High Temperature Elastic Constants of $\alpha$-Fe Single Crystal Studied by Electromagnetic Acoustic Resonance

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Complete set of elastic constants $C_{ij}$ of $\alpha$-Fe single crystal have been investigated from ambient temperature up to 893 K by electromagnetic acoustic resonance. Longitudinal component of elastic constants $C_{11}$ showed linear temperature behavior and the magnitude of elastic softening was approximately 13%. The remaining two shear moduli, $C_{44}$ and $C_{12}$ however showed highly nonlinear behaviors with significant softenings of 50%. On a Blackman diagram, elastic constant ratios at high temperatures move to a limit, $C_{44}/C_{11}=1$ and $C_{12}/C_{11}=0$, where Born’s two lattice instability criteria have been satisfied simultaneously. Violation of Cauchy relation is also significant upon heating.

KEY WORDS: $\alpha$-Fe; high temperature elastic constants; lattice instability; electromagnetic acoustic resonance; violation of Cauchy relation; martensitic phase transformation.

1. Introduction

Martensitic structural phase transformation in Fe-based alloys has frequently been employed in order to control their microstructure and mechanical properties.1) Understanding the mechanism of $\alpha$ to $\gamma$ phase transformation, and vice versa, has therefore been one of the central issues in the research field. Until now, most of experimental studies employ microstructural analysis such as by transmission electron microscopy.1) On the other hand, theoretical analysis uses crystallography, geometry and linear elastic theories.1–3) These experimental and theoretical works can explain some part of the intriguing phenomena while the fundamental mechanism is still unclear.

Elastic constants, $C_{ij}$, are one of the most fundamental physical properties of condensed matters. According to the theory of linear elasticity, $C_{ij}$ is defined as fourth-rank coefficient tensor when we expand thermodynamic potential with respect to strain. In a microscopic point of view, it can be defined as the second spatial derivative of inter-atomic potential at an equilibrium position. The potential is given by an anharmonic function in general so that their second derivatives, elastic constants $C_{ij}$, show strain dependence. On the other hand, the anharmonicity causes thermal expansion since thermal vibration, under a finite excitation energy $k_BT$, would be bounded in the anharmonic energy well. Elastic constants $C_{ij}$ therefore show temperature dependence through thermal expansion strain. This is the fundamental interpretation of temperature dependence of elastic constants $C_{ij}$ within a framework of quasi-harmonic thermodynamics.8) It is therefore reasonable to suppose that elastic constants $C_{ij}$ around the phase transformation point would be a key factor in order to understand the nature of the martensitic transformation.

High temperature elastic constants of $\alpha$-Fe has already been examined from 1931 to 1971 by several researchers.5–10) These studies report $C_{ij}(T)$ in different temperature ranges while the results show inconsistency in the overlapped temperature intervals. Thus re-investigation should be worth while. Recently, Adams et al.11) reported high temperature elastic constants of $\alpha$-Fe measured by acoustic resonance technique, which is, state-of-the-art in $C_{ij}$ measurements. Unfortunately, however, their measurement is limited to 500 K. In this study, we report high temperature elastic constants of $\alpha$-Fe single crystal measured by electromagnetic acoustic resonance (EMAR)12) up to 893 K. The obtained results $C_{ij}(T)$ will be discussed from a lattice dynamical point of view.

2. Experimental Procedure

The material used in this study is cylinder-shaped $\alpha$-Fe single crystal with the dimensions of 9.22 mm diameter and 1.02 mm thick with its purity of better than 99 wt%. One of a cubic direction (100) corresponds to the thickness direction within 1 deg. The specimen is inserted into a solenoidal coil and we mount them into a vacuum chamber with the pressure of approximately $8 \times 10^{-4}$ Pa in order to prevent oxidation of the specimen during the high temperature measurements. Temperature of the specimen is controlled by an electric furnace which has been set in the chamber. Static magnetic field of 0.2 T is applied from a side of the
chamber by pairs of permanent magnets. The solenoidal coil is driven by tone-burst current with the duration of 30 $\mu$s. Free-vibration resonance spectra are measured from 0.1 to 2 MHz up to 1300 K.

Here, we briefly describe the inverse analysis for determining elastic constants $C_{ij}$ from resonance frequencies. Let us consider a time independent Lagrangian $L$ for an elastic body $\Omega$ represented in the following form.

\[ L = \frac{1}{2} \int_\Omega (\rho \omega^2 \delta_{ij} u_i u_j - C_{ijkl} e_{ij} e_{kl}) dV \quad (1) \]

where $\rho$, $u_i$, $e_{ij}$ and $C_{ijkl}$ represent density, displacement vector, elastic strain and full tensor notation of elastic constants, respectively. $\omega$ represents angular frequency of free vibration. According to Hamilton’s principle, free vibration resonance state can be represented as stationary point of the Lagrangian, $\delta L = 0$. In this study we solved the variational problem by approximating the displacement $u_i$ in $\Omega$ by Legendre polynomials with Rayleigh–Ritz method. More details can be seen in several literatures.\(^{12–14}\)

3. Experimental Results

Figure 1 show temperature dependence of free vibration resonance frequencies obtained from $\alpha$-Fe single crystal by EMAR. Most of resonance frequencies showed monotonic decrease with increasing temperature, which indicates elastic softening upon heating. In the present EMAR measurement, we could not determine resonance frequencies between 893 and 1300 K since all resonance peaks disappeared from the EMAR spectra. One of the reasons is increasing in internal friction $Q^{-1}$ in the temperature range. As mentioned previously EMAR excite ultrasound waves with the long duration of 30 $\mu$s. The excited ultrasound waves cause multiple reflections by the specimen surfaces. If frequency of the wave corresponds to a resonance frequency of the medium, vibrational amplitude increases significantly since all excited waves become a standing state. On the other hand, internal friction represents energy dissipation and it turns ultrasound energy into heat if the medium has high $Q^{-1}$. In this case, amplification by multiple reflections is not significant and resonance peaks will disappear from the spectra. The hopping of interstitial impurity atoms is one of the plausible mechanism on the increasing of internal friction $Q^{-1}$. In this case the temperature dependence of $Q^{-1}$ can be estimated from their activation energies in the $\alpha$-Fe lattice. Another possibility is precursor phenomena of the martensitic structural phase transformation. In fact, in our previous study to Ti–Nb based system, continuous increasing of $Q^{-1}$ had been confirmed when temperature approaches to its transformation point.\(^{15}\)

In order to clarify the dominant mechanism of $Q^{-1}$ over 893 K further investigations such as quantitative analysis of impurity elements are required.

Temperature dependence of elastic constants $C_{ij}$ has been summarized in Fig. 2. $C'$ represents shear modulus for a (110) direction on a {110} plane calculated from $C' = C_{11} - C_{12}/2$. According to Fig. 2(a), longitudinal modulus, $C_{11}$, as well as two shear moduli, $C_{44}$ and $C'$, show elastic softening with increasing temperature. On the contrary, off-diagonal component of $C_{12}$ increases monotonically upon heating. These are usual temperature behaviors in a qualitative point of view. Quantitatively, however, we note some interesting results. Figure 2(b) plots temperature dependence of normalized elastic constants. We see that the changes in $C_{11}$ and $C_{12}$ are approximately 11 and 14% while those of $C_{44}$ and $C'$ reach 50%. Thus, softening of the two shear moduli is remarkable and its ratio is almost the same.

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**Fig. 1.** Temperature dependence of free vibration resonance frequencies of $\alpha$-Fe single crystal obtained by electromagnetic acoustic resonance.

**Fig. 2.** (a) Temperature dependence of elastic constants $C_i$ obtained from ambient temperature to 893 K by EMAR. The normalized elastic constants, calculated by dividing ambient temperature values, have been plotted in (b).
4. Analysis and Discussion

It is interesting to discuss the temperature dependence of elastic constants $C_{ij}$ on a Blackman diagram. This diagram plots $C_{12}/C_{11}$ ratio against $C_{44}/C_{11}$. At a room temperature, $(C_{44}/C_{11}, C_{12}/C_{11})$ of α-Fe is $(0.50, 0.59)$ so that it almost satisfy the Cauchy condition; $C_{12}=C_{44}$. With increasing temperature, however, experimental results becomes $(0.31, 0.76)$ indicating severe violation of the Cauchy condition.

The dashed line in Fig. 3 shows the least square fitting of experimental results to a linear function in the Blackman diagram. Surprisingly, as seen from the figure, the intercept coefficient to the $C_{12}/C_{11}$ axis becomes almost unity. It is worthwhile noting that two shear moduli of $C_{44}$ and $C'$ becomes zero at the limit $C_{12}/C_{11}=1$ (or $C_{44}/C_{11}=0$) and which are known as the Born lattice instability criteria. The approaching of $C_{12}$ to this point clearly implies that α-Fe turns to mechanically instable at high temperatures.

Let us also discuss the mechanical stability of high temperature α-Fe from a crystallographic point of view. For this purpose we calculate crystallographic orientation dependence of elastic wave velocities. According to the linear theory of elasticity, wave equation and a harmonic plane wave solution can be cast into the following eigenvalue problem:

$$[\Gamma_{ik} - \rho \omega^2 \delta_{ik}] \nu_k = 0, \quad \Gamma_{ik} = C_{ijk} k_i k_j.$$  

This is called the Christoffel equation. The parameters $\rho$ and $\omega$ are density and angular frequency of the elastic wave, respectively. The $k_i$ and $\nu_i$ represent elastic wave propagation direction (normalized wave vector) and vibration directions. Since the all subscripts take 1 to 3, this equation has three fundamental solutions representing one longitudinal and two transverse elastic waves (transverse 1 and 2). Angular frequency $\omega$ as well as wave velocities $v_i$ for a given wave vector $k_i$ can be calculated from the eigenvalues of the equation. On the other hand, the vibration direction $\nu_i$ is given as the corresponding eigenvectors. It should be worthwhile to note that elastic wave velocity of transverse 1 at 296 K is always greater or equal to that of transverse 2 by the present definition.

Tables 1 and 2 summarize elastic wave velocities for specific crystallographic directions at 296 K and 893 K. For a longitudinal wave the the maximum and minimum wave propagation directions at an ambient temperature are (111) and (100), respectively. On the other hand, those of transverse waves are (100) and (110). As seen from Fig. 2(b), two shear moduli, $C_{44}$ and $C'$, showed significant softening while that of the longitudinal modulus $C_{11}$ is usual. As a result, the change in longitudinal wave velocities is less significant, ranging from $-13.6$ to $-7.1\%$, if we compare it to those of transverse ones; ranging from $-27.4$ to $-16\%$. This is because of the fact that the influence of two shear moduli on a longitudinal wave is generally small. Another notable feature is that the velocities of the transverse 2 are greater or equal to those of transverse 1. Namely, the magnitude of two transverse waves have been exchanged. Precise analysis to the transverse wave velocities revealed that this slightly strange feature occurred around 700 K. Thus, the weak inflection of $C_0(T)$ curve at the temperature would be the reason. Let us now discuss about the crystallographic features of the transverse wave velocities. As seen from the Table 2 two transverse waves show fair anisotropic velocity change; ranging from $-27.4$ to $-20.0\%$ for transverse 1 and that of transverse 2 is from $-27.4$ to $-16.4\%$. Thus, both of the transverse wave velocities and their change from ambient temperature show anisotropic manner. The maximum velocity changes can be seen in (100) and (110).

| Temp. Propagation Direction | Vibration Direction |
|-----------------------------|---------------------|
| Longitudinal | Transverse 1 | Transverse 2 |

| [1 0 0] | [0 1 0] | [0 0 1] |
|---------|---------|---------|
| 296 K   | 0.984   | 0.984   |
| [1 1 0] | [0.58, 0.58] | [0.10, 0.75] |
| 893 K   | [0.82, 0.74] | [0.01, 0.6] |

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|---------|---------|---------|
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| 893 K   | [0.82, 0.74] | [0.01, 0.6] |
directions. Further analysis revealed that the directions on a (110) plane show similar predominant decreasing. This result implies that the directions on a (110) plane is easy to be instable if elastic constants approaches to a limit $C_{12}/C_{11} \rightarrow 1$ and $C_{44}/C_{11} \rightarrow 0$ at high temperatures. However, the relation between the mechanical stability and the $\alpha-\gamma$ martensitic transformation is still unclear yet. For this purpose further investigation such as $C_i(T)$ measurements over 900 K should be worthwhile.

5. Conclusions

In conclusion, we have investigated high temperature elastic constants of $\alpha$-Fe single crystal by electromagnetic acoustic resonance (EMAR). Results of the present study can be summarized as follows.

1. By means of EMAR technique, it has been succeeded in obtaining free vibration resonance spectra up to 893 K. Between 893 and 1 300 K, however, we could not determine resonance frequencies since all peaks disappeared in this temperature range.

2. Temperature dependence of elastic constants $C_{ij}$ has been obtained from 296 to 893 K. Longitudinal component, $C_{11}$, showed an usual linear temperature dependence while two shear moduli, $C_{44}$ and $C''$, represented highly nonlinear manner with the significant change up to 50%.

3. On a Blackman diagram, elastic constant ratios at high temperatures shift to a limit of $C_{12}/C_{11} = 1$ and $C_{44}/C_{11} = 0$. This result implies that high temperature elastic constants of $\alpha$-Fe would change in order to satisfy two Born’s lattice instability criteria simultaneously. As a result, high temperature $C_{ij}$ violate Cauchy condition significantly.

4. Crystallographic orientation dependence of elastic wave velocity has been calculated by numerically solving Christoffel equation. Present analysis revealed that the transverse waves velocity as well as its change from ambient temperature show anisotropic crystallographic orientation dependence. The predominant transverse velocity change has been confirmed on (100), (110) and the directions on a (110) plane.

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