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INTERNAL FRICTION IN QUENCHED β PHASE CuZn AND CuZnAl ALLOYS

* Madrid
A.Ghilarducci and M.Ahlers
Centro Atómico Bariloche - Comisión Nacional de Energía Atómica
8400 S.C.de Bariloche, Argentina

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1. Introduction

The ordering reaction in β CuZn alloys cannot generally be suppressed by quenching (1). However, some short range disorder can be retained on quenching as reported by several investigators (2-5). Notably, Clarebrough (2) observed an internal friction peak in β CuZn at 70°C that decayed with time. Similar aging effects subsequent to quenching have also been noticed while measuring the electrical resistivity (3-5) and the martensitic transformation temperatures (5) of these alloys. Thus Koczak et al (4) detected a small recovery stage between -50°C and 0°C in addition to the main recovery stage between 20°C and 50°C from isochronal annealing curves of resistivity in quenched or electron irradiated Cu-48.4 wt% Zn. The activation energy associated with this small recovery stage was reported to be 30 to 40 kJ/mole. Koczak et al concluded from their results that a point defect exists below 0°C which is mobile and causes atomic interchange. The intention of the present study is to obtain more details concerning these point defects, particularly as quenching and subsequent aging strongly influence the martensitic transformation (5). To this end, internal friction measurements below room temperature were carried out in β CuZn and β CuZnAl single crystals, and the results are reported in this note.

2. Experimental Procedure

Single crystals of Cu-29.61 wt% Zn-4.64 wt% Al and of Cu-45.83 wt% Zn were grown in sealed quartz tubes by the Bridgman method. The crystals were then spark machined to cylindrical samples 2.8 to 3.2 mm in diameter and 55 to 75 mm long. These samples, after chemical polishing were solution treated at 800°C for 3 min, furnace cooled to a temperature T_Q between 100°C and 200°C and subsequently quenched into alcohol at -100°C. The binary CuZn alloy -in contrast to CuZnAl- had to be encapsulated during the heat treatments owing to Zn evaporation. Some samples were plastically deformed by torsioning at room temperature to an angle of 1° per mm length. The samples were then heated to T_Q for 10 minutes and afterwards quenched in the same manner mentioned earlier.

The quenched samples were mounted on a torsion pendulum inside a stainless steel tube that was closed at the lower end and thus could be inserted into a liquid nitrogen bath. During this entire operation the temperature of the sample remained below -50°C. The sample was then heated up at a rate of about 120°C/hour and its internal friction measured as a function of temperature. Temperature was measured by a thermocouple positioned close to the sample. Differences in temperature between the thermocouple and the sample were determined and corrected for by making a heating and a cooling run and comparing the positions of the internal friction peaks. The frequencies employed in the internal friction measurements depended on the sample diameter and length and were in the range 30 to 90 Hertz.

3. Results

The ternary CuZnAl alloy has an ordering transition from B2 to DO_3 order near 150°C. Consequently, samples quenched from above this temperature did not show the superlattice spots in electron diffraction patterns characterizing DO_3 order, whereas samples quenched from below 150°C did exhibit them.

The results of a heating curve of a specimen quenched from T_Q=200°C are shown in figure 1 for an undeformed and deformed CuZnAl sample. Internal friction peaks can be observed at -135°C

* GHILARDUCCI ob SELVA, Adv A.

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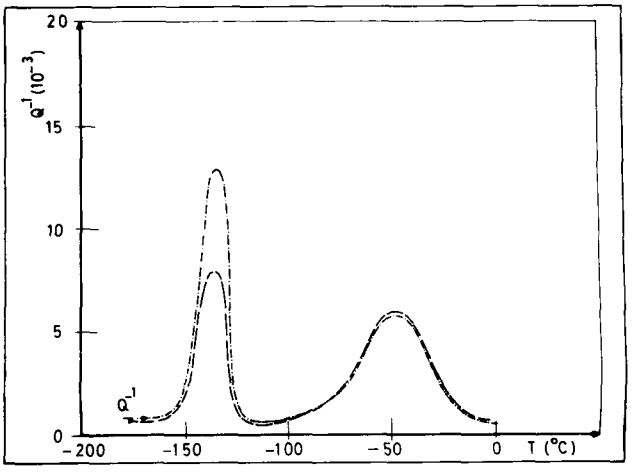

Fig.1: Internal friction Q^{-1} versus sample temperature for a heating cycle after quenching from T_Q=200°C (-·-·-·- deformed, ------ undeformed) CuZnAl. Heating velocity 120°C/h.

and at -50°C. Plastic deformation increases the height of the peak at -135°C, whereas the second peak at -50°C remains unaffected. Varying the time of annealing at T_Q from 5 minutes to 2 hours has no effect on the peaks by way of changing their position or height, implying that no precipitation phenomenon is occurring and the material remains truly as single phase. Binary CuZn also gives rise to similar peaks at -135°C and -50°C. The latter peak, however, is smaller than the one observed in CuZnAl.

When the CuZnAl sample is quenched from well below the T_{DO3} ordering temperature, the peak at -50°C is shifted to -15°C. On quenching from near but below T_{DO3}, peaks at -50°C as well as -15°C appear and superpose each other.

The height of the peaks at -50°C and -15°C is reduced considerably, once the sample has been warmed up to 0°C: when a sample is heated to 0°C at a velocity of 120°C/h and after reaching 0°C is cooled immediately again, the -15°C peak has disappeared and the -50°C peak has decayed to less than 10% of its original peak height. The -135°C peak decays only after longer annealing times above 0°C.

Since the spectrum of CuZn is exhibited by the ternary CuZnAl alloy as well and also as the quenching treatment is more easily carried out on the ternary alloy, the latter alloy was studied more extensively as will be evident from the results reported here.

From the frequency shift of the peak maxima and the shape of the peak profile the activation parameters can be deduced. The results are discussed now for each peak separately:

a) The -135°C peak: The peak position was measured as a function of frequency of oscillation. In figure 2 is shown a plot of $\omega=2\pi f$ versus T^{-1} at the peak position. It will be noticed that in spite of the different thermal treatments all points fall on a straight line with very little scatter. Included in the figure is a value for CuZn also indicativing that the difference in composition has a negligible influence on the peak position. The activation energy as calculated from the slope in the figure is Q=28.1 kJ/mole. Good agreement of this value with the activation energy estimated from the halfwidth of the peaks (29 ± 1)kJ/ mole and from the slope of the peak shoulders (30.5 ± 1.5)kJ/mole confirms that the -135°C peak is a singly activated relaxation peak. The preexponential factor τ_0 in $\omega = (1/\tau_0)\exp(-Q/kT)$ as deduced from figure 2 is $\tau_0 = 1.3\times10^{-14}$sec.

b) The -50°C peak: In CuZnAl this peak is observed by itself after quenching from T_Q=200°C, but appears superposed with the -15°C peak after quenching from 150°C. The shift of the peak position with frequency $\omega=2\pi f$ is shown in figure 3. A value from CuZn is also included in the plot. The activation energy and the preexponential factor as deduced from figure 3 are Q = 42kJ/mole and $\tau_0 = 3\times10^{-13}$sec. The activation energy as calculated from the half width of the peaks, Q = (43.0 ± 1.5)kJ/mole, or from the slope of the peak profile, Q = (43.3±2.5)kJ/mole

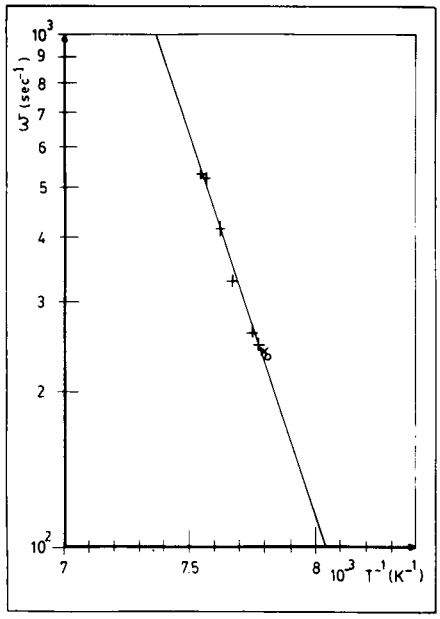

Fig.2: Peak frequency $\omega=2\pi f$ versus T^{-1} for the -135°C peak. (× CuZnAl, quenched from 100°C, + CuZnAl, quenched from 200°C, ○ CuZn quenched from 100°C).

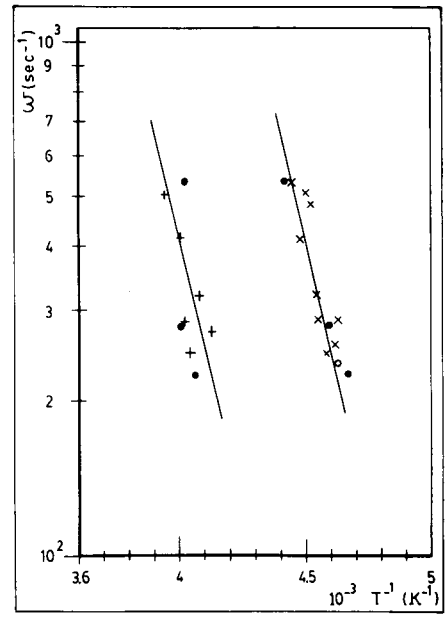

Fig.3: Peak frequency $\omega=2\pi f$ versus T^{-1} for CuZnAl after quenching from 200°C (×), 150°C (●) or 100°C (+) and for CuZn (○).

(the peak is quite symmetric) is only slightly larger than the value calculated from the peak shift data. It is to be noted in figure 3 that the peak position after quenching from 200°C and from 150°C falls on the same line. The activation energy for CuZn as calculated from the high temperature side of the peak profile is (43.4 ± 1.5)kJ/mole.

c) The -15°C peak: The results for quenching from T_Q = 150°C and T_Q = 100°C are essentially the same. However, when T_Q = 150°C there is overlap with the -50°C peak, which renders determination of the peak position in this case less accurate than when T_Q = 100°C. Hence, the data for T_Q = 100°C alone will be used. The peak is assymmetric with the high temperature side having the larger slope. This suggests some annealing out of defects during measurement, being consistent with the observation that the peak has disappeared, once the sample has reached 0°C. Using figure 3, the activation energy and preexponential factor are Q =(44.5 ± 2.5)kJ/mole and $\tau_0 = 3.4\times10^{-12}$sec, respectively. The low temperature side of the peak profile yields an activation energy Q =(44 ± 1.5)kJ/mole.

4. Discussion

The foregoing results imply that defects are retained on quenching which are then responsible for the internal friction peaks observed at subzero temperature. The position of the peak at -135°C is the same in the ternary and binary alloys and is also independent of DO_3 or B2 order. The increase in peak height after deformation and its decay after annealing strongly suggests that the peak is due to the interaction between dislocations and defects. (Hasiguti peaks). Peaks with similar frequency factors and activation energies have also been reported for other metals (7).

The peak position at -50°C or -15°C depends on whether the alloy is B2 or DO_3 ordered but is otherwise not influenced by the composition of the alloys. The peaks do not involve dislocations since their height is not affected by plastic deformation. When analyzing the nature of the defects which lead to the -50°C and -15°C peaks it should be kept in mind that quenching from 100 to 200°C in all likelihood only introduces extra vacancies and some short range substitutional disorder. The defects then could be a) vacancy pairs or vacancy clusters, b) configurations consisting only of substitutional atoms, and c) configurations composed of vacancies and substitutional atoms, in the simplest case a vacancy - substitutional atom pair. The defect is unlikely to be of the first type considering the low quenching temperatures of $T_Q \leq 200$°C.

The second type can also be ruled out for the following reasons: In order to produce internal friction the defect must be able to reorient itself under the applied periodic stress. This is possible only by the corresponding vacancy jumps. The reorientation frequency of a vacancy-substitutional atom configuration depends on the vacancy jump frequencies and on factors which are determined by the geometry of the defect configuration but not on the vacancy concentration which only affects the peak height. A configuration consisting only of substitutional atoms requires for reorientation a vacancy near-by,and thus leads to a reorientation frequency which is proportional to the vacancy concentration. Since a vacancy concentration not higher than 10^{-5} is expected at T_Q=100°C (using reasonable vacancy formation energies (6)) and since the Debye frequency of $\approx 10^{+14}\text{sec}^{-1}$ is an upper limit for the preexponential factor, τ_0 values must be higher than $\approx 10^{-14}\times 10^{5} = 10^{-9}$ sec ,if this defect exists. However, the observed τ_0 are orders of magnitude smaller. Furthermore, if the vacancy concentration influences τ_0, the quenching temperature would change τ_0 and consequently the peak position. But the results of figure 3 prove the contrary as the peak position lie on a straight line, whether quenched from 200°C or 150°C for the -50°C peak, and from 100°C or 150°C for the -15°C peak. From these very general arguments it is concluded that the defect which is responsible for the subzero peak consists of a vacancy-substitutional atom configuration. Experiments are in progress now to clarify the defect configuration in more detail.

Although the vacancies become mobile at subzero temperatures, their mobility remains restricted, since they do not lead to a complete recovery of the quenched in disorder. For this to occur, an activation energy which is 20 kJ/mole higher is required. Koczak et al (4), on the basis of their results assumed that vacancies get completely mobile below 0°C, but get trapped immediately by boundaries and are emitted again only at higher temperatures. Grain or domain boundaries are unlikely trapping centers in the present study where single crystals were used which had large B2 ordered domains (8). Trapping by the formation of vacancy clusters is another possibility that cannot be excluded a priori. However, for vacancy concentrations of the order of 10^{-6}, the vacancies must move rather large distances before they can cluster, implying that a considerable fraction of disorder would be expected to anneal out below 0°C in contrast to the observations, which have shown that B2 order can be quenched from T_Q=150°C and 200°C, taking hours for DO_3 order to appear at room temperature. Thus the assumption that freely moving vacancies are trapped by boundaries or by other vacancies below 0°C is not well substantiated. The alternative is that vacancies are not yet completely free below 0°C and that movement is restricted to lattice sites within a special favorable atom configuration. Only if an additional 20 kJ/mole activation energy becomes available, they start to move through the lattice, leading to the recovery of the quenched in defects.

The type of long range order, DO_3 or B2 influences the peak position (at -15°C or -50°C) either by a change in τ_0 or in Q. Attributing all the differences to τ_0 would require a change in τ_0 by more than an order of magnitude, which seems unlikely unless the configuration changes. On the other hand, an increase of Q by 13% on DO_3 ordering reproduces the displacement of the curves in figure 3. The corresponding change in slope, however, is smaller than the scatter of the experimental results. An increase in Q on more ordering seems reasonable, since ordering lowers the energy of the atoms and thus increases the difference to the saddle point energy.

In summary, the present results have shown that defects consisting of vacancies and substitutional atoms can be quenched in β CuZn, that they interact with dislocations and become mobile at subzero temperatures depending on the type of long range order B2 or DO_3, but only to a lesser degree on alloy composition. The vacancy movement, which is implied, remains restricted, however and becomes free only at higher temperatures.

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