Reversion Phenomena in an Aluminium-4% Copper Alloy*

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Reversion characteristics due to the dissolution of G. P. zones in an Al-4wt% Cu alloy has been investigated by means of the electrical resistivity measurement and tensile tests. When the state of the aged alloy shows the electrical resistivity higher than that in the as-quenched state, the reversion heat treatment results in a decrease in electrical resistivity. On the other hand, when the state of the aged alloy shows the resistivity lower than that in the as-quenched state, the electrical resistivity increases in the initial stages of reversion and the electrical resistivity versus reversion time curve shows a peak. In all cases, the tensile strength decreases by the reversion treatment. It has been concluded that only the dissolution of the G. P. zones is responsible for the reversion.

A complete reversion can only be observed above the minimum temperature, T_{GP} , which depends sensitively upon the ageing temperature and the time corresponding with the stability of the G. P. zones formed during the ageing. Rather complicated reversion characteristics of this alloy reported in the literatures can be fully explained taking into account the stability of the G. P. zones as a function of ageing temperature and time. In Al-4wt% Cu alloy, the highest possible temperature for the formation of the G. P. zones is estimated to be 275°C.

The reversion kinetics shows that the reversion is rate-controlled by the diffusion of copper atoms in the matrix and the activation energy for the reversion is sensitively affected by the excess vacancies introduced in the alloy by quenching before ageing.

(Received August 16, 1971)

I. Introduction

The reversion phenomena in an age-hardened alloy system are closely related to the thermodynamical stability of G.P. zones. It is, therefore, considered as a reliable evidence that so-called low-temperature ageing is independent of high-temperature-ageing and that the G.P. zones are not necessarily formed as nuclei of the precipitates⁽¹⁾. The mechanisms of the reversion discussed by many authors can be classified into two types; one based on the concept of the critical size in the nucleation theory and the other on the metastable phase diagram for the G.P. zones. It appears, however, that no detailed experimental investigations on the reversion have been carried out. Recently, the present authors⁽²⁾⁽³⁾ investigated the mechanism of the reversion in Al-Ag alloys and showed that the mechanism based on the metastable phase diagram for the G.P. zones, rather than that on the critical size, was favorable for the reversion. In the present work, similar experiments have been carried out with an Al-Cu alloy and somewhat different behaviors from those in Al-Ag alloys have been found.

Before the discovery of G.P. zones by X-ray analysis, Gayler⁽⁴⁾ found that an Al-4% Cu alloy age-hardened at room temperature exhibited a reversion phenomenon. Since then, the hardness-reversion has been verified in various aluminium alloys^{(5)~(7)}. Gerold⁽⁸⁾ showed

that the reversion in Al-Cu alloys resulted from the re-solution of G.P. zones into the matrix. Subsequent work by Mondolfo⁽⁹⁾ on the reversion as a function of ageing time revealed that the degree of the hardness-reversion in naturally aged Al-4% Cu alloy decreased with ageing time. Extrapolating his experimental results, he inferred that no reversion would take place if the alloy was aged at room temperature for 5×10^3 hr. He attributed the decrease in the degree of reversion with ageing time to the transformation of G.P. zones into the θ' precipitate. In contrast with his interpretation, it has been shown by Hardy et al.⁽¹⁰⁾ that in this alloy the θ' precipitate is not detected by X-ray diffraction even after ageing for 25000 hr at room temperature. Prakash and Nijihawan⁽¹¹⁾ carried out a similar experiment to that by Mondolfo and showed that the reversion treatment at higher temperature ($> 190^\circ\text{C}$) could result in a complete reversion even after ageing for 5×10^4 hr at room temperature. They interpreted the difference between their results and Mondolfo's taking into account the contributions from the dislocation loops to the age-hardening and its reversion in Al-Cu alloy. However, there remain various experimental results which cannot be explained from such a point of view.

As for the metastable phase diagram of the G.P. zones, Beton and Rollason⁽¹²⁾ verified that there exists the minimum temperature above which a complete reversion is possible. They identified this temperature with the

* This paper was originally published in Japanese in J. Japan Inst. Metals, 35 (1971), 364.

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solvus temperature of the G.P. zones. However, they disregarded the effects of the ageing conditions on the minimum temperature for the complete reversion as will be discussed in section IV.

The present work has been carried out to obtain further information on the reversion behaviors in Al-4% Cu alloy, particularly on the stability and the dissolution kinetics of the G.P. zones.

II. Experimental Procedures

An Al-4.0 wt% Cu alloy was prepared from high purity materials. The cast ingot was homogenized at 540°C for 7 days, cold swaged with intermediate anneals and finally drawn into wires, 1 mm (for the tensile tests) and 0.45 mm in dia. (for the electrical resistance measurements).

The specimens were solution heat-treated at 540°C for 30 min and then quenched into iced-water. The specimens were transferred into liquid nitrogen within 5 sec after quenching. Heat treatments for ageing and reversion were carried out in oil baths (40°~160°C) or nitrate salt baths (170°~280°C).

Electrical resistance measurements were conducted at the liquid nitrogen temperature by a conventional method using two DC potentiometers. The resistance change due to the fluctuation of the temperature of liquid nitrogen was corrected by measuring the resistivity of the dummy specimen.

Tensile tests were carried out at room temperature. The gauge length was 50 mm and the cross-head speed was 1 mm/min.

III. Experimental Results

1. Ageing characteristics

To check the state of the aged alloy before the reversion heat-treatments, ageing curves of the electrical resistance and the 0.2% proof stress were obtained. Figure 1 shows changes of the resistivity on ageing at 40°, 130° and 190°C. On ageing at 40°C, the resistivity increases to a maximum and then decreases, while on ageing at 130°C it decreases almost continuously. On the other hand, the resistivity drops rapidly

Fig. 1 Resistivity ageing curves of Al-4% Cu alloy at 40°, 130° and 190°C.

in the initial stages of ageing at 190°C; until 2000 sec, it retains a value which appears to be constant within an experimental error and then decreases again. Corresponding to the initial rapid decrease of the resistivity at 190°C, the decrease of the strength is observed at 200°C as shown in Fig. 2. This can be attributed to the dissolution of small clusters formed during quenching and the value of the strength after annealing at 200°C for a few sec (8 kg/mm²) can be recognized as being that of the homogeneous solid solution without any clustering of the solute atoms and thus will be referred to that of the completely reverted state of the alloy in the following discussions.

Fig. 2 Strength ageing curves of Al-4% Cu alloy at 130° and 200°C. Hardness ageing curve obtained by Silcock et al. is also shown for comparison.

In Fig. 2 the change of the strength on ageing at 130°C is also shown in comparison with the hardness ageing curve obtained by Silcock et al.⁽¹³⁾ In contrast to the hardness, the strength increases markedly in a very short ageing period followed by a gradual increase. The initial rise in the strength may be considered to be due to the formation of clusters of the solute atoms assisted by quenched-in vacancies. A large increase of the strength after ageing for 100 hr may be attributed to the precipitation of the θ'' phase.

2. Reversion

Experiments of reversion kinetics were conducted with the alloys aged at 40°C for 15 min and at 130°C for 22 hr, and the specimens aged at 130°C for 10 and 100 hr and at 160°C for 10 hr were also used in order to investigate the relation between the stability of the G.P. zones and the reversion. Examples of the resistivity versus reversion time curves are shown in Fig. 3. By the reversion heat treatment, the resistivity of the specimen aged at 40°C decreases monotonously. After a longer reversion treatment, the resistivity approaches a constant value independent of the reversion temperature, T_R . On the other hand, the resistivity versus reversion time curves of the specimens aged at 130°C

(13) J. M. Silcock, H. K. Hardy and T. J. Heal: J. Inst. Metals, 82 (1953~54), 239.

Fig. 3 Resistivity reversion curves of Al-4% Cu alloy aged (a) for 22 hr at 130°C and (b) for 15 min at 40°C.

Fig. 4 Strength reversion curves of Al-4% Cu alloy aged at 130°C for 22 hr.

Fig. 5 A typical example of $\Delta\sigma$ vs T_R relation.

show a maximum; with T_R , the maximum value increases and the reversion time to the maximum, t_m , decreases.

Figure 4 shows the strength versus reversion time curves of the specimens aged at 130°C for 22 hr. In all the reversion curves, the strength decreases rapidly down to the value which depends on T_R , both the speed of the reversion and the decrement of the strength

being larger with increasing T_R . When the reversion temperature is higher than 200°C, the minimum value of the strength attained is lower than that of the as-quenched specimen. When $T_R > 220^\circ\text{C}$, the strength falls down to the value which corresponds to the complete reversion, i.e. 8 kg/mm². In Fig. 5, the relationship between the maximum reversion decrement of the strength, $\Delta\sigma$, and T_R is shown. It can be seen that $\Delta\sigma$ increases with increasing T_R up to 220°C above which $\Delta\sigma$ becomes constant. This result suggests that for the complete reversion, the reversion treatment should be conducted above a certain critical temperature.

3. Activation energy for reversion

It has been shown in the supersaturated Al-Cu alloys the resistivity change accompanied by the formation of the G.P. zones at a constant ageing temperature can be expressed by⁽¹⁴⁾

$$\frac{1}{\rho_0} \frac{d\rho_t}{dt} = \frac{a}{b+t}, \quad (1)$$

where ρ_0 and ρ_t are the resistivities of the specimens quenched and aged for a time, t , respectively, a and b being constants determined by the ageing temperature. The ratio, a/b , represents the initial rate of the resistivity change and is given by

$$a/b = A \exp(-Q_F/kT_A), \quad (2)$$

where A is a constant, Q_F the activation energy for the formation of the G.P. zones and T_A the ageing temperature. From eq. (1), we obtain

$$\rho_0 \frac{dt}{d\rho_t} = \frac{b}{a} + \frac{t}{a}. \quad (3)$$

Then, plotting the reciprocal rate of the resistivity change, $dt/d\rho$, against the time, t , a straight line will be obtained and the value of a/b can easily be determined. Thus, from eq. (2), the activation energy, Q_F , can be estimated.

Figure 6 shows the results obtained by applying eq. (3) to the resistivity-reversion curves of the specimen aged at 40°C (Fig. 3 (b)). In the present case Q_F and T_A in eq. (2) are replaced by Q_R and T_R , respectively, where Q_R is the activation energy for the reversion. Plotting b/a against $1/T_R$, a straight line is obtained as shown in Fig. 7, the slope of which gives 13.6 kcal/mol as the activation energy for the reversion.

The activation energy can also be calculated from the strength reversion curves, if they can be expressed by the Johnson-Mehl equation

$$1 - X = \exp(-Kt^n) \quad (4)$$

$$\text{or} \quad \log \ln \{1/(1-X)\} = \log K + n \log t, \quad (5)$$

where $X = \Delta\sigma(t)/\Delta\sigma$ is the fraction reverted, $\Delta\sigma(t)$ the strength decrement at a time t , K the reaction rate constant and n a constant. As shown in Fig. 8, the strength-reversion curves can be actually replotted

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Fig. 6 Typical examples of $dt/d\Delta\rho$ vs reversion time of Al-4% Cu alloy aged at 40°C for 15 min.

Fig. 7 Arrhenius plot of the reciprocal of the initial rate of resistivity change during reversion of Al-4% Cu alloy aged at 40°C for 15 min, the activation energy being determined to be 13.6 kcal/mol.

Fig. 8 Johnson-Mehl plot of the strength reversion curves of Al-4% Cu alloy aged at 130°C for 22 hr.

Fig. 9 Arrhenius plot of the rate constant K in the Johnson-Mehl equation, the activation energy being determined to be 28.8 kcal/mol.

according to eq. (5). In Fig. 9, the rate constant K obtained from eq. (5) by taking $t=1$ is plotted as a function of $1/T_R$. The slope of the straight line gives the activation energy, 28.8 kcal/mol.

IV. Discussions

1. Reversion and the stability of the G.P. zones

The maximum decrement of the strength, $\Delta\sigma$, by the reversion heat-treatment was found to depend strongly on the ageing time before reversion. Figure 10 (a) shows the relation between the fraction reverted, $\Delta\sigma/\Delta\sigma_m$, and T_R for the specimens aged at 130°C for 10, 22 and 100

Fig. 10 (a) Relation between $\Delta\sigma/\Delta\sigma_{\max}$ and reversion temperature in Al-4% Cu alloy aged at 130°C for 10, 22 and 100 hr, respectively, (b) Ageing time dependence of T_{GP} on ageing at 130°C.

hr, respectively, where $\Delta\sigma_m$ is the difference in the strength between the specimens quenched and completely reverted (see Fig. 2). It can be seen that $\Delta\sigma/\Delta\sigma_m$ is not constant but varies depending upon both T_R and ageing times even if the ageing temperature is fixed. Here again it is shown that for the complete reversion, $T_R > T_{GP}$, where T_{GP} is the critical (minimum) temperature for the complete reversion. Figure 10 (b) shows the dependence of T_{GP} on the ageing time at 130°C. T_{GP} rises in the initial stages of ageing and then reaches a constant value, T_G , after ageing for about 25 hr. T_G can be considered as the upper limit temperature for the presence of the G.P. zones formed at that ageing temperature. The relation shown in Fig. 10 (b) is very much similar to the change of T_M on ageing of an Al-4% Cu alloy obtained from the specific heat measurements by Hirano and Iwasaki⁽¹⁵⁾ suggesting that the reversion observed in the present work is closely connected with the stability of the G.P. zones*.

Estimating from the ageing temperature dependence of $T_M^{(15)-(17)}$, T_G is also expected to depend on the ageing temperature. As shown before, T_G for 130°C-ageing is about 220°C. T_G for 160°C-ageing is determined to be about 230°C. Furthermore, from the results of hardness measurements by Mondolfo⁽⁹⁾ and Prakash et al.⁽¹¹⁾, T_G for room-temperature ageing can be inferred to be between 170° and 190°C. The relation between T_G and T_A can be summarized in Fig. 11. The T_G versus T_A line thus obtained intercepts with the line showing $T_G = T_A$ at 275°C. Thus it can be concluded that the G.P. zones in Al-4% Cu alloy is possible to exist up to, at least, 275°C, in good agreement with the result of the calorimetry by Hirano et al.⁽¹⁵⁾

Considering the new findings on the stability of the G.P. zones described above, various observations on the reversion phenomena in Al-Cu alloys can be consistently interpreted as follows :

(1) Beton and Rollason⁽¹²⁾ regarded T_{GP} of Al-Cu alloys aged at room temperature for 10 days as the

Fig. 11 Ageing temperature dependence of T_G .

(15) H. Iwasaki and K. Hirano : Trans. JIM, 5 (1964), 162.

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(17) K. Asano and K. Hirano : Trans. JIM, 9 (1968), 24; 11 (1970), 225.

* A heat absorption due to the dissolution of the G.P. zones can be observed in the specific heat versus temperature curves obtained in the course of heating the aged alloy. The peak temperature of the heat absorption, T_M , has been recognized as a measure of the stability of the zones.

solvus temperature of the G.P. zones. However, this is not acceptable since they ignored the dependence of T_{GP} on the ageing conditions as shown above. According to Beton et al., the solvus temperature of the zones in Al-4% Cu alloy is 180°C. On the contrary, as can be seen from Fig. 10, only 70% of the strength of Al-4% Cu alloy acquired by ageing at 130°C for 10 hr (it has been confirmed that in this stage of ageing, no ageing products except the G.P. zones are formed) can be reverted at 180°C. The metastable phase diagram determined by Beton et al.⁽¹¹⁾ may be applicable only to ageing at room temperature for 10 days.

(2) Mondolfo's observation that the degree of reversion at 170°C in naturally aged Al-4% Cu alloy decreases with ageing time before the reversion can be explained as follows ; since, as shown previously, the stability of the G.P. zones increases with ageing time, the degree of reversion at a fixed temperature may decrease with ageing time. If the reversion is conducted at temperatures higher than that of Mondolfo, the complete reversion could be observed. In effect, Prakash et al.⁽¹¹⁾ showed that the complete reversion could not be observed at 170°C but at 190°C. Thus it can be noted that changes in the stability of the G.P. zones with ageing time must be taken into account to understand the reversion behaviors.

For the natural ageing, the critical ageing time, t_c , where T_{GP} becomes constant (see Fig. 10(b)) is expected to be so long that T_{GP} cannot be experimentally determined. Assuming that the ageing time variation of T_{GP} precedes at a rate determined by the activation energy for the so-called slow reaction in this alloy, t_c at room temperature can be estimated from the value determined for the ageing at 130°C as follows :

$$\ln t_c = \frac{E}{k} \left(\frac{1}{T} - \frac{1}{T'} \right) + \ln t'_c \quad (6)$$

where E is the activation energy for the slow reaction and is reported to be about 1 eV⁽¹⁴⁾; k is the Boltzmann constant, T and T' are ageing temperatures, t'_c is the value of t_c at T' . Since it is shown by the present work that $t_c = 25$ hr at $T = 403^\circ\text{K}$ (see Fig. 10 (b)), t'_c at $T = 303^\circ\text{K}$ is calculated to be 1.8×10^6 hr (205 years).

(3) Prakash et al.⁽¹¹⁾ attributed a part of the hardness-reversion to the disappearance of dislocation loops. However, judging from the results of the quench-hardening of pure aluminium, the contribution of the dislocation loops to the hardening of aluminium alloy appears to be negligible. Thus the large difference (about 10 VPHN) between the hardness reversions at 170° and 190°C must be explained by the difference in the amount of the G.P. zones to be reverted at different temperatures.

2. Diffusion processes in reversion

In Table 1, the activation energies for the reversion determined by the present work are shown in comparison with the activation energies for the reactions involved in the precipitation and for the diffusion in Al-Cu alloys. In the specimens aged at 40°C for 15 min, the activation energy for the reversion is about one half of

that of the diffusion of Cu in Al and is in agreement with that for the fast reaction of the formation of the G.P. zones. In this ageing stage of the alloy, the migration of Cu atoms in the reversion may be facilitated by the remaining excess vacancies.

Table 1 Activation energies in the Al-Cu system.

Reaction	Activation energy (eV)	Ref.
Slow reaction	0.5~1.0	(14)
Fast reaction	0.5	(14)
Reversion	1 ($T_A=70^\circ\text{C}$) 0.6 ($T_A=40^\circ\text{C}$) 1.3 ($T_A=130^\circ\text{C}$)	(18) This work This work
Diffusion	1.3 1.3	(19) (20)

In connection with this, Kimura et al.⁽¹⁸⁾ showed that the excess vacancies made a considerable contribution to the reversion in Al-4% Cu alloy aged at 70°C for 1000 min. It was also shown that the activation energy was dependent on the length of the reversion treatment, since the concentration of the excess vacancies changed with the reversion time. The present results agree with the above; the activation energy for the reversion after ageing at 40°C is determined to be 0.58 eV by the initial rate method (Table 1) and 0.84 eV by the cross-cut method at $\Delta\rho_r=10\%$.

On the other hand, in the specimens aged for 22 hr at 130°C , where the excess vacancies may be annealed-out almost completely, the diffusion of copper atoms during the reversion will take place via vacancy of equilibrium concentration. This can be proved by calculating the diffusion coefficient of copper atoms during the reversion from the time necessary to complete the reversion and the size of the G.P. zones at the starting of the reversion. Let us suppose that the G.P. zones (assumed to consist of copper atoms of one atomic layer⁽⁹⁾) are embedded in the matrix of the concentration C (atomic fraction) and that the copper atoms must diffuse out in the field of the ellipsoid of revolution around the G.P. zones as shown in Fig. 12 in order to make the G.P. zones dissolved in the matrix. Taking c_0 (atomic fraction) as the average concentration of the alloy, the following equation can be obtained:

$$\frac{3}{2} \left(\frac{R}{r_z} \right)^2 + \left(\frac{x_0 y_0^2}{r_M^3} - \frac{3}{2} \frac{R^2 r_z}{r_M^3} \right) C = C_0, \quad (7)$$

where r_z and r_M are the mean atomic radii in the G.P. zones and the matrix, respectively, x_0 and y_0 are the axes of the ellipsoid of revolution, y_0 being the axis of rotation (Fig. 12). r_z and r_M are assumed to be equal to the atomic radii of pure copper (2.5 Å) and aluminium (2.80 Å), respectively. According to Silcock et al.⁽¹³⁾

Fig. 12 Diffusion field of Cu during reversion.

the radius R of G.P. zones in Al-4% Cu alloy formed on ageing at 130°C for 22 hr is 50 Å. Thus taking $C \approx 0$ and $C_0 = 0.017$ (for 4 wt% Cu), we obtain

$$x_0 y_0^2 = \frac{3}{2} \frac{\left(\frac{R}{r_z} \right)^2 - \left[\left(\frac{R}{r_z} \right)^2 - \frac{R^2 r_z}{r_M^3} \right] C_0}{\frac{C_0}{r_M^3}} = 7.4 \times 10^5 \text{ Å}^3. \quad (8)$$

Equating $(x_0 y_0^2)^{1/3}$ to the diffusion distance, the diffusion coefficient D is calculated by

$$2\sqrt{D t_m} = (7.4 \times 10^5)^{1/3}, \quad (9)$$

where t_m is the time to complete the reversion. Temperature dependence of D thus determined for various reversion temperatures is shown in Fig. 13, compared with the diffusion coefficient, D^* , of Cu in Al

Fig. 13 Arrhenius plot of the diffusion coefficient of Cu atoms during reversion.

(18) H. Shimizu and H. Kimura: Mater. Sci. Eng., 5 (1969~70), 127.

determined by the tracer technique⁽¹⁹⁾⁽²⁰⁾. Both results are in fairly good agreement. Thus it can be concluded again that the reversion is rate-controlled by the diffusion of copper atoms in the matrix with equilibrium vacancies.

V. Conclusions

Reversion behaviors in an Al-4% Cu alloy aged at 40° and 130°C have been examined by electrical resistivity measurements and tensile tests, with the results summarized as follows :

(1) There exists a critical temperature for the complete reversion, T_{GP} , which strongly depends on the ageing conditions, i.e. on the stability of G.P. zones.

(2) From the temperature dependence of T_{GP} , it is shown that the G.P. zones can stably exist, at least, up

to 275°C in this alloy.

(3) The reversion is rate-controlled by the diffusion of copper atoms in the matrix, on which the quenched-in vacancies have an important effect. The activation energy for the reversion in the alloys aged for a sufficiently long period to anneal-out the excess vacancies is determined to be about 30 kcal/mol, in good agreement with the activation energy for the tracer diffusion of Cu in Al.

(4) Taking into account the stability of the G.P. zones as a function of ageing temperature and time, complicated reversion behaviors of this alloy reported in the literatures can be explained consistently.

Acknowledgements

The authors are indebted to Professor H. Kimura for his valuable discussions and encouragement throughout this work. A part of this work was supported by the grant-in-aid from the Keikinzoku-Shogakkai (The Educational Foundation of Light Metals).

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