# Transformation Sequence in a Cu-Al-Ni Shape Memory Alloy at Elevated Temperatures

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Precipitation sequences in a Cu-14 pct Al-4 pct Ni (wt pct) shape memory alloy were studied by means of transmission electron diffraction and microscopy as well as X-ray microanalysis techniques. On aging thin foil specimens up to 550 °C in the electron microscope, an as-quenched sample having a mixture of 2H-type and $DO_3$-type metastable structures transformed to the stable simple cubic $\gamma_2$ phase at or above 450 °C. The remaining matrix either showed precipitates of the fcc $\alpha$-phase on prolonged annealing at 500 to 550 °C for a longer period, or transformed to martensite on cooling below the $M_s$ temperature ($\sim$150 °C).

## I. INTRODUCTION

THE shape memory effect occurs in martensitic alloys but, in some alloys, deleterious aging effects in both the martensite and parent phases occur. The Cu-base shape memory alloys have brought many practical applications although they are susceptible to undesirable aging effects.[1,2] In order to overcome difficulties resulting from aging effects and to achieve long lifetime capacity of the Cu-based shape memory alloys, it is necessary to know the changes which occur in these alloys during aging.

Aging effects in Cu-Al-Ni shape memory alloys have been investigated to some extent.[3-6] There is controversy about the initial structure of the as-quenched alloy. The occurrence of a 2H type metastable phase in the as-quenched $\beta_1$ Cu-14.2 pct Al-4.3 pct Ni (wt pct) alloy has been reported by Otsuka et al.,[4] while a $DO_3$ structure was reported by others.[2,3,5] Aging in this alloy was studied up to 400 °C. In the present work, a Cu-14 pct Al-4 pct Ni (wt pct) alloy was investigated systematically, and aging effects in the electron microscope were observed up to 600 °C. The observed microstructural changes were supported by microchemical STEM analysis, and a transformation sequence is proposed.

## II. EXPERIMENTAL PROCEDURE

A single crystal of composition Cu-14 pct Al-4 pct Ni (wt pct) alloy was prepared using the Bridgman technique, and slices were cut with [001] surface orientation. After mechanical and chemical polishing to a thickness of 0.3 mm, 3 mm discs were punched out. The samples were then homogenized at 850 °C for 48 hours in evacuated quartz capsules and rapidly quenched into iced water (by breaking the capsule after contact with water) in order to avoid precipitation of high temperature phases. As-quenched discs were electropolished at room temperature using a conventional jet polishing technique with an electrolyte consisting of phosphoric acid and water.

Heat treatments and in situ observations were carried out using hot stages of Hitachi H500 and Philips 420 microscopes, operated at 125 or 120 kV. Specimens were aged up to 600 °C for as long as 1 hour followed by cooling to 300 °C for 10 minutes and reheating back to 600 °C. The heating stage could be tilted to ±60 deg about a single axis. Some samples were examined in the microscope at room temperature with a 60-deg tilt, 360 deg rotation goniometer.

## III. RESULTS AND DISCUSSION

### A. As-Quenched Alloy

The as-quenched alloy showed a large volume fraction of ordered matrix phase plus isolated martensite plates. The martensite phase of the binary Cu-Al and the ternary Cu-Al-Ni systems is well documented.[3,6,7] The $M_s$ temperature of the binary alloys gradually decreases with the addition of Ni.[1] The present investigation has focused on precipitation sequences in the nonmartensitic region (i.e., matrix region) during heat treatments.

The as-quenched alloy (nonmartensitic region) shows APB contrast as presented in Figure 1. The corresponding diffraction patterns taken at room temperature are given in Figures 2(a) through (c). These patterns are generally com-
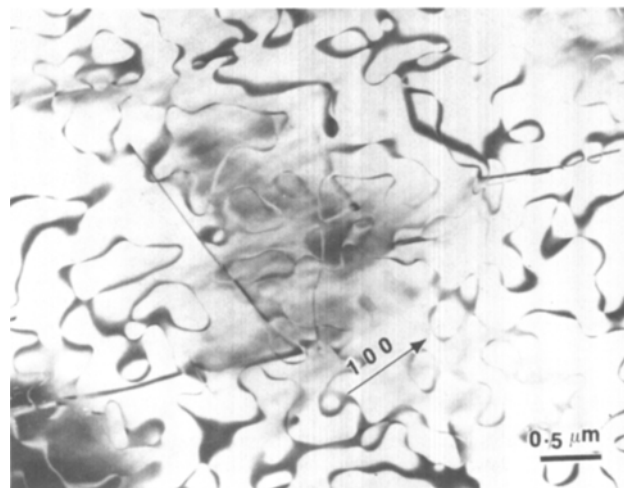
JOGENDER SINGH, HAYDN CHEN, and C. M. WAYMAN are with the Department of Metallurgy and Mining Engineering and the Materials Research Laboratory at the University of Illinois at Urbana-Champaign, 1304 West Green Street, Urbana, IL 61801.

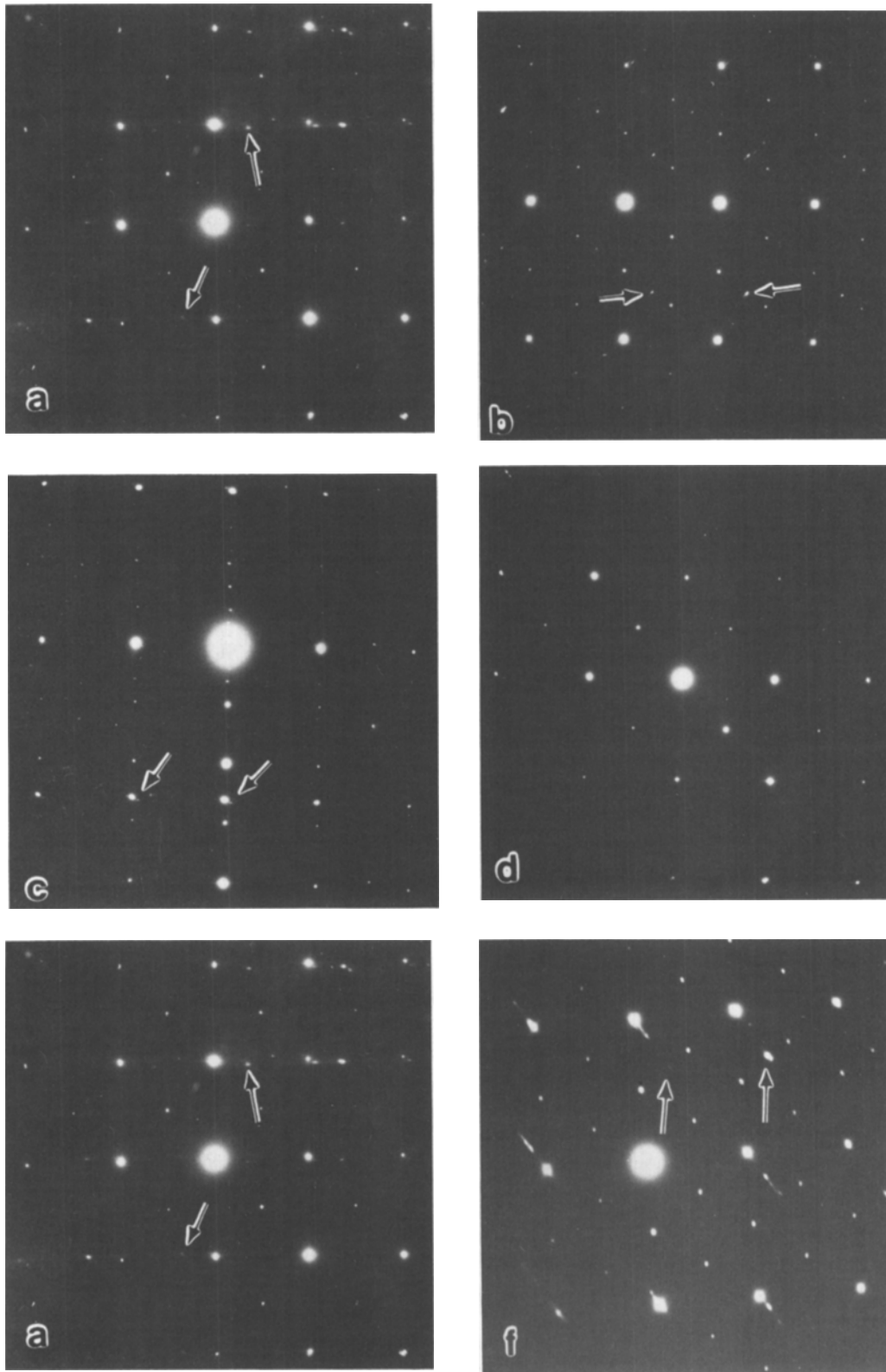Fig. 1 — Electron micrograph of as-quenched sample showing antiphase boundaries (APB's).

Fig. 2 — Electron diffraction patterns of thin foil sample taken at different temperatures: (a) to (c) as-quenched state showing extra spots as marked by arrows; (d) at 500 °C showing the disappearance of extra spots and diffuse streaks; (e) and (f) at 300 °C showing the reappearance of extra spots and diffuse streaks.

plex and consist of features such as fundamental spots, superlattice reflections from the matrix, diffuse streaks, and diffuse spots arising from the intersection of streaks with the Ewald sphere. Additional sharp extra reflections are indicated by arrows.

The early stage transformation of the high temperature $\beta$ phase in an as-quenched sample having the $DO_3$ structure has been investigated by Robertson and Wayman using TEM[8] and Dvorack and Chen employing the X-ray technique.[9] Under two-beam conditions, the alloy exhibited a modulated structure which was more closely related with a "tweed" structure than spinodal decomposition.[8] In addition to the tweed structure, smoothly curved APB's were also observed in the as-quenched alloy. They remain smoothly curved during aging up to ~150 °C. There is evidently little interaction between the APB's and the tweed structure. The occurrence of streaks and diffuse spots in the diffraction patterns has been extensively studied in the Cu-Al-Ni and Cu-Zn-Al systems and shown to be due to a soft transverse acoustic phonon mode.[9,10] We are mainly concerned here with the sharp extra reflections in the diffraction pattern as indicated by arrows in Figure 2.

There are some differences in the initial structure of the as-quenched alloy. Investigators have observed streaks and extra reflections in electron diffraction patterns which generally correspond to 2H or $\omega$-type reflections, and mottled structures in the electron micrographs for many binary and ternary alloys. These are often claimed to be premartensitic or premonitory phenomena.[11,12] Murakami et al.[13] and Otsuka et al.[4] analyzed the extra reflections in as-quenched Cu-Zn-Al and Cu-Al-Ni alloys, respectively, and claimed that all reflections could be explained by the 2H-type structure as proposed by Takezawa and Sato.[14] On the contrary Kuwano and Wayman[3] as well as Dvorack et al.[5] reported the existence of only the $DO_3$ phase in the as-quenched alloy. In order to clarify the as-quenched structure in the current study, a systematic TEM study was carried out which reconfirmed the existence of the 2H-type metastable phase along with the $DO_3$ phase. Since the $DO_3$ phase is a higher temperature metastable phase as compared with the 2H phase, if the quenching rate is not fast enough, then one can expect only the $DO_3$ phase in the as-quenched alloy. The mottled structure was also observed in the martensitic region and corresponded to the 2H type phase. If the 2H type phase represented truly a premartensitic effect for the subsequent martensitic transformation, then it should not appear in the martensitic phase.[4]

In order to examine further the above results, the same thin foil was heated in the TEM to 500 °C for short times (<5 minutes). The corresponding diffraction pattern is shown in Figure 2(d). The extra reflections due to the 2H type phase completely disappeared. On cooling the sample to about 300 °C, the 2H type reflections reappear as shown in Figures 2(e, f). This indicates that the $\beta_1(DO_3) \rightleftarrows 2H$ type phase transformation is reversible. In addition it is also noted that the streaks in the $\langle 112 \rangle_{\beta_1}$ direction behave the same way as the extra reflections. They disappear when the extra reflections disappear and reappear when the extra reflections reappear. Thus the extra reflections and streaks are inseparable phenomena, typically characteristic of this transformation in this alloy.

## B. Heating Stage Work

In order to study aging effects, the thin foil alloy was heated slowly to 450 °C and isothermally held for a longer period (~1 hour) in the microscope. Figure 3 shows electron micrographs taken during the in situ experiment, which indicate the formation of another phase at 450 °C. This phase has been identified as the $\gamma_2$ phase. During formation of the $\gamma_2$ phase, interfacial dislocations are observed at the interfaces between the $\gamma_2$ and $DO_3$ matrix. Under different contrast conditions these interfacial dislocations appear like low angle boundary dislocations suggesting that initial growth of $\gamma_2$ phase is semi-coherent with the matrix.

When the sample was isothermally held between 450 to 500 °C for a longer period (~2 hours), a marked stage of extensive coalescence of the $\gamma_2$ phase was observed. It is clearly evident that the small domains of $\gamma_2$ phase (300 to 500 Å) coalesce into units of ~600 to 700 Å in diameter or more. This process is very rapidly completed and then the
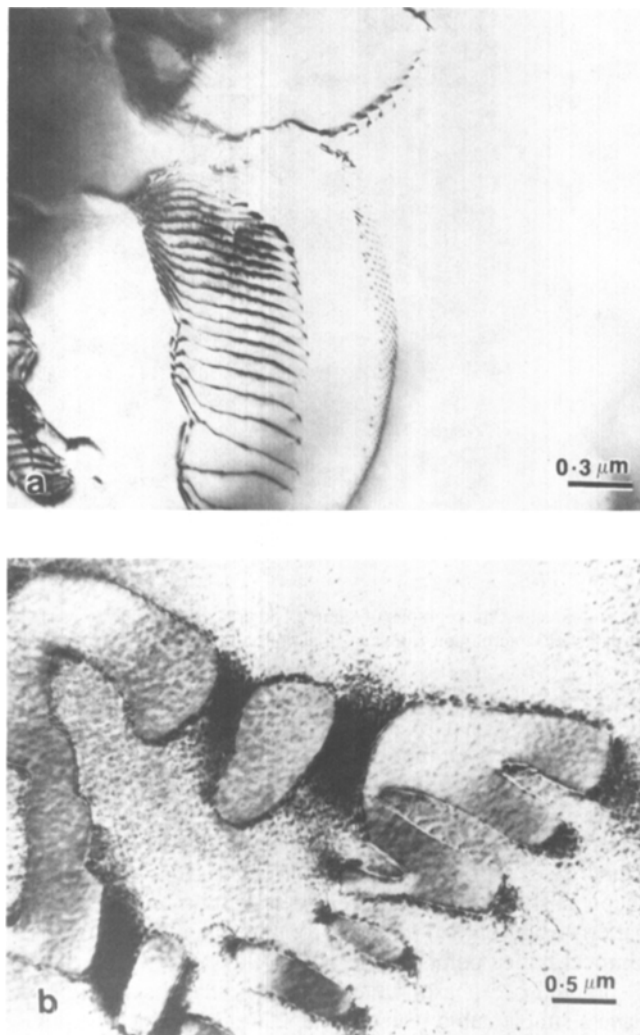


Fig. 3—Electron micrographs taken at 450 °C showing (a) formation of interfacial dislocations between $\gamma_2$ and $DO_3$ phases (matrix); (b) coalescence of the $\gamma_2$ phase.
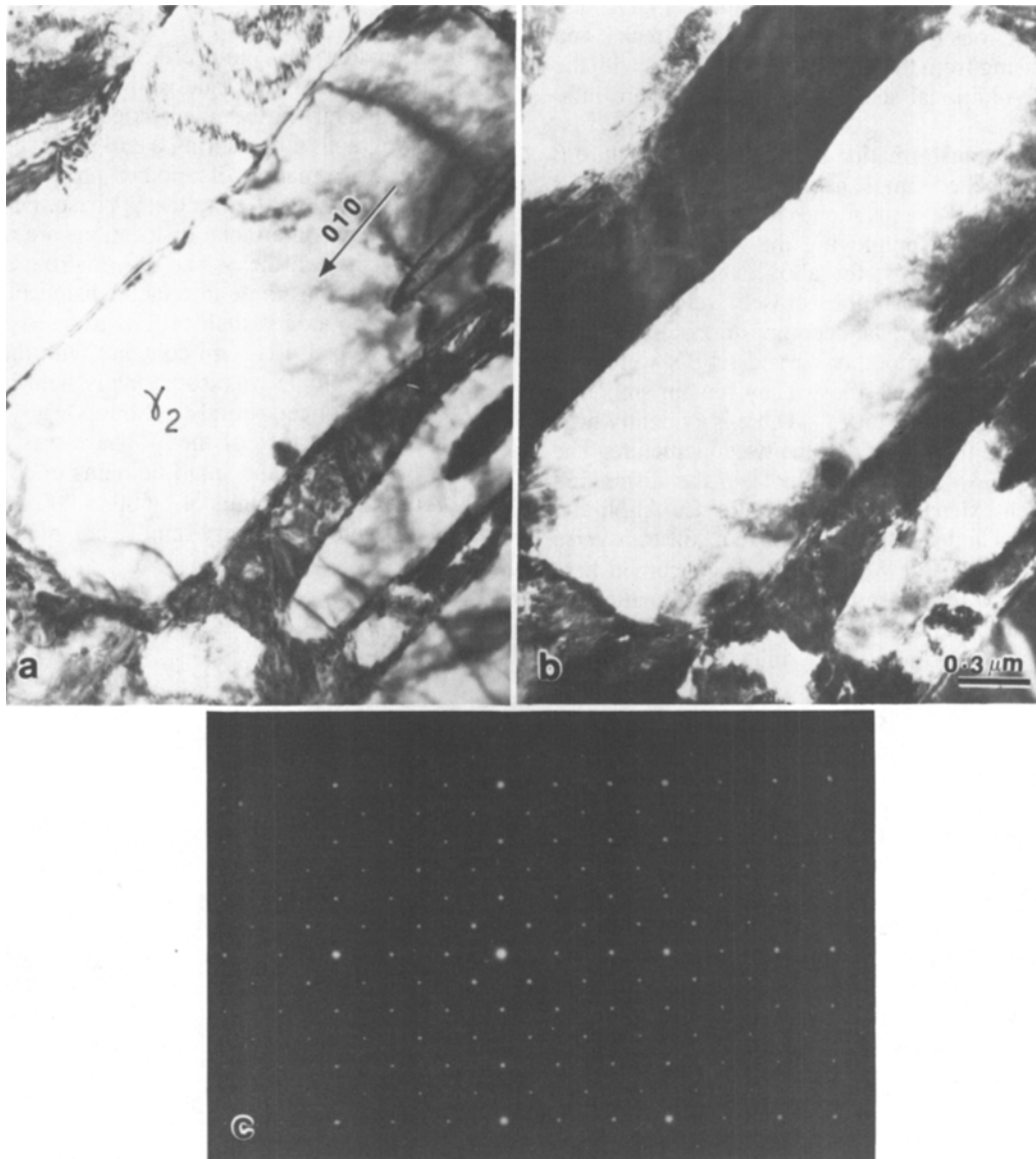
Fig. 4—Electron micrographs of sample taken at room temperature after aging at 500 °C for 1 h in the microscope showing (a) precipitation of $\gamma_2$ phase, (b) dark-field micrograph using $\gamma_2$ reflection, and (c) corresponding diffraction pattern from $\gamma_2$ region with [001] zone axis.

boundaries between the small domains fade out as a mechanism for domain growth.[14]

On isothermal holding between 500 to 550 °C for long times (>30 minutes), the decomposition of the matrix into $\gamma_2$ increases rapidly and the $\gamma_2$ forms a rectangular blocked shape as shown in Figure 4. The corresponding diffraction pattern (Figure 4(c)) taken at room temperature shows reciprocal lattice points of the type $h/3$, $k/3$, $l/3$ (referred to disordered bcc phase) which indicates that the precipitates have a simple cubic structure with lattice parameter equivalent to $3a$, where $a$ is the lattice parameter of the bcc cell. The decrease in amount of ordered DO$_3$ phase with phase separation and coarsening of the $\gamma_2$ phase as an associated process is consistent with the phase diagram.

In order to see the reversion effect on the $\gamma_2$ phase, a cyclic heat treatment was carried out in the microscope. The sample was brought down from ~450 °C to ~150 °C. The

$\gamma_2$ phase did not show any martensitic transformation whereas the matrix undergoes martensitic transformation as shown in Figure 5. This observation indicates that the formation of $\gamma_2$ phase has caused the $M_s$ temperature of the matrix to be higher since the matrix now contains more Cu. This has been demonstrated by STEM X-ray microanalysis as shown in Figures 6(a) and (b) where composition spectra taken from the as-quenched sample and $\gamma_2$ phase are displayed, respectively. They clearly reveal that the $\gamma_2$ phase is comparatively richer in Al atoms compared with the as-quenched sample and confirm that for many alloys including the Cu-Al-Ni system[1,15] there is a drift in matrix composition because of the formation of a high solute content phase at elevated temperature.

The morphology of the $\gamma_2$ precipitate appeared to vary with heating rate. On slow heating the thin foil to 450 °C (20 °C per minute), the microstructure of the $\gamma_2$ phase was
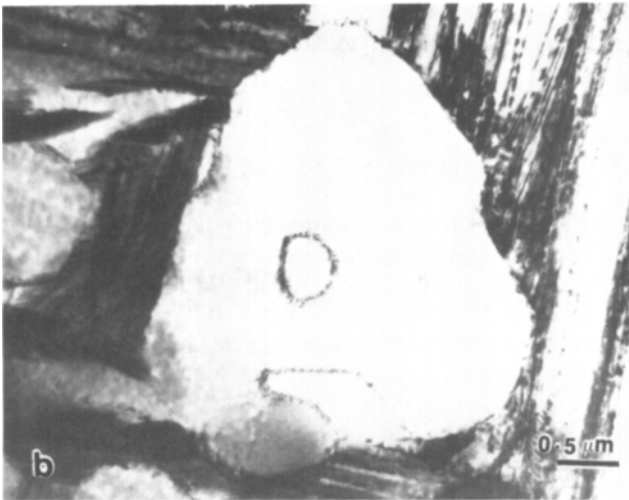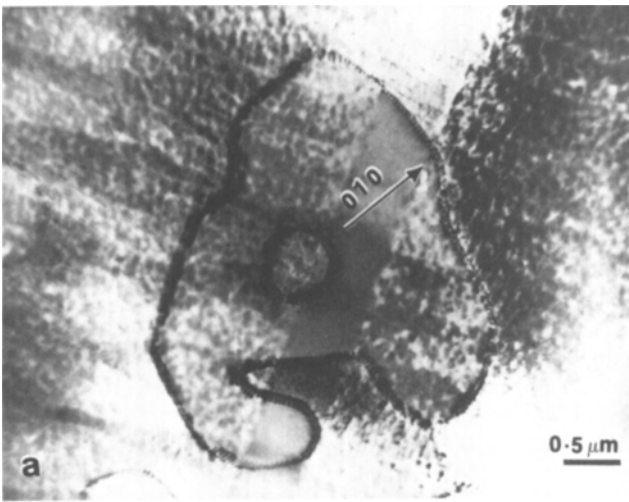
Fig. 7—Concentration variation of Al atoms in the $\gamma_2$ phase with time.

Fig. 5—Electron micrograph (a) taken at 450 °C showing the growth of $\gamma_2$ phase, (b) taken at 160 °C showing martensitic transformation in the matrix.
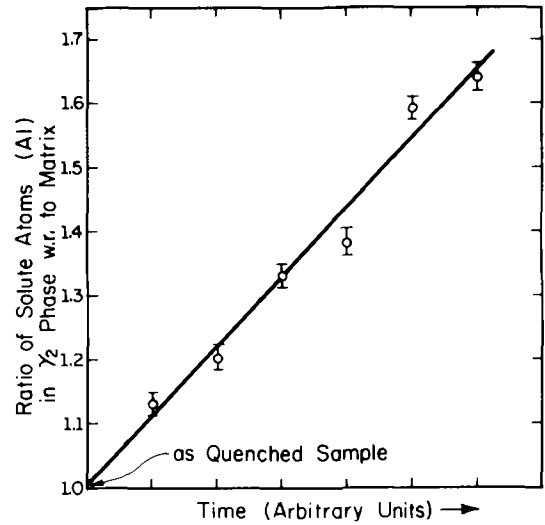
similar to that seen in Figure 3. But for rapid heating (~100 °C per minute), the $\gamma_2$ phase appears in the form of rectangular blocks (Figure 4). When the alloy is aged for a prolonged time (72 hours) the major precipitating phase is $\gamma_2$. It was noted from STEM analysis that the composition of the $\gamma_2$ phase continuously changes as the $\gamma_2$ coarsens. The corresponding STEM X-ray microanalysis of the $\gamma_2$ phase is shown in Figure 7. As the $\gamma_2$ phase is rich in Al atoms (with respect to the matrix) and the concentration in the $\gamma_2$ phase increased with time along with the coarsening, the $\gamma_2$ has not reached equilibrium concentration. It is believed that during the advancement of $\gamma_2$ interfaces, the $\gamma_2$ phase retains Al atoms and probably rejects the excess concentration of Cu and Ni into the matrix. At this stage, the supersaturated matrix would be richer in Cu and Ni atoms, compared with the as-quenched matrix.
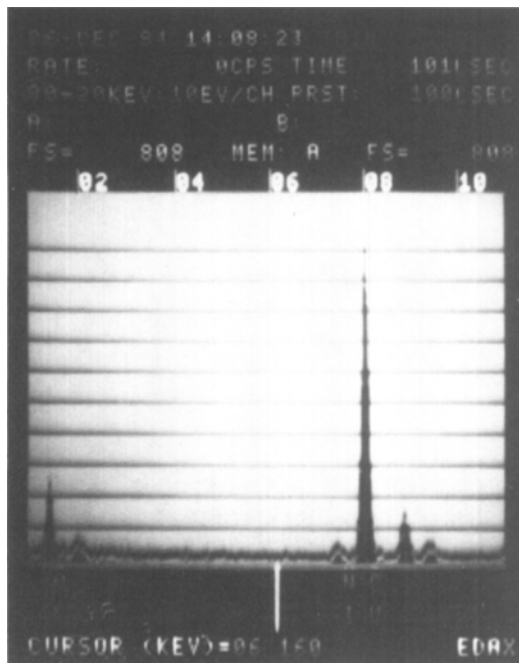


(a)
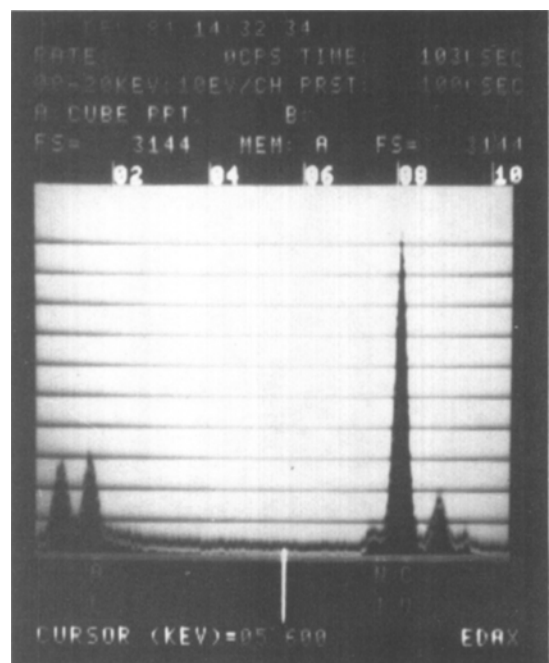
(b)

Fig. 6—Composition spectrum obtained by X-ray microanalysis from (a) as-quenched sample, (b) the $\gamma_2$-phase which is rich in Al atoms.
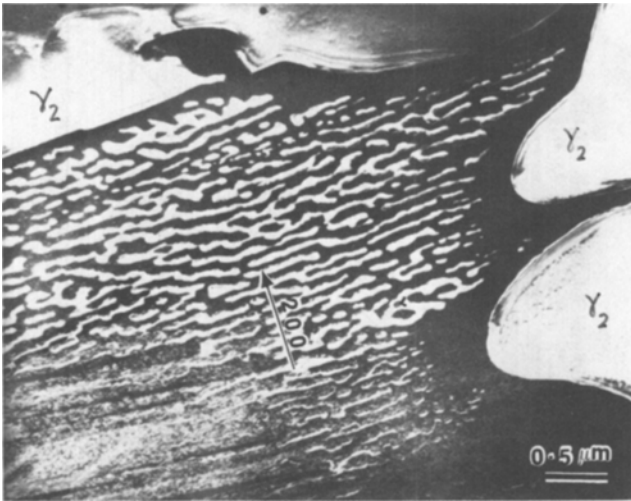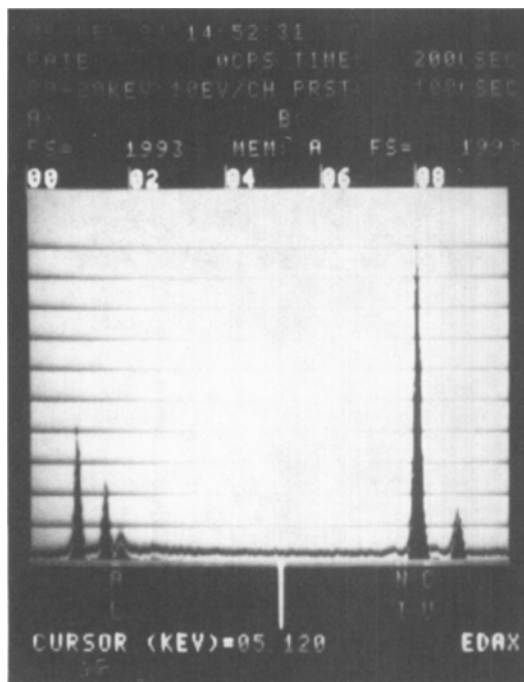
Fig. 8 — Dark-field electron micrograph taken at 550 °C showing precipitation of α-phase (using one of the fcc reflections).

Once the remaining untransformed matrix reached the supersaturated condition after the partitioning of excess Cu and Ni atoms from the $\gamma_2$ phase into the matrix, further precipitation takes place.[16] On aging at 500 to 550 °C, the matrix containing excess Cu and Ni atoms decomposed into solute rich precipitates with more Ni and Al atoms and a depleted bcc matrix as shown in Figure 8. These precipitates have been identified as the α-phase having a fcc structure. It is also revealed that precipitation and alignment of the α-phase in the form of rods occurred about 0.2 $\mu$m away from the $\gamma_2$ phase interface, which indicates long range

redistribution of solute atoms in the matrix. A dark-field electron micrograph using one of the α-phase reflections suggests preferred growth of the α-phase precipitates along the $\langle 022 \rangle$ directions of the matrix and indicates that a certain crystallographic orientation relationship exists between the two phases. The corresponding STEM X-ray microanalysis shows that the α-phase is rich in Ni and Al atoms and the "depleted matrix" contains mainly Cu atoms, as shown in Figure 9. After one cyclic heat treatment of the sample in the electron microscope, the sample was reexamined at room temperature. Domains of the $DO_3$ phase were observed in the "depleted matrix" as shown in Figure 10. The size of the $DO_3$ domains is less than 30 Å. On heating the alloy at and above 600 °C, the α-phase disappears, which indicates that the solvus line for the α-phase of this ternary alloy is about 600 °C. The $\gamma_2$ phase is still stable up to 600 °C. However, decomposition of $\gamma_2$ phase into a mixture of NiAl phase and a copper solid solution have been observed by Singh et al.[17]

## IV. SUMMARY

On rapid quenching, a Cu-14 pct Al-4 pct Ni (wt pct) alloy shows a metastable 2H type structure along with a metastable $DO_3$ structure at room temperature. The 2H type structure disappears on heating at about 400 °C but reappears on cooling around 300 °C. The 2H $\rightleftarrows \beta_1$ type transformation is reversible. Upon heating at 450 to 500 °C, the $\gamma_2$ phase appears. After aging for longer periods, coarsening of the $\gamma_2$ phase occurs by the migration of $\gamma_2$ interfaces, and simultaneous partitioning of solute atoms takes place across the interface. The concentration of solute atoms (Al) increases continuously in the $\gamma_2$ phase as a function of time. When the $\gamma_2$ phase reaches the nearly equilibrium condition,



(a)
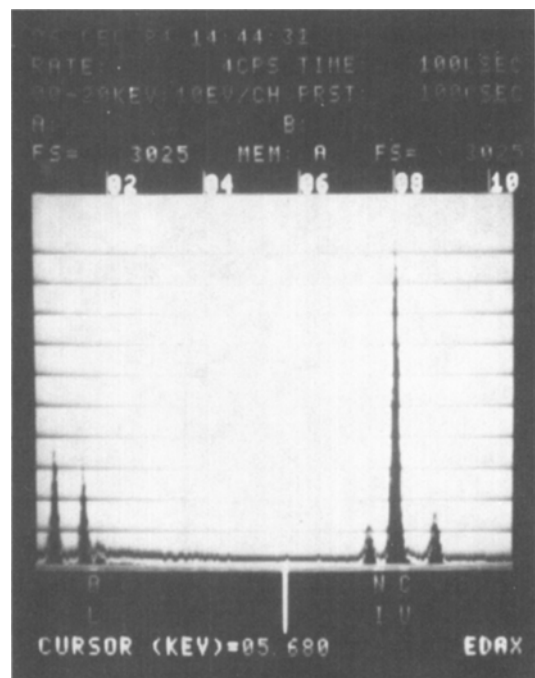


(b)

Fig. 9 — Composition spectrum obtained by STEM X-ray microanalysis at 550 °C: (a) from the α-phase showing Ni enrichment, (b) from the depleted matrix.
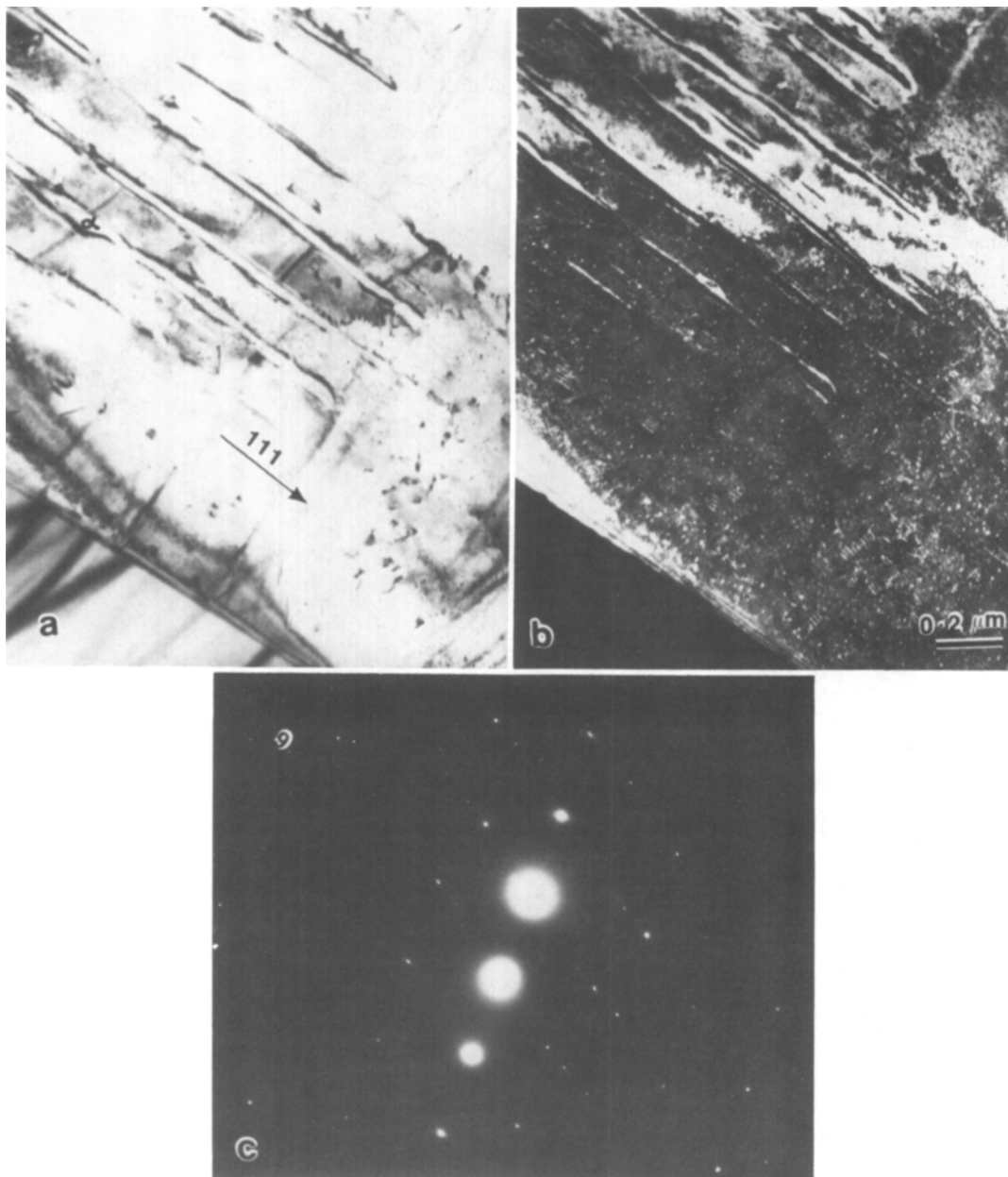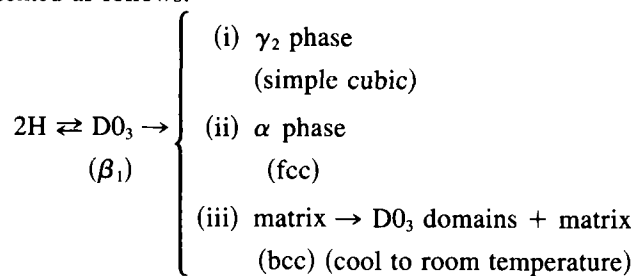
Fig. 10—Electron micrograph taken at room temperature after aging up to 550 °C: (a) bright-field image showing alignment of the $\alpha$-phase, (b) dark-field image using one of the D0$_3$ reflections showing D0$_3$ domains, and (c) corresponding diffraction pattern.

the remaining matrix shows precipitation of the $\alpha$-phase in the form of rods at 500 to 550 °C. The $\alpha$-phase is rich in Ni atoms. On cooling, D0$_3$ domains appeared in the depleted bcc matrix at room temperature.

The overall transformation sequence and products occurring during heat treatment in this ternary alloy can be represented as follows:

$$2H \rightleftarrows D0_3 \rightarrow \begin{cases} \text{(i)} \;\; \gamma_2 \text{ phase} \\ \quad\;\; \text{(simple cubic)} \\ \text{(ii)} \;\; \alpha \text{ phase} \\ \quad\;\; \text{(fcc)} \\ \text{(iii) matrix} \rightarrow \text{D0}_3 \text{ domains + matrix} \\ \quad\;\; \text{(bcc) (cool to room temperature)} \end{cases}$$
$(\beta_1)$

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