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Martensitic transformations and mobility of twin boundaries in Ni_2MnGa alloys studied by using internal friction

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Abstract

Internal friction (IF) was measured in two non-stoichiometric Ni_2MnGa alloys. Several IF peaks attributed to some restructuring of the martensitic lattice were observed below M_s. From the strain dependence of IF, the activation enthalpy for movement of twin boundaries between martensitic domains was estimated to be equal to 0.02–0.04 eV.

Keywords: Ni–Mn–Ga; Internal friction; Differential scanning calorimetry; Phase transformations; Martensite

1. Introduction

Magnetic-field-induced strain (MFIS) has been found in non-stoichiometric Ni_2MnGa alloys, which has given start for numerous studies of magnetic shape memory effect, MSME, (see e.g. [1–4]). It is generally accepted that a controlling mechanism of MFIS amounts to magnetically caused movement of twin boundaries between the martensitic variants that, at the same time, are the magnetic domain walls (e.g. [5–7]). Strain originates from the field-assisted growth of a martensitic variant having the most favourable orientation of its axis of easy magnetization (*c*-axis) in relation to applied field, so that the highest reachable value of strain is determined by the c/a ratio in the martensite lattice. The same effect can be caused by the applied mechanical stress and it is shown that the maximum of mechanical stress needed for twinning, i.e. twinning stress, in these alloys is rather small (e.g. even less than 3 MPa [3,8,9]).

The aforementioned fact suggests that mobility of twin boundaries is an important factor affecting MFIS. So far no attempt has been made for quantitative estimation of this property. Taking into account that internal friction (free decay of enforced vibrations), IF, is extremely sensitive to any softening of the crystal lattice, the aim of the present work was to use the stress-dependent IF in order to estimate the value of the activation enthalpy for movement of twin boundaries in

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Ni_2MnGa alloys. Another purpose was to detect the possible occurrence of restructuring in martensite measuring the temperature dependence of internal friction. Temperature-dependent IF was already successfully used for studies of Ni_2MnGa alloys; transformation of austenite to an intermediate phase above M_s [10] and two-step martensitic transformation [11]. Martensite-to-martensite transformations in Ni–Mn–Ga alloys far below M_s were so far not detected by using IF.

2. Experimental

Two Ni_2MnGa alloys of non-stoichiometric compositions were selected for studies (see Table 1). Their compositions were chosen aiming at obtaining relatively high temperatures of martensitic transformation. Studies of high-temperature compositions of MSM alloys are promising because many fields of practical application of MFIS, e.g. actuators, need to use this effect in a broad temperature range. This was also essential as the present internal friction study concentrated on measuring the magnetically induced motion of twin boundaries in the already formed martensite and, therefore, no disturbance caused by phase transformation could be then allowed. Alloy A was chosen in such a way that the martensitic transformation took place at the magnetic transition, while Alloy B had the martensitic transformation clearly above Curie point. Some magnetic and electric properties of an alloy exhibiting the crystal transformation at the magnetic transition region are presented in [12]. Both alloys were manufactured at AdaptaMat Ltd. by using modified Bridgman method. Their chemical compositions were determined using EDS spectrometer connected to the scanning electron microscope LEO-SEM. The large grained ingots were homogenized for 72 h at 1273 K and then annealed for 48 h at 1073 K followed by cooling in air. The IF samples of $1 \times 1 \times 50$ mm^3 in size for measurements of internal friction were cut by using the sparkle cutting. Since these samples were rather long, it was not possible to cut them to the certain crystal orientations and, therefore, the specimens were cut inside certain grains, longitudinal along the ingot. The specimens were ground from all their long faces and thereafter electropolished in 25% nitric acid–ethanol solution at ambient temperature. Samples for differential scanning calorimetry and magnetic susceptibility measurements were cut from these pieces with slow rotation diamond saw. The temperatures of direct (M_s, M_f) and inverse (A_s, A_f) martensitic transformations and Curie temperature (T_C) were obtained from the measurements of magnetic susceptibility and differential scanning calorimetry with the heating/cooling rate of 2 K/min (Table 1). The average energy connected to the martensitic transformation according to the differential scanning calorimetry (DSC) measurements was estimated to be 9.5 J/g for Alloy A and 13.6 J/g for Alloy B. There were two samples of Alloy B showing low temperature reverse transformation with energy 1.7 J/g at temperatures of 256–262 K, while the other samples did not show any signs of low temperature transformations in DSC measurements (see Fig. 1). The crystal structures of the materials were determined with the Philips X'pert X-ray equipment at ambient temperature. Both of the alloys exhibited the non-layered tetragonal structure; the lattice parameters of Alloy A were $a = b = 5.459$ nm and $c = 6.550$ nm resulting $c/a = 1.200$, and in Alloy B $a = b = 5.462$ nm and $c = 6.576$ nm resulting $c/a = 1.204$.

Measurements of the temperature-dependent IF were carried out by using the automated inverted pendulum in the temperature range of 77–473 K at

Table 1
Chemical compositions of alloys, temperatures of direct and inverse transformations and Curie point

Alloy	Ni (at.%)	Mn (at.%)	Ga (at.%)	M_s (K)	M_f (K)	A_s (K)	A_f (K)	T_C in heating (K)	T_C in cooling (K)
A	54.5	21.5	24.0	373	365	376	384	374	368
B	52.1	27.3	20.6	399	391	401	410	380	380

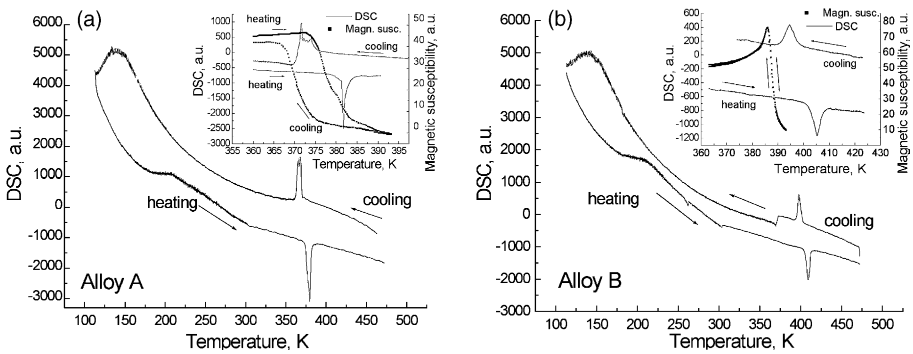

Fig. 1. Martensitic transformations in Alloys A and B according to the data of DSC and magnetic susceptibility. Two steps affecting the slope of the DSC curve at approximately 373 K during cooling and at 203 K during heating are from starting and stopping the cooling pump in equipment.

the strain amplitude of 10^{-6} and the linear heating/cooling rate of 1.5 K/min. The strain dependence of internal friction was measured at constant temperatures within the same temperature range at strain amplitudes of 10^{-6}–10^{-4}. The upper level of strain was limited in order to avoid any strain-induced crystal lattice defects. Martensitic transformation in both alloys was accompanied by a giant acoustic emission that generates vibrations and damping which were beyond the limits of measuring equipment. That is why at some stage of transformation during heating or cooling the measurements were automatically interrupted and started again when the strain amplitudes and damping were back in the controllable range of their values. This unreadable region situated to magnetic transition, so it was not possible to observe its effect on IF.

3. Results and discussion

The transformation behaviour of the alloys is presented in Fig. 1. In both DSC curves, the major transformation peaks are present while in Alloy B one can detect also a small additional peak at 256 K. From inserts of these curves, it can be seen that in Alloy A there is a clear difference of Curie point during heating and cooling (Fig. 1a), while in Alloy B this is not the case.

Fig. 2 shows the temperature dependence of internal friction in both alloys. It is remarkable that the IF values are much larger in Alloy B than in Alloy A.

In Alloy A, the IF curve reveals several maxima (the first, second, third and fourth peaks), whereas neither magnetic susceptibility nor DSC detected any intermartensitic transformations below M_s, M_f in both alloys except a small peak at 256 K for Alloy B (Fig. 1b). The first IF peak corresponds to the austenite-to-martensite transition in both alloys. Also, the second peak is clearly observed in both IF curves for all studied samples. The third and the fourth peaks were not found in Alloy B and also not detected in some Alloy A specimens. This difference between the IF curves measured on several samples of the same alloy suggests some chemical inhomogeneity in spite of the above-mentioned homogenisation treatment.

A clear discrepancy between the data of DSC and IF occurs, which can be explained by a higher sensitivity of IF technique to small restructuring in martensite. On the other hand, one has to take into account that, in contrast to DSC, IF measurements include some small elastic strain of the samples ($\varepsilon \approx 10^{-6}$).

Measurements of strain-dependent internal friction were used in order to obtain knowledge about mobility of twin boundaries in martensite. Usually, the internal friction background is caused by vibrations of dislocations and, e.g., one of possible techniques for studies of the recovery and recrystallisation during heating of cold deformed materials is based on the measurements of the

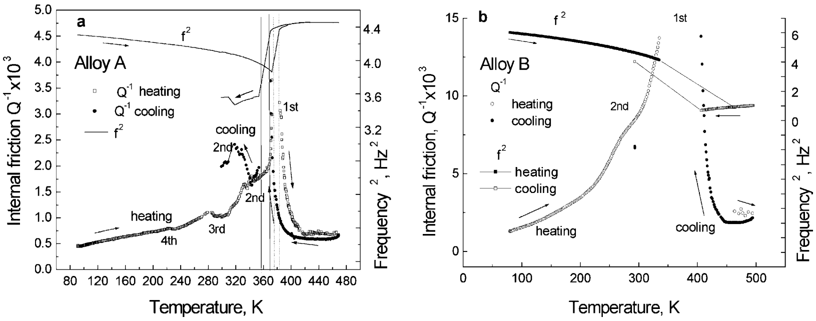

Fig. 2. Temperature dependence of IF in the studied alloys. Measurements could not be done after reaching some degree of martensitic transformation because of a giant acoustic emission. This interruption is shown for heating and cooling by the dotted and solid lines respectively.

internal friction after gradual, step by step, heating to different temperatures.

As shown in a number of studies (e.g. [13]), martensite in the studied Ni_2MnGa alloys is essentially twinned and does not contain the slip dislocations. One can at least state that their density is negligible and, therefore, their contribution to damping is insignificant.

No grain boundaries were observed under optical microscope in the samples for the internal friction. Moreover, even if the samples would consist of several grains, the movement of grain boundaries and, correspondingly, their contribution to damping (the grain-boundary IF peak) occurs at rather high temperatures (e.g., 500–600 °C in Ni-based alloys [14]).

No relaxation phenomena are observed in the studied temperature range (see Fig. 2). And, even if they could occur, a peculiarity of the relaxation internal friction is that its relaxation strength does not reveal any strain dependence (e.g. Snoek-like relaxation) or it is negligible, which is important for the present study. The IF peaks in Fig. 2 are of hysteretic nature, because they are not shifted with the frequency change and exist in the narrow frequency range. Thus, they clearly belong to martensite-to-martensite transformations.

Therefore, in the temperature areas where there is no phase transformations, the only mechanism that can be responsible for the internal friction background is related to the vibrations of twin boundaries.

Thus, the following model is proposed for this case. An increase in the value of internal friction with increasing applied stress/strain amplitude reflects an increase in the area S swept by twin boundaries for one vibration cycle: $S = S_0 e^{-H_{tw}/kT}$, where H_{tw} is the activation enthalpy for the movement of twin boundaries, similarly as it occurs for mobility of dislocations in iron-based alloys (e.g. [15]). Therefore, measuring strain dependent IF at different temperatures and treating the experimental data of $Q^{-1} = Q^{-1}(\varepsilon)_T$ in the Arrhenius coordinates $\ln(Q_\varepsilon^{-1}/Q_0^{-1}) = \ln(S_\varepsilon/S_0) = -H_{tw}/k \cdot 1/T$, one can obtain the value of H_{tw}, i.e. the height of an energy barrier that has to be overcome by the atoms during the movement of twin boundaries.

In Figs. 3 and 4 the strain dependence of IF is presented for both alloys. In both cases, the slope $\Delta Q^{-1}/\Delta\varepsilon$ increases with increasing temperature, which corresponds to an increase in the mobility of twin boundaries. This is in good agreement with twinning stress (stress needed for the growth of a favourable martensitic variant at expense of others) decreasing with the temperature [16]. At the same time, in the both alloys the strain dependence of internal friction reveals peculiarities at large strain amplitudes in the temperature ranges that coincide with those of all the IF peaks shown in Fig. 2a and b, even if they are not always detected in the temperature dependence of IF at $\varepsilon \approx 10^{-6}$. As an example, the strain dependence of internal friction in Alloy A is shown in Fig. 3 for temperatures in between 290 and 353 K. The strain-dependent IF curves move to higher values up to 323 K after which they decrease again at 343 and 353 K. This is clearly due to the effect of the

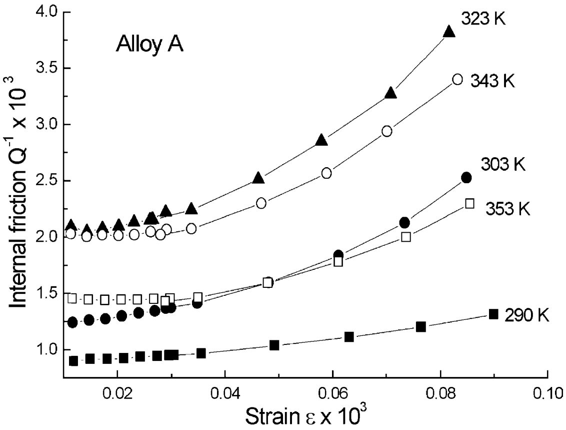

Fig. 3. Change in the strain dependence of internal friction in Alloy A at temperatures in the vicinity of the second transformation in martensite (see Fig. 2).

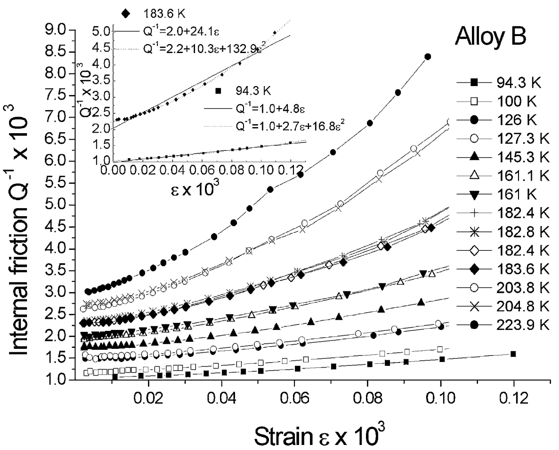

Fig. 4. Strain-dependent internal friction Q^{-1} in Alloy B. Linear and polynomial fits of the $Q^{-1} = Q^{-1}(\varepsilon)_T$ curves measured at different temperatures are shown in the insert.

martensite-to-martensite transformation causing the second IF peak (see Fig. 2a) that increases the background level of the experiment established in the beginning of each measurement at the strain amplitude of 10^{-6}. However, a more important result shown also in Fig. 3 is that the slope of the curve $Q^{-1} = Q^{-1}(\varepsilon)_T$ is always decreased in the temperature range of the discussed second, third and fourth IF peaks. Along with the data of temperature-dependent IF (Fig. 2a, b), this suggests that the lattice of martensite is extremely unstable so that at some temperatures a restructuring (martensite-to-martensite transformation) occurs, which prevents in this temperature range the movement of twin boundaries under the stress caused by the pendulum. The fact that the decrease in the IF slope was always observed, although third and fourth peaks were not detected for some samples of Alloy A and at all not seen for Alloy B, means that the increase in the value of strain above 10^{-6} assists the structural instability of martensite, so that, possibly, the observed phenomenon can be partly characterised as stress-induced martensite-to-martensite transformation. This could explain also why these peaks are not visible in DSC or magnetic susceptibility measurements, where samples are totally unstrained, although the IF technique is obviously more sensitive to structural instability as compared to DSC or MS measurements.

On account of the data of which example was shown in Fig. 3, the measurements of the strain-dependent IF were carried out below 220 K, i.e. at temperatures below the range of any possible structural changes (as revealed in Fig. 2).

An example for the treatment of the obtained experimental data is given in the insert of Fig. 4. One can see that at low temperatures the experimental data can be satisfactorily described by a linear function, whereas the square term becomes stronger with increasing temperature of measurements. Within the frame of the proposed model, an increase of the square contribution to the strain-dependent IF corresponds to an increase in the length of the oscillators, i.e. vibrating twin boundaries. In the low temperature range the length of the twin boundary segments involved into vibrations remains nearly unchanged. Again, this result corresponds with the twinning strain expansion connected to the temperature increase shown in non-layered tetragonal martensite structure [16]. The linear component of the fitting characterises the activation enthalpy for the movement of twin boundaries.

The procedure of treatment in the Arrhenius coordinates is shown in Fig. 5 for Alloy B. Using the data of both linear and polynomial fitting of the experimental curves $Q^{-1} = f(\varepsilon)$, one practically obtains the same values of the activation

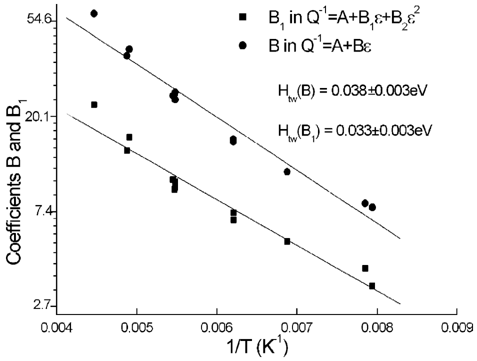

Fig. 5. Data of $\ln \Delta Q^{-1}/\Delta\varepsilon$ as function of $1/T$ in the cases of linear fitting (coefficient B in $Q^{-1} = A + B\varepsilon$) and polynomial fitting (coefficient B_1 in $Q^{-1} = A + B_1\varepsilon + B_2\varepsilon^2$) of the strain dependence of internal friction in Alloy B. The enthalpy of activation for movement of twin boundaries is determined from treating of $Q^{-1} = Q^{-1}(\varepsilon)_T$ in the Arrhenius coordinates $\ln(Q_\varepsilon^{-1}/Q_0^{-1}) = \ln(S_\varepsilon/S_0) = -(H_{tw}/k)\cdot(1/T)$.

enthalpy for movement of the twin boundaries, 0.03–0.04 eV. The values in between 0.02 and 0.025 eV were obtained for Alloy A. These low values of the activation enthalpy are qualitatively consistent with the extremely low stress of twinning in MSM Ni_2MnGa alloys and show how small in this case is the energy barrier for movement of atoms during twinning. E.g., if the interaction of dislocations with impurity atoms would be a controlling mechanism, one could expect the values of the activation enthalpy of about 0.8–1.0 eV (see e.g. [15]).

Another possibility to estimate the enthalpy of activation is related to the analysis of the isothermal transformation kinetics. As first approximation, one can interpret the movement of the twin boundaries under applied mechanical stress, i.e. the growth of a favourably oriented martensitic domain at expense of the others at constant temperature, as some isothermal transformation in martensite. If so, following the formalism of the kinetics analysis of phase transformations described e.g. by Mittemeijer et al. [17], the value of the activation enthalpy can be determined from the values of strain ε_{f_2} and ε_{f_1} (times t_{f_2} and t_{f_1} in [17]) needed to reach two fixed stages of transformation f_2 and f_1 measured at a number of temperatures: $\ln(\varepsilon_{f_2} - \varepsilon_{f_1}) = (H_{tw}/kT) + \text{Const}$. This procedure was fulfilled for Alloy B for different $\Delta\varepsilon = \varepsilon_{f_2} - \varepsilon_{f_1}$, and the values of H_{tw} of 0.04–0.05 eV were obtained.

Consequently, one can state that the movement of twin boundaries in the studied alloys requires extremely small energy, which suggests that they can be promising for obtaining the magnetic-field-induced strain.

4. Conclusions

1. Temperature dependence of internal friction at the strain amplitude of 10^{-6} was measured in two Ni_2MnGa alloys having relatively high temperatures of the austenite-to-martensite transformation. One to three additional peaks of IF were observed below the M_s temperature, which was interpreted as some restructuring in the martensite lattice.
2. The increase in the strain amplitude up to 10^{-4} has led to a marked decrease of the internal friction in three temperature ranges corresponding to three IF peaks in the martensitic temperature range, which is an indirect confirmation of the stress-induced restructuring in martensite that retards mobility of twin boundaries.
3. Under suggestion that twin boundaries in the Ni_2MnGa martensites provide the main contribution to the background of IF, the strain dependence of IF measured at different temperatures was used in order to obtain the value of the activation enthalpy H_{tw} for the movement of the twin boundaries.
4. The values of 0.02–0.05 eV were obtained for the activation enthalpy H_{tw} of the movement of twin boundaries, which suggests a high mobility of twins and refers to a possibility to find the magnetic-field-induced strain in the studied alloys.

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