Some Effects of Parent Phase Aging on the Martensitic Transformation in a Cu-Al-Ni Shape Memory Alloy

N. KUWANO and C. M. WAYMAN

Transmission electron microscopy observations have been carried out for a Cu-14 pct Al-4 pct Ni (wt pct) alloy aged in the thin foil state in an electron microscope. It was found that large cuboidal precipitates of the γ_2 phase and many small domains of a highly ordered phase form in the DO_3 matrix during aging. The small ordered domains form preferentially on matrix antiphase boundaries as well as within the antiphase domains. The formation of γ_2 and the highly ordered phase, both of which are rich in alloy content, depletes the matrix of solute and thus raises the transformation temperatures M_s and M_f. The small domains of the highly ordered phase prevent the propagation and reversion of martensite plates, leading to higher M_s-M_f and A_s-A_f temperature intervals.

I. INTRODUCTION

SHAPE memory alloys Cu-Al-Ni have been of particular interest for over a decade, and practical applications of them have been attempted for various uses. However, Cu-Al-Ni alloys, as with most other Cu-based shape memory alloys, show considerable aging effects[1,2] which have constrained potential applications of them. To overcome difficulties resulting from aging effects and to achieve a long lifetime of shape memory capacity it is important first to clarify details of the structural changes which occur in the alloy during aging.

In the present work a Cu-14 pct Al-4 pct Ni (wt pct) alloy was aged at 673 K in an electron microscope to observe microstructural changes, and it is reported that not only large cuboidal precipitates of the γ_2 phase but also many domains of a highly ordered phase are formed in the DO_3 matrix. These precipitates and domains exert an influence on the subsequent martensitic transformation.

II. EXPERIMENTAL

A single crystal of the Cu-14Al-4Ni alloy was prepared using the Bridgmann technique. A slab was cut from the crystal with a [001] surface orientation, and after mechanical and chemical polishing to a thickness of 0.3 mm, discs 3 mm in diameter were punched out. The discs were sealed in an evacuated quartz capsule, heated to 1073 K and water-quenched to room temperatures, thus obtaining the DO_3 state. The as-quenched discs were electropolished at room temperature using a conventional jet method and an electrolyte containing phosphoric acid and water. The M_s temperature was measured for both bulk and thin foil specimens and found to be 240 to 250 K. It was confirmed initially that products such as a "2H-type phase"[3] and an "ω-like phase"[4] had not formed in thin foils of the as-quenched specimens.

Heat treatments and in situ observations were carried out for the quenched specimens using the heating stage of a Hitachi H500 electron microscope operated at 125 kV. The specimens were aged at 673 K as long as 7.2 to 9.0 ks, cooled to room temperature, and then reheated to 673 K. The heating stage could be tilted to ±60 deg about a single axis.

III. EXPERIMENTAL RESULTS

Figure 1 shows a typical bright-field (BF) image of an as-quenched specimen of the present alloy. Large spear-like plates of martensite are seen. The spear-like martensite is
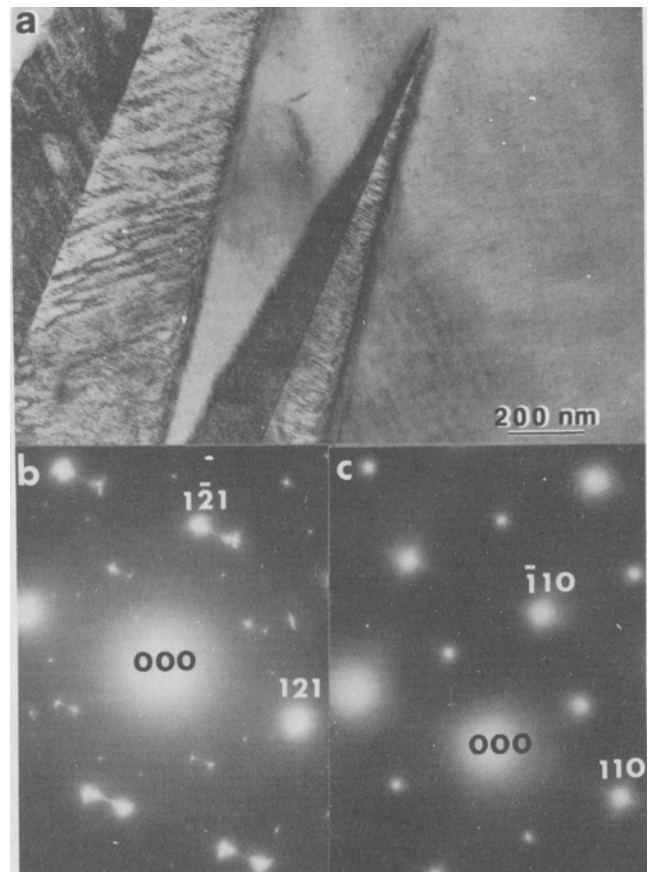

Fig. 1 — Typical BF image and diffraction patterns taken at room temperature for an as-quenched specimen. (a) BF. (b) Diffraction pattern from martensite. Indices are referred to the 2H structure. (c) Diffraction pattern from the DO_3 matrix.

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characteristic of Cu-Al-Ni alloys and has been investigated in detail by others.[5] Since the M_s temperature of the present alloy is about 240 K, which is well below room temperature, and the spear-like martensite is observed only at the thin edges of specimens with the sharp end of the spear running inward, it is suggested that this martensite is formed by the assistance of stresses during or after electropolishing. From the electron diffraction pattern, the matrix is confirmed to have the DO_3 ordered state. In the diffraction pattern shown in Figure 1(c) each DO_3 reflection shows four-fold satellites along $\langle 001 \rangle$, and in the BF image (Figure 1(a)) a basket weave type of structure can be seen, possibly indicative of the start of a spinodal decomposition. A spinodal decomposition has been commonly reported in other as-quenched and aged (at room temperature or slightly above) noble metal beta-phase alloys such as Ag-Cd,[6] Cu-Zn,[7] and Cu-Sn[8] alloys. The decomposition is believed to proceed during or after electropolishing because of a "thin-foil" effect.

Figure 2 shows two DF images of an as-quenched specimen taken with superlattice reflections hkl* = 001 and hkl = ½½½. In Figure 2(a) no antiphase boundaries (APB's) are visible, but for Figure 2(b) typical APB's are clearly seen. This indicates that most APB's in the present alloy have a displacement vector $\mathbf{R} = \langle 001 \rangle a_{bcc'}$, where a_{bcc} is the dimension of the fundamental bcc structure.

It was found from the *in situ* observations that when a specimen was held at 673 K for longer than about 1.8 ks in the heating stage of the electron microscope, large cuboidal precipitates appeared. Figure 3 shows an example of the precipitates formed after aging for 2.4 ks. It has been
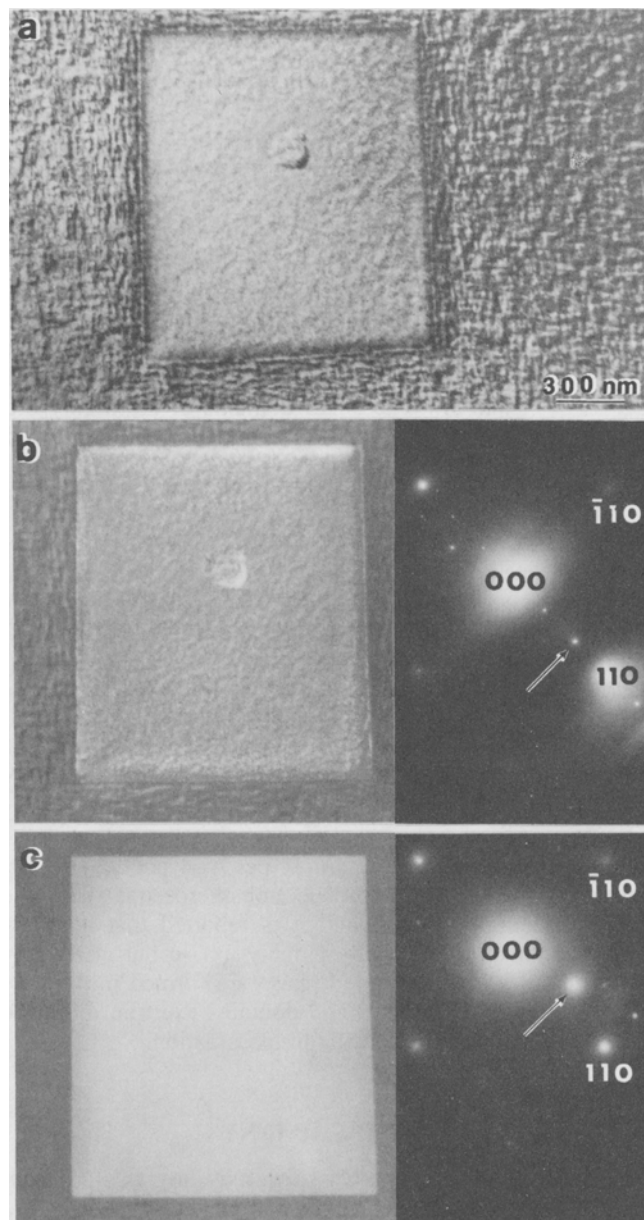

Fig. 3—BF and DF images taken at 673 K for specimen aged at 673 K for about 2.4 ks, revealing cuboidal precipitates of the γ_2 phase. (a) BF. (b) and (c) DF.
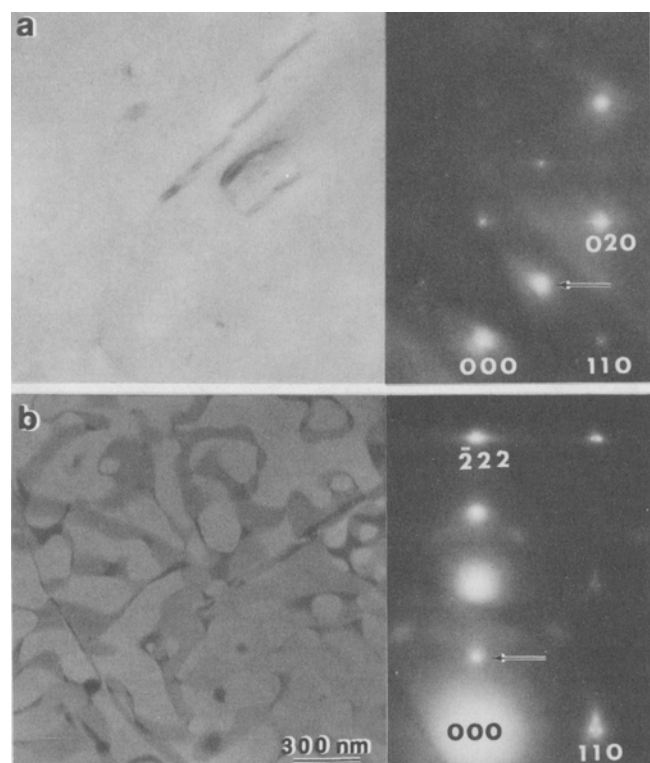

Fig. 2—DF images taken at room temperature for an as-quenched specimen using superlattice reflections. (a) hkl = 010. (b) hkl = ½½½. Arrows in the diffraction patterns indicate the reflections used to take the DF images.

reported[9] that in an aged Cu-Sn alloy large precipitates form with a low symmetry crystal structure and that the superposition of reflections gives a diffraction pattern of apparent cubic symmetry. But this is not the case for the present. The diffraction spots from one cuboidal precipitate appear at every reciprocal lattice point of the type $h/3, k/3, l/3$ (referred to the disordered bcc phase), and the precipitate appears in uniform contrast in dark-field images taken with one of the one-third reflections, as shown in Figures 3 and 4. These results indicate that the precipitate has a cubic structure with lattice dimension $3a_{bcc}$. That is, the cuboidal precipitate is identified with the γ_2 phase. Comparing the images and diffraction patterns in Figures 3 and 4, it is clearly seen that $\langle 100 \rangle$ of the γ_2 is parallel to $\langle 100 \rangle$ of the DO_3 matrix, and that the γ_2 interface corresponds to $\{100\}$. In addition to the γ_2 particles, one can see small domains in the
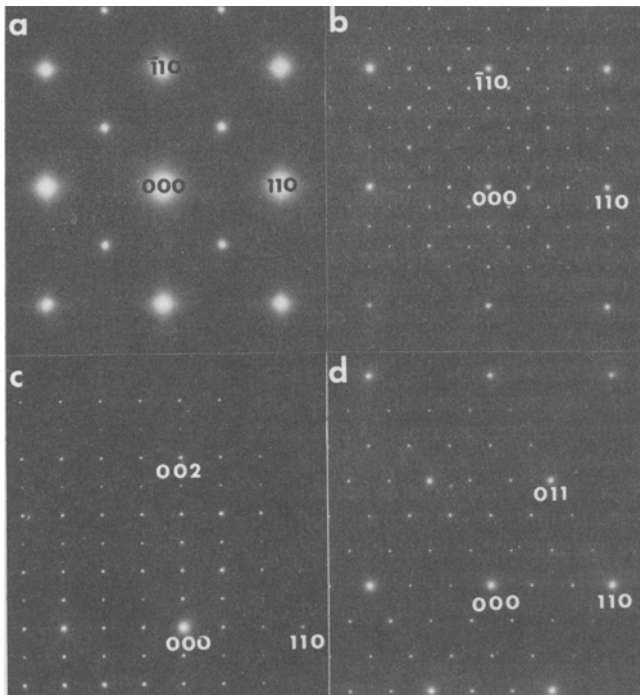
Fig. 4—Typical diffraction patterns from the matrix and γ_2 phase taken at 673 K. (a) DO$_3$ matrix. (b)-(d) γ_2 phase. (a) and (b) were taken using the same specimen orientation.

matrix in Figure 3(a). These domains, as will be shown later, were found to form preferentially on APB's as well as within the antiphase domains; for the latter case they have a tendency to align along $\langle 001 \rangle$. Since there are no additional diffraction spots in the diffraction patterns in cases where such domains appear in the matrix, these domains are believed to be of a highly ordered DO$_3$ or Heusler structure. In this connection, Nakamura et al.[1] have suggested that an aged Cu-Al-Ni alloy orders partially from DO$_3$ to a Heusler structure because of excess solute atoms.

Figure 5 shows a BF image after holding a thin foil specimen at 673 K for 9.0 ks. The thinnest region of the specimen was chosen for Figure 5, and the γ_2 phase was not observed in such a region. In Figure 5 it can be seen that the highly ordered domains have coarsened and have assumed the shape of a "loose" cuboid, some of which have elongated along $\langle 001 \rangle$. One can also see in Figure 5 a band of

18R martensite (β'_1). This martensite propagated from the edge of the specimen inward during heating, and is thus regarded as a stress-induced martensite. It is not surprising that this type of martensite has an 18R structure considering that the type of martensite formed depends on both the composition and the temperature. Stress-induced martensites in Cu-Al-Ni alloys have been investigated in detail, particularly as to their crystallographic aspects.[10,11,12]

On cooling a specimen after aging at 673 K for 7.2 to 9.0 ks in the electron microscope, no change in the γ_2 phase was observed, but martensitic transformation of the matrix started at about 393 K and was completed before room temperature was reached. A typical microstructure of such an aged specimen (taken at room temperature) is shown in Figure 6, where a fine lamellar structure can be seen. From the characteristics of the lamellar structure and the associated diffraction patterns, it is seen that the field of view corresponds to a 2H martensite which is internally twinned with respect to a $\{121\}_{2H}$ plane. But in the diffraction pattern shown in Figure 6, several reflections other than those corresponding to a twinned 2H structure can be seen. These can be attributed to double diffraction and reflections from the DO$_3$ phase. Actually, in a DF image taken with one of the "additional" spots, small domains are imaged as shown in Figure 6(d), revealing that the domains which are highly ordered have formed at the high temperature and are retained to room temperature. Although the aged specimen was undoubtedly martensitic at room temperature, no typical martensitic surface relief could be detected at moderate magnification (32×) using an optical microscope. The reason for this is that the many highly ordered particles have restricted the martensite to form as short segments, thus preventing any large scale surface relief from being detected.

When such a specimen (Figure 6) was reheated, the martensite started transforming back to the parent phase. Figure 7 shows a typical BF image and the corresponding DF image after heating to 673 K. The DF image was taken using a martensite reflection. It can be seen that a significant fraction of the martensite is retained even at 673 K, and that no other products of thermal decomposition are formed.

IV. DISCUSSION

Although the present results must be viewed with the reserve that they have been obtained using thin foils and are
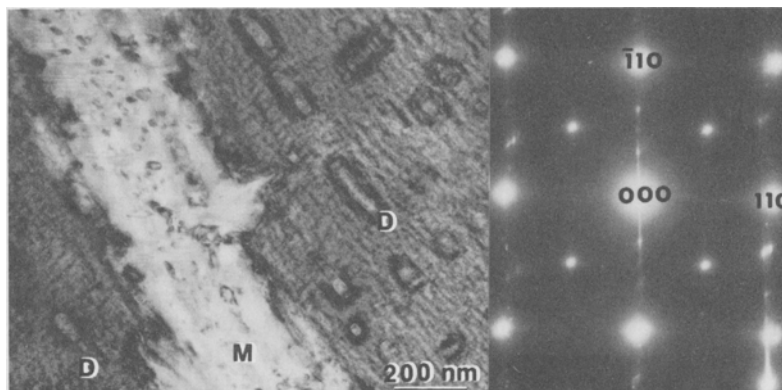

Fig. 5—BF image and diffraction pattern taken at 673 K for specimen aged at 673 K for 9.0 ks. D = domains of highly ordered phase; M = 18R martensite.
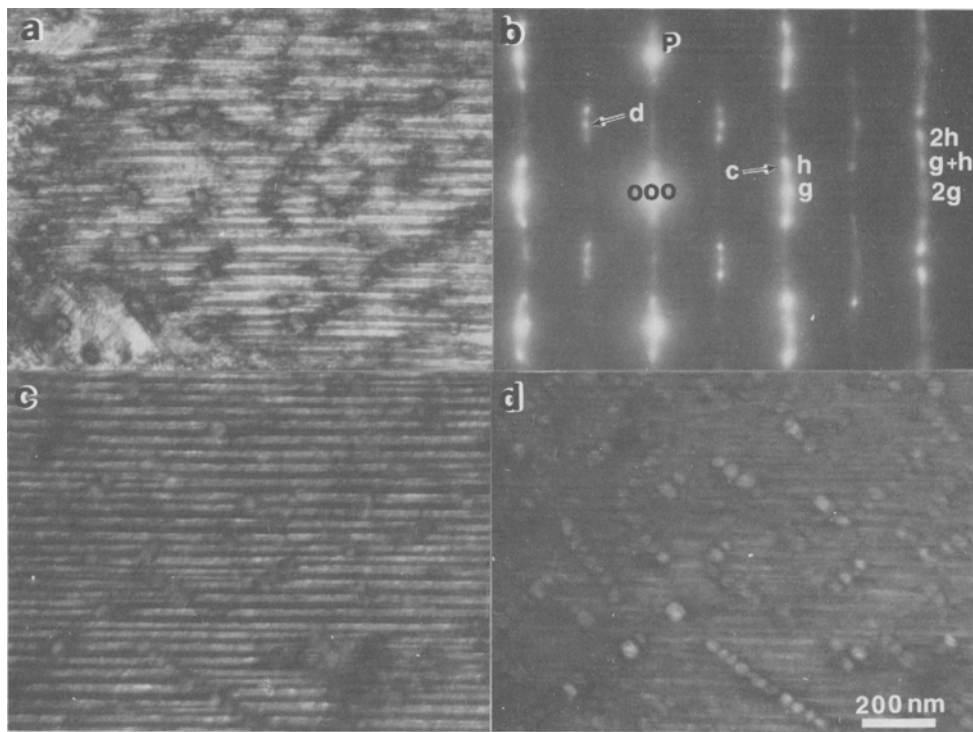
Fig. 6—Typical BF and DF images taken at room temperature for specimen aged at 673 K for 7.2 ks. (a) BF. (b) Diffraction pattern. (c) and (d) DF images. In (b) P = $\bar{1}10$ or $\overline{121}_{2H}$, g = 110, and h = $1\bar{2}1_{2H}$. The reflections indicated c and d were used to take the DF images shown in (c) and (d), respectively.
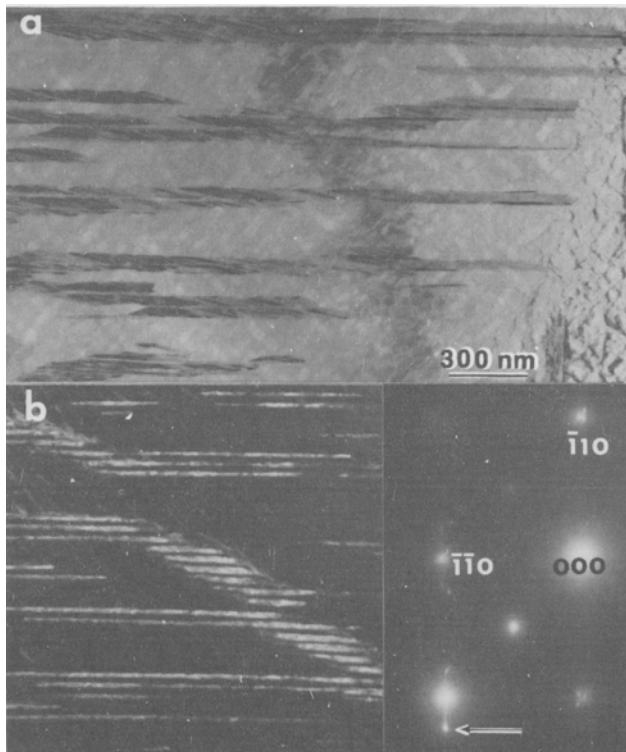

Fig. 7—BF and DF images taken at 673 K for specimen aged at 673 K for 7.2 ks, cooled to room temperature, and then heated to 673 K. (a) BF. (b) DF.

thus subject to thin foil effects, it is seen that the M_s temperature increases from 240 to 250 K to about 390 K after aging at 673 K for 7.2 to 9.0 ks. Since the γ_2 phase and the

highly ordered domains, both of which are rich in solute atoms, formed during aging, the increase in the M_s temperature is considered to be attributed to a decrease in alloy content of the matrix. In fact, it is known that the M_s temperature increases with decreasing matrix solute content.[2] Some investigators[1,13-15] have expressed the view that atomic ordering can influence the M_s temperature. However, in the present alloy where ordering proceeds inhomogeneously, the actual M_s temperature depends on the degree of order in a matrix of low solute content instead of one averaged over the crystal.

The martensite formed in aged specimens was found to have a 2H structure, typical of the usual spear-like martensite although of clearly a different morphology in the present thin foil case. Figure 8 shows the substructure of martensite formed in an as-quenched specimen following cooling in the electron microscope to a low temperature. The martensite is lamellar and quite similar to that formed in an aged specimen. A lamellar γ_1' martensite in a Cu-Al-Ni alloy has been previously reported by other workers.[16] This report and the present results indicate that the martensite morphology depends mainly on the rate of martensite formation rather than on the alloy composition. In other words, the Cu-Al-Ni 2H martensite has a lamellar structure if it is formed rapidly, and a spear-type morphology when formed slowly.

As mentioned above, the formation of the γ_2 phase and the highly ordered domains decreases the matrix solute content, thereby increasing the M_s temperature. In addition to this effect, it was found that the highly ordered domains exert a "mechanical" influence on the martensitic transformation if the domains are densely distributed and coarsen to a size comparable to the width of martensite plates.
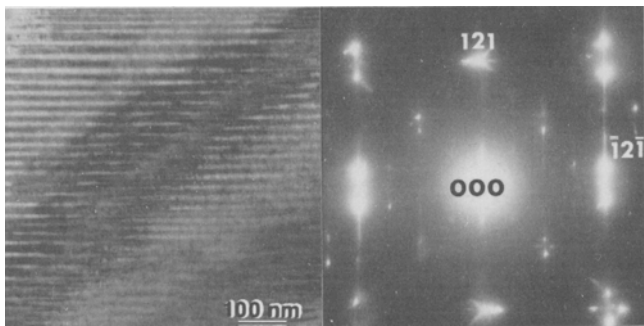
Fig. 8 — BF image and corresponding diffraction pattern taken at 171 K for an as-quenched specimen. Indices refer to the 2H structure.

Figure 9 shows the behavior of martensite in an aged specimen during cooling and subsequent heating in the microscope. In this micrograph, one can see that the highly ordered domains have formed in large numbers on the APB's as well as within them. When the temperature is decreased the martensite plates propagate. But some are restricted from propagating by the highly ordered domains, especially those formed at APB's. At about 373 K (Figure 9(e)) the martensite transformation is nearly complete, although a small amount of the parent phase is retained owing to the blockage effect of the ordered domains. When the specimen was heated again to 673 K, the martensite plates were inhibited from reversing, as seen in Figure 9(f), again because
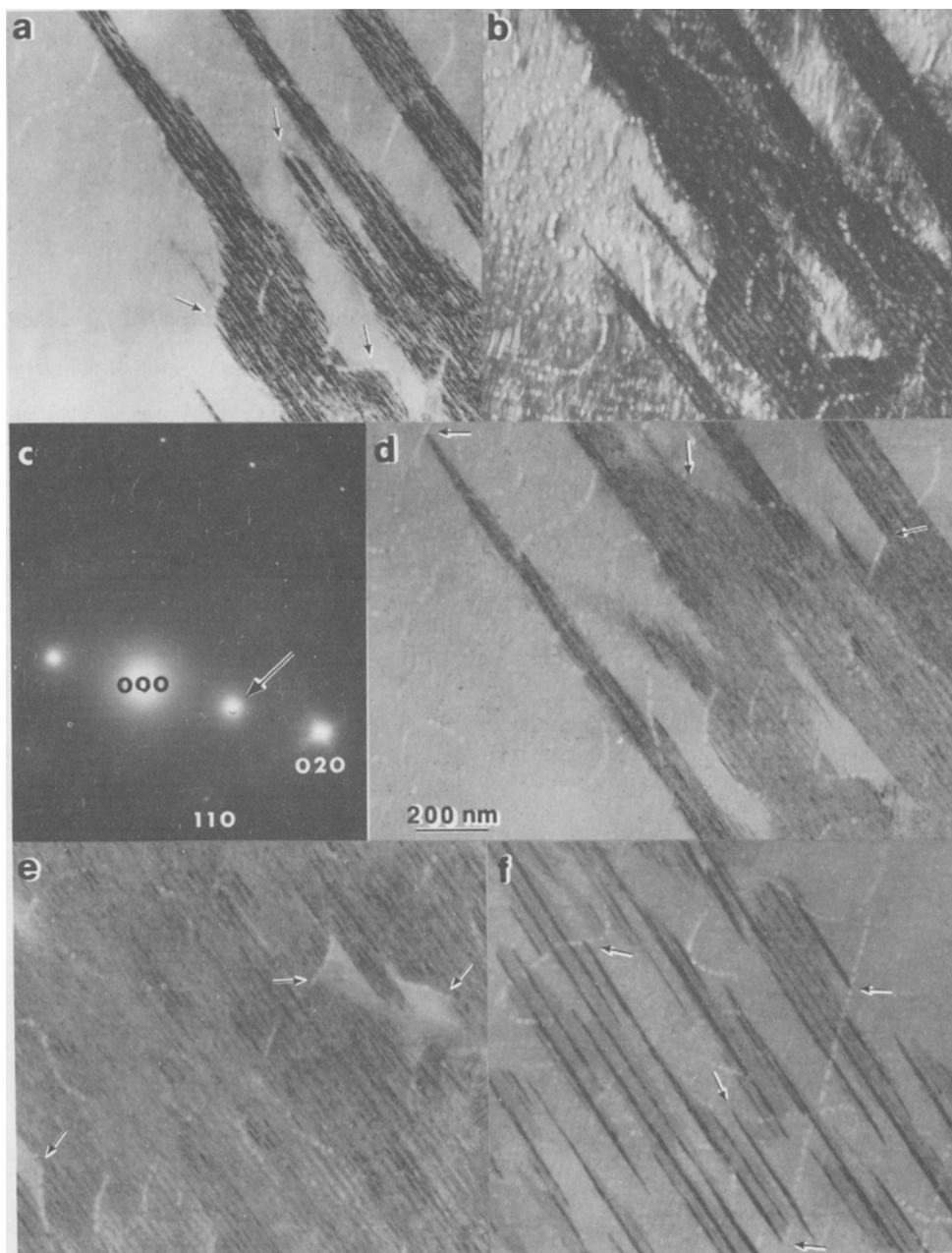

Fig. 9 — Propagation and reversion of martensite in specimen aged at 673 K for 7.2 ks. (a) BF at 393 K. (b) DF at ~376 K. (c) Diffraction pattern for (b). (d) BF at ~373 K. (e) BF at ~368 K. (f) BF at 673 K. (a)-(e) were taken on cooling from 673 K to room temperature and (f) on subsequent heating. The domains of the highly ordered phase are observed to arrest the martensite from propagating or reversing (see arrows).

of the existence of the highly ordered domains. These observations clearly indicate that the highly ordered domains act to increase the temperature intervals M_s-M_f and A_s-A_f. For many alloys including Cu-Al-Ni alloys[1,17] aged at moderate temperature an increase in these temperature intervals has been reported, and correspondingly ascribed to a composition drift in the matrix because of the formation of a high alloy content phase. This is well documented, but in addition to such a "chemical effect", a further "mechanical effect" such as the transformation blockage (forward and reverse) by ordered domains should be taken into consideration insofar as the actual progress of the martensitic transformation is concerned.

When the alloy was aged at 673 K for a prolonged time in the electron microscope, the major "precipitating" components were the γ_2 phase and the highly ordered domains, both forming within the DO_3 matrix. Thus, the matrix was a less-ordered DO_3 or possibly a disordered bcc phase which transformed to martensite well above room temperature. But when a specimen was aged at 573 K no γ_2 phase was detected although highly ordered domains were observed at APB's. But in contrast to this behavior, Dvorack et al. using single crystal X-ray experiments found that the γ_2 phase formed in a similar alloy aged as low as 545 K; further, the alloy aged at 673 K for several hours consisted of the γ_2 and α phases coexistent with small amounts of the disordered bcc phase in addition to some martensite.[18] The apparent discrepancy is believed to be due to the difference in kinetic behavior comparing thin foils and bulk specimens. It may also be related to differences in composition or thermal history.

V. CONCLUSIONS

From the electron microscopy observations of a Cu-14Al-4Ni alloy aged in the thin foil condition in the microscope, we conclude

1. Aging at 673 K results in the formation of large cuboidal precipitates of the γ_2 phase and small domains of a highly ordered phase. Their formation reduces the alloy content of the matrix.

2. The M_s temperature of the aged alloys is much higher than that of an as-quenched specimen because of the decrease in alloy content during aging.
3. Small domains of the highly ordered phase form preferentially on antiphase boundaries and within the antiphase domains. These domains prevent plates of martensite from propagating or reverting and consequently increase the temperature intervals M_s-M_f and A_s-A_f.

ACKNOWLEDGMENTS

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