The Correlations between the Eutectoid Transformation, Order-Disorder Transformation, and Martensitic Transformation in Cu_3Al Binary Alloys

By Norihiko Nakanishi*

In view of the fact that three kinds of phase transformations, i.e. an eutectoid decomposition \( \beta \rightarrow \alpha + \gamma_2 \), an ordering transformation \( \beta \rightarrow \beta_1 \), and a martensitic transformation \( \beta_1 \rightarrow \beta' \) have been observed on isothermal holding and cooling at different rates from the \( \beta \) region in Cu-Al binary alloys, the author has tried to obtain the T/T/T diagrams in order to show the correlations between these three transformations. In the case of tempering the \( \beta' \) martensite formed by water-quenching, the above three transformations have occurred in the reverse direction, and the T/T/T diagrams associated with the tempering process have also been determined.

Specific heat measurements and microscopic observations were carried out, and the X-ray diffraction pattern was used for phase identification during these heat-treatments.

As the result of the experiments, it was verified that the growth of the ordered domains of the Cu_3Al super-lattice occurred below the critical temperature for ordering, \( T_c \), when cooling from the \( \beta \) region, (therefore, the transformation \( \beta_1 \rightarrow \alpha + \gamma_2 \) appeared instead of the eutectoid transformation \( \beta \rightarrow \alpha + \gamma_2 \)) and then the \( \beta' \) martensite contained about 25% aluminium after air-cooling. On the other hand, in the case of tempering of quenched alloys the growth of the ordered domains occurred at temperatures above 400°C, and below 400°C the ordering did not occur, but the precipitation of \( \alpha \) or \( \gamma_2 \) appeared preferentially.

I. Introduction

The eutectoid transformation in Cu-Al binary alloys was proved to be analogous to that in steel as shown in the phase diagram, and the eutectoid and martensitic transformations have been observed when cooling the \( \beta \) phase.\(^{(1)}\)

Wassermann and other investigators have reported that when the alloy is cooled to temperatures below the eutectoid temperature 565°C from the \( \beta \) region, the Cu and Al atoms arrange themselves to form an ordered phase \( \beta_1 \) of the Fe_3Al type, below the critical temperature of ordering (about 520°C).\(^{(2)}\)

The \( \beta_1 \) phase is the so-called metastable super-lattice,\(^{(3)}\) and the formation of \( \beta_1 \) is not arrested even by rapid cooling. Therefore, it was confirmed qualitatively by means of X-ray and electric resistance measurements\(^{(4)}\) that \( \beta \) transformed into \( \beta_1 \) and followed by the transformation, \( \beta_1 \rightarrow \beta' \), when rapidly cooled.

The earliest work on the isothermal transformation for an eutectoid aluminium–copper alloy was published by Smith and Lindlief in 1933,\(^{(5)}\) and in succession this work has been investigated by Mack,\(^{(6)}\) Klier and Grymko,\(^{(7)}\) and Haynes.\(^{(8)}\)

These investigators attempted to clarify the correlations between the eutectoid decomposition \( \beta \rightarrow \alpha + \gamma_2 \) and the metastable transformation \( \beta \) and \( \beta' \).

The author has made a study with respect to the phase transformation in Cu-Al binary alloys by means of dilatometric measurements\(^{(9)}\) and he has found that the formation of \( \beta_1 \) has caused the alteration of the aluminium concentration in the parent phase, and affects the Ms temperature of the \( \beta_1 \rightarrow \beta' \) transformation.

The investigation described in the present paper was designed to obtain the correlations among the eutectoid transformation, order-disorder transformation, and martensitic transformation occurring during isothermal transformation and isothermal tempering.

II. Experimental Methods

Five alloys, containing 23.33 at %, 24.01 at %, 24.62 at %, 24.92 at % and 25.16 at % aluminium, were used for the specimens, whose chemical compositions are shown in Table 1. High purity aluminium and electrolytic copper were melted and cast into sand moulds.

The specimens used for the isothermal transformation were 5 mm in diameter, 10 mm in length

<table>
<thead>
<tr>
<th>Al at %</th>
<th>Al wt %</th>
<th>Fe wt %</th>
<th>Si wt %</th>
<th>Pb wt %</th>
<th>Cu wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.33</td>
<td>11.44</td>
<td>0.03</td>
<td>—</td>
<td>—</td>
<td>Bal</td>
</tr>
<tr>
<td>24.01</td>
<td>11.53</td>
<td>0.07</td>
<td>—</td>
<td>—</td>
<td>Bal</td>
</tr>
<tr>
<td>24.62</td>
<td>12.18</td>
<td>0.08</td>
<td>0.13</td>
<td>—</td>
<td>Bal</td>
</tr>
<tr>
<td>24.92</td>
<td>12.35</td>
<td>0.08</td>
<td>—</td>
<td>0.02</td>
<td>Bal</td>
</tr>
<tr>
<td>25.16</td>
<td>12.49</td>
<td>0.03</td>
<td>—</td>
<td>—</td>
<td>Bal</td>
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</tbody>
</table>

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(1) Obinata: X-ray Metallurgy, (1940), 165.
(2) G. Wassermann: Metallwirt., 13 (1934), 133.
(3) S. Nagasaki: Metal Physics, 5 Special Issue (1959), 41.
(6) D. J. Mack: Trans. AIME, 175 (1947), 240.
(7) E.P.Klier and S.M.Grymko: Trans. AIME, 185 (1949), 611.
and the cylindrical specimens for the specific heat measurement were 20 mm in diameter, 25 mm in length and had a hole 4 mm in diameter in the centre. All the specimens were annealed at 950°C for 20 hrs. in vacuum (10^{-3} \text{mmHg}) before the heat-treatments, and then isothermal holding and tempering in a salt-bath were carried out. For the purpose of microscopic observation, the specimens were mechanically polished, electrolytically etched in a H_3PO_4 solution. And in special cases etched in a FeCl_3 solution again.

The specific heat measurement was carried out after Smith's method. Moreover, various phases which appeared during the heat-treatments were identified by X-ray diffraction.

III. Experimental Results

1. On the isothermal transformation

The phase diagram for the Cu-Al binary system was shown in Fig. 1. The eutectoid composition is about 23.96 at% Al and the eutectoid temperature is 565°C. The eutectoid decomposition $\beta \rightarrow \alpha + \gamma_2$ occurred only during slow cooling. On the other hand, an ordering reaction $\beta \rightarrow \beta_1$ takes place below 500°C in place of the eutectoid decomposition at a cooling rate above 10^{-15} \text{°C/min}. The T/T/T diagrams obtained are shown in Fig. 2~4. There are some characteristic features associated with the difference in respective Al contents.

The “start” and “end” curves for the $\beta \rightarrow \beta_1$ transformation are shown in Fig. 2~4, in which the times at which nodules and sheaths with $\alpha$ first appeared and finally spread out were plotted against the various holding temperatures respectively.

Especially in Fig. 4, the time at which the sheaths with $\gamma_2$ disappeared was plotted for the “end” curve for the $\beta \rightarrow \beta_1$ transformation. Some characteristics in T/T/T diagrams may be pointed out as follows:

1. The “start” curve for the pro-eutectoid $\alpha$ forms a double C shape above and below the critical temperature of ordering (Tc ≈ 500°C), in the 23.33 at% Al-Cu alloy (Fig. 2).

2. Pro-eutectoid $\gamma_2$ appears above Tc, and below Tc the pro-eutectoid $\alpha$ appears in the hyper-eutectoid alloy of 24.62 at% Al content (Fig. 3).

3. In the 25.16 at% Al-Cu alloy (near the Cu_3Al composition), the pro-eutectoid $\gamma_2$ phase which should be expected to appear at and above Tc is not observed at temperatures below Tc, and the eutectoid decomposition occurs directly from $\beta_1$.

4. The “eutectoid start” forms also a double C shape like the pro-eutectoid $\alpha$ in Fig. 2, and the $\beta_1 \rightarrow \alpha + \gamma_2$ transformation occurs in stead of the $\beta \rightarrow \alpha + \gamma_2$ transformation below Tc, as it is shown in Fig. 2~4.

In order to re-examine the complicated phenomena depending on the ordering reaction, which were observed in T/T/T diagrams, the specific heat measurements were carried out with specimens in which the isothermal transformation were accomplished.

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Fig. 1 Phase diagram for eutectoidal Cu-Al alloys.
Fig. 2 T/T/T diagram for 23.33 at % Al-Cu alloy.
Fig. 3 T/T/T diagram for 24.62 at % Al-Cu alloy.
The specific heat vs. temperature curves of the alloys containing 24.01 at% and 24.92 at% Al respectively are shown in Fig. 5, 6. In Fig. 5 (a), the Cp vs. T curve of the $\beta'$ martensite water-quenched from 1000°C is illustrated for comparison;

a heat-evolution appeared at about 250°C, and followed by a heat-absorption above 400°C (its peak at 496°C) and last a large heat-absorption at 565°C. The exothermic reaction that appeared at 250°C is always observed on the tempering process of the $\beta'$ martensite in hypo-eutectoid composition. This phenomenon may be supposed to have a relation to $\alpha$ super-saturated with Al. It is reasonable to think that the peak of heat-absorption that appeared at 466°C corresponds to the $\beta'$ martensite in hypo-eutectoid composition. The abnormal heat-absorption that appeared at 565°C is due to the $\gamma_2 \rightarrow \beta$ transformation. However, it is significant that the peak of heat-absorption occasioned by the $\beta_1 \rightarrow \beta$ transformation is not observed because the exothermic reaction by the $\beta_1 + \beta \rightarrow \alpha + \gamma_2$ cancels the endothermic reaction of the $\beta_1 \rightarrow \beta$ transformation at about 500°C, while an abnormal expansion and an increase on specific resistance occurred by the disordering reaction $\beta_1 \rightarrow \beta$ were evidently observed.

The peak of heat-absorption occasioned by the $\beta' \rightarrow \beta_1$ shifts to the lower temperature side after holding at 490°C, slightly below Tc, for 3 mins., as it is seen at curve (b). The curve (c) shows the case of isothermal holding at 440°C for 30 mins., the peak moves to a lower temperature than at curve (b) and is observed at 360°C. Similarly, this peak is observed at the range 360~370°C in the case of holding at 400°C for 1 hr., as shown in curve (d). At last, the curve (e) shows the case of holding at 350°C for 1 hr., the peak of heat-absorption occasioned by the $\beta' \rightarrow \beta_1$ transformation separates into two peaks at 370°C and 450°C respectively. The specific heat curves after isothermal holding with the 24.92 at% Al-Cu alloy (near the Cu₃Al composition) are shown in Fig. 6. The tendency of reactions is the same as in Fig. 5. First, concerning the water-quenched specimen as shown in curve (a), it is observed that the peak of the heat-absorption occasioned by the $\beta' \rightarrow \beta_1$ transformation appears at 398°C and a small peak of heat-absorption by the $\beta_1 \rightarrow \beta$ transformation appears at 515°C. Secondly, in the case of holding at 450°C for 2.5 hrs. as shown in curve (b) and at 350°C for 7 hrs. as shown in curve (d), the peak of the $\beta' \rightarrow \beta_1$ transformation shifts to a slightly lower temperature side and is observed at 380°C. Finally, as is shown in curve (e), the peak tends to move to a higher temperature side after holding at 325°C for 10 hrs.

The special characteristic shown in the above specific heat curves is in good agreement with the
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The author has already studied the nature of the transformation process \( \beta \rightarrow \beta_1 \rightarrow \gamma \) during cooling at various rates from the \( \beta \) region. Then, the \( C_p \) vs. \( T \) curves of the 24.01 at% Al-Cu alloy which is air-cooled from 900°C are shown in Fig. 7.

Fig. 7 \( C_p \) vs. Temp. curves for 24.01 at% Al-Cu alloy after air-cooling and water-quenching.

The curve (a) shows the \( C_p \) vs. \( T \) curve after water-quenching from 900°C; the peak of the \( \gamma \rightarrow \beta \) transformation is observed at 460°C. On the other hand, at curve (b) which shows the \( C_p \) vs. \( T \) curve for the specimen air-cooled from 900°C, the peak of the \( \gamma \rightarrow \beta \) transformation is observed at approximately 380°C.

Therefore, it may be supposed that an alteration of Al concentration has occurred during the air-cooling, depending on the growth of the ordered domains.

3. On the transformation during tempering

According to experiments with isothermal decomposition and the cooling process of the \( \beta \) phase, it has been observed that the ordering reaction \( \beta \rightarrow \beta_1 \) was formed first and followed by the eutectoid reaction \( \beta_1 \rightarrow \alpha + \gamma \).

In the present case, in order to ascertain the behavior of the ordering reaction during tempering, the \( \beta' \) martensite obtained by water-quenching from \( \beta \) was isothermally held at various temperatures.

The \( T/T/T \) diagrams for the 24.01 at% and 24.92 at% Al-Cu alloys are shown in Fig. 8 and 9 respectively. To determine the “start” and “end” curves for the pro-eutectoid and eutectoid reactions, microscopic observation and analysis of specific heat curves after tempering were carried out, and
X-ray diffraction analyses was made for phase identification.

In Fig. 8 obtained for the 24.01 at % Al–Cu alloy, the pro-eutectoid $\alpha$ is observed, and also the amount of the $\alpha$ decreases rapidly at temperatures below 400°C as shown in Fig. 9. Further it is observed

that the pro-eutectoid $\gamma_2$ tends to precipitate in the 24.92 at % Al–Cu alloy (near the Cu$_3$Al composition).

Thus, it was recognized that the ordering reaction governed the nature and the temperature’s range of transformation above about 380°C.

Some representative Cp vs. T curves after tempering are shown in Fig. 10 and 11. In Fig. 10, curve (a) is the Cp vs. T curve of the $\beta'$ martensite by water-quenching as mentioned above. In curve (b), the $\beta'$ martensite has almost been decomposed during tempering at 500°C for 1 hr., but the heat–evolution is only observed at 250°C, which might be due to the precipitate, $\alpha$. On tempering at 450°C for 5 mins., as shown at curve (c), the peak of heat-absorption by the $\beta' \rightarrow \beta_1$ transformation separates into two peaks in which one is observed at 378°C and the other is observed at 450°C respectively. The same behavior is observed in the specimen tempered at 350°C for 22 hrs., curve (d). On tempering at a lower temperature, 350°C for 8.5 hrs. curve (e). Decomposition of $\beta'$ did not occur during tempering at 350°C for one day.

The Cp vs. T curves after tempering in the alloy containing 24.92 at % Al close to the Cu$_3$Al composition are shown in Fig. 11.

1. A curve (a) shows the water–quenched one as mentioned already.

2. The peak of heat-absorption by the $\beta' \rightarrow \beta_1$ transformation moves to a slightly lower temperature side when tempered at 525°C for 2 mins. curve (b).

3. A sharp peak caused by the $\beta' \rightarrow \beta_1$ transformation is observed at 380°C when tempered at 415°C.
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for 5 mins. curve (c).

Furthermore, on tempering at 405°C for 1 min., the peak by the β'→β₁ transformation tends to separate into two peaks in which one is observed at the higher temperature side of curve (d).

(4) On tempering at 370°C for 5 hrs., the peak again moves to the higher temperature side and is observed at 440°C curve (e), and a little heat-evolution has been observed in the range 200~350°C as shown in curve (c)~(e).

In brief, an interesting phenomenon shown in Fig. 11 is that the β' martensite containing a slightly higher Al content than 24.92 at% has been formed during isothermal tempering at temperatures above 400°C due to the ordering reaction, on the contrary below 400°C, the alteration of Al concentration into the lower side has occurred due to the precipitation of γ₂.

Lastly, some representative microstructures of the 24.92 at% Al-Cu alloy on tempering are shown in Photo. 4, 5. In Photo. 4 the eutectoid decomposition is observed at the grain boundary (dark) and the pro-eutectoid γ₂ is surrounded by the sheath. The needle-shaped α₃, the eutectoid decomposition (dark), and the white region corresponding to Cu₃Al composition are observed in Photo. 5.

IV. Discussion

As it has been shown in Fig. 2~4, the “start” and “end” curves for the β→β₁ transformation in the T/T/T diagrams were determined by means of the microscopic observation, in which some special behaviors of rosette-shaped nodules and the sheaths enveloping the pro-eutectoid precipitates were observed. The author has identified the growth of the rosettes with the development of domains of order β₁. On the other hand, Klier and Grymko have reported that these rosettes and sheaths are not β₁ because a water-quenched alloy containing 11.9 wt% Al has an ordered structure by X-ray test, but does not reveal the metallographic structure such as given above. From the experimental result shown in Fig. 4, it may be considered that the rate of the β→β₁ reaction so increased at temperatures close to 400°C that the rosette-shaped nodules spread out uniformly and joined together. Mack(6) has reported that the Ms point of the martensite transformed from β₁ is 385°C and the Ms point of the martensite transformed directly from β is 93°C in an eutectoid alloy. This could not be recognized during the present study.

According to the results of the dilatometric, electric specific resistance, and specific heat measurements, it is reasonable to think that the Ms point of the martensite transformed by water-quenching is constant and this martensite structure contains the ordered domains which distribute finely within it, and so the Ms point of this martensite does not depend on the Al concentration of ordered domains but is characteristic of the initial Al concentration of the alloy.

Here, the author proposes therefore a free-energy diagram shown in Fig. 12 in order to explain summarily the correlations among the phase transformations during the isothermal holding, during the cooling, and during the tempering.

It is well known that the relationship between the phases in the phase diagram will be explained by the mutual position relation of corresponding free energy vs. composition curve in various temperatures. Free energy curves of α₃, β, γ, β₁, and β' in various temperatures may be assumed to take a relative position as described in Fig. 12 (a)~(g), in which the β₁, β' having the ordered structure form a deep valley shape at 25 at% Al in the free energy curve.

First to the question why the “start” curves for the pro-eutectoid α and eutectoid decomposition formed the double C shape on T/T/T diagram (Fig. 2), and why the pro-eutectoid γ₂ occurred at temperature above Tₑ, but it was eventually replaced by the pro-eutectoid α below Tₑ in the 24.62 at% Al-Cu alloy (Fig. 3), the answer may be given from Fig. 12 (c)~(e). That is, the β phase is more stable than the β₁ phase at Tₑ>T>Tₐₑ, then an equilibrium state between β and α is set up for the 23.33 at% Al-Cu alloy (in Fig. 2 and Fig. 12 (c)), but β₁ becomes more stable than β at Tₑ>Tₐₑ>Ms, then an equilibrium between β₁ and α is set up, causing higher Al concentration within α (Fig. 12 (e)). This is the reason for the double C shape in Fig. 2.

On the other hand, in the 24.62 at% Al-Cu alloy, the pro-eutectoid γ₂ occurs according to the equilibrium state between β and γ₂ at Tₑ>Tₐₑ, and
the pro-eutectoid $\alpha$ occurs at $T_c > T > T_m$ according to the equilibrium between $\beta_1$ and $\alpha$ (Fig. 3 and Fig. 12 (c)–(e)). The eutectoid decomposition occurred directly from $\beta_1$ according to the equilibrium condition between $\beta_1$ and $\alpha$ and $\gamma_2$ at the low temperatures in the 25.16 at% Al-Cu alloy (Fig. 4 and Fig. 12 (c)–(e)). Furthermore, it would be reasonable to think that $\beta_1$ becomes more stable than $\beta$ during cooling, as shown in Fig. 7 and Fig. 12 (c)–(e), causing the precipitation of the pro-eutectoid $\gamma_2$, and then the martensite containing the Al concentrations close to 25 at% is formed.

Thinking about the characteristics obtained in $T/T/T$ diagrams associated with tempering, the $\beta_1$ phase is more stable than the $\beta$ and $\beta'$ phases in the range $T_c \sim 380^\circ C$, as shown in Fig. 12 (e), then the pro-eutectoid $\alpha$ occurs in the 24.01 at% and 24.92 at% Al-Cu alloys. On the other hand, $\beta'$ becomes more stable than $\beta_1$ on tempering at temperatures below 380°C, as shown in Fig. 12 (f), (g), and further it may be assumed that in the temperature range $T \geq \beta' \rightarrow \beta_1$ ($\sim 380^\circ C$) the precipitation of $\gamma_2$ from $\beta'$ is preferred to the precipitation of $\alpha$. Then it may be easily understand that the decomposition reaction of $\beta'$ is extremely delayed in the 24.01 at% Al-Cu alloy and on the contrary the pro-eutectoid $\gamma_2$ appears in the 24.92 at% Al-Cu alloy. Therefore, it is understood that the peak of heat-absorption by the $\beta' \rightarrow \beta_1$ transformation moved to higher temperature side in the 24.92 at% Al-Cu alloy. The $T/T/T$ diagrams associated with tempering in the present study is in good agreement with the one which was published recently by Cope. (11) Although Hull and Garwood (12) have recognized the behavior of the ordered domains in Cu-Al-Ni alloy containing 7.7 wt% Ni, Haynes (8) has proposed another hypothetical diagram.

V. Conclusions

(1) The isothermal transformation diagrams have been formed for the three kinds of alloys containing 23.33 at%, 24.62 at%, and 25.16 at% Al respectively. Summarizing the kinetics of the transformation, it is stated as follows;

$$\text{at } T \geq T_c, \quad \beta' \rightarrow \beta + \alpha + E + \beta_1$$

$$\text{at } T < T_c, \quad \beta' \rightarrow \beta_1 + \alpha + E + \beta_1$$

$\text{Th}$ and $E$ are the holding temperature and eutectoid decomposition respectively.

(2) During the air-cooling of the 24.01 at% Al-Cu alloy from the $\beta$ region, it has been confirmed that the $\beta'$ martensite containing 25 at% Al, which corresponds to a Cu$_3$Al composition, has been formed, following the precipitation of the pro-eutectoid $\alpha$.

(3) The $T/T/T$ diagrams associated with the isothermal tempering of the $\beta'$ martensite for the 24.01 at% and 24.92 at% Al-Cu alloys have been obtained. The kinetics of transformations during the tempering are summarized as follows;

$$\text{at } T \geq T_c, \quad \beta' \rightarrow \gamma_2 + E$$

$$\text{at } T < T_c, \quad \beta' \rightarrow \beta_1 + E$$

$$\text{at } T \geq T_c, \quad \beta' \rightarrow \beta_1 + \gamma_2 + E$$

$$\text{at } T < T_c, \quad \beta' \rightarrow \beta_1 + \gamma_2 + E$$

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