,86}Ga$ alloy is visible in micrographs presented in Figure 4. ATM analyses were performed using a cantilever with a cobalt-coated needle, magnetized in a homogenous magnetic field along its symmetry axis prior to investigations. The alloy sample used in the experiment was polished mechanically. The alloy was also subjected to metallographic tests and analyzed under an atomic force microscope in the contact mode, following etching in a solution containing 2 ml(HNO_3) + 5 g($FeCl_3$) + 99 ml(methanol). The alloy structure is shown in micrographs (Fig. 5). Similar results of microscopic examinations were reported by BESSEGHINI et al. (2001) for the $Ni_{53}Mn_{23,5}Ga_{23,5}$ alloy.

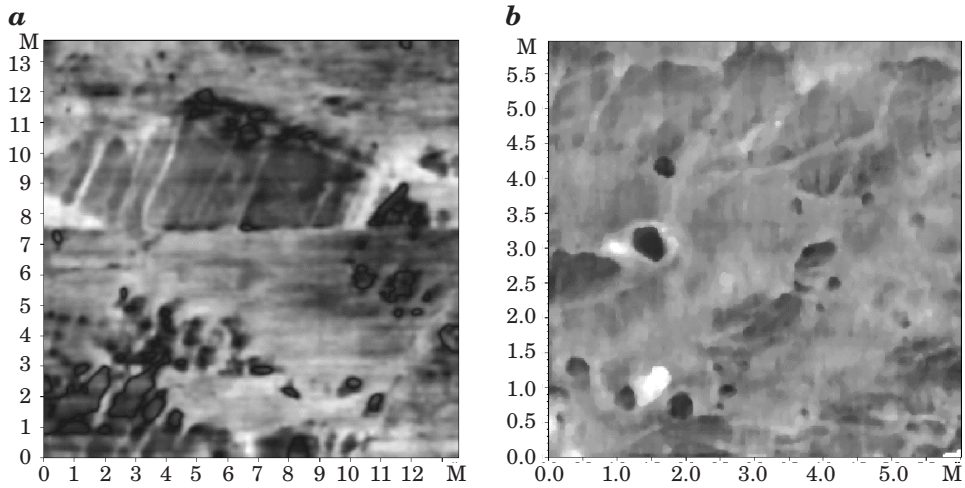

Fig. 4. Phase contrast of a $Ni_{2,14}Mn_{0,86}Ga$ sample: a – scan area – 13.5×13.5 μm, b – scan area – 6×6 μm

The results of microscopic analyses (atomic force and optical microscopy) indicate that grain structure is non-homogenous. Twin structure was not observed immediately after casting. However, the columnar structure of alloy grains suggests that twin structure can be obtained in the $Ni_{2,14}Mn_{0,86}Ga$ alloy after heat treatment.

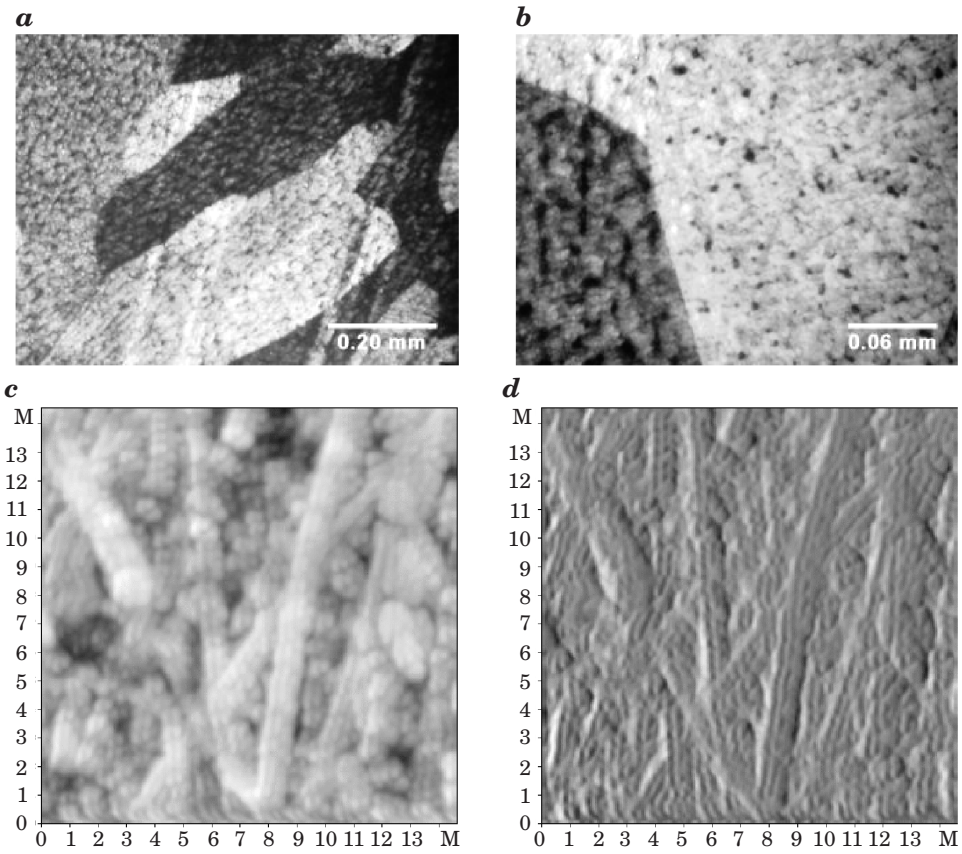

Fig. 5. Micrographs of the $Ni_{2,14}Mn_{0,86}Ga$ alloy: a, b – optical micrography, c, d – AFM micrography (c – "Height" signal, d – DFL signal) – scan area 14.5×14.5 μm

Conclusions

The experimental results suggest that an external magnetic field caused an increase in atom ordering in the crystal lattice in the alloy examined, immediately after casting. The austentic phase symmetry changed from disordered to *Fm3m*. The results of metallographic tests show that grain structure was non-homogenous and that grains were considerably elongated, probably in the direction of carrying away the heat.

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