ORDER-STRENGTHENING IN THE TERNARY ALLOY Cu$_2$NiZn

P. M. BRONSVELD, B. RAMASWAMI, G. J. L. VAN DER WEGEN and J. Th. M. DE HOSSON

1Department of Applied Physics, Materials Science Center, University of Groningen, 9747 AG Groningen, The Netherlands and
2Department of Metallurgy and Materials Science, University of Toronto, Toronto, Canada MSS 1A4

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Abstract—The order-strengthening mechanism in Cu$_2$NiZn was studied by comparing stress-strain curves and electron micrographs of corresponding dislocation structures in disordered, partly ordered and ordered samples. At the low strain level superdipoles were frequently observed showing a whole range of interdislocation distances, which were compared with the calculated equilibrium distance between the dislocations based on a zero force consideration.

Résumé—Nous avons étudié le mécanisme de durcissement par ordre atomique dans Cu$_2$NiZn en comparant les courbes déformation-contrainte avec les structures correspondantes de dislocations dans des échantillons désordonnés, partiellement ordonnés et ordonnés. Pour les faibles déformations, on observe souvent des superdipoles présentant toute une gamme de distances entre les dislocations, que l'on compare avec la distance d'équilibre entre les dislocations, calculée en annulant la force d'interaction.


INTRODUCTION

With the advance of higher-voltage electronmicroscopy it is possible to study in increasingly more detail the microstructure belonging to the special features of a stress-strain curve of a material, be it a metal, an alloy, of f.c.c., h.c.p. or b.c.c. structure, polycrystalline or single crystal, ordered or disordered. In this article we deal with Cu$_2$NiZn a ternary alloy of f.c.c. structure which, at low temperatures, has a modified Li$_2$ ordered structure, and at still lower temperatures a modified Li$_0$ structure. We will concentrate on the typical features introduced by the ordering phenomena: that means we will vary the long-range order parameter and the domain size and study the behaviour of superlattice dislocations. The samples were mostly polycrystalline, some with severe rolling texture: (011) [211] which predetermines already to a certain extent the material as being soft when stressed in the rolling direction.

STRENGTHENING MECHANISM IN ORDERED ALLOYS

The plastic deformation of well ordered alloys with Li$_2$ superlattice like Cu$_3$Au is usually associated with the motion of superdislocations along {111} planes. These superdislocations consist of two unit dislocations of type \( b = \frac{1}{2} a_0 \langle 110 \rangle \) in which \( b_1 \) indicates the Burgers vector of the leading dislocation. Due to the disorder introduced by \( b_1 \), a so-called antiphase boundary is trailing \( b_1 \). This means that the superlattice behind the dislocation is displaced over a displacement vector \( R = \frac{1}{2} a_0 \langle 110 \rangle \) along the {111} plane. This could also happen without the existence of a dislocation. It is then called a thermally introduced antiphase boundary or grown-in domain wall. Although \( R \) is the same in both cases, the difference is a sharp discontinuity in the basic lattice when a dislocation is causing the APB whereas a thermal APB is rather diffuse. Furthermore the APB introduced by the dislocation lies in a {111} plane while for thermally activated APB's {100} planes are often preferred as those planes show a minimum in APB energy. The trailing dislocation \( b_2 \) restores the original superlattice. In equilibrium situations there is a balance between the tendency to keep the APB area as small as possible and the repulsive force between two unit dislocations of the same \( b \). The equilibrium distance between the dislocations enables one to calculate the APB energy (De Groot et al. [1]). However, the situation is more complicated as both unit dislocations may each separate into two partial dislocations of...
type $b_p = 1/6 \ a_0 \ <110>$ according to the equation:
$$\frac{1}{2} \ a_0 \ [110] = 1/6 \ a_0 \ [121] + 1/6 \ a_0 \ [211] \quad (1)$$
In general separation into partials constitutes a defect in stacking sequence, thus a stacking fault (SF). In a superlattice it also causes a disturbance in the ordering of the atoms, a so-called antiphase boundary (APB).

Sastry and Ramaswami [2] calculated the APB energy and the SF energy in ordered and disordered Cu$_3$Au from measurements of the distances between superpartials using the weak beam method (Cockayne et al., [3]). A remarkable result was found namely that the stacking fault energy in ordered Cu$_3$Au is smaller than the stacking fault energy in disordered Cu$_3$Au. They report the following values: $\gamma$ (ordered) = 13.0 $\pm$ 1.5, $\gamma$ (disordered) = 21.5 $\pm$ 3.5 and E (APB) = 39 $\pm$ 5 mJ/m$^2$. Already in 1962 Kear and Wilsdorf [4] reported on dislocation configurations in plastically deformed polycrystalline Cu$_3$Au alloys. After a few percent strain dislocations in disordered Cu$_3$Au are arranged in groups in well-defined slip planes, whereas in ordered alloys the distribution of dislocations is more or less random. Very long, straight dislocation segments observed in the ordered alloy are interpreted in terms of cross-slip of screw dislocations from their slip planes onto cube planes. Their result is important especially with respect to our work as they used polycrystalline samples with (111) [211] texture the same as we did. Cross-slip of screw dislocations onto cube planes parallel to the viewing direction suggest the occurrence of single dislocations whereas the remaining part in the original (111) slip plane is still observed as being a superdislocation.

According to the theory of Stoloff and Davies [5] deformation of ordered alloys is controlled by the motion of superdislocations when the order parameter $S$ is large and it is controlled by unpaired dislocations when $S$ is small. The size of the domains is less important than the value of the APB energy, which itself is dependent on the square of the long-range order parameter. Thom, Lasserre, Reynaud and Coulomb [6] reported results which underline this theory of Stoloff and Davies for Ni$_3$Mn. Koneva et al. [7] reported a big difference in the dislocation structure of Ni$_3$Mn specimens having different domain-sizes and degree of order. Still a significant number of single dislocations appear in a fine domain alloy with a high degree of order. A decrease in the degree of order goes along with an increase in the number of single dislocations. Their presence in the ordered alloy has a considerable influence on its work hardening factor. Single dislocations may be due to the development and growth of antiphase boundary steps on domain boundaries in the process of shear. Once the shear in a certain plane is greater than the domain size the slip plane becomes a mosaic of antiphase boundaries (Popov et al. [8]). Then the movement of a single dislocation does not create excess APB's and since the resistance to dislocation motion due to the overcoming of a forest is less for a single dislocation than for a superdislocation, the formation of an APB mosaic in the slip band further localizes the shear.

Czemichow and Marcinkowski [9] deformed single crystals of Cu$_3$Au in compression to a very high degree of plastic strain in stage II.

Electronmicroscopic observations showed a very high density of superlattice screw dislocations which had cross-slipped onto [100] planes. These cross-slipped superlattice dislocations were for the most part arranged as superdipoles or supermultipoles. On the other hand Sadananda and Marcinkowski [10] described a low strain situation in which dislocations of opposite sign glide in parallel [111]-planes. At high enough frictional force superdipolarizations on parallel slip planes are locked as super multipoles and this super multipole formation is believed to be the principal source of work hardening in our low strained samples.

**SPECIMEN PREPARATION**

An alloy close to the stoichiometric composition of Cu$_3$NiZn was prepared by induction melting of the appropriate amounts of 5N-pure Cu, 4N-pure Ni and 5N-pure Zn in a silica crucible. After a first heat treatment of 10 days at 1000°C in order to homogenize the sample the resulting ingot was rolled down and cut into strips of 120 by 4 by 0.035 mm in thickness. These strips were encapsulated under vacuum in a narrow tube of fused quartz and annealed at 850°C for 4 days. The average grain size of the material was about 0.3 mm. Almost all grains showed a (011) [211] rolling texture.

The composition was checked by means of atomic absorption spectroscopy. Deviation from nominal composition was less than 0.5 at.$\%$. The actual annealing treatment were then carried out ranging from 1000 h at 350°C for the ordered material to 10 min at 560°C for the disordered one. Dislocations were introduced by various elongations of the strips at a constant strain rate of $\dot{\varepsilon} = 3\times10^{-3}$ s$^{-1}$ on a Zwick tensile tester. Discs, 3 mm in diameter, were spark cut and thinned electrochemically by a jet method at room temperature in a 33 vol.$\%$ solution of orthophosphoric acid in water. Subsequently, electrochemical polishing was carried out at $-70$°C in a 33 vol.$\%$ solution of nitric acid in methanol.

The electronmicroscope was a Philips EM 300 operated at 100 kV with a goniometer stage and with both micrograph and video registration.

**RESULTS**

Tensile tests and transmission electromicroscopy were carried out on disordered, partly ordered and ordered Cu$_3$NiZn. In Fig. 1 a stress-strain curve is shown of drawn wire before and after a thermal
Fig. 1. Stress–strain curve of Cu$_2$NiZn. The dashed curve is drawn wire. The full curve the same but after and additional anneal of 2 h at 600°C.

anneal of two hours at 873 K. The annealed curve of this concentrated solid solution consists of a yield point followed by a flat zone characterized by inhomogeneous deformation. The work hardening rate

Table 1. Specific values of the series A, C, E and H

<table>
<thead>
<tr>
<th>Series</th>
<th>Anneal temp. (°C)</th>
<th>Anneal time (h)</th>
<th>Order parameter S</th>
<th>Domain size D (nm)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>560</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>350</td>
<td>10</td>
<td>1</td>
<td>16</td>
<td>3</td>
</tr>
<tr>
<td>E</td>
<td>350</td>
<td>1000</td>
<td>1</td>
<td>33</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>470</td>
<td>50</td>
<td>1</td>
<td>100</td>
<td>3</td>
</tr>
</tbody>
</table>

near 15% strain was measured as being $\theta = 1040$ MPa while the yield and fracture stress were 250 and 570 MPa respectively. Fracture occurred at a strain of 44%. Other samples were treated in such a way that both the degree of order, S, and the size of the domains D, were varied as indicated in Table 1. Figure 2 contains the corresponding stress–strain curves. Curve A resulted from a quench from above the ordering temperature and should thus be characteristic of the disordered state. The corresponding micrograph is given in Fig. 3. A pile-up of dislocations with a slight tendency to appear in pairs forms the most dominant feature. The distance of the pairs varies along the pile-up in agreement with previous observations of Koneva et al. [7]. Due to the high critical temperature of ordering (773 K) it is impossible to freeze-in a situation of complete disorder. The node near A is a 60-degree extended node giving a stacking fault energy of 33 mJ/m$^2$ as was reported earlier by Van der Wegen et al. [11].

In micrograph 4 one notices that already after 1 h

Fig. 2. Comparison of stress–strain curves of Cu$_2$NiZn as a function of the degree of ordering (see Table 1).

Fig. 3. Pile-up of dislocations in Cu$_2$NiZn annealed for 10 min. at 560°C and subsequently quenched. Tensile deformation was 5%. The node near A is a 60° node.
at 350°C superdislocations occur which are strong enough to overcome a dislocation barrier. But the highest initial flow stress occurs after 10 h at 350°C (see curve C), when the ordering domains are still rather small but the long-range order parameter has had time to increase considerably. In micrograph 5 an example is given which contains clearly both superdislocations and superdipoles.

After 100 h the ordering energy is high enough even to cause cross-slip onto \{100\} planes as became obvious from micrograph 6. Part of the superdislocation has apparently cross-slipped out of the sample via a \{100\} plane which is parallel to the viewing direction. A sample kept at 350°C for 100 h and deformed 20% in tension shows also very clearly the existence of superdislocations and superdipoles but no single dislocations. Due to their typical outlook one can recognize a few edge superdipoles near A in micrograph 7(a). Those dipoles are the result of moving screw superdislocations which contain jogs as was described recently for Cu₃Au by Sastry and Ramaswami [12]. A close-up of a more complicated superdipole is given in micrograph 7(b). It was taken with a Philips EM400 T microscope at an accelerating voltage of 120 kV and with a LaB₆ electron gun.

Series E which was ordered for 1000 h at 350°C contained domains of 33 nm in size and of complete ordering within the domains. The initial flow stress is here the lowest of all series. The electronmicrographs 8(a), (b) and (c) show as dominant feature superdipoles described in detail by Sadananda and Marcinkowski.
Near A in the micrographs two such superdipoles are lying close together. The striking feature is that the splitting of the superdipoles along the dislocations line is changing as if the individual domains which are depicted in 8(c) have their tetragonal axis of the Li$_2$O-structure oriented differently going from one domain to the other.

In order to determine the width and height of the superdipoles we imaged a few of them in stereo using a single crystal, first annealed at 350°C for 165 h, compressed 5% along the [123] direction and then again annealed at 350°C for 75 min. Subsequently a sample was spark cut along the (111) plane and prepared for observation in the electronmicroscope. The stereomicrographs 9(a) and 9(b) were taken of the (111) slip plane under a stereo angle of 5° towards either side of [111]. A similar example is given in the stereo micrographs 10(a) and 10(b), but now we are looking in a [223] direction under a stereo angle of ±10°. A third example of a polycrystalline sample with a grain in (110) orientation is given in stereomicrographs 11(a) and 11(b). They were taken with a JEOL 200 CX microscope at an accelerating voltage of 200 kV under a stereo angle of ±20°. A clear
Table 2. Values for $X$, $X_1$, and $Y$ belonging to the superdipoles shown in the stereomicrographs 9, 10, and 11.

<table>
<thead>
<tr>
<th>Micrograph</th>
<th>$X$ [nm]</th>
<th>$X_1$ [nm]</th>
<th>$Y$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>8.5</td>
<td>20.0</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>7.5</td>
<td>22.5</td>
<td>22</td>
</tr>
<tr>
<td>11</td>
<td>1.8</td>
<td>10.5</td>
<td>6</td>
</tr>
</tbody>
</table>

change in $Y$-value from 15 nm to 6 nm is noticeable along the dipole with corresponding changes in $X_1$ and $X$ as if [111] cross-slip had occurred; $Y$ being the distance between the slip planes, $X$ being the distance between the leading partial of one super with respect to the trailing dislocation of the other super (note that under stress they should move in opposite direction), and $X_1$ being the distance between the partials of one superdislocation. The three sets of values are listed in Table 2.

Finally series $H$, which was annealed during 50 h at 470°C and subsequently given a rapid quench to room temperature, stand out because of the absence of a region of inhomogeneous deformation. The corresponding micrograph 12 shows super and single dislocations. However, due to cross-slip onto the planes only part of those single dislocations may be caused by the low value of S introduced by quenching the sample from an annealing temperature just under the critical temperature of long-range order. The similarity with the micrographs made by Kear and Wilsdorf [4] on Cu$_2$Au suggest that especially in this series a large amount of cross-slip has occurred. Therefore a detailed study of the ratio between single and superdislocations turned out to be difficult but for this sample one can state that the majority consisted of superdislocations.

DISCUSSION

Adding elements in solid solution raises the critical resolved shear stress (c.r.s.s.) for slip above that of the pure f.c.c. metal. The c.r.s.s. increases linearly with solute content for small solute concentrations and then deviations occur (Haaseu [13]).

Relative atomic sizes of solvent and solute atoms, their elastic properties, stacking fault energy and local order if present are the important variables in determining the flow stress of solid solutions. The deformation in crystals with a low stacking fault energy like copper alloys is mainly controlled by the collective motion of unit dislocations dissociated into partials on the slip plane with the maximum resolved shear stress. Three groups of dislocations can be observed:

- parallel primary dislocations of the same sign (pile-up's)
- Taylor-type dislocation dipoles on two closely spaced primary slip planes (multipoles)
- complex dislocation arrays due to interaction between primary and locally activated secondaries.

In the case of Cu$_2$NiZn the disordered lattice changes below 773 K into an L1_1-structure and below 650 K from an L1_2- into an L1_0-structure (De Rooy et al. [14]). Due to the occurrence of those superlattices the parallel primary dislocations and the Taylor-type dislocation dipoles consist of superdislocations and superdipoles respectively. The splitting of the unit dislocation into partials in the case of low stacking fault energy is now of secondary importance. In a previous article [1] we published the results of a calculation of the distances between the four partials of a superdislocation in Cu$_2$NiZn. These distances in well-ordered material are $r_s = 4.7$ nm, $r_p = 8.6$ nm while the partials could not be resolved: $r_p < 1$ nm. This should be compared with a distance of $r_s = 1.5$ nm for the splitting of a screw dislocation in pure copper (Cockayne et al. [15]). Also the third group mentioned above is strongly affected by the occurrence of superlattice. Due to the high ordering energy on the planes it is frequently observed that the superdislocations cross-slip onto the planes where the APB energy is much lower. Those cross-slipped superdislocations form obstacles for the ones gliding on the planes. Parallel primary dislocations were found in sample A, micrograph 4, where a pile-up of superdislocations occurs due to the existence of short-range order. Even in short-range ordered alloys there may be a coupling between dislocations (Amelinckx, [16]). But due to the incomplete order successive dislocations show a disordering action which is cumulative. After a small number of dislocations has moved along the glide plane the local order has stabilized. Dislocations tend to follow each other along those planes because this offers the least resistance as order has already been destroyed. This phenomenon leads to coarse slip lines.

Taylor-type dislocation dipoles were the single most dominant phenomenon we encountered in our investigation. The original idea was to measure the distances between the four partials in a superdislocat-

Fig. 12. [100] cross-slip in Cu$_2$NiZn annealed for 50 h at 470°C, quenched to room temperature and deformed 3% in tension.
tion but very often the superdislocation turned out to be a superdipole created by Taylor mechanism and discussed extensively by Lakso et al. [17], Leamy et al. [18] and Sadananda et al. [10]. In the stereo micrographs 9, 10 and 11 examples of such Taylor-type dipoles are depicted. The distances between the dislocations as given in Table 2 may be compared with calculated values based on a zero force consideration similar to the one Sadananda and Marcinkowski [10] performed. The result of such a calculation is given in Fig. 13 for an APB-energy of 40 mJ/m² (Van der Wegen et al. [19]). The difference between the values of superfripoles 9 and 10 with respect to 11 may be due to the additional heat treatment in the former two cases. The APB can become more diffuse so that the distance between the superpartials increases. With respect to the third group we can state from Fig. 6 that even at such a low strain already [100] cross-slip is observed. However, neither the immobilization of the dislocations on {100} planes (Flinn [20]) nor the cross-slip process onto that plane (Kear and Wilsdorf [4]; Thornton et al. [21]) is completely understood. The reason for this is that the cross-slip process depends on the complex dislocation dissociation on {111} planes. This complexity is due to three possible planar faults on {111} namely a superlattice intrinsic stacking fault (SISF), an antiphase boundary (APB) and a complex stacking fault (CSF) consisting of both the APB and the SISF. Instead of only the dissociation reaction of equation (1) two possible dissociation reactions have been proposed for [110] superlattice dislocations on {111} planes:

\[
-\{110\} \rightarrow \frac{1}{2}\{12\bar{1}\} + \frac{1}{2}\{212\} + \frac{1}{2}\{211\}
\]

for Cu₃Au, Ni₃Mn, Ni₃Fe

\[
-\{110\} \rightarrow \frac{1}{2}\{12\bar{1}\} + \frac{1}{2}\{211\} + \frac{1}{2}\{112\}
\]

\[
+ \frac{1}{2}\{112\} + \frac{1}{2}\{121\} + \frac{1}{2}\{211\}
\]

for Zr₃Al, Ni₃Al, Ni₃Ga

Recently Yamaguchi et al. [22] have shown, based on a computer simulation study, that the SISF is always stable, independent of the ordering energy, but that both APB and CSF can become unstable as the ordering energy increases. Which of the two splitting models (2) or (3) is favoured will depend on the difference between the SISF and APB-type fault. However, they argued that in the cross-slip process from \{111\} onto \{100\} planes in both cases the \{112\} screw component is unlikely to have any strong effect on the cross-slip whereas the edge component may affect the orientation dependence of the flow stress (Call et al. [23]).

**CONCLUSION**

In order to describe the results we compare the stress-strain curves for copper, disordered Cu₂NiZn and ordered Cu₂NiZn. In state I the c.r.s.s. for copper is just the lattice frictional force, while the work hardening \(\theta_1\) is mainly determined by the strength of the multipoles. Disordered Cu₂NiZn is similar to copper except for the occurrence of serrated yielding caused by Cottrell-locking, Suzuki-pinning and S.R.O. Ordered Cu₂NiZn is different from disordered Cu₂NiZn in that the multipoles are now supermultipoles; moreover, especially at the onset of ordering the small size of the ordering domains may have an additional effect. Stage II is similar again for copper and disordered Cu₂NiZn with \(\theta_1\) determined by forest dislocations, jogs and multipoles. The ordered alloy has much larger \(\theta_1\) due to \{100\} cross-slip and stronger supermultipoles. Copper has a medium high stacking fault energy, therefore the partials in extended dislocations are not too far apart so that \{111\} cross-slip in stage III can occur, giving a high work hardening at a low transition point \(\tau_{III}\). Disordered Cu₂NiZn has a lower SFE due to alloying and thus \{111\} cross-slip is more difficult giving a higher \(\tau_{III}\). Ordered Cu₂NiZn is dominated by superpartials cross-slipping onto \{100\} planes resulting in a high work hardening rate.

At the moment this investigation is still going on with special emphasis on single crystal work and on the behaviour at higher temperatures.

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