Morphological Change and Recovery during Tempering of $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ Martensite

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The morphological change during tempering the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ martensite (Ll_0 structure) was studied by means of optical and electron microscopy. The morphology of the Ll_0 phase changed from the martensitic structure to the massive one during tempering at 823 K. At the early stage of tempering, new interface boundaries appeared and polygonal grains were formed in a martensite plate due to the polygonization. During further tempering, many subgrains were formed. The volume fraction of the twin decreased gradually in a polygonal grain. At the late stage of tempering, large massive grains appeared and a few thin plates of $(111)_{\text{Ll}_0}$ twins existed as growth faults inside them. The surface relief of the Ll_0 martensite disappeared gradually with the growth process of the massive grains. These phenomena were discussed briefly in relation to the recovery and the recrystallization.

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I. Introduction

A nickel base alloy such as $\text{Ni-Al}^{(1)(2)}$, $\text{Ni-Zn}^{(3)}$ and $\text{Ni-Zn-Cu}^{(4)-(6)}$ undergoes a martensitic transformation from the CsCl(B2) -type cubic phase to the $\text{AuCuI(Ll}_0\text{)}$ -type tetragonal structure. In the $\text{Ni}_{50}\text{Zn}_{50}$ alloy, the starting temperature of the B2 to Ll_0 transformation upon cooling, T_t , is about 1033 K⁽³⁾. The B2 to Ll_0 transformation in this alloy has been reported to be martensitic in the case of quenching and massive in the case of furnace cooling⁽³⁾, because the migration of grain boundary is very fast at a high temperature near 1000 K. In the ternary $\text{Ni}_{50-x}\text{Zn}_{50}\text{Cu}_x$ alloy, the transformation temperature T_t has been reported to decrease with increase in the Cu content, x ⁽⁴⁾. In the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy cooled in a furnace (T_t is about 883 K), the surface relief has been recently observed, suggesting that the migration of grain boundary occurs slowly, compared with that of the binary $\text{Ni}_{50}\text{Zn}_{50}$ alloy⁽⁶⁾.

In nonferrous martensitic alloys such as Cu-Al , Cu-Al-Mn and $\text{Ni-Co-Al}^{(7)-(10)}$, the

tempering process of the martensite phase has been studied by several investigators, and the formation of a complex superstructure or the precipitation of a stable phase has been observed. On the other hand, in the $\text{Ni}_{71}\text{Cu}_4\text{Sn}_{25}$ alloy, the 2H martensite obtained by quenching has been found to change into the massive DO_{19} phase during tempering at 873 K, revealing that the migration of interfaces and the change in crystal structure occur simultaneously during tempering⁽¹¹⁾.

In the ternary $\text{Ni}_{50-x}\text{Zn}_{50}\text{Cu}_x$ alloy, any precipitate has not been observed in the process of aging or furnace cooling⁽⁴⁾. When the Ni-Zn-Cu martensite is tempered at a high temperature below T_t for a long time, the morphology of the Ll_0 phase is expected to change gradually by the migration of interface. In the present work, the effect of tempering on the morphology of Ll_0 phase in the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy was investigated by means of optical and electron microscopy.

II. Experimental

The $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy was prepared by melting the metals (99.9%Ni, 99.999%Cu and Zn) in an evacuated quartz tube and then quenched into water at 273 K after annealing at 1073 K for 245 ks. A specimen for optical microscopy was tempered at 823 K for a

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definite time and then quenched into water. Another alloy specimen was cut and polished mechanically into a disc about 0.2 mm in thickness and 3 mm in diameter. This specimen was quenched from 1073 K to 273 K and then tempered at 823 K for a definite time, followed by quenching into water. Finally, this specimen was electropolished by a jet polishing method using a 20% H_2SO_4 solution in methanol. The electron microscopic observation was carried out at room temperature by a JEM-100CX electron microscope operated at 100 kV.

III. Results and Discussion

Optical micrographs of the quenched and tempered $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloys are shown in Fig. 1(a)-(d). In the quenched specimen, Fig. 1(a), a surface relief revealing the existence of many variants of Ll_0 martensite is observed. In the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 10.8 ks, a mixture of the martensite and the massive structure is observed, as shown in Fig.

1(b) and (c). The size of the martensite plate is dependent on the position of specimen. From an area with a large size of martensite plate, an optical micrograph such as Fig. 1(b) is observed. The plate-like crystals labeled by A and B in Fig. 1(b) are the variants of martensite which have straight boundaries, whereas the grains C and D are the massive ones. The surface relief of martensite plates disappears at a place where the massive grain (e.g. grain C) appears. In a different area with a small size of martensite plate, Fig. 1(c), a different morphology of massive grains is observed. In this micrograph, the variants of the martensite plates, which line up along the horizontal direction, are cut into small pieces by the crossing of massive grains, which grow along the vertical direction. Also in this micrograph, the surface relief disappears at a place where the massive grains grow. In the specimen tempered at 823 K for 108 ks, only the massive grains are observed, as shown in Fig. 1(d). The size of these massive grains seems to be

Fig. 1 Optical micrographs of a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy. (a) Ll_0 martensite in a specimen quenched from 1073 K. (b) and (c) Coexistence of the martensitic and massive structures in a specimen tempered at 823 K for 10.8 ks after quenching from 1073 K. (d) Massive grains in a specimen tempered at 823 K for 108 ks after quenching from 1073 K.

larger than that of the martensite plate. Then, it is suggested that the small massive grains formed in the martensite plates in Fig. 1(b) and (c) grow into large grains during tempering, as observed in Fig. 1(d), and that the morphology of the $L1_0$ phase changes gradually from the martensitic structure to the massive one by the migration of interfaces. This process was also studied by means of electron microscopy, and the results are described in the following.

Electron micrographs of the $L1_0$ martensite tempered at 823 K for 3.6 ks are shown in Fig. 2(a) and (b). In this tempered specimen, an arrangement of dislocations and internal $(111)_{L1_0}$ twins are observed. In Fig. 2(a), dislocations are located separately crossing the internal $(111)_{L1_0}$ twins: These dislocations are expected to make a new interface between polygonal grains, as shown later in Fig. 4 in the process of further tempering. In Fig. 2(b), dislocations gather in a place and are making a network with a shape close to hexagon: This

is considered to be the place where the network of dislocations as shown in Fig. 5 is just forming. These dislocations revealed in Fig. 2 are not observed in the as-quenched specimen, and the number of such dislocations increases during tempering. Then, they are considered to be formed in the process of tempering.

An electron diffraction pattern and micrographs of the $Ni_{40}Zn_{50}Cu_{10}$ alloy tempered at 823 K for 18 ks are shown in Figs. 3 and 4. The diffraction pattern, Fig. 3, indicates that the $L1_0$ martensite has the internal $(111)_{L1_0}$ twins still in the tempered specimen. A bright field image, Fig. 4(a), shows the internal $(111)_{L1_0}$ twins and a new interface boundary together with many boundary dislocations. This boundary crosses the internal twins of the martensite plate. In a dark field image, Fig. 4(b), taken by the $(20\bar{2})_{L1_0}$ spot of Fig. 3, the contrast of the twin variant in the lower area B is brighter than that in the upper area A, suggesting that the upper grain A is slightly bent from the lower one B by the formation of interface boundary. When the specimen was tilted in the electron microscope, a bright field image such as Fig. 4(c) was observed. The contrast of internal twins is seen clearly in the upper area but not in the lower area in this micrograph. Many interface dislocations are arranged at the grain boundary. These results indicate that new polygonal grains are formed by the bending of crystal, i.e. by the

Fig. 2 Electron micrographs taken along the direction close to $[0\bar{1}1]_{L1_0}$ in a $Ni_{40}Zn_{50}Cu_{10}$ alloy tempered at 823 K for 3.6 ks after quenching from 1073 K. (a) and (b) show the arrangement of dislocations in the $L1_0$ martensite having internal $(111)_{L1_0}$ twins.

Fig. 3 Electron diffraction pattern taken along $[1\bar{2}1]_{L1_0}$ direction of a $Ni_{40}Zn_{50}Cu_{10}$ alloy tempered at 823 K for 18 ks after quenching from 1073 K. Suffix T shows twin spot.

Fig. 4 Electron micrographs of a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 18 ks. (a) Bright field image taken along $[\bar{1}21]_{L10}$ direction. A diffraction pattern of this area is shown in Fig. 3. (b) Dark field image taken by $(20\bar{2})_{L10}$ diffraction of Fig. 3. (c) Bright field image tilted from $[\bar{1}21]_{L10}$ direction.

polygonization⁽¹²⁾. The averaged direction of the traces of $(111)_{L10}$ planes in the upper grain A is parallel to that in the lower grain B, suggesting that the axis of rotation of crystals during the polygonization is along $[111]_{L10}$. In the dark field image, Fig. 4(b), the width of the twin variants (dark bands) in the lower

Fig. 5 Electron micrographs of a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 18 ks after quenching from 1073 K showing the interface boundary with the network of dislocations.

grain B becomes slightly thinner than that in the upper grain A, and the interface of the twin boundary is slightly curved. This result suggests that the interface of $(111)_{L10}$ twins migrated and the volume fraction of the twins decreased during tempering in the lower grain B; this may be favorable for the bending of crystals.

Another example of the grain boundary between two polygonal grains observed in the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 18 ks is shown in Fig. 5. A network of dislocations is observed on the grain boundary in this specimen. Traces of the internal $(111)_{L10}$ twinning planes in the grain of the upper area are nearly parallel to that in the lower area. This result also suggests that the direction of the $(111)_{L10}$ trace does not change at the early stage of tempering even by the bending of crystal due to the polygonization.

When the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ martensite was tempered furthermore, polygonal grains containing many small subgrains were observed. Electron micrographs and a diffraction pattern of the alloy tempered at 823 K for 50.4 ks are shown in Figs. 6 and 7. Many grain boundaries and internal $(111)_{L10}$ twins are observed in Fig. 6(a). When the specimen in Fig. 6(a) was tilted in the electron microscope, an electron micrograph shown in Fig. 6(b) was obtained, where four polygonal grains (A, B, C and D) and boundary dislocations were observed. Although the trace of $(111)_{L10}$ plane is slightly

Fig. 6 Electron micrographs of a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 50.4 ks after quenching from 1073 K. (a) Bright field image taken along $[0\bar{1}1]_{L10}$ direction. The diffraction pattern of this area is shown in Fig. 7. (b) Bright field image tilted from Fig. 6(a) showing the grain boundaries among four polygonal grains, A–D.

curved, the averaged direction of the $(111)_{L10}$ trace is not rotated even by the formation of polygonal grains. In this stage of tempering, some of the interface dislocations are located along the direction parallel to the $(111)_{L10}$ trace, indicating that angles among the grain boundaries became larger than those in the early stage of tempering. Many subgrains with the diameter of about 100–250 nm are observed in the polygonal grain. The role of these subgrains in the growth process of the massive grain is unknown at present. The size of polygonal grains in this specimen is about 1000–3000 nm.

In an electron diffraction pattern, Fig. 7, which was taken the specimen in Fig. 6(a), the extra spots indicated by arrows are observed; these cannot be explained by diffraction spots in this zone axis and may arise from another

Fig. 7 Electron diffraction pattern taken along $[0\bar{1}1]_{L10}$ direction of a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 50.4 ks. Suffix T shows twin spot. Arrows represent extra spots. For details of indexing, see ref. (2).

subgrain with a different orientation. This diffraction pattern is quite different from that of the $L1_0$ martensite in a quenched specimen⁽⁵⁾.

The stages of tempering observed in the electron micrographs, Figs. 4–6, may correspond to those of Fig. 1(b) and (c) observed by optical microscopy, where the boundaries of the massive grains grow crossing the martensite plate. Therefore, the shape change accompanying the growth of polygonal grains, i.e. the recovery, is considered to cause the disappearance of surface relief during tempering.

The size of the polygonal grains formed inside the martensite plate in Fig. 6 is smaller than that of the martensite plate. Then, at the next stage of tempering, these polygonal grains are expected to grow into the larger massive grains. An electron micrograph of the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 432 ks is shown in Fig. 8, where the grain boundary and a few plates of the $(111)_{L10}$ twins are observed. In this specimen, the size of the massive grains is larger than that of Fig. 6, and the volume fraction of the twin is very small. The thin plates of $(111)_{L10}$ twins revealed in Fig. 8 are considered to exist as growth faults in the massive grain. In the electron micrograph and the diffraction pattern from this specimen, subgrains and extra spots

Fig. 8 Electron micrograph of the massive grain in a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy tempered at 823 K for 432 ks after quenching from 1073 K.

as presented in Figs. 6 and 7 were not observed, suggesting that they almost disappeared during the growth process of the massive grain. Moreover in the late stage of tempering, the $[111]_{\text{Ll}_0}$ direction of a massive grain was slightly tilted from that of the neighbouring grains; the grains might be slightly rotated during the growth process of the massive grains.

These phenomena observed in the tempering process of the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ martensite are similar to those of the ferrous martensite such as Fe-C and Fe-Cr-Mo⁽¹³⁾⁻⁽¹⁶⁾, where subgrains were formed during the recovery process of the defects structure and also similar to the recovery and the recrystallization process of deformed metals⁽¹²⁾⁽¹⁷⁾.

In a bulk specimen tempered at 823 K for 108 ks, only the massive grains are observed, whereas in a thin foil specimen tempered at 823 K for 432 ks, polygonal grains as shown in Fig. 6 before the stage of recrystallization are sometimes observed depending on a position of specimen. Moreover, the size of massive grain in a bulk specimen, Fig. 1(d), is larger than that in a thin foil. These results suggest that the growth rate of massive grains in a bulk specimen is larger than that in a thin foil, which may be affected by the difference in the thickness between specimens used in these two kinds of observation. Thereby, thin foil specimens are considered to be easier for the relaxation of the nonchemical free energy accompanying the martensitic transformation,

and they do not always need the recrystallization during tempering in contrast with the case of bulk specimen.

These phenomena observed in the process of tempering may occur by the decrease of the nonchemical free energy accompanying the morphological change from the martensitic structure to the massive one. Because the martensite plates have many interfaces and faults, the formation of massive grains may be favorable in order to minimize the total free energy including the interfacial and elastic free energy. This may be the origin of the morphological change during tempering of the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ martensite.

Finally, if the tempered $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ martensite is heated up to the high temperature B2 phase, the massive (or polygonal) Ll_0 grains are expected to change into the massive (or polygonal) grains having the B2 structure by the reverse Ll_0 to B2 transformation. Moreover, during further heating in the B2 phase, they are expected to return immediately to the original large grains of the B2 phase by the recrystallization. An in-situ observation of these phenomena in an electron microscope seems to be very difficult because of the evaporation of Zn atoms at a high temperature. Generally, in metals and alloys with high transformation temperature, the martensitic transformation is considered to occur during quenching and the massive one during slow cooling⁽¹⁸⁾⁽¹⁹⁾. When the martensite phase obtained by quenching is heated very slowly up to the high temperature phase without the precipitation of other phases, similar phenomena to those described above are expected to occur, i.e. the elastic energy of the martensite may be relieved by the recovery and the recrystallization in the temperature range below the transformation temperature. These throw an interesting problem on the morphological study of the phase transformation.

IV. Summary

From the present results, it was made clear that the morphology of the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ martensite changes gradually from the martensitic structure to the massive one

during tempering. This process of tempering is summarized in the following.

At the early stage of tempering, new interface boundaries are induced in the martensite plate by the polygonization, accompanying the release of the strain energy of the martensite plates, and the polygonal grains are formed. During further tempering, angles among the grain boundaries become larger, and many subgrains are formed inside the polygonal grain. The volume fraction of the internal twin decreases gradually in the grain during tempering. At the late stage of tempering, the volume fraction of the twin becomes very small, and the polygonal grain grows into the large massive one, but it contains the thin plates of $(111)_{L1_0}$ twins as growth faults inside itself. The surface relief of the martensite plates disappears with the polygonization and the growth process of the massive grains, i.e. by the processes of recovery and recrystallization.

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