Anomalous attenuation of ultrasound in alloys with heterophase fluctuations

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A mechanism is proposed for the attenuation of ultrasound in systems with disperse inclusions of a low-symmetry phase or regions with a low-developed short-range order. The mechanism is based on an analysis of thermally activated transitions of these regions between various "vacuum" states in the field of an ultrasonic wave. Corresponding experimental data on Ti–Fe and Cu–Mn alloys are explained. © *1994 American Institute of Physics.*

Metastable alloys of transition metals based on titanium and zirconium exhibit several unusual features. One clearly expressed, and so far unexplained, feature is a strong attenuation of ultrasound in a certain composition region[1] ($\Gamma \approx 8$ dB/cm at a frequency of 10 MHz and 21 dB/cm at 25 MHz in $Ti_{1-x}Fe_x$ with $x \approx 0.07$). The increase in attenuation (at $x \approx 0.07$–0.10 for $Ti_{1-x}Fe_x$) is observed in the same composition region as a high-resistance state with a negative temperature coefficient of the resistance. It is not directly related to an α(hcp)/β(bcc) phase transition, from which it is separated along the composition scale. In this letter we offer an explanation for this phenomenon based on a picture drawn in Ref. 2 of the electronic and structural state of titanium alloys.

As was discussed in Ref. 2, a governing feature of this state is the presence of many extremely small particles of an ωphase, which form a superstructure. (These particles make up 30–40% of the volume; their sizes are 20–50 Å.) More precisely, these particles are essentially regions of a short-range "ω-like" order. We will refer to these system as "heterophase fluctuations," as suggested by Krivoglaz.[3] On the basis of experimental results on the scattering of neutrons, x radiation, and Mössbauer radiation in Zr–Nb alloys, and also on the basis of the complete similarity of the structural properties of zirconium and titanium alloys, these fluctuations are generally regarded as dynamic with characteristic times $10^{-11} < \tau \ll 10^{-7}$ s (see a review[4]). In an analysis of the propagation of ultrasound with a frequency $\omega \leqslant 10^7$ s$^{-1} \ll 1/\tau$, however, heterophase fluctuations can be regarded as static, with lattice distortions corresponding to the time average of the displacements of {111} planes, as is manifested as an "imperfection" of the ω phase.[5] An important point is that these distortions can occur in four $\langle 111 \rangle$ directions. Since we are dealing with small particles here, the energy barriers separating these four potential wells are finite, and transitions between them should, in general, be taken into consideration. In this sense, the situation is analogous to the phenomenon of superparamagnetism for small, single-domain particles.[6] Below we discuss a mechanism for the attenuation of ultrasound due to these transitions. We show that the results of Ref. 1 can be explained at

a qualitative level under some plausible assumptions regarding the height of the barriers between wells.

In a model with linear relaxation, the general expression for the attenuation (Γ) of ultrasound by a system of "multiwell" regions is[7]

$$\Gamma = \frac{1}{2c} \frac{\Delta}{(1+\Delta)^{1/2}} \frac{\omega^2 \tau_r}{1+\omega^2 \tau_r^2}, \tag{1}$$

where c is the sound velocity, $\tau_r = \tau(1+\Delta)^{-1/2}$, τ is the relaxation time, which satisfies

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{H}{T}\right), \tag{2}$$

H is the height of a barrier between wells, $\Delta = \delta J/J_u$, $\delta J = J_r - J_u$, and J_r and J_u are the relaxed and unrelaxed compliances, respectively. For a matrix of cubic symmetry, with bulk relaxation ignored, the quantity δJ is given as a function of the direction cosines (γ_i) of the ultrasonic wave with respect to the cube axes by[7]

$$\delta J = \delta J_{\langle 100\rangle} + 3(\delta J_{\langle 111\rangle} - \delta J_{\langle 100\rangle})(\gamma_1^2\gamma_2^2 + \gamma_1^2\gamma_3^2 + \gamma_2^2\gamma_3^2), \tag{3}$$

where $\delta J_{\langle hkl\rangle}$ is the relaxation of the compliance for the $\langle hkl\rangle$ direction. In the case of precipitates of the ω phase with a displacement of planes in $\langle 111\rangle$ directions, we would have $\delta J_{\langle 100\rangle} = 0$. In calculating $\delta J_{\langle 111\rangle}$ we adopt for simplicity a model in which the ω-phase regions are ellipsoids of revolution with long dimension along a $\langle 111\rangle$ direction. The strain of the β–ω conversion in the principal axes of the ellipsoid is $\epsilon_{ij}^0 = \mathrm{diag}(\lambda, -\lambda/2, -\lambda/2)$, $\epsilon_{ii}^0 = 0$, under the condition of volume conservation. The relaxation of the compliances upon the rotation of the axes of the ellipsoids from one $\langle 111\rangle$ direction to another due to ultrasound can thus be written as follows in the self-consistent-field approximation (cf. Ref. 7):

$$\delta J_{\mathbf{n}} = \sum_{pq} \left[\frac{4T}{\Omega_0 f} + \tilde{V}\right]^{-1}_{pq} \lambda_p \lambda_q. \tag{4}$$

Here Ω_0 is the volume per atom, f is the volume fraction of ω regions in the β matrix, $\lambda_p = \Sigma_i \beta_i^2(p)\lambda_i$, β_i are the direction cosines between the principal axes of the tensor $\epsilon_{ij}^0(p)$ and the vector $\mathbf{n}$ ($1 \leqslant p \leqslant 4$ specifies the particular $\langle 111\rangle$ axis), and

$$\tilde{V}_{pq} = V_{pq} - \frac{1}{4}\sum_p V_{pq}, \tag{5}$$

where V_{pq} is a Fourier component of the energy of the interactions between precipitates of types p and q (Ref. 8) with $\mathbf{k}=0$, corresponding to the contribution of image forces. The largest eigenvalue of the matrix, $-\Omega_0 f \tilde{V}_{pq}/4$, coincides with the temperature of an instability of the homogeneous state with respect to an orientational ordering of the precipitates. A simple estimate yields $\Omega_0 ||\tilde{V}_{pq}|| < \Omega_0 J_u^{-1}\lambda^2 \ll T = 300$ K for $\lambda = (1-5) \times 10^{-2}$, so the interaction of precipitates with each other can be ignored. We can then write

$$\delta J_{\langle 111\rangle} = \frac{\Omega_0 f \lambda^2}{3T} \tag{6}$$

Assuming $\lambda = 3.6\times 10^{-2}$, $f \approx 0.3$, $\Omega_0/J_u \approx 3$ eV (J_u^{-1} is on the order of the Young'ss modulus[7]), and $T = 300$ K, we find $\Delta \approx 0.016$. From this result we find, for the absorption maximum ($\omega\tau_r \approx 1$), a fairly large relative attenuation, $c\Gamma/\omega \sim 4\times 10^{-3}$, which agrees in order of magnitude with an experimental value.[1] The soliton model of β–ω conversion has a transition to an imperfect ω phase at $\lambda = 5\times 10^{-2}$, but the experimental data indicate smaller values of λ(Ref. 9).

Using $\Delta \ll 1$ and $H = H_0 N$, where H_0 is the barrier height per cell, and N is the number of cells in an ω-phase region, and introducing the distribution of regions with respect to size, $P(N)$, we find from (1)–(3) and (6)

$$\Gamma = \frac{\Omega_0 f \lambda^2}{2cJ_u T}(\gamma_1^2\gamma_2^2 + \gamma_1^2\gamma_3^2 + \gamma_2^2\gamma_3^2)\int dNP(N)\frac{\omega^2\tau_0 \exp(H_0 N/T)}{1+\omega^2\tau_0^2\exp(2H_0 N/T)}. \qquad (7)$$

The experimental dependence of Γ on ω in the region $\omega \approx 10^7$–10^{11} s^{-1} at $T \approx 300$ K lies between $\Gamma \sim \omega^2$ for the case $\omega\tau \ll 1$ and $\Gamma \sim$ const for the case $\omega\tau \gg 1$ (Ref. 1). It is thus natural to suggest that for the most probable value of N_0 and for $\tau_0 \approx 10^{-12}$ s^{-1} we have $\exp(H_0 N_0/T) \approx (\omega\tau_0)^{-1} \approx 10^4$. For $N_0 \approx 10$–30, this result yields $H_0 \approx 300$–100 K. This estimate looks fairly reasonable, since H_0 must be much lower than the height of the barrier for the ω–β transition, and the latter is on the order of 500 K according to a calculation[10] for Zr at $T = 0$. In other words, according to this model the anomalous attenuation of ultrasound in titanium and zirconium alloys is due to specifically heterophase fluctuations, i.e., regions which contain a few ω-phase cells, not the large precipitates ($N \sim 10^2$–10^3) which may also exist in such alloys.[11] These large precipitates may contribute to the attenuation of ultrasound due to the dynamics of interfaces, which may be predominant in the immediate vicinity of an α–$(\beta+\omega)$ transition. [The first peak on the concentration dependence $\Gamma(x)$, at $x \approx 0.05$ in $Ti_{1-x}Fe_x$ (Ref. 1), may be due to specifically such processes.]

Expression (7) predicts a definite angular dependence of $\Gamma(\gamma_i)$ with a maximum along a $\langle 111\rangle$ direction and a minimum along a $\langle 100\rangle$ direction. This result could be tested in experiments on single crystals.

The mechanism proposed here for the attenuation of ultrasound may operate in other systems with heterophase fluctuations. For example, there are well-known effects of a strong short-range order in Cu–Mn alloys above the temperature of the fct–fcc transition, which are described as regions of tetragonal distortions of the lattice with a size of 20–30 Å (Ref. 12). At the same time, these alloys exhibit clearly defined anomalies in the ultrasonic attenuation near the transition point.[13] We believe that this increase in the attenuation could be explained on the basis of the model proposed here [with $\delta J_{\langle 111\rangle} = 0$ and $\delta J_{\langle 100\rangle} \neq 0$, i.e., with an angular dependence $1 - 3(\gamma_1^2\gamma_2^2 + \gamma_1^2\gamma_3^2 + \gamma_2^2\gamma_3^2)$ instead of (6)], as resulting from processes involving a reorientation of tetragonal axes. One might suggest that in this case $f(T)$ would rise sharply as $T \to T_c$; this rise may explain the maximum in $\Gamma(T)$ near T_c (Ref. 13). A similar idea was expressed in Ref. 14.

Again, we wish to stress that the most important circumstances in this model are the small barrier height H_0 (the transition is of a martensitic type) and the small size of the region. In systems of this sort, any distortion of the lattice would be dynamic because of thermal transitions between "vacua" corresponding to the low-symmetry phase.

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