Journal of Alloys and Compounds 502 (2010) 356–359

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Influence of the experimental technique on the quench temperature dependence of the martensitic transformation temperature in Cu–Zn–Al alloys

F.G. Sesma [a], P. Arneodo Larochette [a,b], J.L. Pelegrina [a,b,*]

[a] Instituto Balseiro, Univ. Nac. de Cuyo, Av. E. Bustillo 9500, R8402AGP S.C. de Bariloche, Argentina
[b] CONICET and Centro Atómico Bariloche, Av. E. Bustillo 9500, R8402AGP S.C. de Bariloche, Argentina

ARTICLE INFO

Article history:
Received 8 March 2010
Received in revised form 14 April 2010
Accepted 23 April 2010
Available online 4 May 2010

Keywords:
Metals and alloys
Martensitic transformation
Order–disorder effects

ABSTRACT

The shift of the martensitic transformation temperatures has been measured in a Cu–Zn–Al alloy as a function of the quenching temperature using different experimental techniques. Results from temperature and stress induced transformations were compared. It was found that the spread of the results is related to the geometry as also to the preparation time characteristic of each experimental method. The evidence of Zn loss by volatilization during the high temperature anneals is also reported.

1. Introduction

About 30 years ago, Rapacioli and Ahlers observed that the characteristic temperatures of the martensitic transformation in Cu–Zn–Al alloys were shifted down when the sample was quenched from different temperatures T_Q [1]. As the whole transformation cycle moved homogeneously, the description could be done in terms of the martensite start temperature M_S. These temperature shifts (ΔM_S) are shown as a function of T_Q as full circles in Fig. 1. The reference transition temperature for the calculation of the shifts was taken from the M_S value for the sample which was slowly cooled from the annealing temperature down to room temperature. The linear departure from zero at low T_Q was related to an increasing degree of $L2_1$ disorder in the high temperature β phase [1]. On the other hand, the behavior above 600 K is determined by the high amount of vacancies that are quenched in, which allow a fast promotion of the $L2_1$ order. A vacancy concentration of up to 10^{-4} has been determined after quenching from 600 K [2]. The relative maximum at around 800 K is related to a change in behavior at the B2 ordering temperature [1].

These results were obtained from measurements of electrical resistance as a function of the temperature. The transformation behavior as a function of T_Q has also been determined by calorimetry [3,4], and these results are shown as crosses in Fig. 1. The martensitic transformation can also be induced by the application of stresses, and its study as a function of T_Q was performed in [5]. In the resolved stress vs. strain graph, a critical resolved transformation stress (τ_T) for the beginning of the transformation plateau can be defined. This stress can be related to the M_S temperature because a linear relationship exists between τ_T and the difference between the working temperature and M_S [6]. In the present work a slope of $d\tau_T/dT = 1.07$ MPa/K has been taken from the mean value of the data in [7]. The experimental points extracted in this way from the stress induced transitions [5] are shown as triangles in Fig. 1. The sets of results show a similar trend, but the complete picture presents a big scatter, mainly at the highest quenching temperatures. The samples used to construct Fig. 1 have different shapes and also a spread of ordering temperatures which are presented in Table 1 together with the corresponding M_S. The former values were obtained from an interpolation of precise determinations of the ordering temperatures as a function of composition in [8]. The M_S are the experimental values except for the compositions in [5], which were assessed from the ratio of the transformation enthalpy and entropy as a function of composition, according to [9].

The aim of the present work is to analyze whether the scatter observed in Fig. 1 arises from these different characteristic temperatures or whether they are a consequence of the different experimental techniques. In the latter case, the geometry of the samples and/or the concomitant time for each measurement could influence the results.

It is known that due to the high vapor pressure, Zn can vaporize from Cu–Zn alloys when a high enough temperature is reached [10,11]. It is usual to state that in Cu–Zn–Al alloys this loss is negligible due to a protecting aluminum oxide layer on the surface of

---

[*] Corresponding author at: Centro Atómico, R8402AGP San Carlos de Bariloche, Argentina. Tel.: +54 2944 445272; fax: +54 2944 445299.

E-mail addresses: sesmaf@ib.cnea.gov.ar (F.G. Sesma), arneodo@cab.cnea.gov.ar (P.A. Larochette), jlp201@cab.cnea.gov.ar (J.L. Pelegrina).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.04.166

Table 1
B2 and L2$_1$ ordering and reference martensitic transformation temperatures for the samples from which figure 1 was constructed and for the present work.

#	C_{Zn}	C_{Al}	T_{B2} [K]	T_{L21} [K]	M_S [K]
[1]	0.20	0.14	828	577	180
[3]	0.158	0.161	810	658	260
[4]	0.16	0.16	811	655	265
[5] △	0.2809	0.0995	845	416	−49
[5] ▽	0.2526	0.1137	846	474	16
Present work	0.1873	0.1463	823	604	168

the samples. In fact, in [1] the change in M_S has been found to be independent of the number of the previous reheating and quenching cycles. This will be another aspect analyzed in the present work.

2. Experimental

A Cu–18.73 at% Zn–14.63 at% Al alloy was prepared inside a sealed fused silica tube with an Ar atmosphere. This composition was selected in order to have an M_S temperature accessible to our experimental systems, with low enough ordering temperatures to enhance the disorder retained by the quench. The ordering temperatures and the experimental M_S are presented in Table 1. Two single crystals with a diameter of 6 mm and a length of nearly 10 cm (denoted as crystals 1 and 2) were grown by the Bridgman method, also in sealed fused silica capsules with an Ar atmosphere. They had an orientation near $[1\,4\,28]_\beta$ for crystal 1 and $[0\,2\,5]_\beta$ for crystal 2.

The effect of the long range order on M_S was evaluated in the following way. The degree of long range order was modified by quenching samples from temperatures T_Q between 373 and 1073 K. The M_S temperatures were then determined by three different techniques: stress–strain measurements, differential scanning calorimetry and electrical resistance as a function of the temperature.

A cylindrical sample was spark machined from each single crystal for the stress–strain experiments in tension. They were denoted as S1 and S2 (the number indicates the single crystal used for its preparation). They had Schmid factors of 0.497 and 0.485, respectively, which will be used to calculate the critical resolved transformation stresses. The tensile specimens had a central part of 3 mm diameter, a gauge length of 15 mm and thicker shoulders at the ends, appropriate to insert them into the grips of an Instron 5567 deformation machine. The strain was applied using a cross head speed of 1 mm/min, working at 253 K in an Instron 3119-005 temperature chamber. A time of 7 min was permitted to pass between the placement of the sample in the chamber and the application of the load, to assure that the specimen had reached the working temperature.

For differential scanning calorimetry, a disc shaped sample was cut from each single crystal. They were denoted as C1 and C2, having a diameter of 6 mm and a thickness of 0.75 and 0.34 mm, respectively. A Cu disc of similar shape was used as the reference sample. Their surfaces were mechanically polished with silicon carbide paper of grit 600. The non-commercial calorimeter has been described in detail elsewhere [12]. Cooling was provided by a Dewar containing liquid nitrogen. Typical cooling rates were around 2–3 K/min.

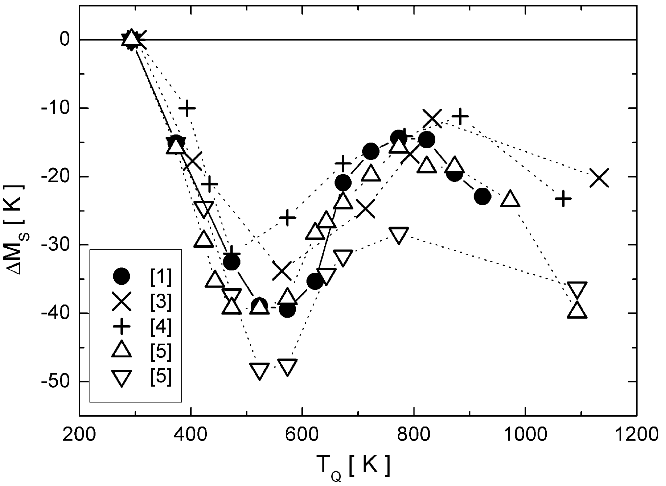

Fig. 1. Shift of the martensitic transformation temperature as a function of the quenching temperature. Data from electrical resistance [1], calorimetry [3,4] and stress–strain [5] measurements. The lines are a guide to the eye.

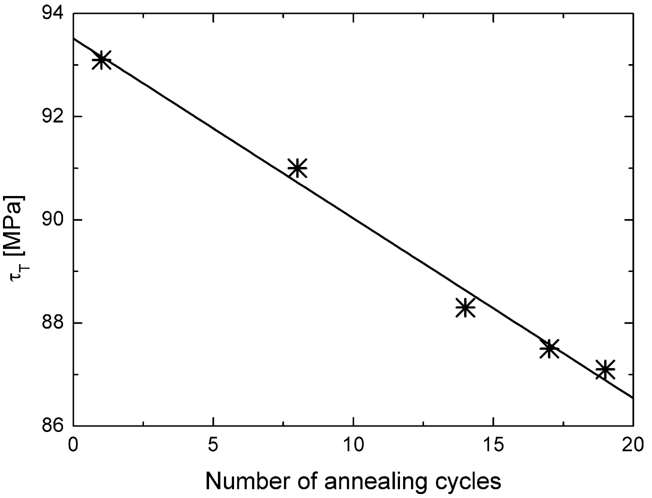

Fig. 2. Variation of the critical resolved transformation stress as a function of the number of the annealing cycles in the specimen. The data points belong to sample S2 after a quench from 773 K.

The electrical resistance measurements were performed on a sample of 25 mm length, 3 mm width and 1.5 mm thickness. It was identified as R1, because it was cut from single crystal 1. The standard four probe method was used, with a direct current of 150 mA. The four Cu wires were spot welded to the sample, as also the chromel alumel thermocouple. Cooling was provided by a Dewar containing liquid nitrogen. Typical cooling rates were around 6–10 K/min. The six cables were removed after each measurement and the damaged surface was mechanically polished with silicon carbide paper of grit 600, before the next heat treatment.

The general procedure was the following: the sample was first homogenized by annealing it in an electrical furnace at 1073 K for 15 min. It was then cooled in air to the desired T_Q and quenched in water at room temperature. No sealed capsules were used for this procedure and the temperature was monitored with a chromel alumel thermocouple placed inside a hole in a brass block of 4 mm × 7 mm × 12 mm in good contact with the specimen. After the quench, the sample was prepared and introduced into the corresponding equipment and the martensitic transformation was induced. This latter step required a mounting time which is dependent on the experimental technique. In order to avoid further atomic rearrangements, it is important to minimize the interval between the quench and the moment at which the sample reaches a temperature below around 273 K, at which the diffusion processes can be neglected. Typical mounting times were about 2 min for the tensile tests, 7 min for calorimetry and around 25 min for electrical resistance measurements.

3. Results and discussion

The values of the critical resolved transformation stress τ_T as a function of the number of the annealing cycles performed on sample S2 are shown in Fig. 2. Only the data which correspond to a quench from 773 K are presented. It can be seen that τ_T decreases linearly 6 MPa after 18 thermal treatments. It is to be noted that the present analysis takes into account only the time at 1073 K and not the following cooling and quenching procedures. A linear fit of these data gives a variation rate of (-0.35 ± 0.02) MPa per anneal, which has been used to refer all τ_T measurements to the original one, i.e. before the first anneal. For sample S1 a variation rate of (-0.49 ± 0.05) MPa per anneal has been found. Using the linear relationship between the critical resolved transformation stress and the temperature mentioned in the introduction, these slopes can be associated with a positive M_S temperature shift of 0.33 and 0.46 K per anneal, respectively.

A similar determination was performed with the samples for calorimetry and electrical resistance measurements. In agreement with the previous results, an increase of the M_S temperature with the number of annealing cycles was found. The corresponding variation rates are 0.44, 1.1 and 0.45 K per anneal for samples C1, C2 and R1, respectively. The greater value presented by sample C2 seems to be related to its higher surface to volume ratio of around 6.6 mm^{-1}. The other samples have ratios between 1.3 and 3.3 mm^{-1}, and scat-

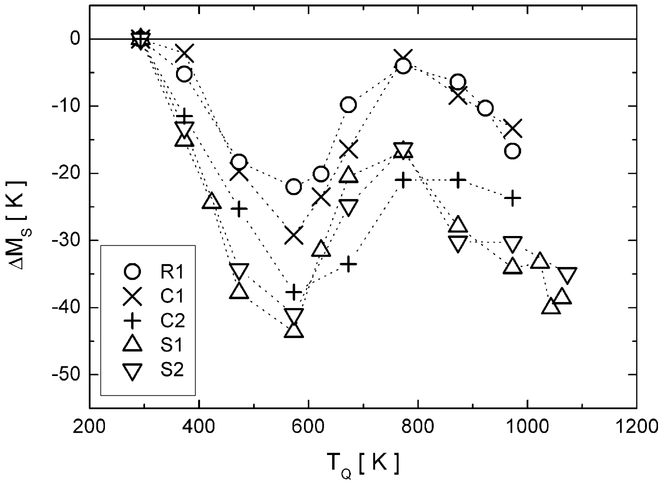

Fig. 3. Shift of the martensitic transformation temperature as a function of the quenching temperature. Data from electrical resistance (R1), calorimetric (C1 and C2) and stress–strain (S1 and S2) measurements. The lines are a guide to the eye.

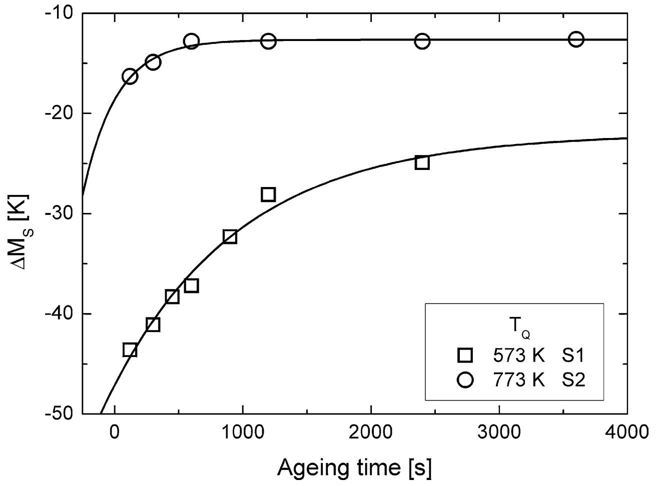

Fig. 4. Shift of the martensitic transformation temperature as a function of the previous ageing time at room temperature. Stress–strain measurements performed on S1 and S2 after a quench from 573 and 773 K, respectively.

ter around a clearly lower value of the variation rate. Whether the orientation of the crystal also plays a role cannot be deduced from the present experiments. The origin of this M_S increment has to be related to a loss of Zn during the anneal, since all other effects of the thermal treatments are erased by the high temperatures. It is to be noted that in the worst case of sample C2 the amount of volatilized atoms is only around 300 ppm per anneal. This is a good indication of the sensitivity of the martensitic transformation on composition in Cu–Zn–Al alloys.

From the previous results it was possible to calculate the original M_S for each specimen, being of 173, 174, 179, 182 and 185 K for samples C1, R1, T1, T2 and C2 respectively. If again these temperature shifts are attributed to Zn loss during the preparation of the alloy and the growth of the single crystals, then a composition of Cu–18.38 at% Zn–14.69 at% Al can be calculated for the highest M_S. This loss of 0.75 at% Zn with respect to the original composition imply an increase of 5 K and a decrease of 3 K in the L2$_1$ and B2 ordering temperatures, respectively. Experimentally, these shifts in the ordering temperature can be considered negligible because they fall well within the scatter of the reproducibility of the quenching temperature.

In Fig. 3 are shown the M_S shifts as a function of T_Q for the five samples using the three different experimental techniques. All of them were corrected to take into account the Zn loss using the coefficients presented above. It can be seen that a similar spread of the data is obtained as in Fig. 1, although all the tested samples for Fig. 3 have the same ordering temperatures. Therefore, the scatter in Fig. 1 is mainly a consequence of the different experimental techniques rather than of the spread of the ordering temperatures of the samples compared there.

It can be seen from Fig. 3 that the samples tested mechanically (up and down triangles) follow the same trend, showing within experimental scatter a similar M_S shift for each T_Q. This can be taken as an indication that the degree of disorder retained by the quench does not depend on the crystallographic orientation of the tensile axis. Additionally, it can be observed that the electrical resistance values (full circles in Fig. 3) present in the majority of cases, the smallest values of the M_S shift. This result could also have been expected, since this sample spent the highest amount of time at room temperature in order to spot weld the six cables for the measurement.

In the case of the calorimetric samples (crosses in Fig. 3), the M_S shift is different for each sample. In a first approximation it can be assumed that this is not due to the crystal orientation, as suggested by the results of the mechanical tests. Instead, it has to be attributed to their different sizes, in particular the thickness. It can be seen that the sample with the smaller thickness presents the more pronounced shifts in M_S, which as explained in the introduction is related to a lower degree of L2$_1$ order. In β phase Cu–Zn–Al alloys the diffusion processes are controlled by vacancies. Therefore, it can be suggested that for a thinner sample the vacancies reach faster the sample surface, leaving the material without the possibility of increasing the degree of long range order. A simple argument will be given that supports this hypothesis. As presented in [13], the average distance d that a vacancy migrates until it is annihilated at a sink is given by

$$d = \frac{\sqrt{3}}{4} a\sqrt{N} \qquad (1)$$

where a is the lattice constant and N is the number of its jumps. N is related to the vacancy migration energy E_m and to the temperature T, according to [13]

$$N = z\tau\nu_0 \exp\left(-\frac{E_m}{kT}\right) \qquad (2)$$

being z the coordination number, τ the average relaxation time, ν_0 the Debye frequency and k the Boltzmann constant. In the present case, for each quenching temperature all variables in Eqs. (1) and (2) are constants, and therefore, the ratio of the relaxation times (τ_1 and τ_2) for the two thicknesses (h_1 and h_2) is given by

$$\frac{\tau_1}{\tau_2} = \left(\frac{h_1}{h_2}\right)^2 \sim 5$$

Thus, the sample with the smaller thickness stops the ordering process five times faster and the M_S shifts should resemble those of samples measured at shorter times after the thermal treatment. This is the reason for a behavior of C2 similar to that of S1 and S2, which had reached low temperatures very fast in the measuring chamber. In spite of the results for the tensile specimens, it cannot be excluded from the present results that they depend also on the crystallographic orientation of the sample. In the stress samples, the cylindrical surface assures a quite similar distribution of diffusion paths for both samples. On the other hand, the two circular surfaces are predominant in the calorimetric samples and the effectiveness of each vacancy jump could depend on the crystal orientation.

It can be seen from Fig. 4 that the shift in M_S is reduced by ageing at room temperature previous to the stress induced transformation.

The squares correspond to sample S1 after a quench from 573 K, whereas the circles belong to sample S2 after a quench from 773 K. It has to be noted that after each transformation the sample was annealed again, quenched and aged. The data were corrected for the loss of Zn. The behavior can be described with one exponential time constant of 1000 s, reaching an asymptotic value of −22 K for sample S1, and 260 s and −13 K respectively for S2. It can be seen from this figure how important is to minimize the time between the thermal treatment and the measurement to detect the M_S shifts. In this context mechanical testing appears to be the more suitable technique.

A similar M_S difference of 13 K has been measured in Cu–Zn–Al melt spun ribbons between a slowly cooled sample and another one quenched from above the ordering temperature [14]. This difference has been rationalized in terms of the energy changes which introduce the presence of $L2_1$ antiphase boundaries on each phase. However, the higher asymptotic value of this sample S1 cannot be ascribed to the antiphase boundaries, because a smaller density of antiphases is obtained after a quench from below the ordering temperature [15]. Therefore, in this latter case, the M_S shift is probably due to a higher remaining $L2_1$ disorder of the structure, which a lower concentration of vacancies was not able to eliminate.

4. Conclusion

The shift of the martensitic transformation temperatures as a function of the quenching temperatures in a Cu–Zn–Al alloy has been studied by three experimental techniques. From the present results it can be concluded that:

1. The spread of the data presented in the literature mainly arises from the specimen geometry and the characteristic preparation times concomitant to each measuring method.
2. The spread is slightly influenced by the location of the ordering temperatures. The principal requirement is the $L2_1$ order temperature to be low enough to allow the retention of some degree of disorder by a quench.
3. Zn is lost during the high temperature anneals.

Acknowledgements

This work was supported by the ANPCyT, CONICET, CNEA and Universidad Nacional de Cuyo, Argentina. Fruitful discussions with M. Ahlers, H.E. Troiani and G.M. Castelluccio are gratefully acknowledged.

References

[1] R. Rapacioli, M. Ahlers, Acta Metall. 27 (1979) 777–784.
[2] R. Romero, A. Somoza, Ll. Mañosa, A. Planes, J. Phys. IV France 112 (2003) 471–474.
[3] A. Planes, J.L. Macqueron, R. Rapacioli, G. Guénin, Philos. Mag. A 61 (1990) 221–231.
[4] M. Jurado, L. Mañosa, A. Planes, Phys. Rev. B 48 (1993) 3540–3543.
[5] A. Planes, R. Romero, M. Ahlers, Acta Metall. Mater. 38 (1990) 757–763.
[6] R. Romero, M. Ahlers, J. Phys.: Condens. Matter 1 (1989) 3191–3200.
[7] R. Romero, J.L. Pelegrina, Phys. Rev. B 50 (1994) 9046–9052.
[8] F. Lanzini, R. Romero, M. Stipcich, M.L. Castro, Phys. Rev. B 77 (2008), 134207 1–8.
[9] J.L. Pelegrina, M. Ahlers, Acta Metall. Mater. 40 (1992) 3205–3211.
[10] H.E. Troiani, J.L. Pelegrina, M. Ahlers, Phys. Status Solidi (a) 156 (1996) 93–106.
[11] H.E. Troiani, J.L. Pelegrina, M. Ahlers, Philos. Mag. A 78 (1998) 1253–1267.
[12] V. Torra, H. Tachoire, J. Therm. Anal. 36 (1990) 1545–1577.
[13] W. Salgueiro, R. Romero, A. Somoza, M. Ahlers, Phys. Status Solidi (a) 138 (1993) 111–118.
[14] J.L. Pelegrina, L.M. Fabietti, A.M. Condó, G. Pozo López, S.E. Urreta, The influence of microstructure on the martensitic transformation in Cu–Zn–Al melt spun ribbons, Philos. Mag. (2010).
[15] R. Rapacioli, M. Ahlers, Scripta Met. 11 (1977) 1147–1150.