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Temperature dependence of elastic properties of cubic and orthorhombic phases in Cu–Al–Ni shape memory alloy near their stability limits

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Abstract

Elastic constants reflect the fundamental thermodynamic properties of the crystal lattice in solids. Essential information on the phase stability of transforming materials can be deduced from their temperature and stress dependencies. In this work, temperature dependence of all elastic constants of the cubic austenite and orthorhombic 2H martensite phases of the Cu–Al–Ni alloy in the transformation temperature range determined by resonance ultrasonic spectroscopy are reported. All measurements were performed on the same sample, existing first as a martensite single crystal (measurement during heating) and, after the reverse transformation took place, as the austenite single crystal (measurement during cooling). It was found that some elastic constants of the austenite phase (C') and martensite phase (C_{55}, C_{MS}) significantly soften when approaching transformation temperatures. The martensite softening is by far more pronounced. While the austenite softening appears solely in the directions $\langle 1\,1\,0\rangle_A$ (C' modes), the 2H martensite softens in the lattice corresponding directions $[1\,0\,0]_M$ and $[0\,0\,1]_M$ (C_{55} modes) as well as along directions from a zone crossing the basal plane characterized by a elastic constant C_{MS} newly introduced in our earlier related work. The elastic anisotropy of the both phases significantly increases when approaching transformation temperatures, the anisotropy factor of martensite increases about ten times more strongly than in the case of austenite.
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1. Introduction

Shape memory alloys (SMA) exhibit diffusionless first-order martensitic phase transitions induced by the change of temperature and/or stress. The elastic constants of the austenite and martensite phases in SMAs are of interest from two main 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 modelling 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 the elastic constants of the low symmetry martensite phases in SMAs were reported in the literature.

We have recently measured elastic constants of bcc austenite and orthorhombic 2H martensite phases in Cu–Al–Ni single crystals [1]. The alloy had T_0 temperature near room temperature so it could exist at room temperature as austenite or martensite single crystal depending on thermomechanical history. Multiple prism shaped martensite single variant samples were prepared by a successive compression deformations via twinning in the martensite state. The elastic constants of both phases at room temperature were evaluated by an ultrasonic pulse-echo technique using a newly proposed method, in which the acoustic wave velocities are measured in general crystal directions on prism shaped specimens and complete set of elastic constants is evaluated by optimization based inverse method. It was found that the 2H martensite crystal partially inherits the soft acoustic modes of the austenite and hence its elastic properties.

In this paper, we present results of an extension of the previous work focusing the temperature dependence of elastic constants of both austenite and martensite phases near the transformation temperature range. From the point of view of lattice stability, the

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temperature dependence of the elastic constants is more important than their absolute values. Second motivation for the present work was that the earlier pulse-echo evaluated constants of 2H martensite phase [1] slightly disagreed with literature data [6] widely used throughout the SMA community, and we needed a verification by another independent experimental technique. The resonance ultrasound spectroscopy (RUS) method (described in detail in Ref. [2]) was used as such independent experimental method in this work. Natural frequencies of free elastic vibrations of a small single crystal specimen are measured for a number of sample's normal modes. Elastic constants are calculated in two steps. First, the natural frequencies are calculated from the estimated elastic constants, and then nonlinear inversion procedure is employed to find the required elastic constants from the measured natural frequencies. The RUS method is thus principally different from the pulse-echo method. The calculation inversion methods have essentially improved recently. Temperature dependence of elastic constants can be very conveniently measured by the RUS method because complete set of all constants is obtained from a single measurement. Temperature dependence of elastic constants of series of NiTi alloys prior to martensite transformation was systematically investigated by the RUS recently [3]. It was found that 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, partial results including temperature dependence can be found in [3]. Cu–Al–Ni alloy in austenite phase exhibits higher elastic anisotropy ($A = C_{44}/C' \sim 12.5$) compared to NiTi ($A = 2.8$). As a results of this, the frequency band, in which the necessary number of resonances must be evaluated [4], widens significantly. Because of that, only few references on the Cu–Al–Ni elastic constants measured by RUS method can be found in the literature (austenite [5], 2H martensite [6]). Many authors however reported temperature dependencies of elastic constants of Cu–Al–Ni austenite (Table 4 in [1]), all concluding that only the C' constant softens upon cooling.

A solution of the problems stemming from the difficulties arising when applying the RUS method to highly elastically anisotropic materials is suggested and discussed in our earlier related work [7]. The proposed approach is based on a consideration of large number of eigenfrequencies while performing the accuracy and sensitivity analysis of the employed inverse calculation procedure and adopting a suitable optimization method.

2. Cu–Al–Ni single crystal

A single crystal of Cu–13.8Al–4.1Ni (numbers indicate wt.%) alloy was grown by the Bridgman method. The transformation temperatures were determined by DSC as $M_s(2H) = 288$ K and $A_s = 313$ K and the mass density was evaluated as $\rho = 7.055 \times 10^3$ 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 prism shape, whereas main care was taken to assure very good parallelism of opposite faces. The general prism shape (Fig. 1) is described by distances d_i of the opposite sides (1 μm in precision) and outside nor-
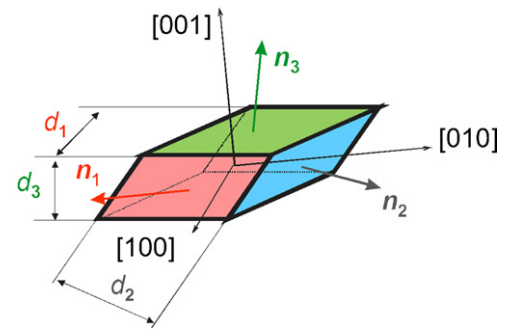

Fig. 1. Shape of specimen for RUS measurement which is described by outward normals $\boldsymbol{n}_1, \boldsymbol{n}_2, \boldsymbol{n}_3$ to surfaces with respect to the crystallographic axes (austenite or martensite) and corresponding distances between parallel surfaces d_1, d_2, d_3.

mals $\boldsymbol{n}_i = [\cos \varphi_1^i, \cos \varphi_2^i, \cos \varphi_3^i]^\mathrm{T}$ of (out of parallel) faces with respect to the principal axes of the crystal. The crystal lattice orientations were determined by back-reflection Laue method with an averaged accuracy better than 0.5°.

The martensite single crystals were prepared from the parent austenite specimen by the compression technique described in [1]. This method enables to obtain repeatedly several single crystal variants of the 2H martensite phase from a single austenite specimen. Only one martensite variant crystal, however, is sufficient for the RUS technique used in the present work. The martensite crystal has a shape of a highly non-rectangular prism with arbitrary crystallographic orientation of face normals. The measured values are compared with values calculated theoretically from the shape strain due to bcc-2H martensitic transformation [1], orientation and dimensions of the austenite prism and lattice correspondence (Fig. 2) between austenite (bcc: $a_o = 0.5835$ nm) and 2H martensite (orthorhombic: $a = 0.4389$ nm, $b = 0.5342$ nm, $c = 0.4224$ nm). The crystallographic data of the phases were taken from the literature [8]. Very good agreement between the measurement and calculation was achieved which indicated that true martensite single variant crystal had been obtained.
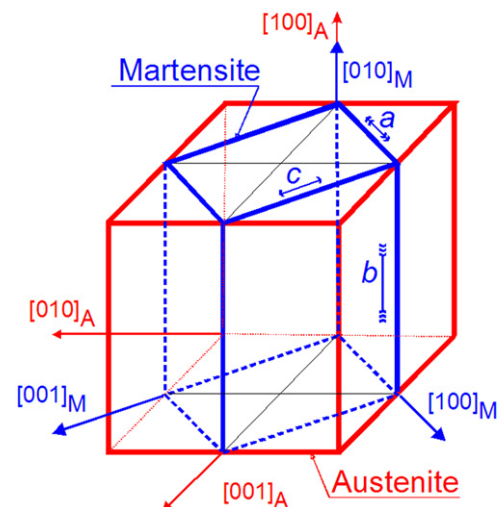

Fig. 2. Lattice correspondence between the bcc austenite and one variant of the 2H orthorhombic martensite phase.
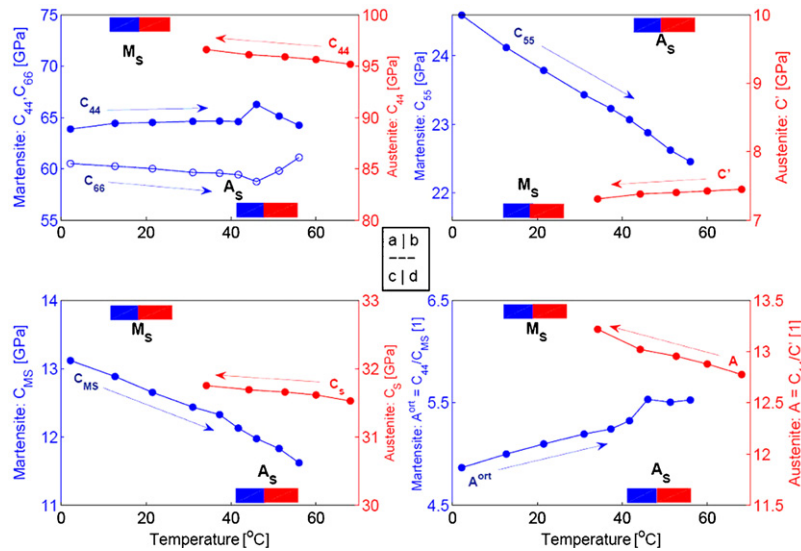
Fig. 3. Temperature dependence of elastic coefficients of the austenite and 2H martensite phase in Cu–Al–Ni alloy, coupled together according to Table 2: (a) C_{44}^A and C_{44}^M, C_{66}^M, (b) C' and C_{55}^M, (c) C_S and C_{MS}, and (d) the elastic anisotropy factor of austenite (A) and 2H orthorhombic martensite (A^{ort}).

3. Elastic constants measurement by the RUS technique

RF lock-in amplifier (Stanford Research System SRS-844) and synthesized function generator (DS-345), enabling measurement of spectral response in 120 dB dynamics are used in the experimental set up of the RUS measurement. The single crystal specimen was positioned in a holder between two piezoelectric transducers and whole ensemble was placed in an environmental chamber. The elastic constants of both austenite and martensite phases were evaluated from the measured resonant frequencies by the inversion procedure based on Ritz method generalized for non-rectangular shaped samples using simplex optimization algorithm (MParallel code [7]). The first 60 resonances of the specimen in the frequency range 0.15–1 MHz were identified in the spectra measured at preselected temperatures during heating of the 2H martensite as well as during cooling of austenite crystals. The frequency resolution was better than 50 Hz.

The obtained values of elastic constants for the austenite (at $T = 32\,°C$) and 2H martensite phases (at $T = 25\,°C$) agree quite well with the values measured earlier by pulse-echo method at room temperature [1]. As we can see from the temperature dependence austenite coefficients (Fig. 3), the C_{44} and C_{12} are increasing, C' decreases and anisotropy parameter A increases with decreasing temperature in agreement with earlier literature reports, cited in [1]. The combinations of elastic coefficients C' (C_S) correspond to the global (local) minima on the velocity surface of the qT2 transverse acoustic wave [1] (Fig. 4a). $C' = (C_{11} - C_{12})/2$ is a absolute minimum (pure shear in $\langle 1\,1\,0 \rangle_A$ $\{1 - 1\,1\}_A$ polarization), C_S (for combination of constants see Eq. (14) in [1]) is a minimal shear constant in the $\{1\,1\,0\}_A$ planes.

The elastic tensor of the martensite have following correspondence to the crystallographic axes: $x_1 \| [1\,0\,0] \sim a$, $x_2 \| [0\,1\,0] \sim b$, $x_3 \| [0\,0\,1] \sim c$, where a, b, c are the lattice parameters. By this representation, we can conclude from Table 2 that C_{11}, C_{22}, C_{33}, C_{44}, C_{66} diagonal elastic coefficients of the martensite phase as well as the coefficient C_{12} practically

do not change with temperature—they can be regarded as constants within 2% range. The C_{13} and C_{23} coefficients show a somewhat stiffening trend whereas the low valued C_{55} coefficient exhibits very strong softening with increasing temperature.

(a) Wave velocity [x 10^3 ms^{-1}]

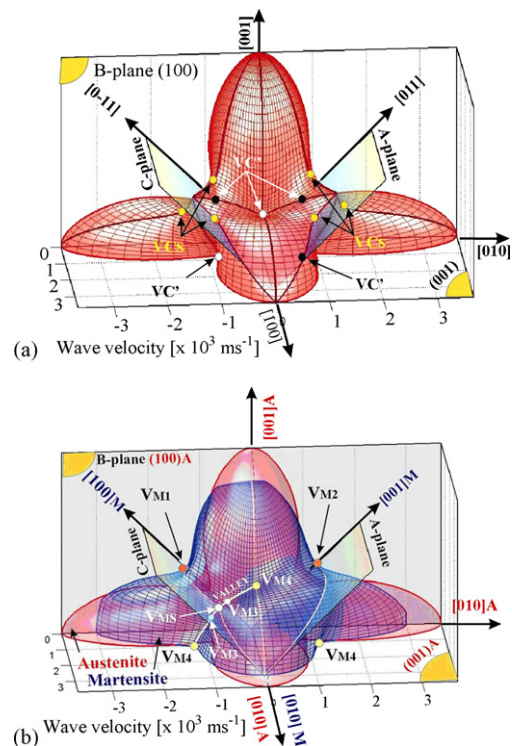(b) Wave velocity [x 10^3 ms^{-1}]

Fig. 4. Orientation dependences of velocity surfaces of qT2 acoustic waves calculated from elastic constants measured at room temperature [1]. (a) One quadrant of spherical polar diagrams for the austenite with global minima (VC') and saddle points (VC_S); (b) the comparison of the velocity surfaces of austenite and the martensite matched together using the lattice plane correspondence. The martensite surface has global minima at V_{M3}, saddle points at V_{MS} and local minima at V_{M1}, V_{M2} directions.
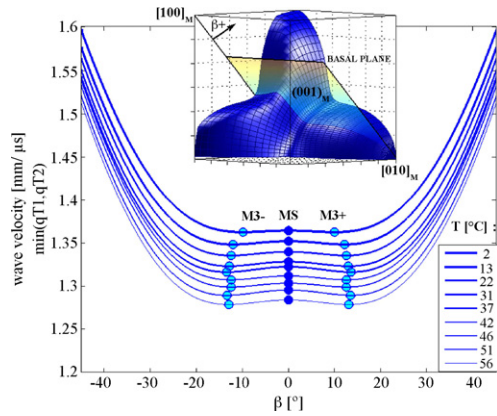
Fig. 5. Evolution of the shape of the valley on martensite qT2 velocity surface with increasing temperature calculated using the 2H martensite elastic constants in Table 2.

It is generally accepted that the pre-transformation processes are revealed as softening of specific shear acoustic modes [1]. However, this is not necessarily well represented by the elastic constants C_{ij}, therefore combinations of austenite constants C' and C_S were evaluated. Hence, it is convenient to represent crystal elasticity for investigation of structural transitions using surface of minimal velocities of quasitransverse wave (qT2 velocity in Fig. 4a). The low valued special points on the velocity surfaces of both austenite and martensite phases are suspected as candidates for softening and possibly related to the important directions of incoming structural changes [1]. As found in previous work [1], the stiffening C_{55} coefficient corresponds to the local minima V_{M1} and V_{M2} on the martensite qT2 velocity surface (Fig. 4b). The global minima were found in two V_{M3} points within a deep valley on the martensite velocity surface centered around the V_{MS} saddle point. The martensite constant C_{MS} corresponds with minimal shear velocity in the basal plane. Let us take the velocity V_{MS} as characterizing the behavior of the valley upon heating. The calculated temperature dependence of C_{MS} (Fig. 3b) reveals significant softening of C_{MS} with increasing temperature, i.e. the martensite valley becomes deeper upon heating (Fig. 5).

4. Elastic property changes with bcc-2H martensitic transformation

When the bcc ↔ 2H martensitic transformation takes place, the crystal structure changes and there is a discontinuity in elastic properties. Let us have a closer look on this discontinuity. We recall that $C = V^2\rho$, where V is the acoustic wave velocity and ρ is the mass density. Based on the analysis of the velocity surfaces for austenite and lattice correspondent martensite variant, the correspondence (Table 1) between specific elastic constants of austenite and martensite at specific directions was suggested [1]. The subscripts A, M denote austenite and martensite, respectively, wherever they can be mistaken. The temperature dependencies of coupled low valued elastic coefficients of austenite and martensite phases are plotted in Fig. 3. Let us discuss the behavior of elastic constants upon approaching the stability limit of the respective structures—upon cooling (heat-

ing) for austenite (martensite), respectively. It can be seen that: (i) while the C_{44}^A increases, the martensite constants C_{44}^M, C_{66}^M coupled to C_{44}^A remain approximately independent on temperature (Fig. 3a), (ii) both the coupled C' and C_{55}^M constants decrease when approaching the stability limits but the softening is much stronger in case of the martensite (Fig. 3b), (iii) while the C_S slightly increases, the C_{MS} strongly decreases (Fig. 3c) towards the stability limit. Finally, the elastic anisotropy of both austenite and 2H martensite phases (characterized by the anisotropy factor $A = C_{44}^A/C'$ for cubic crystals and by the ratio $A^{ort} = C_{44}^M/C_{MS}$ for 2H martensite (introduced in [1])) increases towards the stability limits (Fig. 3d), though the increase is stronger in the martensite case. In order to present the obtained information on temperature changes of elastic properties of both phases in a concise manner, the normalized slope of temperature dependencies $d\{\log[X(T)]\}/dT$ (X denotes the corresponding elastic constant or anisotropy factor) was calculated and the results are summarized in Table 2. We may conclude that, when the crystal approaches its stability limits, the elastic properties of the 2H martensite change by far more strongly than those of the austenite. Softening of the elastic coefficients in some crystal directions is dominant. The maximal softening occurs in directions C' of the austenite and in directions C_{MS} of the martensite which have not a lattice corresponding relation.

Strictly speaking, in view of Fig. 4, the change of elastic properties of a structure approaching its stability limit and going through the transformation range is characterized by continuous and discontinuous distortion of qT2 velocity surfaces in Fig. 4, respectively. In this respect, we were concerned by the temperature dependence of elastic coefficients of the 2H martensite in a wide range of directions around the velocity V_{MS} (corresponding with the elastic constant C_{MS}) where the martensite phase is softest and softens most strongly. These soft directions form a valley crossing the basal plane on the qT2 velocity surface in

Table 1
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	C_{44}^M, C_{66}^M
C'	C_{55}^M
C_S	C_{MS}

Table 2
Slopes of temperature dependencies of elastic constants and anisotropy factors

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

Fig. 4b. This valley may be represented by a set of wave velocity minima, which may be found in planar sections $(h\,0\,l)_M$ making a sheaf of planes with the common line $[0\,1\,0]_M$ in dependence on angle β between the $(h\,0\,l)_M$ plane and the basal $(0\,0\,1)_M$ plane. This evolution of the velocity profile with increasing temperature is plotted in Fig. 5 (only for the $[0\,1\,0]_M$ quadrant). The valley deepens with increasing temperature without any important distortion of its shape. There are two global qT2 velocity minima in the valley (denoted M3) centered symmetrically around the MS saddle point out of the basal plane. The M3 points have general direction given by instantaneous elastic properties of the martensite, they represent no special or pure modes, whereas the MS point is a pure shear mode in the basal plane (principal plane of symmetry). This together with the fact that the deepening valley does not change its shape upon heating are the reasons why the softening of the C_{MS} value was taken as a measure of the 2H martensite softening. The analysis of this experimental information in view of the stability 2H martensite structure and approaching martensitic phase transformation is beyond the scope of this experimental paper and will be published elsewhere.

5. Conclusions

Temperature dependences of all elastic constants of the cubic austenite and orthorhombic 2H martensite phases in Cu–Al–Ni shape memory alloy were determined by resonance ultrasonic spectroscopy. The measurements were performed on the same Cu–Al–Ni single crystal, existing first as a martensite single crystal (heating) and, after the transformation took place, as the austenite single crystal (cooling).

It was found that some elastic constants of the austenite phase (C') and martensite phase (C_{55}, C_{MS}) significantly soften when the measurement temperature was approaching the transformation temperatures upon cooling and heating, respectively. The martensite softening upon heating is by far more pronounced and has a different character than the austenite softening upon cooling. While the austenite softening appears solely in the directions $\langle 1\,1\,0 \rangle_A$ (C' modes), the 2H martensite phase softens in the directions $[1\,0\,0]_M$ and $[0\,0\,1]_M$ (C_{55} modes) as well as in the general directions located within the valley on martensite qT2 velocity surface crossing the basal plane (best characterized by the newly introduced C_{MS} soft mode). The rates of elastic softening of the 2H martensite structure during heating are largest in these specific directions.

Acknowledgements

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