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Magneto-elastic attenuation in austenitic phase of Ni–Mn–Ga alloy investigated by ultrasonic methods

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ABSTRACT

Magneto-elastic ultrasound attenuation in single crystals of a Ni–Mn–Ga is studied by ultrasonic methods at different temperatures, ranging from temperatures above the Curie point down to the vicinity of the premartensitic transition temperature. The conventional pulse–echo method is used for analysis of the attenuation of longitudinal waves only, whereas the attenuation related to shear motion is investigated by the resonant ultrasound spectroscopy (RUS). Because of the strong attenuation (increasing with the distance from the Curie point), the analysis of the resonant spectra obtained from RUS measurements must be done in successive steps, tracing individual resonances from above the Curie point into the region of higher attenuation. This method is also verified as appropriate for accurate determination of the c' elastic coefficient. The overall character of the attenuation is shown to be strongly anisotropic and different for longitudinal and shear waves.

1. Introduction

Thermal dependencies of elastic coefficients are widely accepted as sensitive precursors of structural transitions in single crystals of solids. For the shape memory alloys (SMAs), where the transitions have the character of martensitic (shearing) mechanisms, the behaviors of shear moduli in the vicinity of the transition temperature are of particular interest. As shown for single crystals of different SMAs [1–3], the anisotropy factor of these alloys increases systematically towards the transitions temperatures both in the high-temperature (highly symmetric, austenitic) phases and in the low-temperature (low-symmetry, martensitic) phases, which indicates the softening of the crystal along the crystallographic planes in which the transitions are expected to occur. Such hypothesis can be supported by the increase of ultrasound attenuation close to the transition temperature (e.g. [1]), where these softest modes start to be strongly dissipative.

Such an experimental investigation is significantly complicated for Ni–Mn–Ga alloy, where two different ferroic phenomena: the ferroelasticity (the shape memory) and the ferromagnetism are coupled. The strong ultrasound attenuation of magneto-elastic nature embarrasses significantly the determination of thermal dependencies of elastic coefficients [4,5], especially of those shear moduli which are closely related to the transition mechanism.

This paper aims to investigate the elastic properties, especially the magneto-elastic attenuation, of Ni–Mn–Ga by means of ultrasonic methods. On contrary to the previous works published on the Ni–Mn–Ga alloy, not only the pulse–echo measurements are applied, but this conventional method is complemented by the non-contact resonant ultrasound spectroscopy (RUS) technique [6–9]. The reasons for such extension are following:

1. The RUS technique is extremely sensitive to the $c' = (1/2)(c_{11} - c_{12})$ coefficient of the cubic material (see [8,9] for further details), which is the coefficient with the most dramatic changes with temperature in the vicinity of the martensitic transition, and which cannot be determined accurately from the pulse–echo measurements.
2. The experimental outputs of the RUS technique contain a directly interpretable, quantitative information about the attenuation in the material (the quality factor of particular resonances). Moreover, the RUS method also enables the determination of the attenuation dependence on the frequency.

2. Examined specimens

Three specimens of the near stoichiometric Ni–Mn–Ga alloy were used for the experiments. Two of them were 4.4 mm thick tablets (cylindric, 15 mm in diameter) suited for pulse–echo mea-

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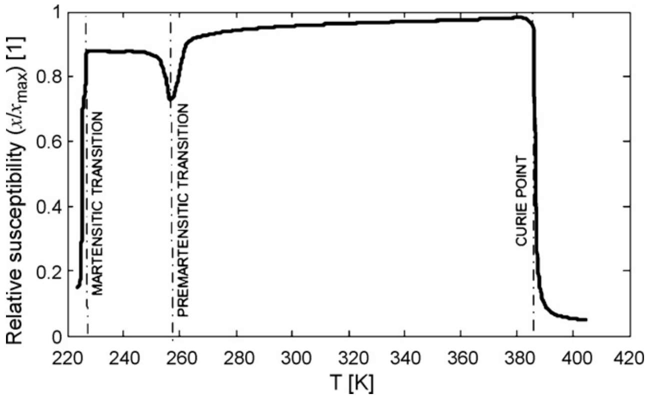

Fig. 1. Thermal dependence of magnetic susceptibility of the examined material.

surements in directions [1 0 0] and [1 1 0]. The last specimen was a 7.7 mm × 5.6 mm × 4.4 mm rectangular parallelepiped for resonant ultrasound spectroscopy measurements. This specimen was cut approximately along the principal (i.e. {1 0 0}) planes, the exact orientations were determined by X-ray Laue method.

The all specimens were produced by directional solidification method and delivered by the Laboratory of Engineering materials, Helsinki University of Technology. The magnetic properties of the material were estimated by the susceptibility measurements with temperature (Fig. 1). The Curie point was evaluated at 385 K, the rapid dropdown of the susceptibility at 257 K indicates the *premartensitic transition* [10–12].

3. Applied ultrasonic methods

Two different ultrasonic methods were applied: the longitudinal modes were investigated by the pulse–echo method, the shear modes by the resonant ultrasound spectroscopy.

3.1. The pulse–echo technique

The pulse–echo method can be used for convenient determination of all independent elastic coefficients of cubic materials, whenever the [1 1 0] and [1 0 0] directions are reachable for the measurements. In our case of the two tablets of the Ni–Mn–Ga alloy (one enabling the pulse–echo measurement in direction [1 0 0], the other in [1 1 0]), we restricted ourselves to measurements of the longitudinal modes only (36Y–LiNbO$_3$piezoelectric transducers at 18 MHz were used). The temperature range of the measurement covered the interval between the temperature of the premartensitic transition T_{pM} and the Curie point T_{C}. Analogously to [4,5], we have obtained nearly constant value of the longitudinal phase velocity in the [1 0 0] direction in this interval. The behavior of the longitudinal velocity in direction [1 1 0] was similar, with a small dropdown around T_{pM}. At the room temperature, the values were $v_{\varphi[1\,0\,0]} = 3.89\,\mathrm{mm}\,\mu\mathrm{s}^{-1}$and $v_{\varphi[1\,1\,0]} = 5.42\,\mathrm{mm}\,\mu\mathrm{s}^{-1}$, which gives (for density $\rho = 8.120\,\mathrm{g\,cm}^{-3}$) values of elastic coefficients $c_{11} = 121.2\,\mathrm{GPa}$ and $c_{\mathrm{L}} = 235.4\,\mathrm{GPa}$. These results are comparable to those obtained earlier by Stipcich et al. [5] and Manosa et al. [4].

Compared to the phase velocities, the thermal dependencies of the attenuation coefficients are much more dramatic. From the pulse–echo measurement, we have determined the evolution of the attenuation coefficients of longitudinal waves in directions [1 0 0] and [1 1 0] during two thermal cycles between the premartensitic transition temperature and the Curie point. The attenuation coefficients were determined from the envelopes of the first, the second and the third detected echoes. The course of this coefficient with temperature was fully reproducible, following nearly the same paths during heating and cooling and during the both applied cycles. The results are shown in Fig. 2. Obviously, the attenuation is anisotropic – the strong attenuation in the [1 0 0] direction has a significant maximum at about 295 K and than decreases towards the Curie point; the indubitably weaker attenuation in the direction [1 1 0] decreases towards the premartensitic transition temperature, where it changes discontinuously. On the other hand, the attenuation in this direction seems to be unaffected by the Curie point at all.

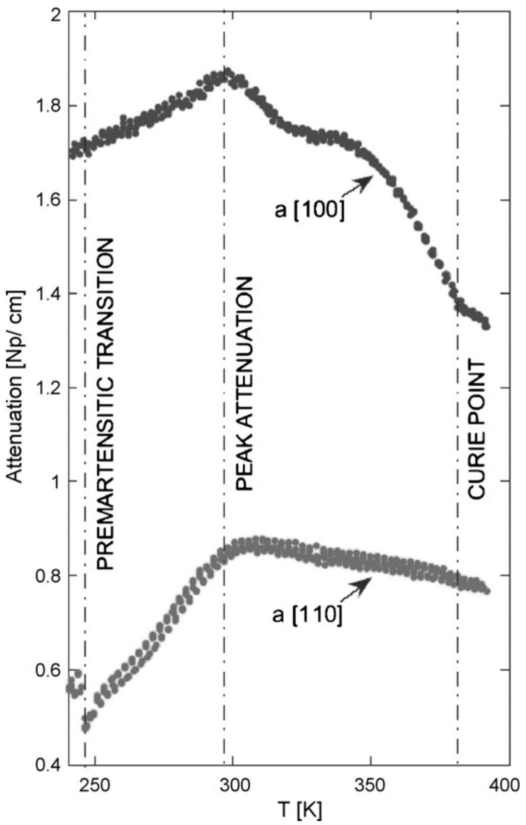

Fig. 2. Thermal dependencies of the attenuation of longitudinal waves in [1 0 0] and [1 1 0] directions of Ni–Mn–Ga single crystals.

3.2. Resonant ultrasound spectroscopy

The RUS method [6–9] is based on an assumption that the resonant spectrum of free elastic vibrations of a small specimen with well-defined geometry contains a sufficient information on the elastic properties of the examined material. Unlike for the pulse–echo method, the outputs of RUS measurement cannot be directly recalculated into elastic coefficients (i.e. no explicit relations are available), but the sought coefficients c_{ij} must be determined inversely using numerical search methods.

For strongly anisotropic cubic materials (anisotropy factor $c_{44}/c' > 10$), as the single crystals of Ni–Mn–Ga are, the RUS method has been shown to be extremely suitable for determination of the c' coefficient, fairly suitable for c_{44}, but nearly unable to determine c_{L} with acceptable accuracy [8,9]. In the light of this finding, the RUS method seems to be a proper complement to the pulse–echo measurements, which are, as discussed above, much more suitable for determination of c_{L} or c_{11} than of c'.

For the examination of the Ni–Mn–Ga single crystal, the fully non-contact arrangement of RUS was used: the specimen was laid on a cork wood underlay (i.e. on material with extremely low acoustic impedance), which was placed in a thermal cham-

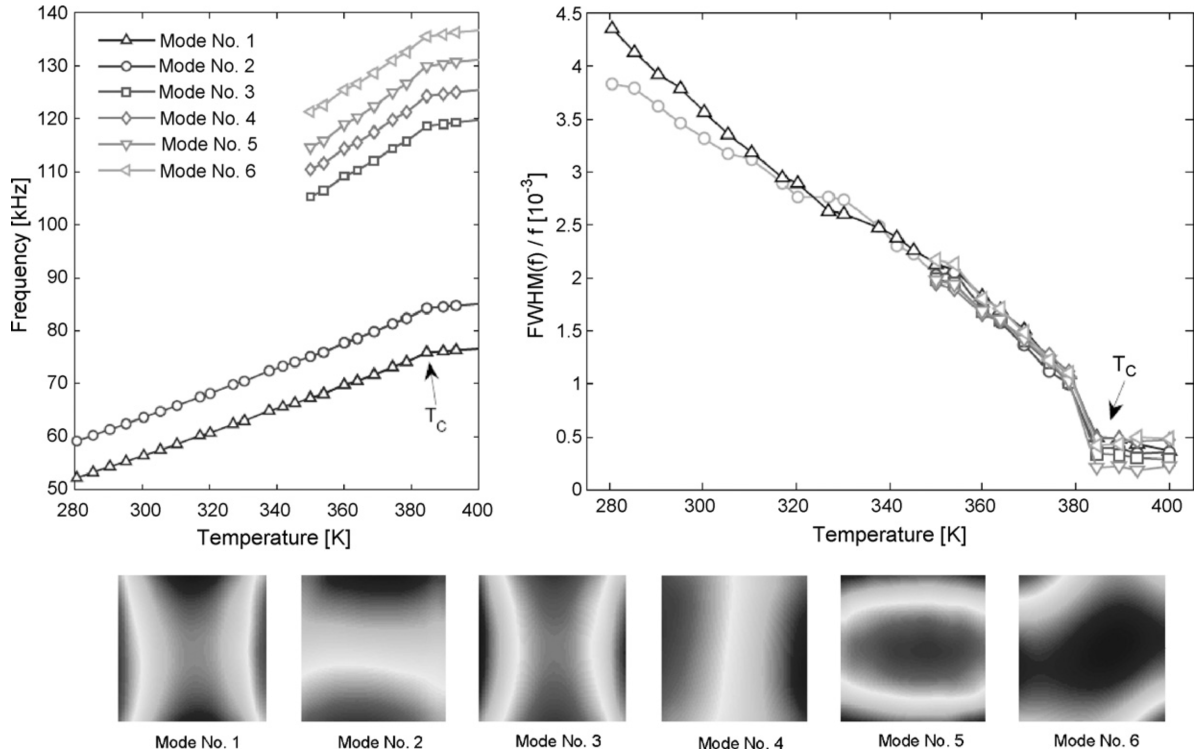

Fig. 3. Thermal dependencies of the peak locations (on the left) and of the attenuation for first six identified modes of RUS spectra (the shapes of the modes are outlined in the lower row). T_C indicates the Curie point.

ber with two silica glass windows enabling the access of two laser beams to the specimen, one for excitation of the vibrations and one for their detection. The elastic vibrations in the specimen were excited by sequences of pulses of an unfocused infrared laser beam (Nd:YAG, General Photonics Corporation TWO-45Q, nominal wavelength 1064 nm) from the side of the specimen. The vibrations were recorded by scanning red-light laser vibrometer (Polytec OFV-2570 equipped by a scanning unit consisting of two dielectric mirrors on motorized positional stages) on the upper surface of the specimen. Such fully non-contact arrangement gives significantly higher quality of the obtained resonant spectrum than the classical arrangement, where the specimen is placed between two piezoelectric transducers, and the results can be, thus, strongly influenced by the contact forces between the specimen and the transducers. Moreover, the measurements in wide temperature intervals can be also biased by thermal dependencies of properties of the transducers.

The RUS measurements were performed between T_{pM} and T_C. Upon cooling, the first resonant frequency moves from 76.1 kHz above the Curie point down to 60.1 kHz at 317 K. The rest of the spectrum drifts in a similar way. Such dramatic changes of the resonances with the temperature cannot be ascribed to the thermal expansion of the specimen, which is about $18.10^{-6}\,\mathrm{m\,K^{-1}}$ [14].

The resonant spectra of the specimen were recorded by the following strategy:

- At 393 K (i.e. safely above the Curie point), the specimen was scanned in the full 20×20 grid to identify accurately the resonant frequencies as well as the shapes of 37 vibrational modes. Such information was sufficient for determination of the c' and c_{44} coefficients.
- Then, the specimen was heated up to 398 K, from where the temperature was decreased in successive steps of approximately −5 K till a 280 K temperature was reached. At each temperature, the surface of the specimen was scanned by a sparse 3×3 grid, which was not sufficient for the identification of the shapes of the vibrational modes, but enabled reliable determination of the spectra.

At 393 K, the full scan data were used for determination of the shear elastic coefficient by conventional RUS inversion procedure stabilized by the knowledge of the shapes of the modes (for more details, see [7–9]). The results are $c' = (6.9 \pm 0.1)$ GPa and $c_{44} = (97.7 \pm 4.7)$ GPa (i.e. the anisotropy factor c_{44}/c' is approximately 14), which is comparable to the results in [4,5]. The spectra at lower temperatures were subjected to further analysis in order to obtain the thermal dependencies of c' and of the attenuation parameters.

4. RUS data analysis

The locations and full width at half maximum (FWHM) values of individual peaks were identified at each temperature by fitting the (complex) spectrum by function

$$F(f) = \sum_{n=1}^{N} \frac{A_n(\mathrm{FWHM}_n/2)e^{\mathrm{i}\phi_n}}{\mathrm{i}(f - f_n) + (\mathrm{FWHM}_n/2)}, \tag{1}$$

where f_n is the resonant frequency of the n-th mode in the group, A_n and ϕ_n are corresponding amplitude and phase, and FWHM_n is the full width at half maximum of the n-th mode, which was chosen as a parameter for characterizing the attenuation of each mode. Values of f_n, A_n, ϕ_n and FWHM_n were obtained by simplex search algorithm implemented in MATLAB. The analysis was performed in successive steps, starting at the highest temperature (above the Cure point), and then fitting the spectra at lower and lower temperatures. As initial guesses for the search at each temperature, the values obtained in the previous step (i.e. at the previous, higher temperature) were used. This enabled the first pair of peaks to be accurately traced down through the whole temperature interval, and the next peak

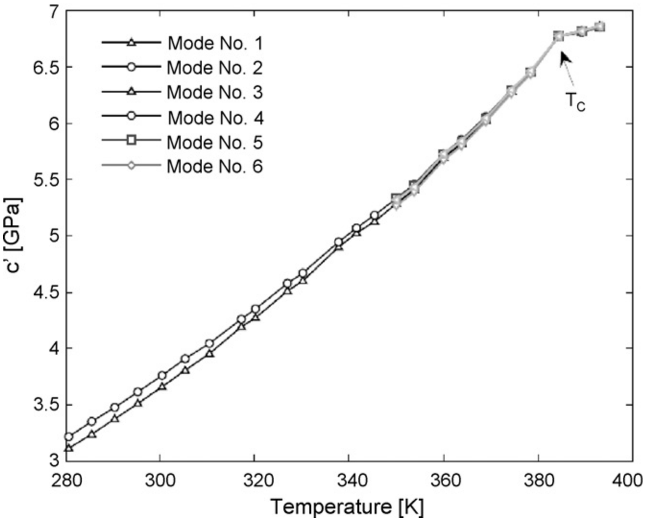

Fig. 4. Thermal dependence of the c' elastic coefficient. T_C indicates the Curie point.

quadruplet to be traced down to $T = 353$ K (below this temperature, the algorithm was able to localize the peaks and fit the amplitude of the spectrum, but the evaluated phases ϕ_n were not agreeing sufficiently with the experimental results and the FWHMs were not obtainable with sufficient accuracy). The obtained thermal dependencies of the peak locations and the attenuation for the first six modes are shown in Fig. 3.

4.1. *Thermal dependencies of c' and FWHM*

The resonant frequencies from the beginning of the spectrum correspond to the softest modes of vibrations and are, thus, sensitively dependent only on the coefficient c' [8]. This enabled us to recalculate directly the dependence of the location of the first peaks on temperature into the curve of thermal dependence of this coefficient shown in Fig. 4 (approximately the linear relation between the resonant frequencies f_n and $\sqrt{c'}$ can be assumed).

The decrease of c' with decreasing temperature is nearly linear, with a significant change of the slope at the Curie point. This corresponds well to the previous measurement of Zhao [12], who performed the measurement of c' by cantilever oscillation method at lower frequency. The corresponding attenuation characteristics (the right of Fig. 3) shows, similarly to the attenuation coefficient for the longitudinal waves in the [1 0 0] direction, significant increase below the Curie point. However, there is no *peak attenuation* for this quantity, although some mild changes in the slope between 320 and 350 K may indicate some relation to the thermal behavior of the attenuation of the longitudinal waves in the [1 0 0] direction again. Such character of the attenuation related to the c' coefficients differs significantly from the low-frequency attenuation reported in [12], which forms a narrow, localized peak around the Curie point.

5. Summary

The combination of two different ultrasonic method was applied for analysis of the elastic properties and magneto-elastic attenuation of single crystal of Ni–Mn–Ga shape memory alloy in the temperature interval between the premartensitic transition temperature and the Curie point. The attenuation of longitudinal waves was investigated by conventional pulse–echo measurements, whereas the non-contact resonant ultrasound spectroscopy was firstly applied to the measurement of slow shear vibrational modes. The pulse–echo technique revealed the strongly anisotropic character of the attenuation: While the attenuation of longitudinal waves in the [1 0 0] direction decreases significantly towards the Curie temperature T_C but seems to be fully insensitive the premartensitic transition temperature T_{pM}, the attenuation in the [1 1 0] direction jumps discontinuously at T_{pM} but does not reflect anyhow the magnetic transition at T_C. In the [1 0 0] direction, peak attenuation at about 300 K was observed.

The thermal dependence and the attenuation of the softest shear mode (c') was estimated by tracing the resonant frequencies of the first six modes from above T_C downwards, the corresponding attenuation was shown to have similar character as the attenuation of longitudinal waves in the [1 0 0] direction (slope jump and rapid increase at T_C, slowdown of the increase at about 350 K) but without any peak attenuation.

In general, the used ultrasonic methods were shown to be appropriate tools for analysis of strongly temperature dependent and anisotropic attenuation in the austenitic phase of Ni–Mn–Ga.

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