Phase Transformation of Zn-4Al-3Cu Alloy during Heat Treatment

B.J. LI and C.G. CHAO

The phase transformation in Zn-4 Al-3 Cu alloy employing various solution-treatment temperatures (230 °C to 325 °C) was studied by means of microhardness, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The starting microstructure of the as-cast Zn-4Al-3Cu alloy consists of an α phase (aluminum-rich, fcc structure) in the η matrix (zinc-rich, h.c.p. structure) prior to solution-treatment. A platelike ε phase with 3-μm length and 0.5-μm thickness was found in the η phase matrix after solution-treating the as-cast material at 240 °C for 1 hour. The ε phase was then dissolved gradually back into the η matrix above that temperature. A four-phase transformation, $\alpha + \varepsilon \rightarrow T' + \eta$, was observed from the temperature 250 °C to 310 °C, wherein the T' phase formed at the interface of ε platelet and η phase matrix. This T' phase was further identified as a rhombohedral structure. As the solution-treatment temperature was increased to above 310 °C, the ε phase was completely dissolved back into the η matrix and numerous β phase particles were distributed uniformly in the η matrix. The β phase subsequently decomposed at room temperature to a fine α phase embedded in the η matrix. For the materials solution-treated above 250 °C, the microhardness of the η matrix increased in 40 minutes during natural aging, which was associated with the formation of fine ε phase of 0.15-μm diameter. The orientation relationship between this fine ε phase and η phase was determined as $[\bar{1}011]_\eta$ // $[\bar{1}011]_\varepsilon$, $(01\bar{1}2)_\eta$ // $(01\bar{1}2)_\varepsilon$.

I. INTRODUCTION

THE Zn-4 Al-3 Cu alloy is a widely used commercial material for fabricating various construction parts through die casting. It is also a useful mold material in the trial mold applications for stamping and injection molding. The addition of copper results in an increase of strength of the alloy; however, the material will suffer dimensional instability over a period of time at ambient temperature. The dimensional expansion is related to the copper-rich ε phase precipitated in the η matrix during aging at slightly elevated temperature after casting.[1]

The phase transformations of heat-treated Zn-Al-Cu alloys have been well investigated in the isothermal process by many researchers, such as Köster,[2] Gebhardt,[3] and Murphy.[4] As a result, most of the ternary phase diagrams were established. The aging of zinc alloys containing 19 to 38 pct Al and 0 to 4 pct Cu take place in the following reactions suggested by Savaskan and Murphy[5] and Löbery:[6]

$\beta + \varepsilon \rightarrow \alpha + \eta$ at ~276 °C (eutectoid reaction)
$\alpha + \varepsilon \rightarrow T' + \eta$ at 268 °C (four-phase reaction)

One can see in the preceding reactions that the β phase is unstable at room temperature after quenching. It decomposes into α and η phases in 10 hours.[5] Some investigations[4,7] indicated that the ε phase was a stable phase at the temperature above 268 °C and would be replaced by a stable phase T' during long-time aging below 268 °C. In contrast, Kovacheva *et al.*[8] found that the ε phase dissolved in η phase above 260 °C through the measurement of differential thermal electromotive force in Zn-Al-Cu alloy. The crystal structure of T' phase (58 pct Al, 30 pct Cu, 12 pct Zn) present in the high-aluminum and high-copper zinc alloys was investigated by Arndt and Moeller[9] and Murphy.[10] They had established that T' has a rhombohedral structure (a = 8.68 Å, α = 27.4 deg) with CsCl-type cells. Most of the investigations were concentrated in the high-aluminum zinc alloys. However, little work has been done on phase transformation of Zn-Al-Cu alloy with lower aluminum content.

From the equilibrium ternary phase diagram of Zn-Al-Cu alloy,[4] it can be inferred that in Zn-4Al-3Cu alloy, the η phase (zinc-rich, hcp structure), ε phase ($CuZn_4$, hcp structure), and α phase (aluminum-rich, fcc structure) are the stable phases below eutectoid temperature. On the other hand, the stable phases are β, η, and ε phases above that temperature.

In the present work, the phase transformations of the primary η phase in an as-cast Zn-4 Al-3 Cu alloy during solution-treatment are investigated.

II. EXPERIMENTAL PROCEDURE

The alloy used in this study was Zn-4Al-3Cu alloy. Its alloy composition was analyzed by atomic absorption spectroscopy. The alloy was melted in vacuum and poured at 450 °C into a preheat permanent mold, then aged at room temperature for a period of more than 6 months before solution-treatment. The naturally aged specimens were defined as ''as-received'' specimens. For the measurements of electrical resistivity, 0.5 × 2.0 × 30-mm samples were

B.J. LI, formerly Graduate Student, Institute of Materials Science and Engineering, National Chiao Tung University, is Scientist, Materials Research Laboratories, ITRI, Hsinchu 31015, Taiwan, Republic of China. C.G. CHAO, Professor, is with the Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan, Republic of China.

Manuscript submitted October 27, 1997.

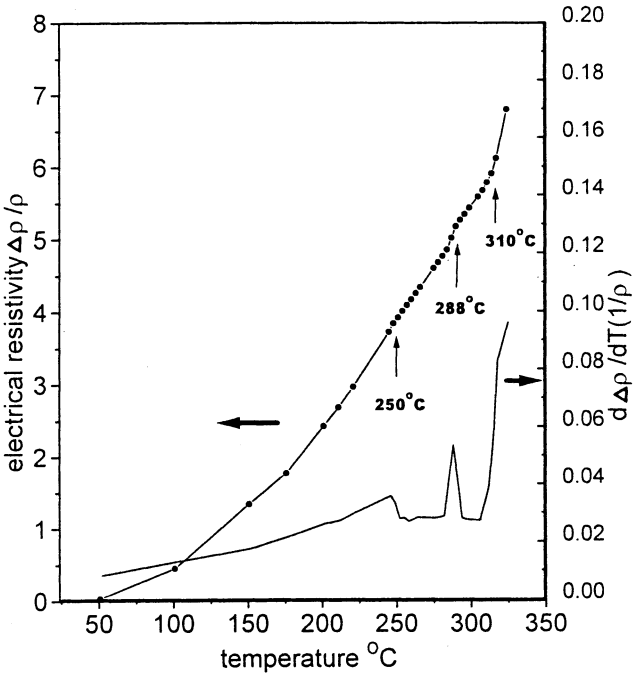


Fig. 1—The variations of relative electrical resistivity ($\Delta\rho/\rho$) and its temperature derivative ($d(\Delta\rho/\rho)/dT$) from 50 °C to 325 °C for the as-received alloy.

machined from the as-received billets. The electrical resistivity of the sample was monitored using a standard four-point probe technique from 50 °C to 315 °C. The as-received specimens were solution-treated at various temperatures (from 230 °C to 315 °C) for 1 hour in an inert gas atmosphere and then quenched in water.

Microhardness measurement was conducted using a Mitutoyo (Kanagawa, Japan) MVK-G1 hardness tester equipped with a Vicker's diamond pyramid indenter. Scanning electron microscopy (SEM) was used to examine the morphology, and electron probe microanalysis (EPMA) was carried out to measure the composition of the η matrix. The phases in the alloys were identified by SIEMENS* D5000 X-ray diffractometer with nickel - filtered Cu K_α radiation, scanning at a speed of 0.01 deg and a step time of 20 seconds.

*SIEMENS is a trademark of Siemens Electrical Equipment, Toronto.

Thin film specimens for transmission election microscopy (TEM) were prepared by means of a double-jet electropolisher with an electrolyte made up from 30 mL of perchloric acid, 250 mL of 2-butoxyethanel, and 700 mL of ethanol. The polishing temperature was kept between −15 °C and −25 °C, with a current density in the range of 0.3 to 0.7 A/cm^2. The TEM analysis was performed on a JEOL* 2000FX scanning transmission electron microscope operating at 200 kV.

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

III. RESULT

A. *Electrical Resistivity*

Figure 1 illustrates the variation of relative electrical resistivity ($\Delta\rho/\rho$) and its derivative with respect to temperature $d(\Delta\rho/\rho)/dT$ from 50 °C to 325 °C for the as-received alloy. It can be seen that the $d(\Delta\rho/\rho)/dT$ value increases gradually with increasing temperature and then experiences a sudden drop at 250 °C to a value, which remains unchanged between 250 °C to 310 °C except a unique peak at 288 °C. Beyond 310 °C, the $d(\Delta\rho/\rho)/dT$ value rises precipitously.

B. *X-Ray Diffractograms*

The X-ray diffractograms obtained from all the specimens are shown in Figure 2. It is clear that ε phase appears in all the solution-treated specimens, in addition to α and η phases, which were originally present in the as-received specimen. The (0002) reflection of ε phase appears at 42.5 deg for the specimen quenched from 240 °C. However, another reflection of ε phase (indicated by ε* in Figure 2) appears at 42.0 deg for the specimen solution treated above 240 °C.

Upon examining the X-ray diffraction (XRD) data, it was found that (0002) reflection of η phase shifted from 36.4 to 37.1 deg as the solution-treatment temperature was increased from 240 °C to 300 °C. The characteristic (433) reflection of the T' phase appeared at 44.8 deg for both solution-treatment temperatures, 280 °C and 300 °C. As the solution-treatment temperature was increased to 315 °C, the $(002)_\alpha$ and $(002)_\beta$ reflections began to appear. These $(002)_\alpha$ and $(002)_\beta$ reflections became more pronounced for the solution treatment extended to 24 hours at 315 °C. Figure 3 is an X-ray diffractogram of specimen solution treated at 315 °C for 24 hours and aged at room temperature for 90 days. The β phase disappeared after 90 days of natural aging (compared with Figure 2).

C. *Microstructure*

Figure 4 shows the backscattered electrons image (BEI) of the as-received material. The contrast in the BEI depends principally on the atomic number of elements present in different phases. It shows the as-cast structure of the naturally aged alloy, which consists of primary dendrites (η phase) and eutectic structure of β and η. The α phase (dark phase) precipitated in η matrix. According to the literature,[1,11] the α phase formed in the central regions of zinc-rich primary dendrites (η phase) immediately after casting.

The micrographs obtained from the specimens solution treated at 240 °C and 280 °C are shown in Figures 5 and 6, respectively. Platelike precipitates in η matrix (3-μm length and 0.5-μm thickness) are observed both in Figures 5 and 6. The composition of the platelike precipitate analyzed by EPMA is 84.0 pct Zn-1.0 pct Al-15.0 pct Cu (by weight), which is similar to that of ε phase.[6] The white phase of irregular shape in the eutectic region was also identified by EPMA to be an ε phase. In Figure 6(b), globular precipitates (dark, indicated by an arrow) also exist in addition to the ε platelets.

Figure 7 shows the BEI of the specimen solution treated at 315 °C × 24 hours. Numerous spherical particles (indicated by an arrow in Figure 7) are uniformly distributing throughout the η matrix without the presence of ε platelets. When solution-treatment temperature was increased to 350 °C, the lamellar eutectic structure was transformed to irreg-

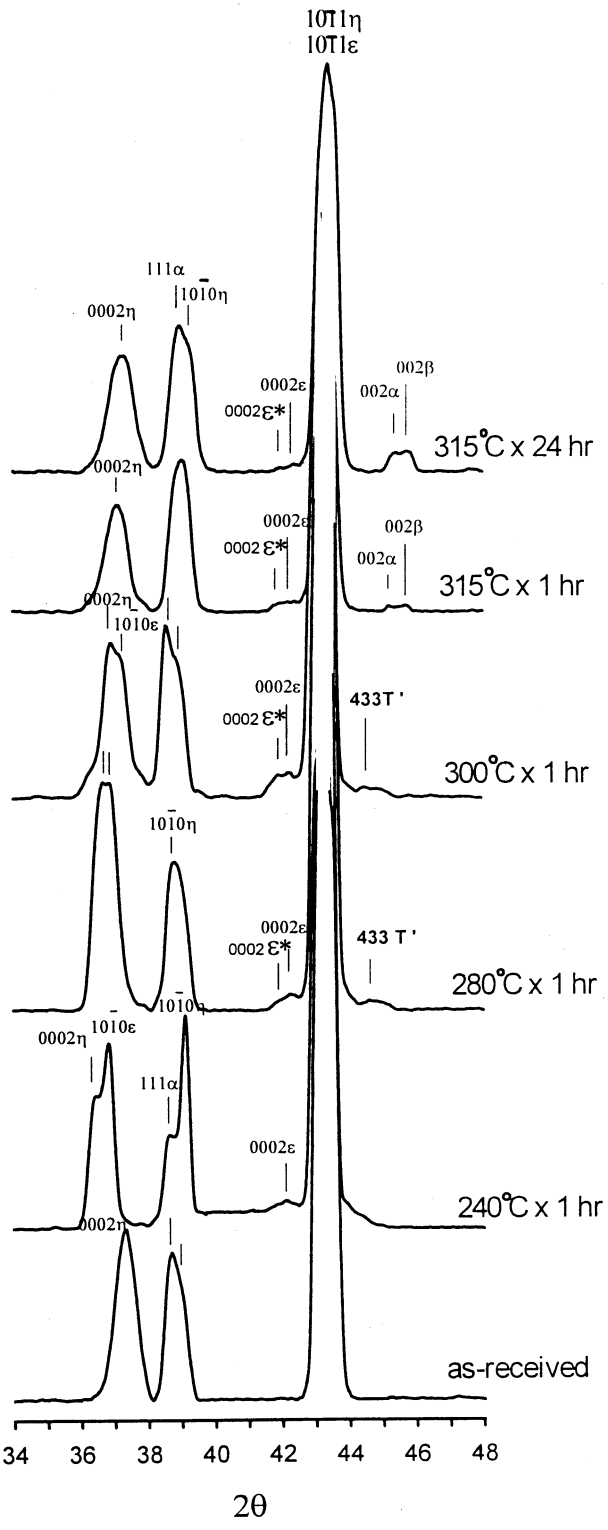


Fig. 2—X-ray diffractograms of specimens solution treated at various temperatures. It shows the $(433)_{T'}$ peak formed in the specimen solution treated at 280 °C and 300 °C, respectively. The phase indicated by ε^* is the same structure as the ε phase.

ular β phase, as shown in Figure 8. In addition, some globular β phase can also be observed in the η matrix.

The compositions of the η phase analyzed by EPMA with various solution-treatment temperatures are listed in Table I.

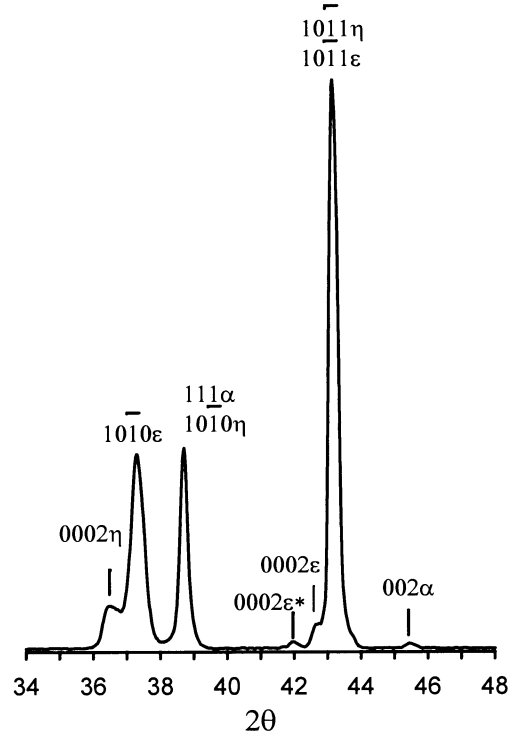


Fig. 3—X-ray diffractogram of specimen solution treated at 315 °C for 24 h and aging at room temperature for 90 days. It shows that no β phase presents in the specimen.

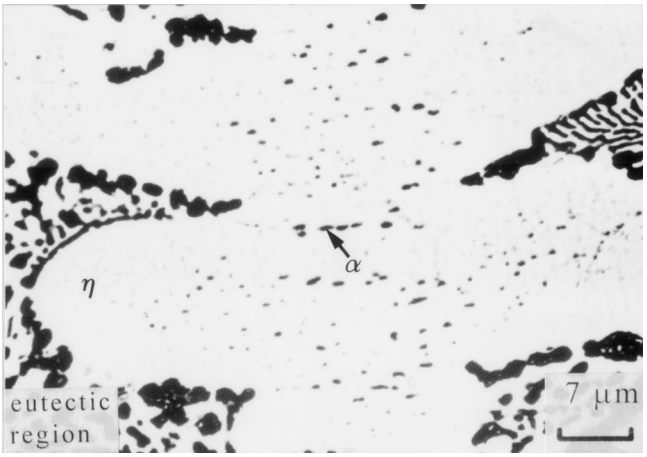


Fig. 4—BEI of as-received Zn-4Al-3Cu alloy. It shows that the as-cast structure of the naturally aged alloy consists of primary dendrites (η phase) and eutectic structure (β and η).

D. *TEM Observation*

Figure 9(a) shows that the T' phase formed at the interface between ε phase and η matrix in the specimen solution treated at 300 °C. In addition, some α phase is also observed. Figure 9(b) is the selected area diffraction pattern (SADP) from the [111] zone of T' phase, indicating the first-order Laue zone ($hu + kv + lw = 1$) of the T' phase, which is attributed to the relatively large lattice parameter ($a = 8.68$ Å) associated with the rhombohedral structure.[12] This led to the identification of {001}, as shown in Figure 9(b). Figure 10(a) is a TEM bright-field micrograph of the η matrix pertaining to the specimen solution treated at 280 °C and then naturally aged. It shows numerous precipitates

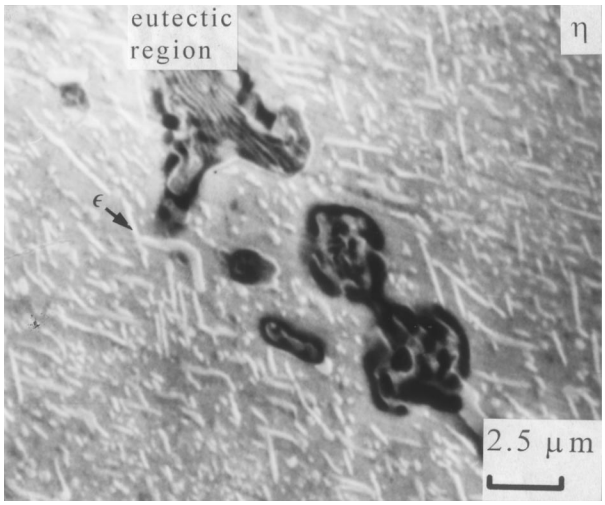
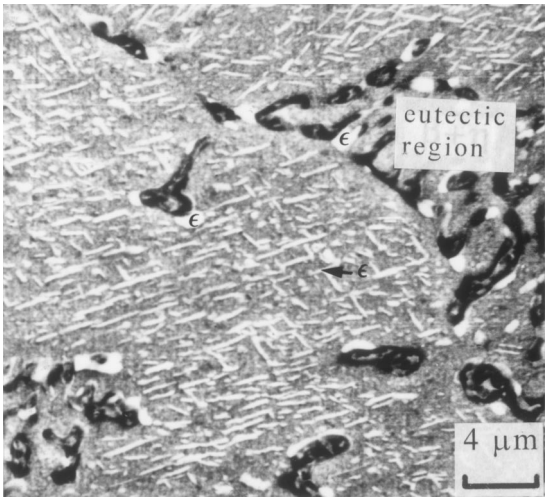
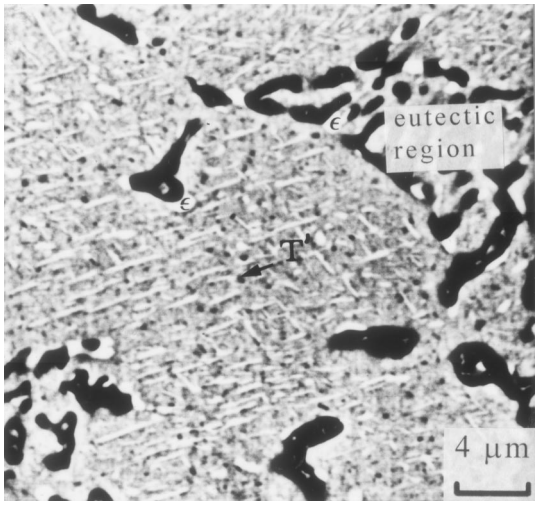


Fig. 5—Micrograph of the specimen solution treated at 240 °C. It shows ε platelets in the η matrix.



(*a*)



(*b*)

Fig. 6—(*a*) Micrograph and (*b*) BEI of the specimen solution treated at 280 °C. It shows that T' phase and ε platelets exist in the η matrix.

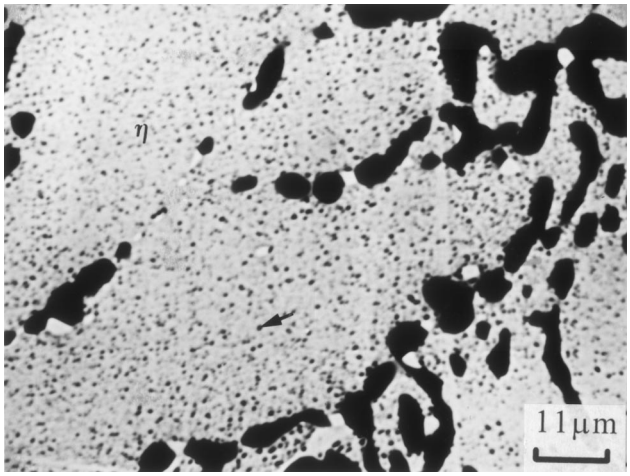


Fig. 7—BEI of the specimen solution treated at 315 °C for 24 h. It shows a distribution of β particles throughout the η matrix.

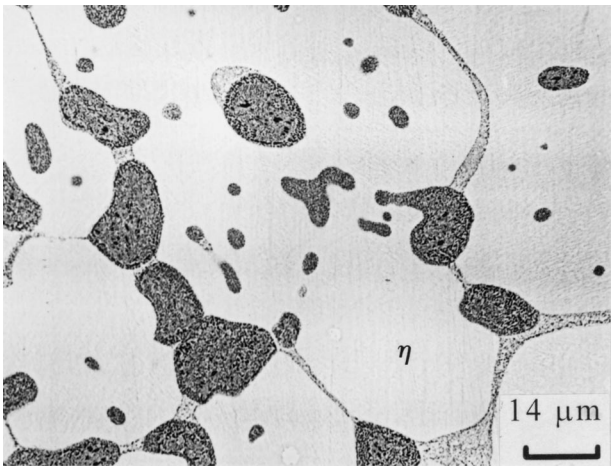
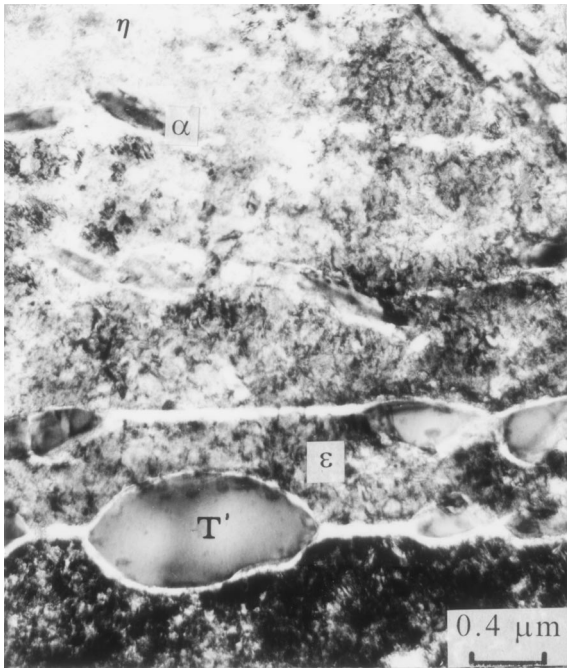


Fig. 8—BEI of the specimen solution treated at 350 °C. It shows irregular β phase instead of lamellar β phase in the eutectic region and some globular β phase presents in the η matrix.

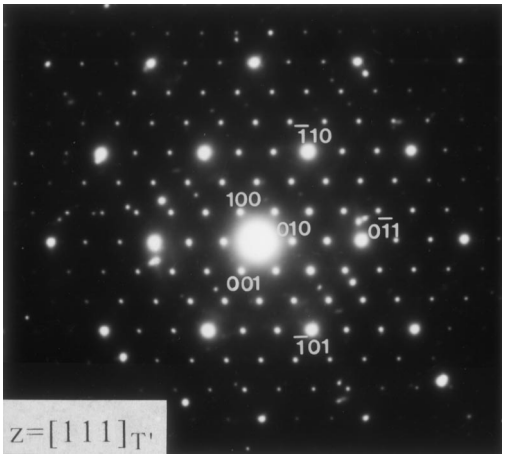
Table I. The Composition of η Matrix with Various Solution-Treatment Temperatures

Composition (Wt Pct)	Al	Cu	Zn
as-received	1.5 ± 0.1	3.8 ± 0.2	94.7 ± 0.2
240 °C × 1 h	1.9 ± 0.1	2.4 ± 0.2	95.7 ± 0.3
280 °C × 1 h	1.4 ± 0.2	3.1 ± 0.3	95.5 ± 0.4
300 °C × 1 h	1.3 ± 0.1	3.3 ± 0.2	95.4 ± 0.2
300 °C × 6 h	1.2 ± 0.1	3.5 ± 0.1	95.3 ± 0.2
350 °C × 1 h	0.5 ± 0.1	4.0 ± 0.1	95.5 ± 0.2

in the η matrix. Figures 10(b) and (c) are SADPs from the $[\bar{1}011]$ zone and $[\bar{2}\bar{2}43]$ zone of η matrix, which show the precipitate is a hcp structure. Figure 11(a) shows the bright-field TEM image of one of the numerous particles indicated by the arrow in Figure 7. The TEM micrograph shows the particle under high magnification, with a boundary (indicated by white triangles) separating itself from the η matrix. It can be seen that there are two phases present in the particle. The SADP (Figure 11(b)) identifies these two phases to be η phase and α phase.



(*a*)

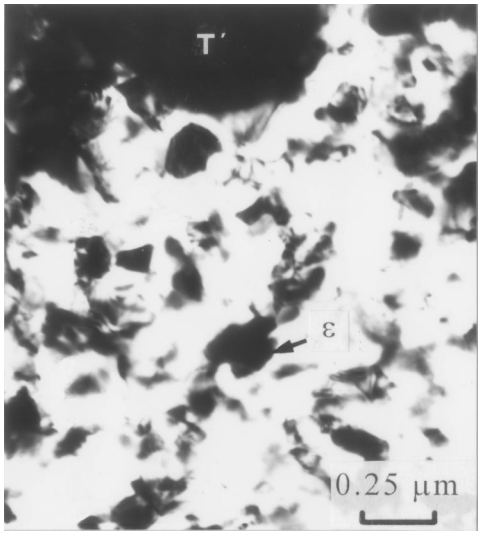


(*b*)

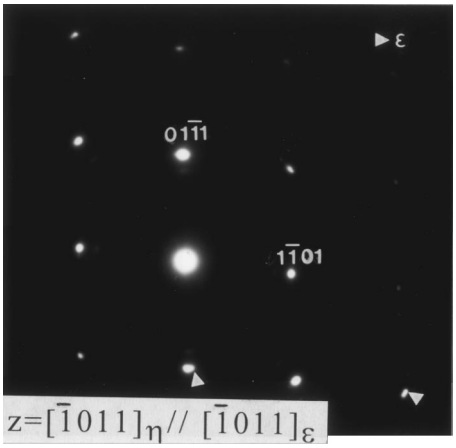
Fig. 9—(*a*) TEM bright-field micrograph derived from the specimen solution treated at 300 °C. It shows that the *T*′ phase forms at the interface between the ε platelet and η matrix. (*b*) SADP from [111] zone of *T*′ phase; the first-order Laue zone reflection spots are shown.

E. *Microhardness*

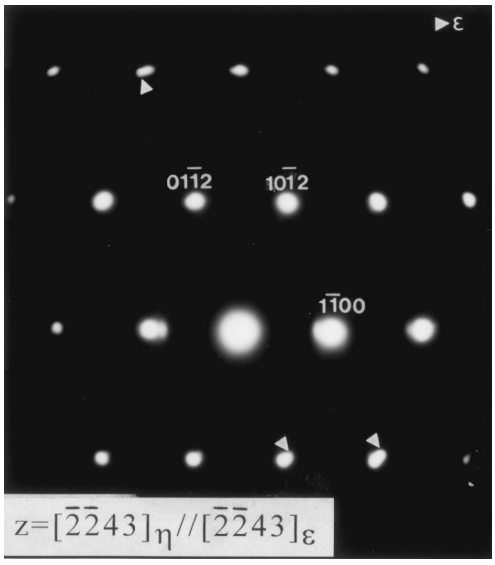
Figure 12 shows that the microhardness of η matrix is increased from HV124 to HV140, which took place in 40 minutes during natural aging after 280 °C solution treatment. However, in the case of solution treatment at 240 °C; the microhardness was kept unchanged. Figure 12 also shows that both microhardness and time derivative of relative electrical resistivity ($d(\Delta\rho/\rho)/dt$) show a similar trend during natural aging for the specimen solution treated at 280 °C. The maximum microhardness attainable during natural aging for various solution-treatment temperatures is shown in Figure 13. It can be clearly seen that the full potential of the solution plus aging treatment can only be realized for a solution-treatment temperature above 250 °C.



(*a*)

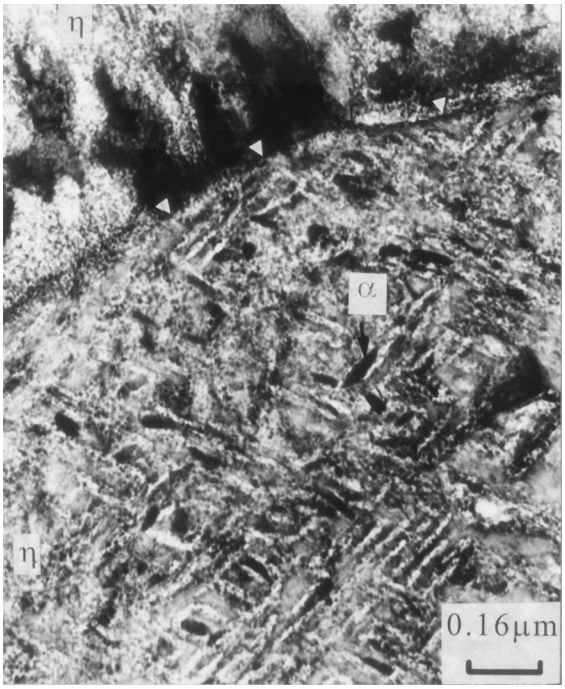


(*b*)

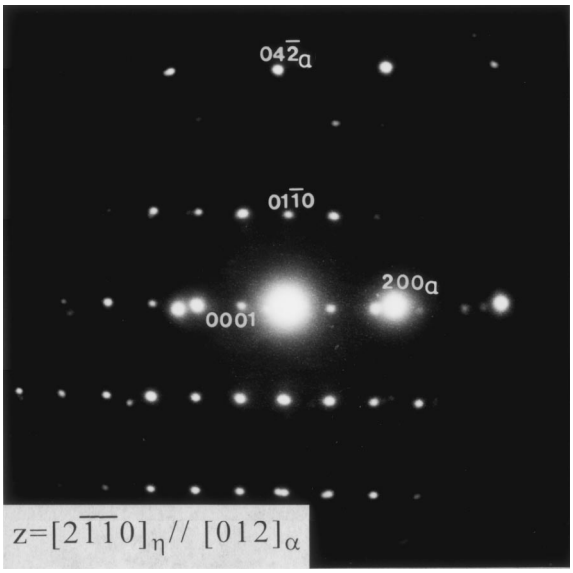


(*c*)

Fig. 10—(*a*) Convention TEM bright-field micrograph derived from the specimen solution treated at 280 °C and then natural aged for about 10 days. (*b*) SADP of [1011] zone of η matrix. The fine precipitate is ε phase with the same structure as η phase (hcp). (*c*) SADP from $[\overline{2}243]$ of η matrix.



(*a*)



(*b*)

Fig. 11—(*a*) TEM bright-field micrograph of a particle (indicated by white triangles) shown in Fig. 7. (*b*) SADP from the [$2\bar{1}10$] zone of the η phase; the diffraction spots from the [012] zone of the α phase are shown. It shows the particle is η phase embedded by tiny α phase.

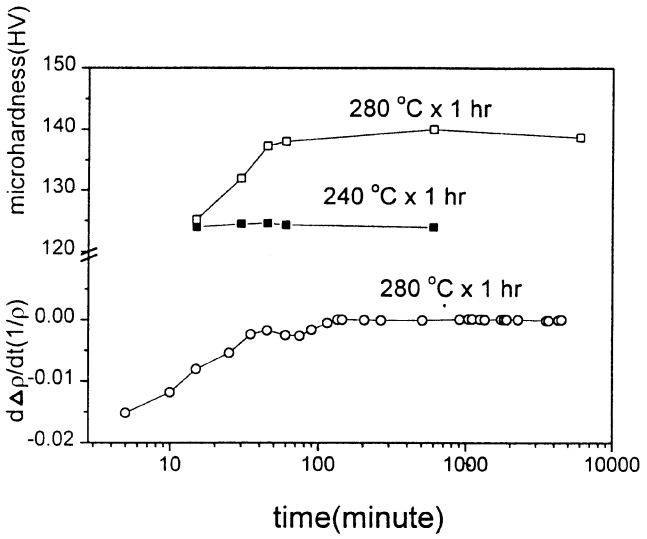


Fig. 12—The microhardness and the time derivative of relative electrical resistivity *vs* aging time during natural aging for the specimens solution treated at 240 °C and 280 °C, respectively.

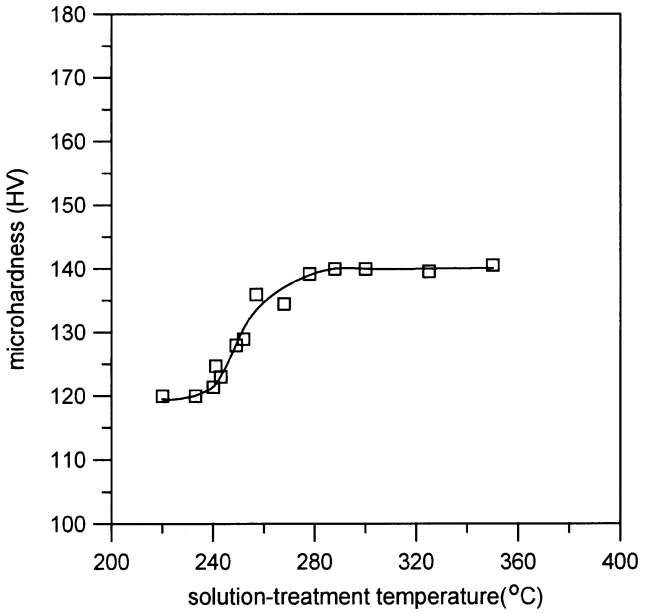


Fig. 13—The relationship between maximum microhardness of the η matrix attainable during natural aging and solution-treatment temperature.

IV. DISCUSSION

A. *Solution Treatment*

For the specimen solution treated at lower temperature (240 °C), the copper content in the η matrix was decreased from 3.8 pct (as-received) to 2.4 pct (240 °C solution treatment). The decrease of copper content in η matrix was associated with the formation of ε phase, which was identified by the result of EPMA and further confirmed by X-ray diffractograms in Figure 2.

It is well known that the electrical resistivity of an alloy is principally influenced by the solute content in the matrix. In Figure 1, one does not see the expected rise of $d(\Delta\rho/\rho)/dT$ between 250 °C and 310 °C, except a peak at 288 °C, which is eutectoid transition temperature. This anomaly can be understood by the following rationalization. As the solution-treatment temperature was increased from 250 °C to 310 °C, the copper content in the η matrix was increased (due to the dissolution of ε phase[8]); at the same time, the aluminum content in the η matrix was decreased (due to the formation of T' phase). The effect associated with the increasing copper content on resistivity was balanced off by that associated with the decreasing aluminum content. As a result, relatively constant value of $d(\Delta\rho/\rho)/dT$ was observed in Figure 1. It is also interesting to note that T' phase was observed to form at the interface between ε phase and η matrix for the specimen solution

treated at 300 °C (Figure 9). It is, therefore, speculated that the T' was formed involving the four-phase transformation, $\alpha + \varepsilon \rightarrow T' + \eta$, in the temperature range of 250 °C to 310 °C

For the solution treatments above 310 °C, the morphology of precipitates in η matrix changed entirely. Neither ε platelet nor T' phase was found in the η matrix. Instead, numerous β particles were seen, as indicated in Figure 7. The β phase decomposed to α and η phases at room temperature, as confirmed by TEM (Figure 11). The formation of β phase (80.1 pct Zn, 28 pct Al, 1.9 pct Cu) resulted in the increase of copper content and the decrease of aluminum content in the η matrix. There was a rapid increase of the copper content in η phase from 3.1 pct for the specimen quenched from 280 °C to 4.0 pct for the specimen quenched from 350 °C (listed in Table I). This was accompanied by the rapid increase of $d(\Delta\rho/\rho)/dT$ above 310 °C. The SEM observation coupled with EPMA analysis demonstrates that the ε phase is unstable above 250 °C and dissolves rapidly above 310 °C. The observation contrasts with the previous work by Murphy,[4] who showed the ε phase is a stable phase above 268 °C. However, the finding of this research is in agreement with that of Kovacheva *et al.*[8]

B. *Natural Aging*

As the solution treatment was increased to above 250 °C, the fine ε phase precipitated in the η matrix rapidly during natural aging due to the highly saturated η matrix with copper. Therefore, this resulted in an increase of microhardness. The negative value of $d(\Delta\rho/\rho)/dt$ in Figure 12 indicates that the resistivity of the specimen decreased due to the precipitation of the ε phase during natural aging. The SADP (Figure 10(b)) shows that there is a small angle between $(01\bar{1}1)_\varepsilon$ and $(01\bar{1}1)_\eta$. The result is similar to the previous work by Durman and Murphy,[13] who showed that the fine ε precipitate is semicoherent with η matrix, in addition to $(01\bar{1}0)_\varepsilon$ // $(01\bar{1}0)_\eta$, and $[0001]_\varepsilon$ was 4.5 deg from $[0001]_\eta$. The c-axis lattice parameter of η phase calculated from XRD data was decreased from 4.93 Å for the specimen quenched from 240 °C to 4.84 Å for the specimen quenched from 280 °C. This is believed to be caused by the large misfit of interplanar spacing at [0001] direction $((d_\varepsilon - d_\eta)/ d_\eta = -12.4$ pct), as suggested by Durman and Murphy. The c-axis lattice parameter of the fine ε phase (indicated by ε* in Figure 2) calculated from the XRD data is 4.30 Å, which is larger than that of the regular ε phase (4.25 Å). The increase of c-axis lattice parameter of the fine ε phase is believed to be associated with the constraint stress imposed by the semicoherent interface between the fine ε phase and η matrix. It is, therefore, concluded that the formation of fine ε phase is through the process of precipitation during natural aging after solution-treatment above 250 °C.

V. CONCLUSIONS

The phase transformations of Zn-4 Al-3 Cu were studied. The main results obtained from this work are as follows.

1. The ε platelets form with 3-μm length and 0.5-μm thickness for the specimen solution treated at 240 °C for 1 hour.
2. The four-phase transformation, $\alpha + \varepsilon \rightarrow T' + \eta$, occurs for the solution-treatment temperatures from 250 °C up to 310 °C. Furthermore, the T' phase forms at the interface between ε platelet and η matrix.
3. As the solution-treatment temperature is increased to above 310 °C, numerous β particles are distributed uniformly throughout the η matrix. The β phase subsequently decomposes to α and η during natural aging.
4. As the solution-treatment temperature is increased to above 250 °C, the microhardness of the η matrix increases in 40 minutes during natural aging due to the precipitation of fine ε phase.

REFERENCES

1. B.J. Li and C.G. Chao: *Metall. Mater. Trans. A*, 1996, vol. 27A, pp. 809-18.
2. W. Köster: *Z. Metallkd.*, 1941, vol. 33, pp. 278-83.
3. E. Gebhardt: *Z. Metallkd.*, 1941, vol. 33, pp. 297-305.
4. S. Murphy: *Z. Metallkd.*, 1980, vol. 71, pp. 96-102.
5. T. Savaskan and S. Murphy: *Mater. Sci. Technol.*, 1990, vol. 6, pp. 695-703.
6. K. Löhberg: *Z. Metallkd.*, 1983, vol. 74, pp. 456-57.
7. E. Gebhardt: *Z. Metallkd.*, 1942, vol. 34, pp. 208-15.
8. R. Kovacheva, R. Dobrev, S. Zadgorski, and A. Lilova: *Mater. Charact.*, 1993, vol. 31, pp. 217-24.
9. H.H. Arndt and K. Moeller: *Z. Metallkd.*, 1960, vol. 51, pp. 596-600.
10. S. Murphy: *Met. Sci.*, 1975, vol. 9, pp. 163-68.
11. M. Durman, K. Sawalha, and S. Murphy: *Mater. Sci. Eng.*, 1990, vol. A130, pp. 247-56.
12. K.W. Andrews, D.J. Dyson, and S.R. Keown: *Interpretation of Electron Diffraction Patterns*, Rank Precision Industries Ltd., London, 1971, pp. 31-49.
13. M. Durman and S. Murphy: *Acta Metall. Mater.*, 1991, vol. 39, pp. 2235-42.