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PLASTICITY OF CLOSE PACKED LONG-RANGE ORDERED Cu-Zn-Al SHAPE MEMORY ALLOYS

M. Ahlers*, A. Cuniberti‡, R. Romero‡

*Centro Atómico Bariloche, 8400 S.C. de Bariloche, Argentina
‡IFIMAT, Facultad de Ciencias Exactas, Universidad UNCPBA, Pinto 399, 7000 Tandil, Argentina

Abstract

The critical resolved shear stress (CRSS) for plastic deformation of Cu-Zn-Al 18R martensitic single crystals with an electron concentration e/a = 1.48 has been determined as a function of temperature between 80K and 470K. It has been found that below room temperature the CRSS depends little on temperature, but that above this temperature it increases with T. These results are discussed in relation to the plasticity of $L1_0$ ordered Ti-Al single crystals, and the great similarity between both alloys systems is stressed.

Introduction

Long range close packed alloys have found widespread interest due to their favorable plasticity at high temperatures (1). The anomalous positive temperature dependence of the critical resolved shear stress (CRSS) in $L1_2$ ordered A_3B compounds has been rationalized by the Kear-Wilsdorf mechanism (2), which assumes a favourable splitting of the superdislocation which does not lie in its slip plane. A similar positive temperature dependence has been found also in $L1_0$ ordered Ti-Al single crystals even if instead of superdislocations, dislocations with an ordinary Burgers vector are mobile (3,4). In this case the Kear-Wilsdorf model cannot be applied and alternative mechanisms have been proposed (5), some of which rely on a splitting of the ordinary dislocation in a plane inclined to the glide plane, or on dislocation reactions that lead to sessile dislocations.

Close packed long range ordered single crystals can also be obtained by stress inducing the martensitic transformation in B2 or $L2_1$ ordered Cu-Zn and Cu-Zn-Al alloys (6). Depending on the composition, different structures can be induced from the high temperature B2 phase: the face centered 3R, orthorhombic 9R or hexagonal 2H, with stacking sequences ABCABC, ABCBCACAB or ABAB, respectively. When the high temperature phase has $L2_1$ instead of B2 order, the number of close packed layers in the unit cell must be doubled, leading to 6R or 18R martensite. For 2H the number of layers remains unchanged. The martensite inherits the atom distribution of the high temperature phase since it is the product of a diffusionless martensitic transformation. By permitting diffusion in the martensite after the transformation, the atom distribution is changed. This change is associated with a change in lattice spacings (7), which also influences the plasticity of the martensite (8).

The macroscopic deformation behavior of Cu-Zn-Al alloys with an

electron concentration e/a = 1.48 and M_s between 280K and 316K has been studied at room temperature and is reported elsewhere (8). An analysis of the dislocations responsible for slip at room temperature has also been performed (9). In the present paper the influence of temperature on the plasticity of the 18R martensitic single crystals is reported. The temperature extends from 80K to 470K. The upper limit in temperature is determined by the retransformation temperature of the β phase, or by the temperatures at which phase decomposition of the metastable martensite occurs.

Experimental Procedure

Single crystals of the β phase material were grown by the Bridgman method in sealed quartz tubes, starting with 5N pure metals. The alloy compositions and the measured transformation temperatures M_s are listed in table 1.

Table 1

alloy number	at%Cu	at%Zn	at%Al	M_s [K]
1	69.52	12.96	17.52	316
2	69.92	12.16	17.92	336
3	69.91	12.17	17.92	380

The single crystals remained for several hours at a homogeneisation temperature close to the melting point, and were then quenched into water at room temperature. Cylindrical samples of 4mm diameter and 11mm length were cut by spark machining. From each crystal several samples could be cut. The samples were polished chemically in a solution of 50% HNO_3 in water. In order to obtain single crystals of the martensitic phase, samples of alloys 1 and 2 were heated to 1100K and subsequently quenched into water at 350K. At this temperature a martensitic single crystal was induced by applying compressive stresses. The single crystal was retained by cooling under stress to below the M_f temperature. Samples of alloy 3 were quenched into glycerine at 420K and the martensite was induced subsequently at 360K. The crystals were then el electropolished in a solution of 10% HNO_3 in CH_3OH at 278K. Due to the martensitic transformation the single crystal had changed its shape and the end faces were no longer normal to the sample axis. This was rectified by an additional mechanical grinding of the sample ends to right angles. All deformation experiments were done in compression. The end faces of the samples were covered with a thin teflon film and were lubricated with silicon grease, in order to reduce the friction of the sample ends.

The orientation of the martensitic single crystals was determined in the following way: First the orientation of the sample axis and of an additional surface mark was determined in the β phase at temperatures above M_s, using the x-ray Laue method. Since the orientation of the most favorable variant which is induced by compressive stresses is known, it is then possible to determine the orientation of the sample axis with respect to the orthorhombic axes system of the martensite. By an additional Laue photo in the martensite phase, the location of

the orthorhombic axes could be verified and if necessary corrected[4]

Samples of alloys 1 and 2 were studied at temperatures between 80K and 406K, those of alloy 3 between room temperature and 473K. In order to deform the martensite above the M_s temperature, alloys 1 and 2 were heated under stress to avoid the retransformation. It was made sure that this stress did not exceed the stress for plastic deformation. Samples of alloy 3 were first stabilized, leading to an increase in M_s. To this end the samples were heated, the heating being stopped intermittently for 30min at 393K, 433K and 473K. This treatment increased the retransformation temperature to above 473K. It is known that the stabilisation does not revert on cooling, although it increases with increasing temperature (10). Therefore the properties of the alloys are not expected to change further by diffusion below 470K.

Experimental Results

a) Nonstabilized samples (alloys 1 and 2). The results of temperature change experiments are shown in figure 1. The samples were deformed at a given temperature T_1 to a strain less than 2% and were unloaded. The temperature was then changed to T_2 and the deformation continued. Sometimes small yield points were observed after temperature (or strain rate) changes. When they appeared the stress at the yield point was taken. The stress change from T_1 to T_2 was found to be closely the same as that from T_2 to T_1. The difference was less than 2% of the total stress. In order to make sure that the stress differences were not affected by the amount of plastic deformation the temperature cycling was mostly done between room temperature and a second temperature To. Figure 1 shows that below room temperature the critical stress increases only slightly with decreasing temperature to 80K. Above room temperature an increase in the critical stress is noted

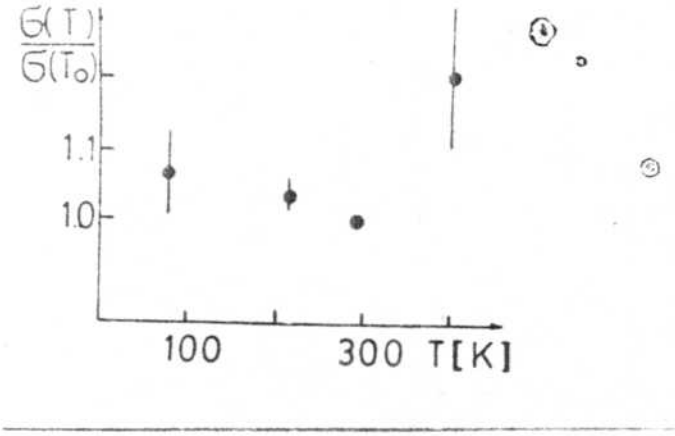

Fig.1: Temperature dependence of the shear stress for alloys 1 and 2 of different orientations obtained from temperature change experiments. Strain rate $\dot{\epsilon} = 8.10^{-4}\ s^{-1}$. Reference To = 293K.

Strain rate experiments were performed at room temperature between strain rates $\dot{\epsilon} = 10^{-3}\ s^{-1}$ and $\dot{\epsilon} = 10^{-5}\ s^{-1}$. The results show a large scatter and a value of the strain rate sensitivity

$$S = \frac{1}{T}\frac{d\ln\sigma}{d\ln\dot{\epsilon}} = (4.5\pm0.5)\ 10^{-5}K^{-1}$$

was obtained. This leads to an activation volume

$$v = kT \frac{d\ln\dot{\epsilon}}{d\tau} = (4\pm0.4)\ 10^{-27}\ m^3$$

Here σ is the yield stress and τ the critical resolved shear stress.

Surface observations of the crystals deformed at the different temperatures show slip line traces which are homogeneously distributed on the surface, as reported for the crystals deformed at room temperature (8). They correspond to slip on the (0018)o close packed plane, with a shear direction in all cases parallel to [010]o of the orthorhombic martensite.

b) Stabilized martensite: In figure 2 are shown the results of some temperature change experiments for samples of alloy 3, with axes orientations given in the unit triangle with respect to the β phase. It can be seen that also for the stabilized martensite the critical shear stress increases with temperature. No yield point is seen, but serrations are present. In figure 3 are collected all the results. It can be noted that although the CRSS increases with temperature, there

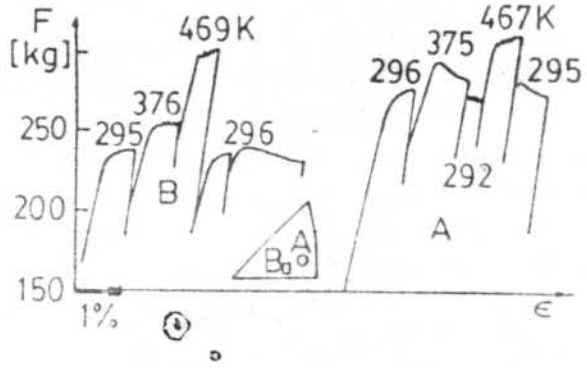

Fig. 2: Force F versus strain ϵ from temperature change experiments. Orientations A and β of alloy 3

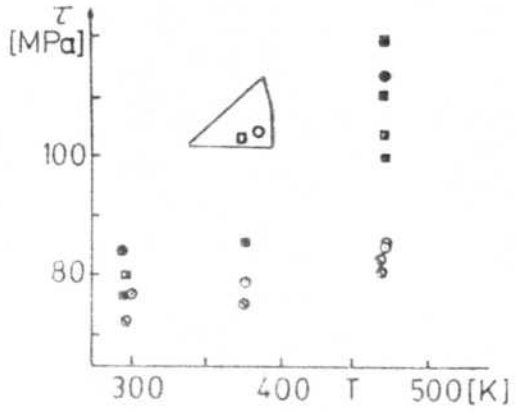

Fig.3: CRSSτ as a function of T for alloy 3. Each symbol denotes a sample, square and round symbols correspond to the square and circle in the triangle.

is a large scatter from sample to sample of a given orientation, and between the two different orientations. The stress increase and decrease when going from lower to higher temperature, and vice versa, are similar in magnitude (the same symbols in figure 3 at a given temperature, whenever present, correspond to the two directions in temperature change). The critical stress at room temperature of the nonstabilized martensite is not significantly different from that of the stabilized one, (77±11MPa) (8). Earlier (8), an increase had been reported for alloys stabilized at lower temperatures (315K). Whether this difference is due to the different degree of stabilisation, or is an orientation effect is not clear.

Strain rate sensitivity measurements have also been performed at 293K and 467K for sample orientation A of figure 3. However, the scatter is quite large and only an upper limit can be given. At 293K a sensitivity $S \leq 4.10^{-5}\ K^{-1}$ is found for changes in strain rate from $8.10^{-4}\ s^{-1}$ to $8.10^{-5}\ s^{-1}$, and $s \leq 2.10^{-5}K^{-1}$ for the inverse change. At

467K S remains small, or even gets smaller, $s \leq 1.3.10^{-5}$ K^{-1} for changes between 8.10^{-4} s^{-1} and 8.10^{-5} s^{-1}.

Surface observations of the stabilized martensite show slip traces which are distributed much more inhomogeneously than observed for the nonstabilized martensite. In addition to the slip traces occasionally some other traces have been observed, which have also been reported for nonstabilized martensite, and which have been denominated $(\bar{1}28)o$ slip. The mechanism by which they form is not yet understood (8). In some of the present samples of orientation A and B deformation bands on the (010)o plane with displacement vector parallel to [001]o have also been observed at all temperatures. These bands have not been seen in nonstabilized samples of similar orientations. Whether they are due to slip, twinning or phase transformation has not yet been analyzed. When they appeared, the temperature change experiments were discontinued.

Discussion

In figure 4 is shown the fct 6R unit cell, obtained after the transformation from the high temperature $L2_1$ ordered phase. The 18R is obtained by introducing stacking faults on each third close packed plane. The dislocations which are responsible for slip move on the

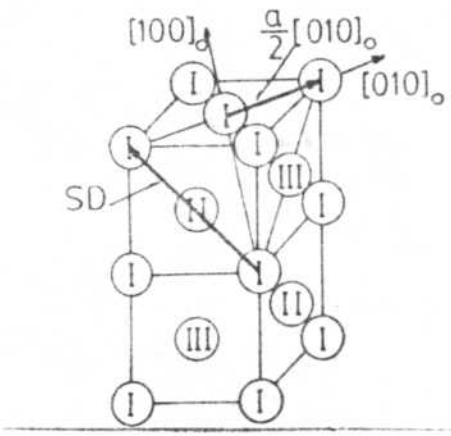

Fig.4: The fct 6R unit cell from which 18R is derived by adding stacking faults on each thirdbasal plane. Sublattice I occupied by Cu, II occupied by Al and Zn, III occupied by the remaining Cu and Zn. For inherited B2 order sites II and III have the same occupation probabilities, and a L1o cell is obtained. A basal plane (0018)o and the orthorhombic [100]o and [010]o directions are indicated. Ordinary Burgers vector for L1o is (a/2)[010]o, and for a superdislocation denoted by SD.

basal plane and have the Burgers vector parallel to [010]o. In the 18R martensite with the inherited $L2_1$ order, the dislocations have been found to be split into two pairs of Shockley partials separated by an antiphase boundary due to the difference in sublattice II and III occupation probability (9). Superlattice dislocations with Burgers vector parallel to SD of figure 4 have not been observed (8,9), which is to be expected since their Schmid factor is unfavorable (8). By quenching in the β phase, different degrees of order on II and III sublattices can be induced. This, however does not influence the CRSS (8). This indicates that the presence of the antiphase boundary between the two pairs of dislocations does not or very little influence the CRSS.

The most important result reported in this paper is the positive

temperature dependence of the CRSS above room temperature. Unfortunately the temperature dependence of the CRSS cannot be followed to temperatures exceeding about 500K, since diffusional processes change the microstructure of the metastable martensitic alloys. Even for temperatures below 500K care has to be exercised in interpreting the results, as will be discussed in the following: The nonstabilized samples when being heated to 400K can start to stabilize depending on the quenched-in vacancy concentration (10). Stabilisation has been found to increase the CRSS, for a stabilisation temperature of 315K at least (8). It is unlikely, however, that this stabilisation is responsible for the increase in CRSS at 400K, shown in figure 1. This is based on the observation that once stabilisation has occurred at a higher temperature, it does not revert at lower ones (10). Therefore, if an increase had occurred at 400K, it would remain present after continuing the deformation at room temperature, contrary to the observations which show that the change in stress on going from room temperature to 400K is, within experimental scatter, the same as that for a change from 400K to room temperature.

In order to measure the CRSS at higher temperatures the samples have to be stabilized at temperatures at which other changes in the microstructure can occur. It cannot be excluded that this has occurred to some extent in the samples which have been stabilized at 473K. This may be the reason for the serrated stress strain curves of figure 2 and for the inhomogeneous slip line distribution. These changes may also affect the temperature dependence of the CRSS and the reason for the large scatter. It is unlikely however that is is the sole cause of the positive temperature dependence of the CRSS, which is also present in the nonstabilized alloys. It is concluded therefore that the positive temperature dependence of the CRSS above room temperature is an intrinsic effect of the long range ordered 18R martensite.

It is interesting to compare the present results with those for L1$_0$ ordered Ti-Al single crystals. For certain crystal orientations the ordinary slip system is activated, viz a $(0018)_o\,[010]_o$ system in the present notation (3,4). The room temperature values of the CRSS and its strain rate sensitivity S are very similar, the CRSS being 80 MPa for Ti-Al (3) versus (77 ± 11)MPa in the Cu-Zn-Al alloys (8), and $S = 4.10^{-5}\ K^{-1}$ versus $(4.5\pm0.5)10^{-5}K^{-1}$. In Ti-Al a strong increase in CRSS of 50% below 200K is measured, and a decrease in dislocation density with the ordinary Burgers vector $\frac{a}{2}\,[010]_o$ is observed by transmission electron microscopy (4). No such strong increase in CRSS has been found in the Cu-Zn-Al alloys, and slip line analysis shows that the slip direction remains $[010]_o$ down to 80K. If indeed the dislocations in Ti-Al become immobile at low temperature due to a splitting or dislocation reactions on planes other than the slip plane, no such mechanism is expected to occur for the 18R martensite for which only one set of basal planes exists, and whose translation Burgers vectors are small only if they lie in the basal plane. In the fct 6R martensite this argument does not hold any more, and a stronger increase in CRSS on lowering the temperature is feasable. Experiments to this end are in progress now.

Above room temperature the CRSS of the Ti-Al single crystals increases by 17% between 300K and 500K. This is compared with (20 ± 10)% for the non-stabilized Cu-Zn-Al crystals between 293K and 400K, and 12% to 60% between 293K and 470K for the stabilized ones. Thus, the temperature coefficients of the CRSS are similar for the Ti-Al and the Cu-Zn-Al single crystals. These results indicate, that whatever factor controls the CRSS and its positive temperature dependence, it is probably similar in the martensitic Cu-Zn-Al and in the L1o ordered Ti-Al.