Intrinsic ultrasonic attenuation during the martensitic transformation of Cu–Zn–Al

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Abstract. Ultrasonic attenuation has been measured using a broad-band immersion pulse-echo technique on Cu–Zn–Al alloys. The use of two different polishing conditions of the surface of the sample has enabled the effect of surface distortion associated with the martensitic transformation undergone by these alloys to be quantified. The behaviour of the ultrasonic attenuation coefficient as a function of both frequency and temperature is presented. The results are interpreted in terms of the scattering of the ultrasonic beam caused by the co-existence within the material of regions with different acoustic impedances.

1. Introduction

Ultrasonic techniques have been widely used in the investigation of many properties of different materials and indeed they are a powerful tool to investigate phase transitions in the solid state. The determination of the behaviour of the elastic constants as a function of temperature and pressure has helped enormously in the comprehension of many phase transitions [1–4]. A less quantitative, but nevertheless important, insight can be obtained by measuring ultrasonic attenuation; knowledge of the phenomena causing energy losses provides valuable information for a better understanding of the transformation mechanism [5, 6].

Martensitic transformations have always received considerable attention. Much theoretical effort has been made in order to describe the mechanism driving martensitic transformations [7, 8]; theoretical models based on Landau expansions in terms of strain and strain derivatives have been developed and have shown the necessity of a better experimental knowledge of the elastic behaviour of materials undergoing martensitic transitions. Several measurements have already been made on the behaviour of second- and third-order elastic constants as a function of temperature [9, 10]. However, measurements of ultrasonic attenuation during the transformation are still scarce [11–13] and, in some cases, contradictory results are obtained. One reason for the lack of measurements is the difficulty of making them properly because the growth of martensitic phase results in a surface relief which modifies the coupling between the sample and the transducer.

Previously [14] we analysed the effect of surface distortion on the measurement of ultrasonic attenuation during the martensitic transformation of Cu–Zn–Al. The results showed that samples having a flat surface in the high temperature phase (β phase for Cu–Zn–Al alloys) exhibited a different attenuation behaviour with temperature from those having a flat surface in the martensitic phase. In particular, the attenuation versus temperature curve showed a maximum if the surface effects competed with those of the bulk. These observations made evident the importance of measuring in such a way that surface effects could be eliminated so that the intrinsic attenuation could be obtained.

A possible way to reduce surface effects is to employ non-contact transducers; Szente and Trivisonno [15] used electromagnetic acoustic transducers to investigate the martensitic phase transformation in sodium. For a typical pulse-echo technique [16] with piezoelectric transducers, preliminary results of the authors [17] demonstrated that the use of an immersion technique resulted in a remarkable reduction of the effects of surface distortion.

The aim of this paper is to present proper measurements of the intrinsic ultrasonic attenuation as functions of temperature and frequency during the martensitic transformation of Cu–Zn–Al.

2. Experiment

Cylindrical monocrystalline samples with 13 mm diameter and 10 mm thickness were investigated. Single crystals (Cu–13.7 Zn–17.0 Al at.%) with nominal temperature of transformation (M_s) about 300 K were cut with their upper and lower faces parallel to the (110) planes of the cubic parent phase.

In order to retain the metastable β phase at ordinary temperatures, samples were annealed for 300 s at 1120 K and then quenched in boiling water. Such heat treatment has been shown to inhibit both internal stresses and precipitation of equilibrium phases, which would result in a modification of the ultrasonic signals propagated through the sample [18]. This thermal treatment was followed by an ageing process for more than 12 h at 340 K to ensure a final state in which all the reordering processes were complete.

The final preparation of samples was achieved by mechanical polishing (1 μm alumina powder). This polishing was performed either at a temperature at which the sample was completely in the β phase or at a lower temperature at which the sample was completely transformed into martensite. In this paper, these two different polishing conditions will be denoted β-polishing and M-polishing, respectively.

Ultrasonic attenuation measurements were performed by a broad-band, immersion, pulse-echo method [16]. The sample and two identical longitudinal piezoelectric broad-band transducers (Panametrics V112) were immersed in a water tank. One transducer was used to generate the ultrasonic pulse and to detect the reflected echoes. The second transducer detected the pulses transmitted through the sample.

The transmitter was electrically excited by means of a pulser–receiver unit (Panametrics P5052) which, in turn, was also used to amplify the signals coming from the receiver. The amplified signals were displayed on the screen of a digital oscilloscope (Tektronix 7D20) interfaced via an IEEE488 bus to a personal computer (HP Vectra). The computer was used for both data acquisition and data treatment. Each signal transferred from the oscilloscope to the computer was an average over 50 acquisitions to reduce the electrical noise.
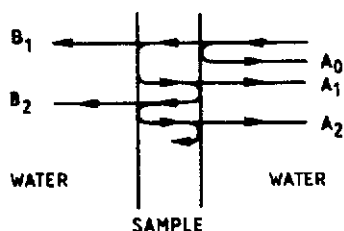
Figure 1. Transmitted and reflected pulses in a typical immersion pulse-echo measurement.

The transition was thermally induced by heating and cooling the water bath, and the temperature was measured by a thermocouple directly attached onto the lateral surface of the sample.

Ultrasonic measurements were complemented by other measurement techniques commonly used to study the martensitic transformation, such as calorimetry, acoustic emission and optical microscopy. These will not be discussed in this paper.

3. Data treatment

The signals suitable of being exploited in a pulse-echo immersion experiment are shown in figure 1. The first transmitted pulse (B_1 in figure 1) has a shorter path through the sample than the reflected echoes and, as a consequence, it has a greater amplitude. Moreover, transmitted signals are less affected by surface imperfections than reflected ones. For these reasons we have restricted our quantitative analysis to the first transmitted pulse.

For a single crystal in the β phase with a proper surface (β-polishing), the attenuation in the frequency range of investigation (<20 MHz) is very weak and this state will be taken as our reference state. The attenuation coefficients will then be given as differences from the attenuation coefficient corresponding to this state: α^β, which in many cases can be considered negligible.

Transmitted pulses have been digitized with a sampling rate of 500 MHz at different temperatures and stored on computer hard disk. The numerical fast Fourier transform has been calculated and the resulting spectrum has been divided by the spectrum of the transmitted pulse in the ground state. By doing this, the desired ultrasonic attenuation coefficient α at temperature T and frequency f is given by:

$$\alpha - \alpha^\beta = -\frac{20}{L} \log \frac{B_1(f, T)}{B_1^\beta(f, T_0)} \tag{1}$$

where L is the sample thickness, $B_1(f, T)$ is the value, at a frequency f, of the modulus of the Fourier spectrum for the first transmitted pulse at a temperature T, and $B_1^\beta(f, T_0)$ is the same quantity at a temperature T_0 ($=310$ K) when the sample is in the β phase having been β-polished.

The transducer used behaves in a broad-band way in the frequency range from 2 to 20 MHz but since the numerical Fourier transform is poor for frequencies above 15 MHz, the ratio between spectra is affected by a significant error and we have restricted our analysis to the range 2 to 14 MHz.

It is worth pointing out that the small diameter of the transducers (~6 mm) can result in losses by diffraction of the ultrasonic beam which are especially significant for low
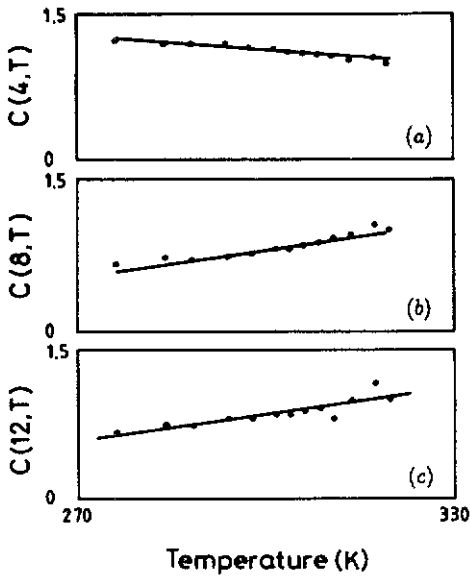
Figure 2. Relative sensitivity of the transducers as a function of temperature for (*a*) 4 MHz, (*b*) 8 MHz and (*c*) 12 MHz.

frequencies. With our procedure, these effects are cleared away because we consider ratios of signals having identical diffraction losses.

The sensitivity of broad-band transducers can vary with the temperature. In order to determine the evolution of our experimental set-up with temperature, we have investigated the transmitted pulse through a Cu–Zn–Al single crystal similar to the samples to be studied but having a different composition so that the martensitic transition takes place more than 150 K below the range of operation ($M_s = 130$ K). Figure 2 shows the ratio between the Fourier spectra:

$$C(f, T) = \frac{B_1^{\beta}(f, T)}{B_1^{\beta}(f, T_0)} \tag{2}$$

as a function of temperature for three selected frequencies. The evolution of $C(f, T)$ with temperature cannot be neglected and is different for each frequency. As a first approximation we have fitted the temperature dependence to linear functions:

$$C(f, T) = a(f)T + b(f) \tag{3}$$

and we have found the coefficients listed in table 1.

Equation (1) must be corrected for by the evolution of the transducers with temperature $C(f, T)$, and the final expression used to calculate α reads:

$$\alpha(f, T) = -\frac{20}{L} \log \frac{B_1(f, T)}{B_1^{\beta}(f, T_0)} C^{-1}(f, T). \tag{4}$$

4. Results

The use of two polishing conditions enables us to quantify the effect of surface distortion on the measured ultrasonic attenuation coefficient. When the sample was β-polished,

Table 1. Coefficients obtained for the linear fit $C(T, f) = a(f)T + b(f)$ to the evolution of the transducer sensitivity.

Frequency (MHz)	a (K^{-1})	b
2	−0.004	2.28
3	−0.005	2.73
4	−0.005	2.64
5	−0.003	2.73
6	0.003	0.03
7	0.007	−1.23
8	0.009	−1.60
9	0.011	−2.50
10	0.012	−2.83
11	0.011	−2.50
12	0.009	−1.85
13	0.013	−1.85
14	0.017	3.12
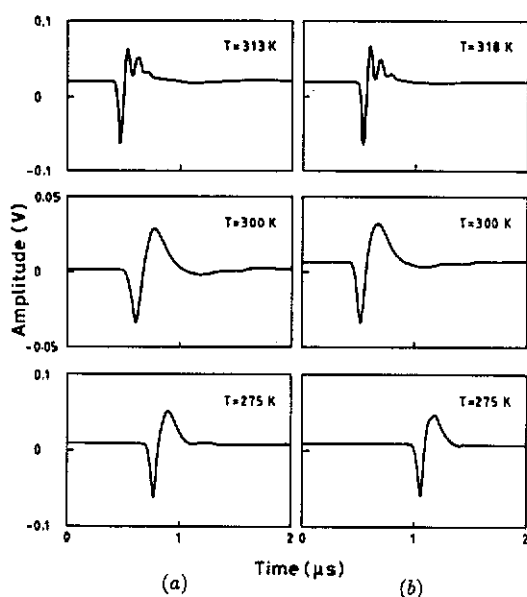
Figure 3. Examples of transmitted pulses at different temperatures during the martensitic transformation of a (*a*) β-polished and (*b*) *M*-polished single crystal.

the surfaces of the sample are flat in the β phase but wrinkled in the martensite phase. Thermoelasticity of the transformations ensures that in the case of a sample polished in martensite (*M*-polishing), the surface becomes flat each time that the sample is completely transformed into martensite, and the surface is wrinkled in the β phase. Therefore, a comparison of the transmitted pulses in the β phase for the two polishing conditions, allows an evaluation of the pure effect of surface distortion. This procedure has shown that the decrease of the amplitude of the signal due to surface distortion is
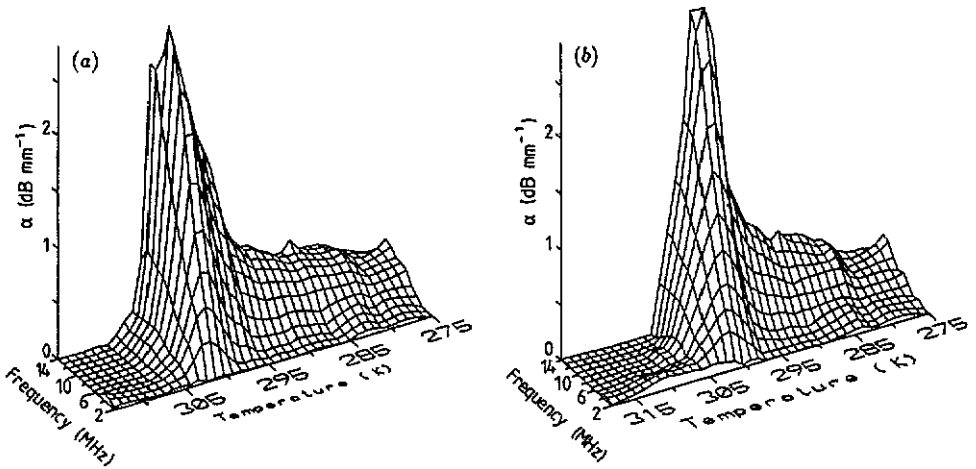
Figure 4. Ultrasonic attenuation coefficient as a function of temperature and frequency during the martensitic transformation of a (*a*) β-polished and (*b*) *M*-polished single crystal.

always less than 0.5 dB over the frequency range studied. This result is in contrast to previous measurements [14] with the transducer directly attached to the sample, and is a clear indication that the use of an immersion technique drastically reduces the effect of surface distortion.

Figure 3 shows examples of transmitted pulses recorded at different temperatures for a single crystal after having been (*a*) β polished and (*b*) *M*-polished. Using equation (4) we have obtained the ultrasonic attenuation coefficient as a function of both frequency and temperature. Results are shown in figure 4(*a*) for β-polishing and 4(*b*) for *M*-polishing. The two different polishing conditions give analogous behaviour for $\alpha(f, T)$. This confirms once again the fact that the use of an immersion technique enables one to neglect surface effects in measuring ultrasonic attenuation.

Figure 4 reveals that for single crystals ultrasonic attenuation is more important in martensite than in the β phase and is maximum at a temperature within the range of transformation. Previous experiments [14] showed that the existence of this maximum could be masked or even suppressed in experiments in which the transducer was in direct contact with the sample.

The amount of material transformed as a function of temperature has been obtained by calorimetric techniques. Figure 5 shows transformed fraction and ultrasonic attenuation at 10 MHz as a function of temperature. The curves show that the maximum attenuation is reached at a small percentage of the transformed volume.

5. Discussion

5.1. Attenuation in martensite

The present results have confirmed that for single crystals the attenuation in martensite is higher than in the β phase. This increase in attenuation can be quantified by analysing the transmission of ultrasound in both phases when the surface is not distorted. This requires a determination of the ratio between the Fourier spectra of the transmitted pulse in martensite, after *M*-polishing, and the Fourier spectrum of the transmitted pulse
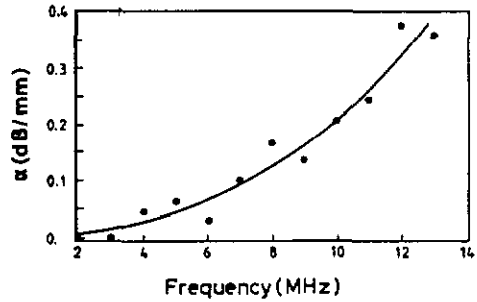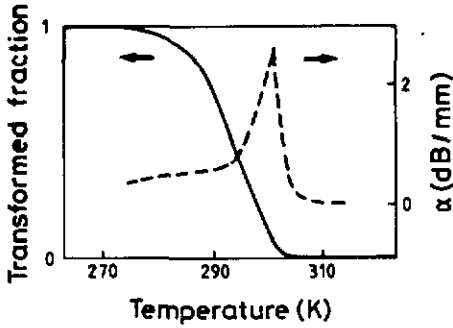
Figure 5. Transformed fraction (full curve) and ultrasonic attenuation coefficient at 10 MHz (broken curve) for a β-polished single crystal as a function of temperature.

Figure 6. Ultrasonic attenuation coefficient as a function of frequency for a *M*-polished single crystal at 275 K. The full curve is the best fit of a function $Af^2 + Bf^4$.

in β phase, after β-polishing. This is nothing more than a section, at low temperature, of the graph shown in figure 4(*b*).

Figure 6 shows the result of such a computation at a temperature of 275 K, and shows that the ultrasonic attenuation coefficient increases with frequency.

For Cu–Zn–Al alloys, the low-temperature phase is degenerate and martensitic structures with different crystallographic orientations (usually called variants) can be induced. Indeed, for a stress-free thermally induced martensitic transformation, as many as 24 of these variants co-exist at low temperature and the martensite exhibits a multi-domain structure [19]. As a result, the martensitic phase is inhomogeneous from an acoustical point of view. Previous works have attributed the attenuation in the martensitic phase to the scattering of the ultrasonic beam by these martensite variants [11, 14].

For scattering losses, phenomenological approaches [20] predict that the ultrasonic attenuation coefficient increases with the second or fourth power of frequency, depending on the size of the scattering element. In order to check the validity of the assumption that the attenuation is caused by scattering, we have fitted our data to the following frequency dependence:

$$\alpha = Af^2 + Bf^4.$$

This fit gives the values $A = 0.17 \; 10^{-2}$ dB mm^{-1} MHz^{-2} and $B = 0.34 \; 10^{-5}$ dB mm^{-1} MHz^{-4}.

According to Papadakis [20], the *A* and *B* coefficients for cubic crystals are given by:

$$A = (16\pi^2\mu^2/525v_l^2\rho^2)D \tag{5}$$

and

$$B = 8\pi^3\mu^2/375v_l^3\rho^2(2/v_l^5 + 2/v_t^5)T \tag{6}$$

where ρ is the density, v_l and v_t the longitudinal and transverse sound velocities, respectively, D and T the average diameter and volume of the scattering elements, respectively, and $\mu = C_{11} - C_{12} - 2C_{44}$ (C_{ij} are the elastic stiffnesses in Voigt notation).

The second power dependence applies when the average size of the scattering elements is of the same order as the wavelength of ultrasound, and the fourth-power

dependence applies when the scattering elements are smaller than the ultrasound wave-length.

Unfortunately the lack of a complete set of elastic data for Cu–Zn–Al martensite makes it impossible for an exact evaluation of these coefficients. However, a rough estimate can be made using the elastic data for the β phase. Taking $C_{11} = 130$ GPa, $C_{12} = 118$ GPa, $C_{44} = 86$ GPa, $v_1 = 5 \times 10^3$ m s^{-1}, $v_t = 3 \times 10^3$ m s^{-1} and $\rho = 7.76 \times 10^3$ kg m^{-3} [21], comparison with scattering coefficients A and B obtained in the present work gives average sizes of the scattering elements ranging from ~0.4 to ~3 mm. These values are perfectly consistent with typical sizes of martensite domains found in Cu–Zn–Al single crystals observed in optical microscopy experiments, thus supporting the assumption that in the martensitic phase ultrasonic attenuation is mainly due to wave scattering.

5.2. Attenuation during transformation

As shown in figure 4 the ultrasonic attenuation coefficient shows a maximum at a temperature within the range of the transformation. To account for a decrease in the amplitude of ultrasonic pulses we consider scattering of the ultrasonic beam. As discussed in the previous section, as the transformation proceeds, a number of martensite and β regions co-exist in the solid. The difference in the elastic properties of the two phases results in different acoustic impedances that produce reflections and refractions of the ultrasonic beams at the interfaces and therefore, a sharp increase in attenuation is produced on starting the transformation. On further decreasing the temperature, β domains progressively transform into martensite ones and, on average, the martensite domains are smaller. This reduction in the domain size implies that scattering passes from an intermediate (or stochastic) domain to a Rayleigh one. Since ultrasonic attenuation is maximum for stochastic scattering, a decrease in temperature results in a decrease in the ultrasonic attenuation. Another factor to consider is that, for Cu–Zn–Al, the martensitic phase is less anisotropic than the β phase [22]. This, again, implies that the attenuation will be higher for a co-existence of both β and martensite domains than for co-existence of different martensite variants.

For a scattering mechanism, the ultrasonic attenuation is expected to be maximum when the wavelength of ultrasound is of the same order than the average size of the scattering elements. This implies that, in our experiments, for high frequencies (small wavelength) maximum attenuation is expected when the average size of the domains is small; that is the ultrasonic attenuation peak for high frequencies must be located at low temperatures. This is the behaviour found in the present experiments (figure 7).

Further support for the assumption that ultrasonic attenuation during martensitic transformation is caused by scattering of the ultrasonic beam comes from experiments on polycrystals. For any mechanism other than scattering, similar behaviour should be expected for polycrystals and single crystals, regardless of the size of the grains. On the contrary, a scattering mechanism is extremely sensitive to the microstructure of the sample. When the size of grains is large (initial grain scattering is not yet in the stochastic domain) a maximum in the attenuation versus temperature curve is still expected but for small grain size (smaller than ultrasound wavelength) the ultrasonic attenuation must decrease without any maximum [23]. We have measured the acoustic behaviour of Cu–Zn–Al polycrystals with a composition close to the studied single crystals, with average grain sizes ranging from 0.2 to 3 mm. Figure 8 shows the ultrasonic attenuation at 10 MHz as a function of temperature for crystals with extreme grain sizes (a complete set of data
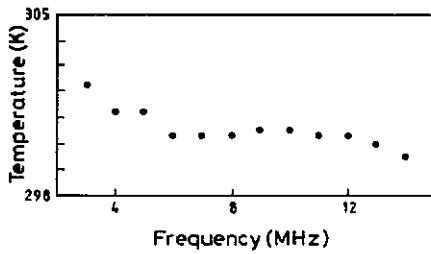
Figure 7. Temperature of the maximum ultrasonic attenuation as a function of frequency.
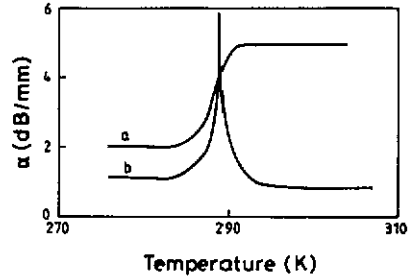

Figure 8. Ultrasonic attenuation at 10 MHz as a function of temperature for Cu–Zn–Al polycrystals with mean grain sizes of (*a*) 0.2 mm and (*b*) 2 mm.

will be presented in a future work [24]). The observed behaviour agrees well with the scattering mechanism described above.

It is worth noting that other typical mechanisms causing energy losses as, for example, damped vibration of interfaces or relaxational mechanisms do not interpret our experimental results. Considering a damped vibration of interfaces, the maximum attenuation should be comparable to that found in internal friction measurements; it should be enhanced at low frequencies and dependent on both the amplitude of the strain and on the cooling rate [25, 26]. The ultrasonic attenuation maximum found in this work is independent of the amplitude of the ultrasound and of the cooling rate; moreover, it decreases as frequency is reduced. These findings prove that the mechanism is different from the one causing internal friction maxima. If relaxational mechanisms are considered, the ultrasonic attenuation maxima would be expected to shift towards higher temperatures when the frequency of ultrasound increases [27, 28]. As shown in figure 7 this prediction does not fit with our experimental observations. Therefore, we can conclude that the most likely cause of the ultrasonic attenuation during martensitic transitions is the scattering of ultrasonic waves by the martensite variants.

6. Conclusions

(i) The use of an immersion technique has enabled a reduction of the effects associated with surface distortion in measuring ultrasonic attenuation. These effects have been quantified using two different polishing conditions and have been shown to be negligible in the measurement of ultrasonic attenuation during a thermoelastic martensitic transition.

(ii) In the martensitic phase, the increase of ultrasonic attenuation with frequency can be explained by the scattering of the ultrasonic beam caused by martensite domains.

(iii) For single crystals, the ultrasonic attenuation is maximum for a temperature within the range of transformation. The behaviour of ultrasonic attenuation as a function of temperature can be explained by taking into account the scattering caused by the coexistence of β and martensite regions.

Acknowledgment

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