

On the evaluation of temperature dependence of elastic constants of martensitic phases in shape memory alloys from resonant ultrasound spectroscopy studies

Michal Landa^{a,*}, Petr Sedlák^{a,c}, Petr Šittner^b, Hanuš Seiner^{a,c}, Luděk Heller^{a,b}

^a *Institute of Thermomechanics Academy of Sciences of the Czech Republic, Dolejškova 5, Prague 8, CZ 182 00, Czech Republic*

^b *Institute of Physics Academy of Sciences of the Czech Republic, Na Slovance 2, Prague 8, CZ 182 21, Czech Republic*

^c *Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Trojanova 13, Prague 2, CZ 120 00, Czech Republic*

Received 17 May 2006; received in revised form 8 November 2006; accepted 31 December 2006

Abstract

Elastic constants of austenite and martensite phases in shape memory alloys reflect fundamental thermodynamic properties of these materials—i.e. important physical information can be deduced not just from the values of the constants but, mainly from their temperature and stress dependencies. As regards to the parent austenite phase, such information is available in the literature for most of the known shape memory alloys. For the martensitic phases, however, only few reliable experimental data exist, due to the experimental difficulties with the preparation of martensite single crystals as well as due to the difficulties with the ultrasonic measurement of elastic properties of strongly anisotropic media with low symmetry. In this work, the temperature dependence of all elastic constants of cubic austenite and orthorhombic 2H martensite phases in Cu–Al–Ni alloy determined by resonance ultrasound spectroscopy (RUS) is reported. Experimental and theoretical improvements of the RUS method which had to be made to perform the successful measurements on strongly anisotropic and martensitic phases are discussed.

© 2007 Published by Elsevier B.V.

Keywords: Modal resonant ultrasound spectroscopy; Elastic properties; Shape memory alloys; Martensitic transformation

1. Introduction

The elastic constants of austenitic and martensitic phases in shape memory alloys (SMAs) have been subject to continuous research for two basic reasons: (i) essential information on the phase stability can be deduced from their temperature and stress dependencies; (ii) knowledge of elastic constants is very important for modeling the SMA functional behaviors, since the martensite crystal domains in activated SMAs interact elastically. However, due to the experimental difficulties with preparation of martensite single crystals, only few reliable complete sets of the elastic constants of the low symmetry martensitic phases in SMAs have been reported in the literature. Another specific problem for the resonance ultrasound spectroscopy (RUS) method is that the phases in SMAs are commonly strongly elastically anisotropic (martensitic phases possess additionally low crystal and elastic symmetry). Hence, we needed to improve

the conventional RUS experimental technique and method to be able to evaluate reliably and efficiently the elastic constants of SMAs including their temperature and stress dependencies. We have developed a comprehensive methodology consisting of: (i) the preparation of single variant martensite specimens of general crystallographic orientation, (ii) determination of the crystallographic orientation, and (iii) pulse-echo [1] and RUS methods (modified experiment and evaluation procedures) for determination of elastic constants of phases in SMAs. Elastic constants of austenite and 2H martensite phases in Cu–Al–Ni evaluated by modified pulse-echo technique were reported in [1]. The present work focuses the work done to optimize the RUS method for measurement of temperature dependence of elastic constants of phases in the same Cu–Al–Ni single crystal.

2. Cu–Al–Ni single crystal

A single crystal of Cu–13.8Al–4.1%Ni (wt.%) alloy was grown by the Bridgman method. The transformation temperatures were determined by DSC as M_s (2H) = 288 K

* Corresponding author. Tel.: +420 26605 3672; fax: +420 28658 4695.
E-mail address: ml@it.cas.cz (M. Landa).

and $A_s = 313$ K and the mass density was evaluated as $\rho = 7.055 \times 10^3 \text{ kg m}^{-3}$ [1]. Due to the thermal hysteresis, this crystal may exist at room temperature either in the bcc austenite or in the 2H martensite phase. The specimen was spark cut in the austenite phase in a cuboid shape. Care was taken to assure very good parallelism of the opposite sample faces. The martensite single crystals were prepared from the parent austenite specimen by the compression technique described in [1]. Due to the fact that orientation of the crystal axes of martensite lattice with respect to sample coordination system can be modified by applying compression deformation, this method enables us to obtain repeatedly several single crystal variants of the 2H martensite phase from a single austenite specimen. The originally cuboid austenite sample can exist as six different prism shaped martensite samples [1]. The dimensions of the samples as well as the orientation of crystal lattices were measured by back-reflection Laue X-ray method with an average accuracy better than 0.5° . The prism shapes and crystal lattice orientations are described by distances d_i of the opposite faces ($1 \mu\text{m}$ in precision) and face normals $\mathbf{n}_i = [\cos \varphi_1^i, \cos \varphi_2^i, \cos \varphi_3^i]^T$ pointing outwards. The geometrical parameters of the sample used in the evaluation procedure thus combine partial information on the sample shape and crystal lattice orientation [1].

In contrast to the pulse-echo method [1], only one martensite variant crystal is needed to evaluate all martensite elastic constants by the RUS technique in a single measurement. This makes it very effective for evaluation of temperature dependence of martensite elastic constants. Fortunately, it is not a problem that the martensite crystals commonly possess highly non-rectangular prism shapes with arbitrary crystallographic orientation of face normals. The measured values of the geometrical parameters are compared with those calculated theoretically (from the lattice parameters; bcc: $a_0 = 0.5835$ nm; 2H orthorhombic martensite: $a = 0.4389$ nm, $b = 0.5342$ nm, $c = 0.4224$ nm, [8]), shape strain due to bcc–2H martensitic transformation, orientation and dimensions of the austenite prism and lattice correspondence between austenite and martensite) in earlier work [1]. A very good agreement between the measurement and calculation was achieved indicating that true martensite variant single crystals were indeed obtained.

3. Modified ultrasonic techniques for measurement of elastic constants in SMAs

3.1. Pulse-echo method

The fact that the Cu–Al–Ni crystal may exist at room temperature as cubic austenite in cuboid shape or as a martensite single crystal in prism shape, depending on thermomechanical history, and that multiple prism shaped martensite single variants (needed for the pulse-echo method to evaluate all elastic constants) can be prepared from a single austenite crystal, is essential for the modified pulse-echo method proposed in [1]. This provides the advantage that propagation velocities of acoustic waves in various martensite crystal directions can be measured on a single piece of material (in a form of various prism

shaped specimens). Complete set of martensite elastic constants is determined by optimization based inverse method [1] from measurement on several samples. The main advantage is that one obtains the elastic constants of austenite and martensite phases from measurements on the same piece of material at the same temperature. The results allow to discuss [1], for example, the inheritance of the soft acoustic modes and elastic properties from the austenite to the 2H martensite phase. One can use efficiently the modified pulse-echo method to measure stress dependence of elastic constants or to evaluate the change of elastic constants in situ during stress induced martensitic transformation.

3.2. RUS method

The pulse-echo ultrasonic method is however quite laborious and inconvenient for evaluation of temperature dependence of all elastic constants. Because of this, significant effort has been made in the literature to develop the RUS method convenient for evaluation of temperature dependence of elastic constants using single crystal samples. Temperature dependence of elastic constants of series of NiTi alloys prior to martensite transformation was recently investigated systematically by resonant ultrasound spectroscopy (RUS) method in [2]. It was found that both C' and C_{44} elastic constants of the austenite phase soften upon cooling. Elastic constants of the monoclinic B19' martensite phase are not known yet, although partial results including temperature dependence are available.

In case of strongly elastically anisotropic Cu based SMAs such as Cu–Al–Ni, however, it is experimentally difficult to employ the standard RUS method for reliable determination of all elastic constants. Because of this, only few references on elastic constants of phases in Cu–Al–Ni measured by RUS can be found in the literature (austenite [3], 2H martensite [4]). Temperature dependencies of elastic constants of Cu–Al–Ni austenite published in the literature (Table 4 in [1]) suggest that only the C' constant softens upon cooling, in contrast to NiTi where both C' and C_{44} soften. No data are available in the literature concerning the temperature dependencies of elastic constants of 2H martensite.

In our earlier paper [5], we employed the conventional RUS method (Fig. 1) for the measurement of temperature dependence of elastic constants of both austenite and martensite phases in Cu–Al–Ni near the transformation temperature range. Natural frequencies of free-elastic vibrations of a small single crystal specimen were measured for a number of sample's normal modes. Elastic constants were calculated in two steps. First, the natural frequencies were calculated from the estimated elastic constants, and then nonlinear inversion procedure was employed to find the required elastic constants from the measured natural frequencies. In the conventional RUS method [6], a prism single crystal specimen is supported by two transducers at its opposite corners. One serves for an excitation and the second for a detection of the sample response. When applied to relatively weakly anisotropic crystals (such as Si, Fe, Cu, cubic NiTi), this experimental setup ensures quite reliable detection of the first 20–30 resonances which are sufficient for stable determination of all elastic constants. In case of strongly anisotropic

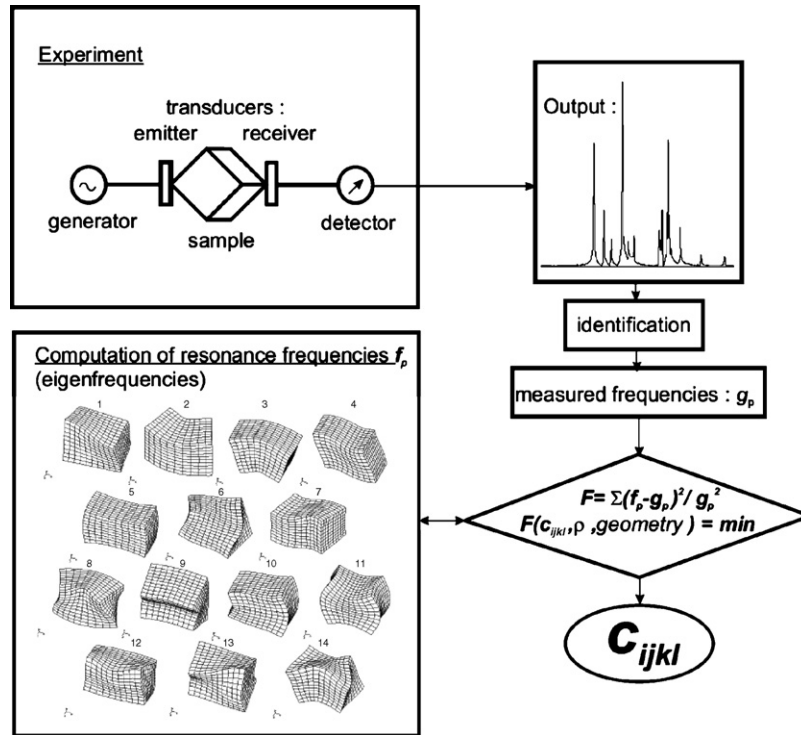


Fig. 1. Schematic depiction of resonant ultrasound spectroscopy method.

crystals, however, the frequency band in which large number of resonances must be evaluated (60 and more) significantly widens [5]. The excitation and identification of the complete proper sequence of resonance frequencies in such wide frequency bands is extremely difficult. In addition, the standard RUS measuring procedure based on the frequency sweeping of harmonic excitation and lock-in detection of received signal is time consuming, and computation demands increase rapidly with growing number of resonance frequencies needed, as well.

This is why we have proposed and employed the following experimental and theoretical improvements of the RUS method (Fig. 2):

- (i) The chirp signal technology was used instead of sweeping harmonic excitation. In this way, the complete frequency spectrum is expressed instantly as a transfer function between the received and excitation signals.

- (ii) The point-to-point noninvasive measurement of vibrational sample response was carried out by laser interferometry technique first introduced in [7]. Main advantage of this is that we avoid omitting of some resonances in detected signal near node points (zero-valued points of vibrational modes (see Fig. 3)) by averaging the magnitudes of measured spectra from different points on the sample surface. In addition, the information on the amplitude and phase variations (Fig. 3) over the specimen surface provided by the laser interferometer can be used to evaluate the shape of vibrational eigenmodes (Fig. 1) which improves significantly the identification of the resonance frequencies in the spectra and facilitates the regularization of the inversion procedure.

- (iii) The efficiency of the inverse computation of the elastic constants is improved by the derivation of the first and second derivatives (Hessian) of the error function characterizing a measure of the distance between the measured and calculated resonant frequencies.

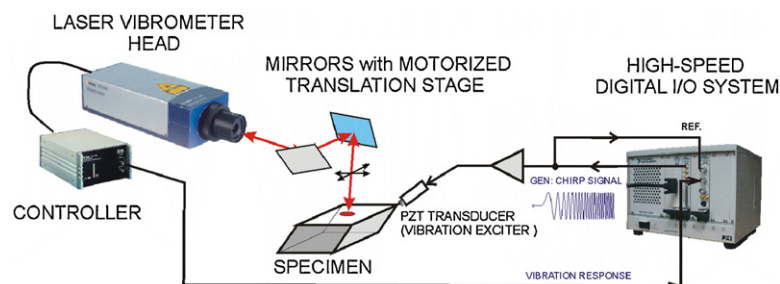


Fig. 2. RUS-laser measurement setup.

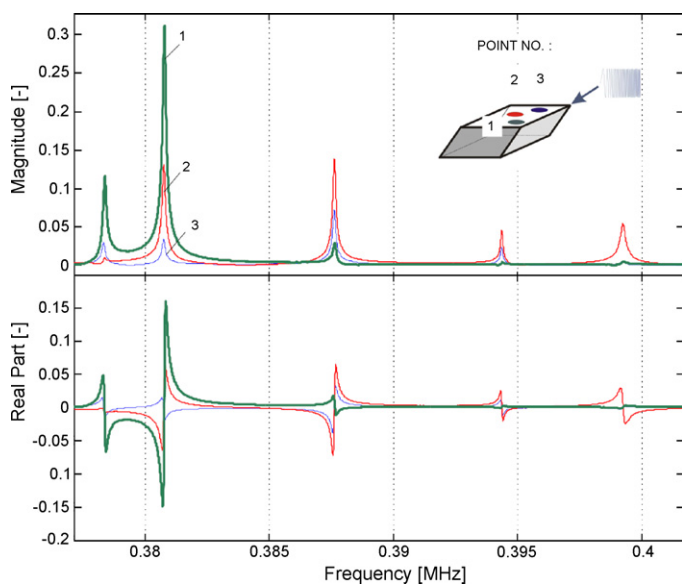


Fig. 3. Part of multipoint measured spectra.

The modified experimental setup (Fig. 2) is based on the high-speed digital I/O system National Instruments. The broadband chirp signal is generated by the high frequency D/A converter. After amplification, the signal is transferred to the sample by a miniature piezoelectric transducer placed on the sample corner which excites ultrasonic vibrations. The displacement responses are detected in multiple points on one of the sample surfaces by means of the laser interferometer (Polytec OFV-2570) equipped with a self-made scanning unit consisting of two dielectric mirrors placed on motorized positional stages (precision up to 1.25 μm).

The elastic constants of both austenite and martensite phases were evaluated from the measured resonant frequencies and resonant modes by the inversion procedure. For the calculation of resonance spectra of a parallelepiped sample, the standard Ritz method was adopted. Legendre orthogonal polynomials as basic functions ensure good numerical stability and accuracy of the calculation. Novel hybrid architecture of the inverse problem solution was proposed. It combines gradient and simplex method. Furthermore, the efficiency of the inverse computation was improved by deriving the analytical expression of the gradient and the Hessian of the objective function. More than 100 resonances of the specimen in the frequency range 0.15–1 MHz were identified in the spectra measured at each preselected temperatures during cooling of the austenite and during heating of the 2H martensite crystals. The frequency resolution was better than 50 Hz.

Table 1
Elastic constants (GPa) of 2H martensite Cu–Al–Ni at room temperature

| | C_{11} | C_{22} | C_{33} | C_{44} | C_{55} | C_{66} | C_{23} | C_{13} | C_{12} |
|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| This work | 180.6 | 158.9 | 257.1 | 65.8 | 23.7 | 60.2 | 96.9 | 73.5 | 144.4 |
| [1] | 184.5 | 151.5 | 238.6 | 66.4 | 22.9 | 60.5 | 86.9 | 70.1 | 140.4 |
| [5] | 182.2 | 151.0 | 237.0 | 64.5 | 23.8 | 60.0 | 87.2 | 67.9 | 140.5 |
| [4] | 189 | 141 | 205 | 54.9 | 19.7 | 62.6 | 124 | 45.5 | 115 |

See [1] for crystallographic details-coordinate systems in which the elastic tensor of martensite is expressed.

The obtained values of elastic constants of cubic austenite (at $T=32^\circ\text{C}$) agree quite well with the values measured on the same material in our earlier papers [1,5]. The elastic constants of 2H martensite phases (at $T=25^\circ\text{C}$) are compared with previous measurement [1,4,5] in Table 1. The differences in elastic constants C_{33} , C_{44} , C_{23} , C_{12} and C_{13} are not negligible. They may possibly be attributed to the imperfectness of the martensite single variant crystals that are rather difficult to avoid. Frequently, during the compression loadings used to bring the martensite crystal into the single variant form, we obtained a very fine twinned structure (compound twins). It is rather difficult to distinguish such structural state from a single variant case. Frequently, we have therefore measured the elastic constants erroneously. Elastic constants of such twinned sample related to the $(010)_M$ plane (i.e. C_{22} , C_{13} , C_{55}) have indeed similar values to that of the single variant sample but other constants differ significantly. Thus, measurement on uncompletely detwinned martensite can lead to the error in evaluation of these elastic constants. The problem is that it is rather difficult to completely drive the compound twin interfaces out from the sample and particularly to verify that the sample is completely detwinned. Dedicated diffraction techniques [9] were applied to check whether the sample is really an interface-free martensite variant single crystal. Other error sources, such as experimental uncertainty or chemical composition inhomogeneity, etc., are much less likely. The modification of the standard RUS method facilitates precise evaluation of temperature dependence of elastic properties of arbitrary anisotropic crystals with general crystallographic orientation. This is demonstrated below for the case of austenite and 2H martensite phases in Cu–Al–Ni.

4. Results

The elastic anisotropy of both investigated phases may be expressed in a form of acoustic wave phase velocity diagrams, plotted in Fig. 4a and b, where important directions and related elastic constants are marked. The subscripts A, M denote austenite and martensite, respectively, wherever they can be mistaken. The slow quasi-shear wave velocity surface (qT2, colored in Fig. 4) is important for characterization of premartensitic changes [2,3,5]. The relative decrease of the qT-wave velocity is shown in Fig. 4c and d as a positive part of $[v_{\text{ref}}(\mathbf{n}) - v(\mathbf{n})]/v_{\text{ref}}(\mathbf{n})$, where $v_{\text{ref}}(\mathbf{n})$, and $v(\mathbf{n})$ are phase velocities of qT2 wave mode evaluated in the same wave vector direction \mathbf{n} from the measurement at temperatures: far (T_{ref}) and the nearest (T) to the transition temperature, respectively.

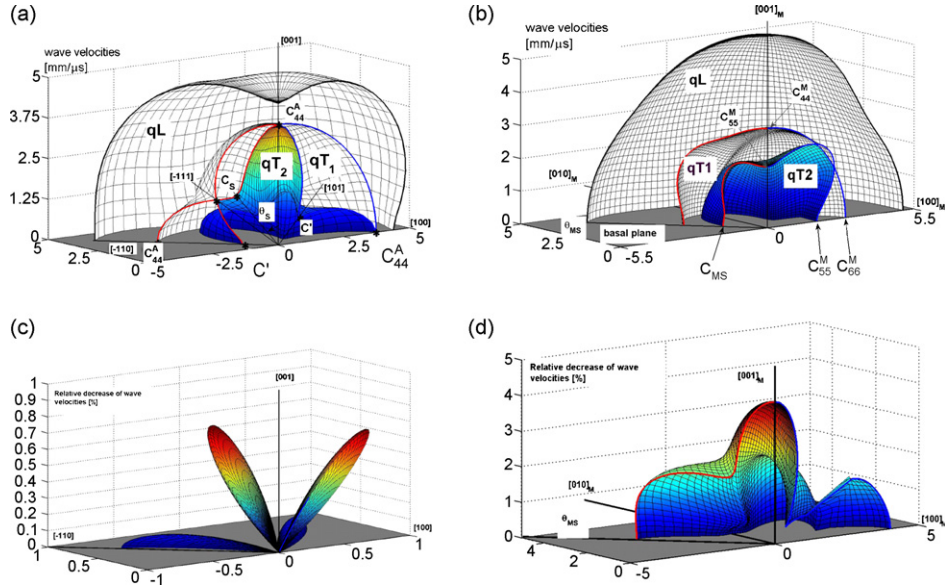


Fig. 4. Part of phase velocity surfaces of (a) austenite and (b) martensite; relative decreases of phase velocity of qT2 waves with the temperature change about 30 °C towards to the phase transition temperature: (c) austenite and (d) martensite.

For the study of pre-transformation softening of elasticity, the parts with increasing velocities near to the transition temperature, i.e. $[v_{\text{ref}}(\mathbf{n}) - v(\mathbf{n})]/v_{\text{ref}}(\mathbf{n}) < 0$, are unimportant, and they are ignored in the plots. The absolute value of temperature difference $T_{\text{ref}} - T$ was the same (approximately 30 °C) for cooling of the austenite as well as for heating of the martensite. It may be seen, that qT2 shear wave velocity relative decrease in the austenite is localized around directions corresponding with C' , whereas in the case of martensite, the decrease is distributed more broadly.

Temperature dependences of the important elastic coefficients of the austenite (measured upon cooling) and 2H martensite (measured upon heating) phases are shown in Fig. 5.

Table 2

The correspondence between specific elastic constants of bcc austenite and 2H martensite at specific directions introduced in [1]

Austenite (A) ... martensite (M)

$C_{44}^A \dots C_{44}^M, C_{66}^M$
 $C' \dots C_{55}^M$
 $C_S \dots C_{MS}$

The combination of austenite elastic coefficients $C' = (C_{11}^A - C_{12}^A)/2$ corresponds to the global minima on the velocity surface [1] of the qT2 transverse acoustic wave representing pure shear in $\langle 110 \rangle_A$ direction with $\{1-10\}_A$ polarization. The saddle point on the qT2 austenite surface [1] is characterized by the

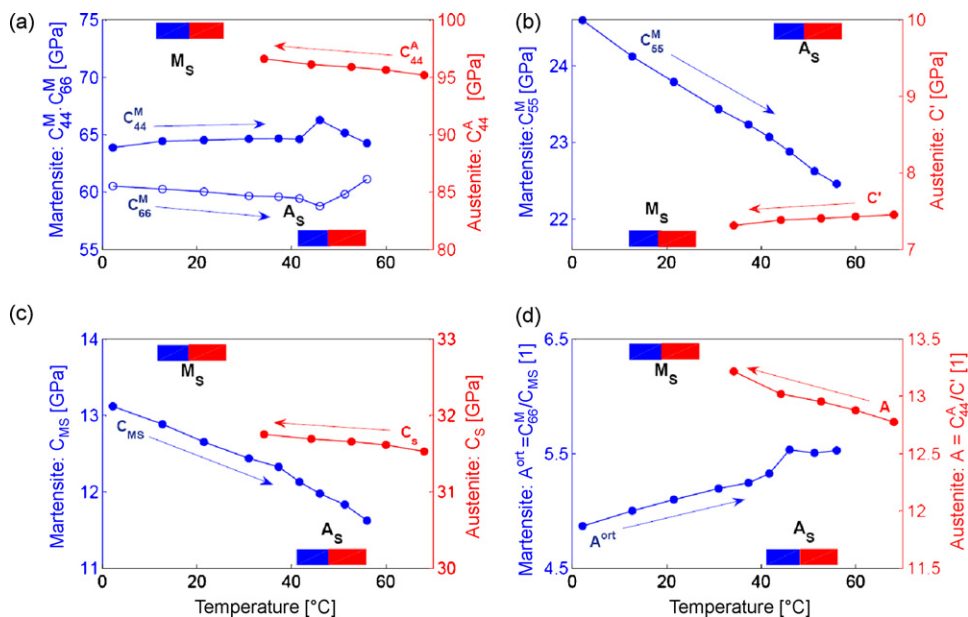


Fig. 5. Temperature dependence of elastic coefficients of the austenite and 2H martensite phase in Cu–Al–Ni alloy, coupled together according to Table 2: (a) C_{44}^A and C_{66}^M, C_{55}^M , (b) C' and C_{55}^M , (c) C_S and C_{MS} , and (d) the elastic anisotropy factor of austenite (A) and 2H orthorhombic martensite (A^{ort}).

Table 3
Slopes of temperature dependencies of elastic constants and anisotropy factors $\{\log[X(T)]\}/dT$

| Austenite $-d\{\log[X(T)]\}/dT$ (%/°C), X | | | | Martensite $d\{\log[X(T)]\}/dT$ (%/K), wX | | | | |
|---|--------|-------|-------|---|----------|----------|----------|-----------|
| C_{44} | C' | C_S | A | C_{44} | C_{66} | C_{55} | C_{MS} | A^{ort} |
| 0.041 | -0.053 | 0.020 | 0.095 | 0.030 | -0.014 | -0.166 | -0.219 | 0.249 |

X denotes the corresponding elastic constant or anisotropy factor.

constant C_S introduced earlier in the literature. Its definition in terms of combination of elastic coefficients can be found e.g. in [1]. As we can see, with decreasing temperature, the austenite elastic coefficient C_{44}^A increases (Fig. 5a), C' decreases (Fig. 5b), C_S slightly increases (Fig. 5c) and the anisotropy factor A significantly increases (Fig. 5d) in agreement with earlier literature data. It was observed, as regards the martensite phase, the diagonal elastic coefficients of C_{11}^M , C_{22}^M , C_{33}^M , C_{44}^M , and C_{66}^M as well as the coefficient C_{12}^M practically do not change with the temperature (these constants can be regarded as constants within 2% range), the C_{13}^M and C_{23}^M coefficients show a somewhat stiffening trend, whereas the low valued C_{55}^M coefficient exhibits very strong softening with increasing temperature. In addition to this, however, the martensite elastic tensor reveals most significant softening in crystal directions characterized by elastic coefficient C_{MS} . This coefficient corresponds to symmetrical position (on the martensitic basal plane) between two local minima on the velocity surface transverse acoustic wave qT2 in the martensite phase and characterizes a kind of valley on this surface introduced in detail in [1] including its definition in terms of combination of elastic coefficients. This valley on the martensite velocity surface becomes significantly deeper with increasing temperature upon heating. Softening of the elastic coefficients in the crystal directions C_{55}^M and C_{MS} thus dominates the behavior of the martensite elasticity upon heating.

The behavior of the martensite elasticity upon heating (softening of C_{55}^M and C_{MS} coefficients) may be compared with the austenite softening in the following way: when the bcc \leftrightarrow 2H martensitic transformation in Cu–Al–Ni takes place, the crystal structure changes. There is an obvious discontinuity in elastic properties accompanying the martensitic transformation. Based on the analysis of the velocity surfaces for the austenite and lattice correspondent 2H martensite variant, the correspondence between specific elastic constants of austenite and martensite in specific crystal directions (Table 2) was suggested in [1].

Fig. 5 was arranged in such a way that the mutually corresponding coupled elastic coefficients are plotted together in each subfigure. It should be pointed out that:

- (i) while the C_{44}^A increases upon cooling, the martensite constants C_{44}^M , C_{66}^M coupled to C_{44}^A remain practically independent on the temperature (Fig. 5a) upon heating,
- (ii) both the coupled C' and C_{55}^M constants decrease when approaching the stability limits, but the softening of the martensite constant is by far much stronger (Fig. 5b),
- (iii) C_S increases only slightly upon heating, but C_{MS} decreases strongly (Fig. 5c) upon heating,
- (iv) the elastic anisotropy of both austenite and 2H martensite phases (characterized by the anisotropy factor $A = C_{44}^A/C'$

for cubic crystals and $A^{ort} = C_{44}^M/C_{MS}$ for 2H martensite) strongly increases as temperature approaches the stability limits (Fig. 5d) of austenite and martensite structures, respectively.

There is not enough space to discuss the physical meaning of the softening of elastic constant in this paper. Let us only compare the softening of austenite and martensite phases quantitatively. For this purpose, the normalized slopes of the temperature dependencies of the elastic constants were calculated as summarized in Table 3. One may conclude that, when the crystal approaches its stability limits due to temperature change, the elastic properties of the 2H martensite change by far more strongly than those of the austenite.

5. Conclusions

A modification of resonance ultrasound spectroscopy method facilitating precise evaluation of elastic constants of arbitrary elastically anisotropic materials (as common for SMAs) was proposed. Since samples in the shape of prisms with general crystallographic orientation of faces can be used, the modified RUS method is applicable and very convenient for measurement of elastic constants of both austenite and martensite phases in SMAs.

The temperature dependencies of all elastic constants of the cubic austenite and orthorhombic 2H martensite phases in Cu–Al–Ni shape memory alloy is reported. The measurements were performed on the same single crystal piece, existing first as a martensite single crystal (during heating) and, after the transformation took place, as the austenite single crystal (during cooling).

It was found that the heated martensite crystal softens in two different crystal directions (corresponding to the two low valued elastic coefficients C_{55}^M and C_{MS}). The elastic properties of the 2H martensite change by far more strongly than those of the austenite. The elastic anisotropy of the both phases increases when approaching stability limits of the crystal lattices by changing temperature.

Acknowledgements

Supports from the Marie-Curie Research Training Network MULTIMAT (MRTN-CT-2004-505226), the project No. 101/06/0768 of the Czech Science Foundation and the institutional project of IT ASCR CEZ: AV0Z20760514 are greatly acknowledged.

References

- [1] P. Sedlák, H. Seiner, M. Landa, V. Novák, P. Šittner, L. Mañosa, *Acta Mater.* 53 (2005) 3643–3661.
- [2] X. Ren, N. Miura, J. Zhang, K. Otsuka, K. Tanaka, M. Koiwa, T. Suzuki, Yu.I. Chumlyakov, M. Asai, *Mater. Sci. Eng. A* 312 (2001) 196–206.
- [3] A. Planes, Ll. Mañosa, *Solid State Phys.* 55 (2001) 159.
- [4] M. Yasunaga, Y. Funatsu, S. Kojima, K. Otsuka, T. Suzuki, *Scripta Metall.* 17 (1983) 1091–1094.
- [5] M. Landa, P. Sedlák, P. Šittner, H. Seiner, V. Novák, *Mater. Sci. Eng. A* 462 (2007) 320–324.
- [6] A. Migliori, J.L. Sarrao, *Resonant Ultrasound Spectroscopy*, J. Wiley and Sons, Inc., NY, 1997.
- [7] H. Ogi, K. Sato, T. Asada, M. Hirao, *J. Acoust. Soc. Am.* 112 (2002) 2553–2557.
- [8] K. Otsuka, C.M. Wayman, K. Nakai, H. Sakamoto, K. Shimizu, *Acta Metall.* 24 (1976) 207–226.
- [9] P. Molnár, P. Šittner, V. Novák P. Lukáš, this volume.