The Effects of Annealing on the Mechanical Properties of Cu-Ni-Zn Alloys

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The effects of annealing on the mechanical properties of Cu-Ni-Zn alloy single crystals with the compositions $\text{Cu}_{(1-2x)}\text{Ni}_x\text{Zn}_x$ and $\text{Cu}_{(0.75-x)}\text{Ni}_x\text{Zn}_{0.25}$ (in at%) were studied. The annealing temperature was 573 K.

Results obtained are as follows.

(1) In the group 1 alloys (Cu-5Ni-5Zn, Cu-10Ni-10Zn and Cu-15Ni-15Zn) the annealing effects are not significant and CRSS (critical resolved shear stress) changes with the deformation temperature similarly to the quenched specimens.

(2) In the group 2 alloys (Cu-20Ni-20Zn and Cu-25Ni-25Zn) CRSS increases with the annealing time below 573 K and above it CRSS decreases steeply to the level of quenched specimens.

(3) In the group 3 alloys (Cu-5Ni-25Zn and Cu-15Ni-25Zn) CRSS increases by annealing below 573 K (Cu-15Ni-25Zn) and it has a peak at about 850 K.

(4) The transmission electron micrographs of annealed specimens of the group 2 alloys indicate that they deform by the movement of superlattice dislocations below 573 K. The separation of them has a tendency to increase with the deformation temperature and above 573 K dislocations move as unit ones, because the separation of superlattice ones becomes too large to move as a pair.

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I. Introduction

It was considered that Ll_2 type superlattice would be formed in the Cu-Ni-Zn alloy⁽¹⁾⁽²⁾. Due to the similarity in the atomic scattering factor of copper, nickel and zinc, X-ray diffraction method is not effective to detect the formation of the long range order in Cu-Ni-Zn alloy. However, the development of the neutron diffraction method made it possible to confirm the existence of long range order at the composition close to the stoichiometric Cu_2NiZn ⁽³⁾⁽⁴⁾. The transmission electron microscopy also verified the existence of superlattice dislocations in the annealed and deformed Cu-Ni-Zn alloy of the composition close to Cu_2NiZn ⁽⁵⁾.

In the quenched state Cu-Ni-Zn alloy can be treated as the ternary solid solution, though once annealed at the temperature below T_c (critical temperature for long range order) mechanical properties will change drastically by the formation of long range order. So far,

the polycrystalline Cu-Ni-Zn alloy of the composition close to Cu_2NiZn exhibited anomalous increase in the yield stress by annealing below T_c ⁽⁵⁾⁽⁶⁾. On single crystals of Cu-Ni-Zn alloy CRSS (critical resolved shear stress) was examined on specimens initially quenched from the disordered state. They obtained the anomalous increase in CRSS at 523~573 K⁽⁷⁾. Though the effects of the formation of long range order on the mechanical properties for the wide temperature range are still insufficiently known in Cu-Ni-Zn alloy.

In the present paper, single crystals of various compositions of Cu-Ni-Zn alloys were prepared to supply to the tensile deformation, because the characteristics in the deformation appear more sensitive in single crystals than in polycrystallines. The temperature dependence of mechanical properties especially CRSS and that of the dislocation structures were studied in relation to the effects of the formation of long range order.

II. Experimental Procedure

Seven Cu-Ni-Zn alloys with the compositions of $\text{Cu}_{(1-2x)}\text{Ni}_x\text{Zn}_x$ and $\text{Cu}_{(0.75-x)}\text{Ni}_x\text{Zn}_{0.25}$

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Table 1 The composition of Cu–Ni–Zn alloys (at %).

	Cu	Ni	Zn
(1) NZ-0505	90.2	5.1	4.7 (balance)
(2) NZ-1010	79.6	9.8	10.6 (balance)
(3) NZ-1515	69.8	15.0	15.2 (balance)
(4) NZ-2020	59.5	19.8	20.7 (balance)
(5) NZ-2525	48.9	24.4	26.7 (balance)
(6) NZ-0525	70.1	5.1	24.8 (balance)
(7) NZ-1525	59.7	15.1	25.2 (balance)

Zn_{0.25} were prepared as shown in Table 1. After homogenized at 1173 K for 86.4 ks, ingots were cold rolled to a thickness of 1.5 mm. Single crystals of $1.5 \times 4 \times 280$ mm³ were grown by the Bridgmann method under the argon gas atmosphere. Among them only those oriented for the single slip were supplied to the mechanical test. To avoid the fluctuation in the mechanical properties owing to the compositional variation along the growth axis, only the central part of single crystals (about 150 mm length) was cut to the every 30 mm length to supply to the tensile test. They were shaped electrolytically to the tensile specimens and heated in silica tubes filled with the argon gas at 1173 K for 86.4 ks.

As T_c in Cu₂NiZn was reported to be 700~800 K⁽¹⁾⁽²⁾, specimens were quenched from 1073 K after held for 1.8 ks to obtain homogeneous solid solutions.

Previously it was found that the maximum in the yield stress in the polycrystalline Cu₂NiZn appeared by annealing at 623 K⁽⁵⁾ and single crystals of NZ-2020 and NZ-2525 initially quenched from 1073 K had the maximum at 523~573 K⁽⁷⁾. Therefore, the annealing treatment in the present experiment was performed at 573 K at most up to 360 ks to obtain the most predominant change in the mechanical properties from those in the quenched state.

Specimens were deformed in tension with 20 mm gauge length and the cross section $(1.0 \sim 1.2) \times (3.5 \sim 3.7)$ mm² at the initial strain rate 4.2×10^{-4} s⁻¹ using an Instron type testing machine, between 77 K and 1073 K. Above the room temperature specimens were deformed in the electrical furnace with the argon gas atmosphere.

To observe the deformed structure some of the specimens were deformed 10% in the shear strain and quenched as quickly as possible after unloading, to minimize the recovering of the deformed structure. They were chemically thinned in conc. HNO₃, and finally thinned electrolytically in HNO₃/CH₃OH=1/2 or H₃PO₄/C₂H₅OH=9/1 solution. Thin foils were observed in a JEM-200 electron microscope operating at 200 kV.

III. Results

1. The temperature dependence of CRSS

The temperature dependence of CRSS in Cu–Ni–Zn alloy single crystals initially quenched from 1073 K was shown elsewhere⁽⁷⁾. In this section, in addition to them, CRSS for specimens annealed at 573 K up to 360 ks is represented. CRSS was at first measured on six virgin crystals at the room temperature, however, CRSS obtained scattered $\pm 5\%$ from the average of that. Then, the repeated tests were made over the wide temperature range to obtain the precise temperature dependence of CRSS and to ensure the correspondence with CRSS due to the individual tests. Of course, the repeated tests were made in the strain range where the work hardening rate was small, that is, in the stage 1. CRSS from the individual and repeated tests well agreed within the experimental errors. Therefore, in figures typical value of CRSS from the repeated tests is represented in relation to the testing temperature.

Seven Cu–Ni–Zn alloys are divided into three groups. The group 1 contains NZ-0505, NZ-1010 and NZ-1515, which have little change in CRSS by annealing at 573 K. The group 2 contains NZ-2020 and NZ-2525 which change CRSS resulting from the formation of long range order. The group 3 contains NZ-0525 and NZ-1525, one of them changes CRSS by annealing, though it does not concern to the formation of long range order. Figure 1 indicates the temperature dependence of CRSS for the group 1. There are no significant changes in CRSS between the quenched and annealed states. Therefore, it is considered

Fig. 1 The temperature dependence of CRSS for NZ-0505, NZ-1010 and NZ-1515.

that the group 1 alloy behaves as the ternary solid solution in both quenched and annealed states, from the viewpoint of the mechanical properties.

In Fig. 2 the temperature dependence of CRSS for the group 2 is represented. CRSS in both NZ-2020 and NZ-2525 changes similarly with the temperature. In the low temperature range below 400 K, CRSS increases and the temperature dependence of it decreases with the annealing time. The intermediate temperature range situates between 400~900 K. In the quenched specimens a peak in CRSS appears at about 573 K, which is explained in relating to the formation of short range order during the heating before the deformation initiates⁽⁷⁾.

In the intermediate temperature range of annealed specimens there exists the region where CRSS little depends on the temperature as high as 573 K and above 573 K it decreases steeply to the level of quenched specimens. In detail, a small peak is observed at about 523 K for NZ-2020 and at about 573 K for NZ-2525 in specimens annealed for 360 ks. For the shorter annealing time the peak in CRSS tends to shift to the lower temperature.

There may be a question that if specimens are annealed at the higher temperature below T_c , the peak in CRSS will shift to the higher temperature. To make clear the question

(a)

(b)

Fig. 2 The temperature dependence of CRSS for NZ-2020 and NZ-2525. (a) NZ-2020, (b) NZ-2525.

specimens annealed at 673 K for 360 ks were tested. The results are shown in Fig. 2(b) as a dotted line. One is able to know the similar dependence of CRSS to the deformation

temperature on the specimens annealed at 573 and 673 K. Especially the point where CRSS begins to decrease coincides for both specimens. Therefore, the annealing temperature adopted is considered reasonable, that is, the growth of long range order is most predominant at 573 K.

The temperature dependence of CRSS for the group 3 is illustrated in Fig. 3. There can be observed the strong reverse temperature dependence in the intermediate temperature range, which would result from the solute dragging motion of dislocations as reported on Cu-Al⁽⁸⁾, Cu-Zn⁽⁹⁾ and Cu-Si⁽¹⁰⁾ solid solutions. In NZ-0525 there is little difference in CRSS between the quenched and annealed states. However, in NZ-1525 a small peak in CRSS appears at 573 K in the quenched specimens, and CRSS below 573 K is increased considerably by annealing.

3. The dislocation structure

The dislocation structure of Cu-Ni-Zn alloys initially quenched and deformed at 300 K are shown in Photo. 1. As the solute concentration increases, specimens of the group 1 and group 2 tend to deform by Lüders band propagation in the stage 1. All of the specimens form piled up dislocation arrays, however, as the solute concentration increases slip bands become more and more localized and concentrated. The number of dislocations emitted from a source increases and the distance between the dislocation arrays decreases as the

Fig. 3 The temperature dependence of CRSS for NZ-0525 and NZ-1525.

solute concentration increases. While, in the group 3 alloy concentrated slip bands and distinct dislocation piled up arrays are observed even in the low solute concentrated alloy, resulting from the lower stacking fault energy.

Next, as the representative of the group 2 alloy in the annealed state, the effects of deformation temperature on the dislocation structure were examined on NZ-2525 annealed for 360 ks. For NZ-2525 annealed for shorter time and NZ-2020 similar results are expected, though the temperature where the dislocation structure changes, shifts to the lower temperature.

Photo. 1 The dislocation structure of quenched specimens deformed at 300 K. (a) NZ-0505, (b) NZ-1515, (c) NZ-2525, (d) NZ-0525.

Photo. 2 The dislocation structure of NZ-2525 deformed at various temperatures. (a)~(d) annealed at 573 K for 360 ks. (e) and (f) quenched from 1073 K. (a) at 300 K, (b) at 433 K, (c) at 503 K, (d) at 573 K, (e) at 573 K, (f) at 773 K.

Photograph 2(a) was taken from a foil cut parallel to the primary slip plane and Photo. 2(b)~(f) were taken from the specimens with the same axis though the primary slip plane and slip direction inclined from the foil surface.

Photograph 2(a) is the dislocation structure at 300 K. Long straight screw dislocations and curved edge ones which compose the superlattice dislocations, indicate the features of deformed structure in the L_2 type ordered

structure⁽¹¹⁾⁽¹²⁾. The electron per atom ratio, e/a , of the group 2 alloys is unit, therefore, the stacking fault energy of them will be almost same as that of copper. In fact, the expanding of dislocation nodes are not detected in the electron microscope. The separation of Shockley partials in a superlattice dislocation cannot be resolved, so only dislocation pairs are observed. The similar dislocation structure is also observed in the fully ordered Cu_3Au single crystals⁽¹³⁾. The separation of superlattice dislocation r is reported 13.0 nm in Cu_3Au . In case of NZ-2525 15~30 nm for the screw, and 20~40 nm for edge dislocations are obtained as r .

From Marcinkowski *et al.*⁽¹³⁾, if neglecting the separation of Shockley partials, r is expressed as

$$r = 3Gb^2/2\pi E_{\text{or}} \text{ for the screw dislocation}$$

$$r = 3Gb^2/2\pi(1-\nu)E_{\text{or}} \text{ for the edge dislocation}$$

where G is the shear modulus, b is the strength of dislocation, E_{or} is the antiphase boundary energy. Therefore, the difference in r between the edge and screw dislocations is qualitatively explained from the theory. In the equation E_{or} is expressed as $E_{\text{or}} = E_{\text{or}}^{s=1} \cdot S^2$ ($E_{\text{or}}^{s=1}$ is antiphase boundary energy for the fully ordered state). Assuming $E_{\text{or}}^{s=1}$ is as same order as Cu_3Au , 75 mJ/m², substituting $r=20$ nm for the screw dislocation and 30 nm for the edge one, about 0.6 is obtained as S . The neutron diffraction experiments by Hirabayashi *et al.*⁽³⁾ estimated $S=0.88$ and that by Vrijen *et al.*⁽⁴⁾ estimated $S=0.43$ for zinc atom though copper and nickel suborder was almost unit. Therefore, the obtained value of S seems acceptable.

Photograph 2(b)~(d) represent the dislocation structures deformed at 433 K, 503 K and 573 K, respectively. In Photo. 2(b) and (c) superlattice dislocations are still predominant, however, r apparently increases with the temperature, and the pure edge and pure screw components diminish. Though the slip plane and slip direction incline from the foil surface, roughly estimated r for screw dislocations are 50 nm at 433 K and 60 nm at 503 K. At last at 573 K as shown in Photo. 2(d) superlattice dislocations and piled up dislocation arrays of unit dislocations coexist. Therefore, 573 K

corresponds to the temperature, below which superlattice dislocations take precedence, and above which superlattice dislocations cannot move as pairs and move as unit dislocations.

The dislocation structures at 573 K are somewhat different between the quenched (Photo. 2(e)) and annealed (Photo. 2(d)) states. In Photo. 2(d) superlattice dislocations are still isolated and wavy, in contrast to Photo. 2(e) which shows the group of paired straight dislocations multiplied on the same slip plane. Then, the difference in the dislocation structure is considered to result from the difference in the degree of order.

Photograph 2(f) is the typical dislocation structure at 773 K. Piled up dislocation arrays are observed again. And above the transition point from the intermediate to the high temperature range the uniform dislocation arrangement is observed.

In NZ-1525, one of the group 3 alloys, CRSS increases below 573 K by annealing. To study the reason of this phenomena, thin foils were observed in the electron microscope. Photograph 3(a) and (b) represent the dislocation structures in specimens deformed at 300 K in quenched and annealed (360 ks) states. Photograph 3(a) exhibits the typical piled up arrays of dislocations.

Photograph 3(b) also shows the piled up arrays of dislocations, though in detail, groups of paired dislocations are observed along the slip trace. They would be multiplied on the same slip plane and the contrast of dislocations exhibits that they are the same sign. Such pairs are observed near the head of a planar array and degenerate as the number of dislocations that have passed along a glide plane increases. Cohen *et al.*⁽¹⁴⁾ proposed theoretically that these configuration of dislocations should be observed in alloys containing the short range order. It is obvious that the dislocation structure and arrangement greatly differ from those of the group 2 alloys which deform as the long range ordered alloys. Therefore, the origin of the increase in CRSS in the annealed NZ-1525 is considered to be due to the existence of short range order, when the degree of long range order is small.

Photo. 3 The dislocation structure of NZ-1525 deformed at 300 K. (a) Quenched from 1073 K. (b) Annealed at 573 K for 360 ks.

IV. Discussion

Vrijen *et al.*⁽⁴⁾ examined the degree of order by the neutron diffraction method and obtained the image of antiphase boundary by the transmission electron microscopy. They found that zinc atom ordered below 753 K, but the ordering of copper and nickel atoms started at the lower temperature and the ordering reaction was much slower. The transmission electron microscopy indicated that at 623 K the contrast between the domain boundary became weaker and above 703 K the image of the antiphase boundary became invisible. The results imply that the degree of order begins to decrease at 623 K. The neutron diffraction experiment due to Hirabayashi *et al.*⁽³⁾ also described that ordering reaction was very slow at 573 K and hard to get the

perfect order. These two experiments suggest that by annealing at 573 K one is able to get maximum order but it is hard to have the perfect order. And above 573 K as suggested by Vrijen *et al.*⁽⁴⁾ the degree of order for copper and nickel atoms will decrease and the microstructure developed at 573 K will become unstable, resulting in the decreasing of CRSS above 573 K.

Davies *et al.*⁽¹⁵⁾⁽¹⁶⁾ proposed that as decreasing in the degree of order the separation of superlattice dislocation increased and when it became larger than 100 nm, unit dislocations forming the superlattice dislocation were forced to move independently. In case of Fe₃Al and FeCo-2V⁽¹⁵⁾⁽¹⁶⁾ a peak in the flow stress appeared at the intermediate degree of order whether tested at the room temperature or at the elevated temperature. However, the peak in the elevated temperature test shifted to the higher degree of order, that is to the lower temperature comparing to the case of the room temperature test. They considered that the peak corresponded to the point above which dislocations no longer moved as superlattice dislocations and in the elevated temperature test the thermal activation might aid the dissociation of superlattice dislocations. Recent study on Cu₃Au Morris *et al.*⁽¹⁷⁾ reported that the separation of superlattice dislocation r depended on the shear modulus and the degree of order. As the shear modulus decreases with the temperature, it will act to decrease r with the temperature. In this experiment degree of order will not change below 573 K during testing, therefore, the situation is different from the case of Cu₃Au.

The degree of order in NZ-2525 is intermediate even by annealing for 360 ks, then r is rather large at the room temperature. Probably due to the thermal activation r increases with the temperature and it reaches to the critical value ~ 100 nm at 523 $\sim$ 573 K. Above that temperature the degree of order also begins to decrease, so dislocations move as unit ones. Though as the unit dislocations encounter the resistance to nucleate the antiphase boundary CRSS at 573 $\sim$ 800 K for NZ-2525 and at 573 $\sim$ 650 K for NZ-2020 is somewhat higher than that in the quenched specimens.

REFERENCES

- (1) W. Shüle and H. Kehr: *Z. Metallk.*, **51** (1960), 711.
 - (2) W. Köster: *Z. Metallk.*, **51** (1960), 716.
 - (3) M. Hirabayashi, S. Hoshino and K. Sato: *J. Phys. Soc. Japan*, **20** (1965), 381.
 - (4) J. Vrijen, P. Bronsveld, J. Veen and S. Radelaar: *Z. Metallk.*, **67** (1976), 473.
 - (5) S. Yoshioka, Y. Nakayama and T. Ito: *J. Japan Inst. Metals (in Japanese)*, **33** (1969), 557.
 - (6) W. Köster and W. Konzelmann: *Z. Metallk.*, **54** (1963), 132.
 - (7) S. Yoshioka, Y. Nakayama, T. Ito and K. Fukunaga: *J. Japan Inst. Metals (in Japanese)*, **37** (1973), 1243.
 - (8) H. Suzuki and E. Kuramoto: *Proc. Int. Conf. on Strength of Metals and Alloys*, Supplement to *Trans. JIM*, Vol. 9 (1968), p. 697.
 - (9) M. Asano, O. Izumi and E. Tanaka: *Trans. JIM*, **9** (1968), 349.
 - (10) S. Yoshioka, Y. Nakayama, T. Ito and H. Mabuchi: *J. Japan Inst. Metals (in Japanese)*, **36** (1972), 393.
 - (11) B. H. Kear: *Acta Met.*, **12** (1964), 555.
 - (12) B. H. Kear: *Acta Met.*, **14** (1966), 659.
 - (13) M. J. Marcinkowski, N. Brown and R. M. Fisher: *Acta Met.*, **9** (1961), 129.
 - (14) J. B. Cohen and M. E. Fine: *J. Physique Rad.*, **23** (1962), 749.
 - (15) N. S. Stoloff and R. G. Davies: *Acta Met.*, **12** (1964), 473.
 - (16) N. S. Stoloff and R. G. Davies: *Progress in Mat. Scie.*, **13** (1966), No. 1.
 - (17) D. G. Morris and R. E. Smallman: *Acta Met.*, **23** (1975), 73.
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