Effects of Cold Working on Precipitation in Age-hardenable Alloys

By

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Experiments have been carried out to examine the effects of cold working on the rate of precipitation in high purity copper alloys and aluminium alloys with measurements of electrical resistance, micro-hardness and thermo-electromotive force, X-ray Laue photographs and small angle scatter method. The correlation between cold working and the excess vacancies retained in quenching was investigated in water quenched and air cooled specimens.

The experiments provided evidence that cold working accelerates the process at higher ageing temperatures, and that at lower ageing temperatures the rate of precipitation of cold worked specimens is less than that of unworked materials. In Al–Ag and Al–Cu alloys, the formation of zones was hindered and the precipitation of the more stable intermediate phases γ' or θ' was accelerated. The suppressive effect of cold working is thought to be a general phenomenon in age-hardenable alloys, because the effect is also found in alloys such as Cu-Cr alloys in which the precipitation sequence is simple.

The mechanism of retarding by cold working is due to two effects: one is the sweeping out of the quenched-in vacancies, which are necessary for solute diffusion, by the motion of jogs in dislocations during cold working, and the other is the formation of many smaller clusters of enriched solute atoms which were formed by the stronger binding interaction energies between solute atoms and the lattice defects introduced by cold working.

Introduction

It is generally believed that the rate of the ageing process is almost invariably increased by plastic deformation due to the increase in the rate of nucleation along the slip planes and accelerated diffusion by the introduced lattice defects. But the inverse evidences have also been found that cold working may hinder the precipitation at low ageing temperatures in Al–Cu[1,2], Al–Zn[2], Cu–Be[3] and carbon steel[4,5].

H. K. Hardy and T. J. Heal[6] have suggested that the overall effect of plastic deformation is to speed up the rate of change towards the most stable precipitate and that the formation of less-stable coherent precipitates may actually be hindered. On the other hand, in carbon steel, it was reported that the precipitation of either the meta-stable ε carbide or the more stable cementite was retarded by cold working

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and that, when alloys with small particles of cementite were cold worked, the precipitates again went into solution.

In Al–Cu alloys, A. Berghezan[2] reported that the suppressive effect by cold working was more remarkable in air cooled alloys than in water quenched materials. On the other hand, J. M. Silcock[7] has found that in Al–Cu alloys cold working decreases the rate of formation of G.P. zone (1) in quenched crystals but increases the rate of zone formation in slowly cooled or reverted crystals.

The present work has been carried out to examine systematically the effects of cold working on the rate of precipitation in high purity copper alloys and aluminium alloys with measurements of electrical resistance, micro-hardness and thermo-electromotive force, X–ray Laue photographs and small angle scatter method. The correlation between cold working and the excess vacancies retained in quenching was also examined in water quenched and air cooled specimens. And finally, to ascertain the experimental results, the binding energies between solute atoms and lattice defects were calculated.

Experimental Procedures

Preparation of alloys: For copper alloys, ingots weighing about 800 g were obtained by the following method: Pieces of copper of 99.997% purity were put into a pure graphite crucible and this crucible was heated in a high frequency furnace under an atmosphere of purified hydrogen. After being melted and deoxidized, the hydrogen gas was driven out by introducing argon. The alloying elements were added to the molten copper. The melt was stirred and cast into a chill mould under argon gas in order to prevent contamination. The chemical analysis of the specimens is given in Table 1. The ingots were hammered and cold rolled. The specimens were prepared by drawing to 1.4 mm diameter.

Table 1. Compositions of the binary copper alloys.

Solute element	Fe	Co	Cr	Ag	Be	Ti	Mg	Sn
wt %	1.29	2.75	0.30	5.04	0.42	1.72	1.03	5.00
at %	1.46	2.96	0.37	3.03	2.89	2.27	2.65	2.74

The aluminium alloys utilized in these experiments were melted in graphite crucibles with a lining of magnesia under an atmosphere of inert argon gas by using 99.995% purity aluminium. After the alloying elements were added, it was cast into a chill mould. Ingots of alloys weighing about 500 g were obtained. The compositions of the alloys are shown in Table 2. To examine the effects of cold working in the presence of small quantities of cadmium, Al–4.00 wt% Cu alloys containing 0.05 wt%

Table 2. Compositions of the binary aluminium alloys.

Solute element	Ag	Ag	Mn	Mg	Si	Cu	Cu*
wt %	3.15	16.51	1.56	4.40	0.83	1.80	4.00
at %	0.81	4.71	0.77	4.86	0.80	0.77	1.74

* with or without Cd addition (0.05 wt %)

Cd were also prepared. The ingots were drawn into 1.3 mm diam. wire for measurements of electric resistance and rolled into the sheets of approximately 10 mm in width and 1 mm in thickness for X-ray diffraction technique. The large-grains for Laue method were prepared by the strain-anneal method.

Solution treatment and cold working: The copper alloys were heat treated under an argon atmosphere to prevent oxidation. The Cu-Fe, Cu-Co and Cu-Cr alloys were solution treated for 48 hr at 1000°C, and the other copper alloys for 48 hr at 850°C. These alloys were quenched in water at room temperature. To examine the effect of the cooling rate, water quenching, air cooling and direct quenching in an oil bath at 250°C were compared in the Cu-Ti alloys.

The aluminium alloys were solution treated for 24 hr at 530°C, except the Al-Mn alloys which were treated for 24 hr at 650°C, and then quenched in water at room temperature. Air cooled specimens were added for the Al-3.15 wt% Ag, Al-1.80 wt% Cu and Al-4.00 wt% Cu alloys.

The plastic deformation for wire specimens was carried out immediately after solution heat treatment by drawing through dies to the required diameters with a small amount of reduction for each pass at a slow drawing rate. And the sheet specimens for X-ray technique have been cold worked by simple extension or cold rolling. The degree of cold working in wire specimens is represented by the reduction in area, but for the specimens with large grains for Laue method the degree of extension is measured in the grain. In the case of the cold rolling of sheets, it was shown in the reduction of thickness.

Resistance measurements: To minimize the contact resistance, the following methods were employed: In copper alloys specimens of 20 cm length were silver-soldered at two points at each of the two ends with copper leading wires. In order to avoid incorrect heating during the silver-soldering, the specimens were water cooled except for the two ends to be soldered. In aluminium alloys, the copper leading wires were attached to the specimens fixedly by small silver bolts.

The voltage was measured precisely with a potentiometer, and the current by using a potentiometer and a standard resistance of 0.01 ohm. The changes in the electrical resistance of the specimen were determined while heating it at a constant rate of 2°C per minute. In copper alloys, the changes in electric resistance during the isothermal ageing could be measured by this method. As the aluminium alloys would be expected to show a considerable variance in measured values by the method described above owing to the large temperature dependency of the electrical resistivity, the specimen and a standard material were connected in series and the ratio of the voltages of both wires were measured under a certain current. The furnace cooled alloys of the same composition as the specimens were used as the standard materials. These standards had not shown any changes of resistance during the ageing at 70° and 110°C. The errors in these resistance-measuring methods were less than ± 0.4 pct.

Micro-vickers hardness measurements: The micro-vickers hardness was measured on the section of wire specimens by using "Durimet" micro-vickers hardness tester under a load of 500 g. The hardness number was taken as the average of four generally close values.

Thermo-electromotive force measurements: Thermo-electromotive force was determined with a potentiometer on the specimens of Cu–Fe alloys paired with pure annealed copper under a constant temperature difference between 0° and 70°C. The electromotive force of the other alloys were too small to examine.

X-ray Laue method: Laue method is generally recommended for a rapid survey of the ageing process. The large-grain specimens of Al–Cu and Al–Ag alloys were examined with a $[100]_{Al}$ axis parallel to the X-ray beam. Satisfactory photographs were obtained by Cu radiation with exposures of 30 min at 60 mA, 35 kVp using a collimeter 5.5 cm in length and 0.5 mm bore with a specimen to film distance of 3.5 cm.

X-ray small angle scatter method: Al–Ag alloys containing 16.51 wt% Ag have been investigated qualitatively with small angle scatter method. The specimens were polycrystalline foils near the thickness of 0.10 mm. The final thickness was reduced by a combination of cold rolling and etching. It was found suitable to etch in H_2F_2 solution and remove a black film with HNO_3 solution.

The CuK_α radiation was monochromated with a LiF crystal monochromator. The excessive blackening from the direct beam was prevented by using a cover of thin brass strip as a beam stop placed on the film. With the X-ray tube operating at 45 kVp and 60 mA legible patterns were obtained by 8 hr exposures with a specimen to film distance of 8 cm. Cold working was done by simple extension and cold rolling.

Experimental Results

1. *Effects of cold working after water quenching on the change in electrical resistance with heating.*

On the effects of cold working after water quenching in Cu–Ti, Cu–Cr and Cu–Fe

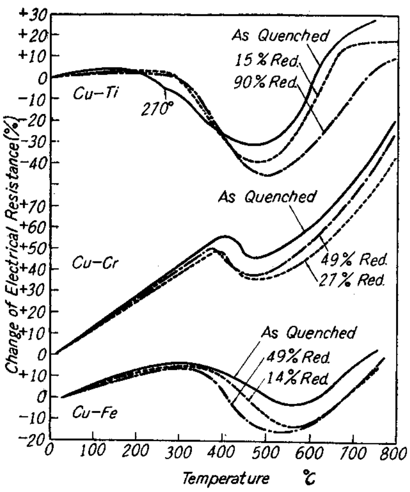

Fig. 1. Effect of cold working on the electrical resistance change of copper alloys in heating at a constant rate (2°C/min).

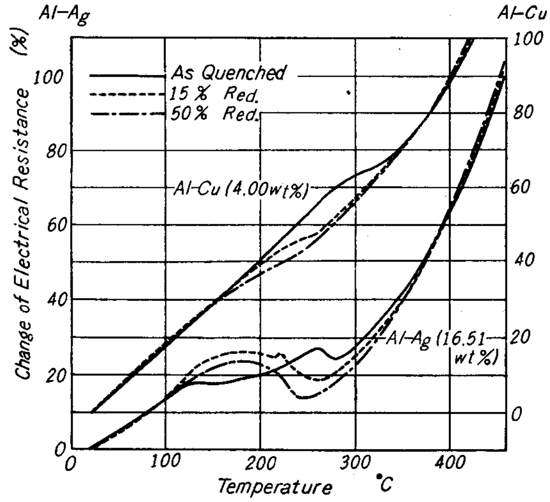

Fig. 2. Effect of cold working on the electrical resistance change of aluminium alloys in heating at a constant rate (2°C/min).

alloys, Fig. 1 shows the electrical resistance changes during heating at a constant rate of 2°C per minute. Fig. 2 shows those of Al–4.00 wt% Cu and Al–16.51 wt% Ag alloys.

The stable precipitate in Cu–Ti alloys is said to be the compound Cu_3Ti with a deformed hexagonal close packed structure by E. Raub[8]. The existence of a less stable intermediate phase in the Cu–Ti alloys was suggested from previous experiments[9]. In Fig. 1, for the unworked Cu–Ti alloys, the first stage decrease due to precipitation of the intermediate phase is shown to occur from about 150°C and to be followed through the knick point at 270°C by the second stage decrease due to a more stable phase precipitation. But, only single stage decrease curves were observed for the cold worked specimens.

In Cu–Cr alloys the decrease of electric resistance due to precipitation in the cold worked specimens begins at a lower temperature than in the unworked specimen. And in Cu–Fe alloys, the mode of the resistance changes has the same appearance as those in Cu–Cr alloys. The ageing process in Cu–Cr alloys is considered to be simple[10,11], since the stable precipitate is not an intermetallic compound but a pure metallic phase. And in Cu–Fe alloys, according to R. B. Golden and M. Cohen[12], the first precipitates are considered to be face-centred cubic iron in registry with the matrix lattice on the basis of measurements of their magnetic properties.

In Al–16.51 wt% Ag alloys shown in Fig. 2, the first stage decrease due to rapid growth of G.P. zones begins at about 100°C in unworked alloys but at about 160°C in the worked specimens. But the relation between cold working and the silver rich spherical zones, which are postulated to be formed during quenching by C. B. Walker and A. Guinier[13], is not clear. On the other hand, the decrease of resistance due to the precipitation or γ' phase is shown to occur at 260°C in unworked alloys and at 220°C in worked specimens.

In Al–4.00 wt% Cu alloys, although the effects of cold working at lower ageing temperatures than 150°C are not so remarkable, the decrease of resistance due to the precipitation of θ' phase is shown to occur at 290°C in unworked specimens, at 190°C in 15 pct cold drawn specimens, and at 170°C in 50 pct drawn materials.

2. *Effects of cold working after water quenching on the micro-hardness and thermo-electromotive force changes in isothermal ageing*

In order to verify the effects of cold working on the precipitation hardening, the micro-hardness was measured in Cu–Ti and Cu–Cr alloys.

Fig. 3 shows the micro-hardness changes in isothermal ageing of Cu–Ti alloys at temperatures of 220°, 320°, 420° and 520°C. Wire specimens were cold drawn up to 90 pct reduction after water quenching. It is shown in Fig. 3 that, on ageing at 520°C, the time to attain peak hardness becomes much shorter and the appearance of the two stages in the ageing curves of as-quenched specimens is made weaker by cold working. On ageing at 420°C, it is clear that the time to attain the first peak hardness is slightly longer in the cold worked specimens, when compared with the curves at 520°C. Furthermore, the rate of hardening of the alloys aged at 320° and 220°C is also slower than that of the unworked specimens. These results seem to suggest that the precipitation is retarded by cold working at

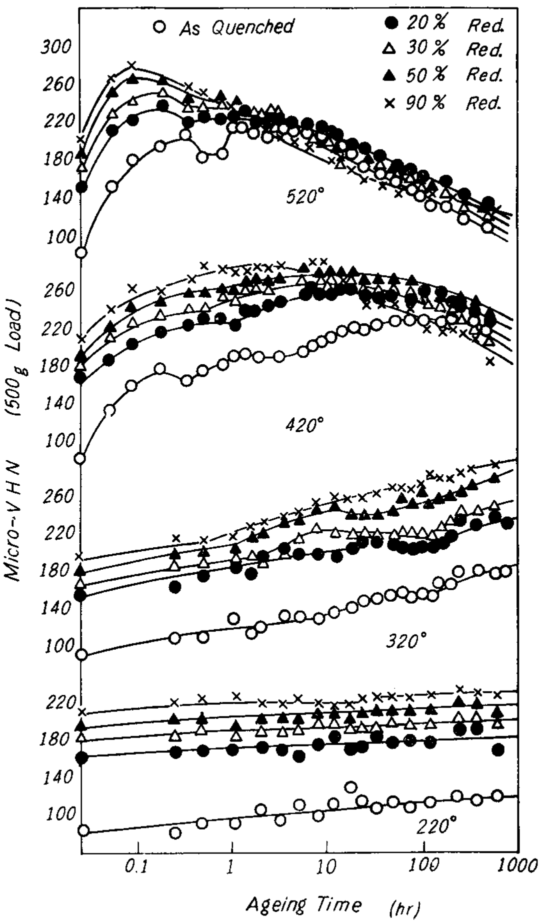

Fig. 3. Effect of cold working on the micro-hardness change of Cu–Ti alloys in isothermal ageing at 220°~520°C.

lower ageing temperatures at which the hardness change is not so remarkable.

Fig. 4 gives the micro-hardness changes in isothermal ageing of Cu–Cr alloys at temperatures 320°, 370°, 420° and 470°C. According to W. Gruhl and R. Fisher[11], no remarkable effect of cold working on the precipitation in Cu–Cr alloys was observed from measurements of hardness. In Fig. 4, it is clear that at each ageing temperature the time to attain the peak hardness is shorter as the degree of cold working increases.

Fig. 5 shows the effects of cold working on the thermo-electromotive force of the Cu–Fe alloys paired with annealed pure copper at a 70°C temperature difference. The amount of thermo-electromotive force increase by cold working is very small. On ageing at 420°C, the thermo-electromotive force in the 14 pct and 50 pct cold worked specimens decreases more rapidly than in the as-quenched specimen. On the contrary, on the ageing at 220°C, the value of the thermo-electromotive force in the 14 pct cold worked specimen is not only larger than that of the quenched specimen, but the difference in the thermo-electromotive force between these two specimens during ageing is also

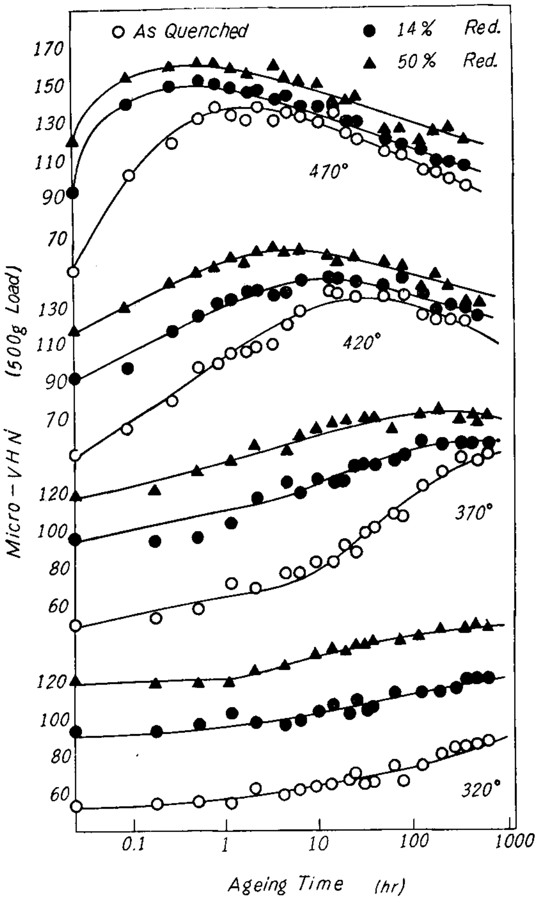

Fig. 4. Effect of cold working on the micro-hardness change of Cu–Cr alloys in isothermal ageing at 320°∼470°C.

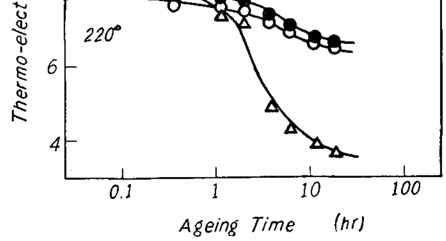

Fig. 5. Effect of cold working on the thermo-electromotive force of Cu–Fe alloys paired with pure copper at a 70°C temperature difference.

larger than before ageing. At 220°C, a rapid decrease of thermo-electromotive force occurs in 50 pct cold drawn material after ageing 30 min.

3. *Effects of cold working after water quenching on the electrical resistance change in isothermal ageing*

Fig. 6 shows the electrical resistance changes in isothermal ageing of Cu–Ti alloys at the temperatures 220°, 320°, 420° and 520°C. The decrease in electrical resistance at each annealing temperature is shown as a percentage of the electrical resistance value obtained by assuming no precipitation to occur during heating to the annealing temperature. Therefore, in the case of higher ageing temperatures in which precipitation may actually occur, the standard value was obtained by extrapolation from the experimental values at lower ageing temperatures. Hereafter, this value for the decrease in electrical resistance will be used. On ageing at 520°C, the electrical resistance decreases more and more rapidly as the degree of cold deformation increases as shown in Fig. 6. At 420°C, on the contrary, the rate of decrease of cold worked specimens in the early stage is less than that of unworked materials. This tendency becomes more remarkable on ageing at 320° and 220°C, particularly when the reduction is lower.

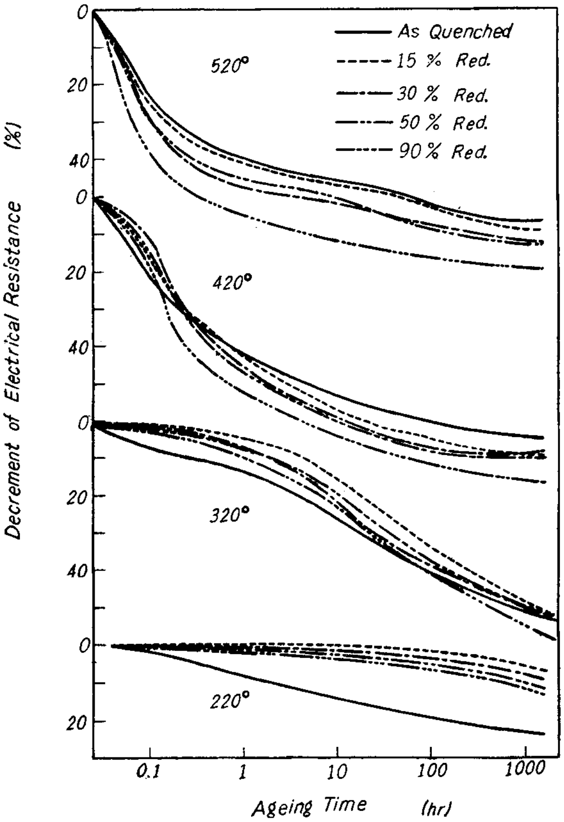

Fig. 6. Effect of cold working on the electrical resistance change of Cu–Ti alloys in isothermal ageing at 220°~520°C.

According to A. H. Geisler[14], the increased resistance during ageing at lower temperatures is observed in the alloys having large disregistry between matrix and precipitates. This increase due to coherency strain is superimposed on the normal decrease in resistance accompanying depletion of solid solution. In cold worked specimens, the increase of resistance due to coherency strain is less than in unworked materials and the recovery of resistance will occur. Therefore, the smaller decrease observed in cold worked alloys indicates that ageing is hindered in these specimens.

From the above experimental results, it is quite possible that the rate of precipitation in cold worked specimens at lower ageing temperatures below 320°C is less than that of unworked specimens, and that at higher temperatures cold working accelerates the process. And these results can be compared with those in Fig. 1.

Fig. 7 shows the analogous results in Cu–Cr alloys. On ageing at 420°C, the rate of decrease of the electrical resistance in cold worked specimens is more rapid than in unworked alloys, but when cold drawn by 50 pct reduction the total electrical resistance decrease is less than in the absence of cold working. On ageing at 320°C, the resistance of cold worked alloys decreases more rapidly. Since the precipitation process may correspond to the electric resistance decrease, the effect of cold working is to speed up the rate of decomposition at higher annealing temperatures. On the contrary, at lower ageing temperatures such as 220°C, the decrease in resistance of cold worked specimens is less than that of the unworked alloys. Therefore, the suppressive effect by cold working was also proved in the alloy system, although not so remarkable as in the Cu–Ti alloys.

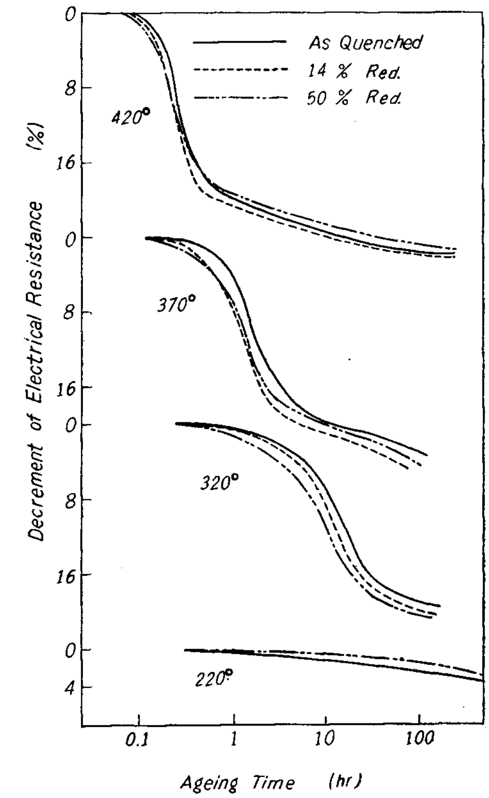

Fig. 7. Effect of cold working on the electrical resistance change of Cu–Cr alloys in isothermal ageing at 220°∼420°C.

Similar experiments were carried out upon the high purity copper (99.997%). The wire specimens were annealed for 30 hr at 850°C, quenched into water at room temperature and cold drawn to 50 pct. Fig. 8 shows the changes in the electric resistance of pure copper on ageing at 170°C. The decrease of the resistance becomes

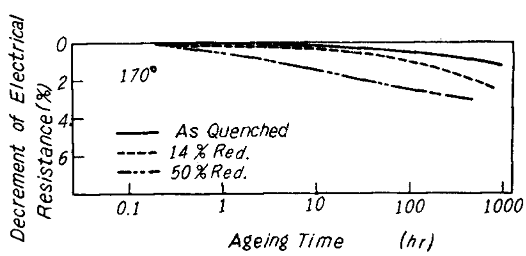

Fig. 8. Effect of cold working on the electrical resistance change of copper of high purity in isothermal ageing at 170°C.

larger as the degree of deformation increases. This result is different from that in age-hardenable copper alloys mentioned above.

To examine further these effects of cold working, experiments have been carried out in isothermal ageing at 175°C for various copper alloys in Table 1. These results are shown in Fig. 9, 10 and 11. In Cu-Fe alloys, shown in Fig. 9, the rate of decrease in the electrical resistance of the as-quenched specimens is more rapid than in 15 pct worked materials, but is slower than in 50 pct worked alloys. From this result, it is known that precipitation in the alloys is retarded by a small degree of cold working. In Cu-Co, Cu-Cr, Cu-Ag and Cu-Ti alloys (Fig. 9 and 10), the rate of decrease of resistance in cold worked alloys is less than that of unworked specimens. In Cu-Ti alloys, shown in Fig. 10, the effect of retardation by cold working was the most appreciable; for example, in ageing 10 days, the decrease is 13.5 pct in as-quenched, 1.5 pct in 15 pct cold worked and 2.2 pct in 50 pct cold worked specimens. In these alloys cold working after water quenching retards the rate of ageing at 175°C, although it is some ambiguous in Cu-Be, Cu-Mg and Cu-Sn alloys

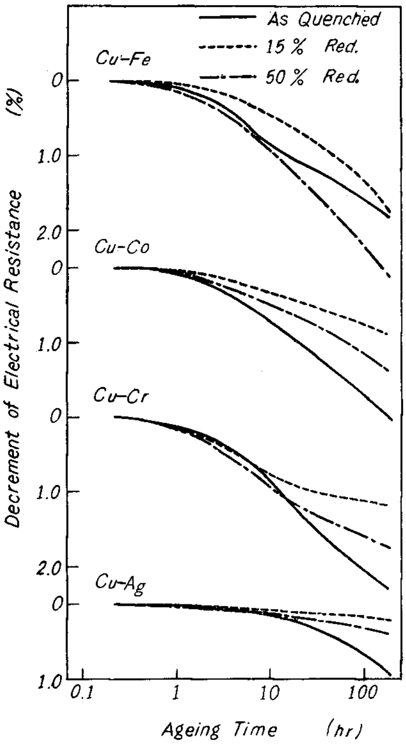

Fig. 9. Effect of cold working on the electrical resistance change of Cu-Fe, Cu-Co, Cu-Cr and Cu-Ag alloys in isothermal ageing at 175°C.

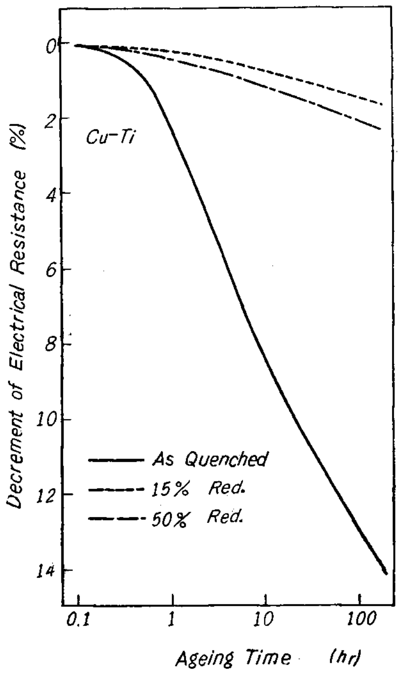

Fig. 10. Effect of cold working on the electrical resistance change of Cu-Ti alloys in isothermal ageing at 175°C.

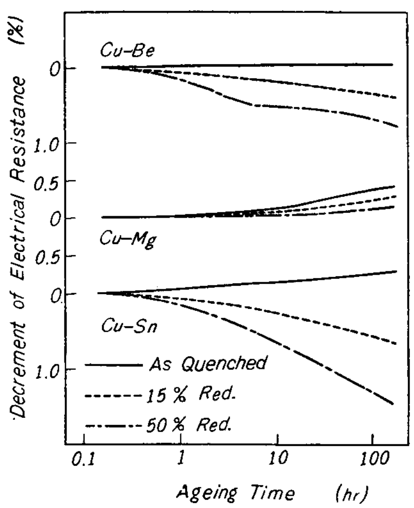

Fig. 11. Effect of cold working on the electrical resistance change of Cu-Be, Cu-Mg and Cu-Sn alloys in isothermal ageing at 175°C.

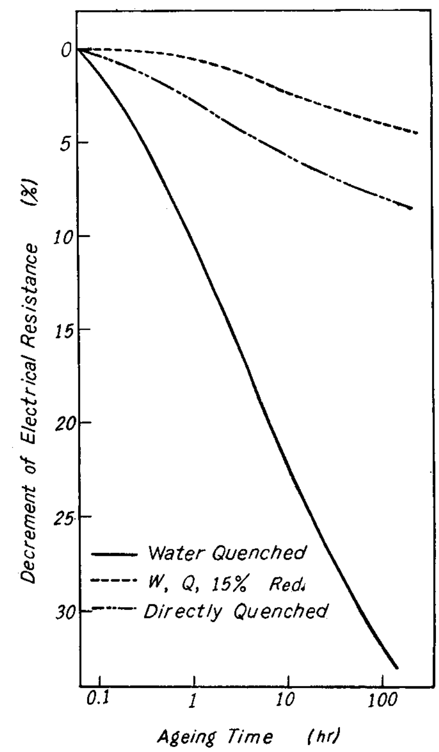

Fig. 12. Effect of direct quenching on the electrical resistance change of Cu-Ti alloys in isothermal ageing at 250°C.

which show the substantial resistance increases in water quenched alloys as shown in Fig. 11.

In order to examine the effects of quenching strains in the ageing process, the changes in the electrical resistance of Cu-Ti alloys were measured in isothermal ageing at 250°C for the following three cases: water quenched, cold drawn after water quenching and directly quenched in an oil bath at 250°C. These results are shown in Fig. 12. In ageing of 10 days, the decrease in resistance is 32.5 pct in water quenched, 4 pct in 15 pct cold drawn after water quenching and 8 pct in directly quenched specimens. These results indicate that the ageing process at 250°C may be accelerated by quenched-in vacancies as discussed later.

In aluminium alloys shown in Table 2, the effects of cold working in isothermal ageing at 70° and 110°C were investigated by resistance measurements. Fig. 13 and Fig. 14 show these results. The resistance of water quenched Al-3.15 wt% Ag and 16.51 wt% Ag alloys decreases in isothermal ageing at 70° and 110°C. The rate of decrease in 15 pct cold worked specimens is less than that of unworked materials. The difference in concentrations of solute in these alloys has little effect on the suppressive behaviour of cold working. In Al-Mn alloys, the resistance increases during ageing are shown in both unworked and worked specimens at 70° and 110°C,

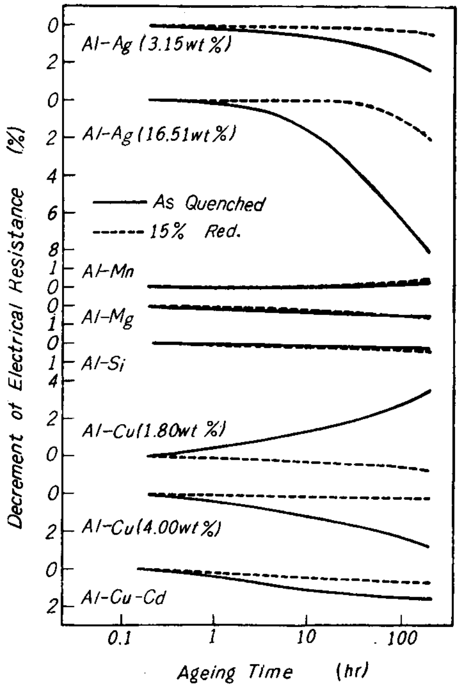

Fig. 13. Effect of cold working on the electrical resistance change of aluminium alloys in isothermal ageing at 70°C.

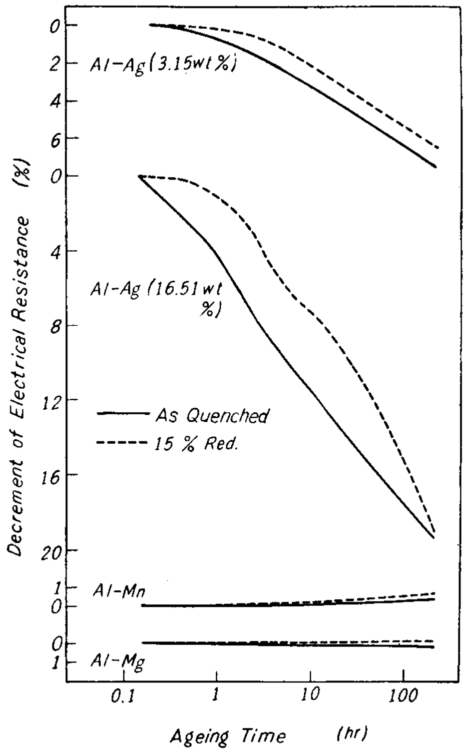

Fig. 14 (1). Effect of cold working on the electrical resistance change of aluminium alloys in isothermal ageing at 110°C.

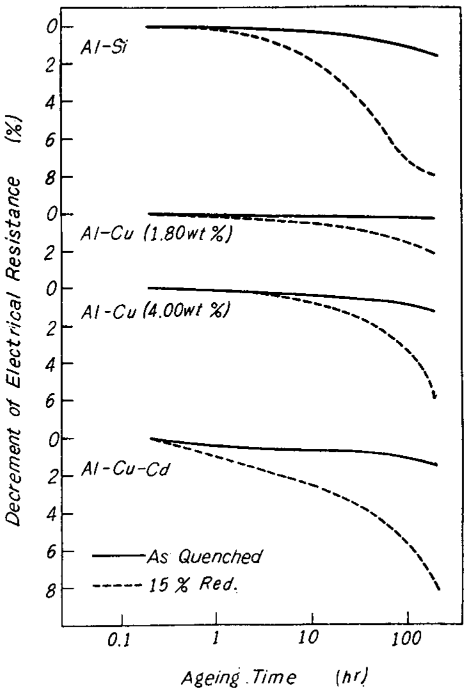

Fig. 14 (2). Effect of cold working on the electrical resistance change of aluminium alloys in isothermal ageing at 110°C.

In the alloys, cold working seems to increase the precipitation rate. In Al–Mg and Al–Si alloys, the effects of cold working are not apparent in ageing at 70°C. And at 110°C, the effect of cold working seems to be retardation in Al–Mg and acceleration in Al–Si alloys. In Al–1.80 wt% Cu alloys, the resistance increases in water quenched alloys and decreases in cold worked materials at 70°C. And at this temperature, in Al–4.00 wt% Cu alloys, the rate of decrease in resistance of cold worked specimens is less than in unworked alloys. And at 110°C, the rate of decrease in cold worked Al–Cu alloys is more rapid than in unworked materials.

In the ternary Al–Cu–0.05 wt% Cd alloys, the retarding effect of cold working in the ageing at 70°C is smaller than in the binary Al–Cu alloys. H. K. Hardy[15] found that at low temperatures the ternary Al–Cu–Cd alloys showed a slower rate of formation of G.P. (1) and (2) than the corresponding binary alloys, and that at elevated temperatures ternary additions accelerated the rate of precipitation of θ'. To examine the effects of a Cd addition, the decrease in electric resistance at the ageing time of 10 days in binary and ternary alloys either unworked or worked are summarized in Table 3. In the ageing at 70°C, the decrease of quenched binary

Table 3. Effects of cold working and Cd (0.05%) addition on the decrease in electrical resistance of Al–4.00 wt % Cu alloys in isothermal ageing of 10 days at 70°C and 110°C.

Ageing temp. °C	Degree of working	Al–Cu	Al–Cu–Cd
70°	As quenched	2.8%	1.5%
	15% Red.	0.3%	0.9%
110°	As quenched	1.3%	1.5%
	15% Red.	6.0%	8.0%

alloys is larger than that of quenched ternary materials. This indicates that the addition of Cd retards the ageing process at 70°C. But in cold worked alloys, the decrease is larger in ternary alloys. In the ageing at 110°C, the Cd addition may accelerate the rate of decomposition in both unworked and worked specimens. In Table 3 it may be understood that cold working weakens the suppressive effects of Cd additions in the ageing at 70°C and that either cold working or Cd additions accelerate the rate of decomposition at 110°C.

4. *Effects of cold working after air cooling*

Fig. 15 shows the effects of cold working on ageing at 150°C in air cooled Cu–Ti alloys, compared with that in water quenched materials. For an ageing of 10 days, the decrease in the resistance is 2.1 pct in air cooled and 1.8 pct in cold worked specimens. On the other hand, the decrease is 12.8 pct in water quenched specimens and 1.5 pct in specimens subjected to cold working respectively.

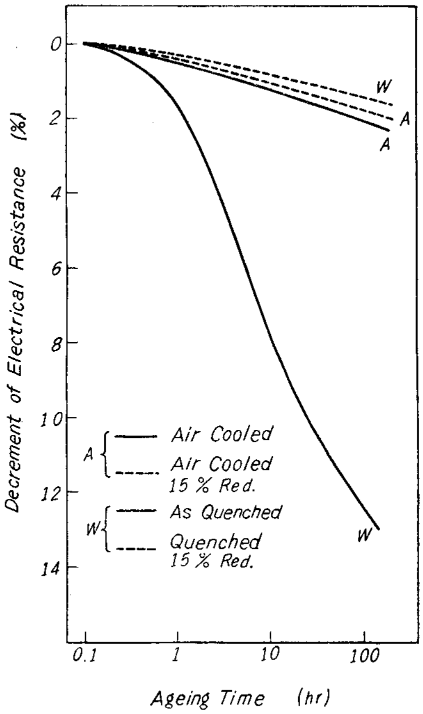

Fig. 15. Effect of cold working after air cooling on the electrical resistance change of Cu-Ti alloys in isothermal ageing at 150°C, as compared with that after water quenching.

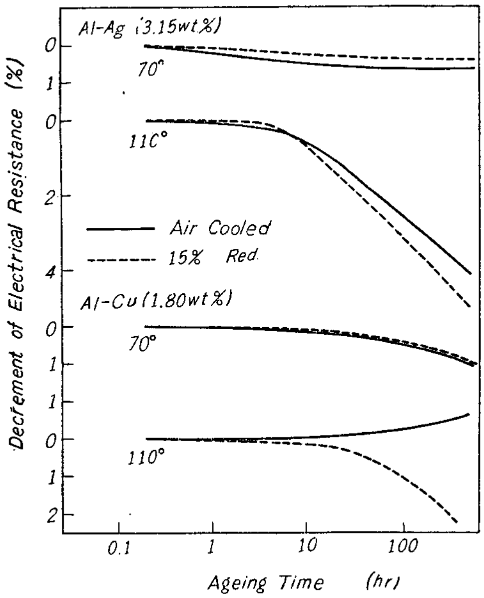

Fig. 16. Effect of cold working after air cooling on the electrical resistance change of Al-0.81 at% Ag and Al-0.77 at% Cu alloys in isothermal ageing at 70° and 110°C.

Fig. 16 shows the results of the same investigation for the Al-3.15 wt% Ag and Al-1.80 wt% Cu alloys in the course of isothermal ageing at 70°C and 110°C. For comparison with the water quenched alloys shown in Fig. 13 and 14, the decreases in electric resistance after 10 days ageing are shown in Table 4. In this table, the minus sign indicates a decrease and the plus sign an increase in the resistance. In

Table 4. Effects of cold working on the electrical resistance change of water quenched and air cooled Al-0.81 at % Ag and Al-0.77 at % Cu alloys in isothermal ageing of 10 days at 70°C and 110°C.

	Al-0.81 at % Ag		Al-0.77 at % Cu	
Ageing temp. °C	70°	110°	70°	110°
Water quenched	−2.4%	−7.5%	+3.4%	−0.3%
Water quench, 15% Red.	−0.5%	−6.4%	−0.8%	−2.1%
Air cooled	−0.7%	−3.2%	−0.7%	+0.4%
Air cool, 15% Red.	−0.4%	−4.1%	−0.6%	−1.7%

Al–Ag alloys, the decreases of air cooled specimens are smaller than those of water quenched alloys. This indicates that the air cooled alloys have a slower rate of ageing. The suppressive effects due to cold working in air cooled Al–Ag alloys are smaller than in water quenched specimens. At 110°C, the decrease of the worked Al–Ag alloys in larger than that of the unworked materials after 5 hr as shown in Fig. 16. In air cooled Al–1.80 wt% Cu alloys, the decrease in resistance occurs for ageing at 70°C and cold working retards the rate of decrease. The behaviour at 110°C is analogous to that at 70°C in water quenched alloys. For a proper understanding of the structural changes in Al–Cu alloys, X-ray studies were carried out as discussed later.

5. *X-ray Laue photographs*

According to G. D. Preston[16], the first change in the supersaturated Al–Cu alloys during ageing is the formation of G.P. zones, which consist of copper rich regions of plate-like shape formed on {100} planes of the aluminium matrix. Owing to their limited thickness, the zones produce streaks on the X-ray patterns. In Al–Ag alloys, the platelets of γ' phase on {111} planes of the matrix produce streaks on the Laue films[17]. The effects of cold working after water quenching or air cooling in the course of isothermal ageing at 70° and 110°C have been studied in Al–Ag and Al–Cu alloys with Laue photographs. The cold working was done by simple extension of several percent.

In the Al–Ag alloys, the length of diffuse scattering surrounding the lattice spot of the aluminium matrix diminishes and the intensity increases as ageing progresses[18]. The (000) reciprocal lattice point is surrounded by a spherically symmetric, shell-liked region of scattering power. The small angle scatter method was also employed for Al–16.51 wt% Ag alloys. These results will be shown later. The orientations of axes of specimens employed and the degree of working are given respectively in Fig. 17 and Table 5.

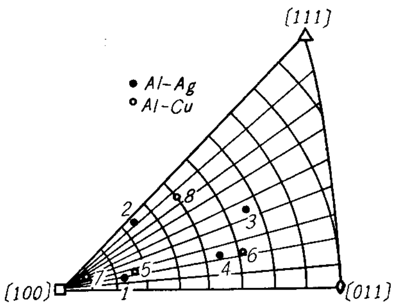

Fig. 17. Orientations of axes of specimens employed in Laue method.

Table 5. Specimen numbers in Fig. 17 and degree of working by simple extension for Laue method.

	Al–Ag (3.15%)		Al–Ag (16.51%)		Al–Cu (1.80%)		Al–Cu (4.00%)	
Specimen No.	1	2	3	4	5	6	7	8
Ageing temp. °C	70°	110°	70°	110°	70°	110°	70°	110°
Degree of extension	4.5	8.3	5.0	5.3	6.3	5.3	4.5	7.5 7.5*

* air cooled specimen,

In Al–3.15 wt% Ag and 16.51 wt% Ag alloys, the legible difference between unworked and worked specimens could not be observed even after one month of ageing at 70°C. The effects of suppression by cold working at this ageing temperature were observed notably in measurements of resistance. The spots of matrix in cold worked alloys elongate in a radial direction, giving rise to the appearance known as asterism. By changes in the length and intensity of the diffuse scattering surrounding {131} lattice spots, the rate of ageing of cold worked alloys could be compared with that of unworked materials for ageing at 110°C. The rate of growth of zones in 8.3 pct cold worked Al–3.15 wt% Ag alloys seems to be slower than in unworked materials. Photo. 1 is a Laue photograph of Al–16.51 wt% Ag crystal in water quenched state. Photo. 2 shows a photograph taken after 5.3 pct cold working in the same alloys. Photo. 3 and 4 represent photographs of the alloys shown in Photo. 1 and 2, aged 20 days at 110°C respectively. In these photographs, it is observed that the rate of growth of the zones in cold worked alloys is slower than in unworked materials. In cold worked specimens as in Photo. 4, the weak streaks are found to pass through {131} spots. And these streaks follow great circles through the poles of planes of the type {111}. These results indicate that in cold worked Al–Ag alloys the growth of zones is hindered and the precipitation of γ' phase is accelerated. The diffuse scattering due to zones in air cooled Al–16.51 wt% Ag alloys is small and intense owing to the rapid growth of zones during cooling. Therefore, the zones are too large to study the effects of cold working after air cooling.

For Al–Cu alloys, the results of Guinier and Preston have been traced for the convenience of our further experiments. Streaks through the spots of matrix running in $[100]_{Al}$ directions are obtained. These streaks are due to G.P. zones (1). G.P. zone (2) was first detected by Guinier[19], who found that the streaks due to G.P. (1) developed intensity maxima. This structure is reported to be tetragonal, with $a=4.04$ and $c=7.7$ Å. On the θ' precipitate, Preston[20] reported the existence of short streaks liking θ' and matrix spots on his Laue photographs.

In Al–1.80 wt% Cu alloys, the Laue photographs of water quenched specimens and specimens which were 6.3 pct cold worked after quenching are shown respectively in Photo. 5 and 6. The changes in the patterns of these specimens for ageing at 70°C are summarized in Table 6. "Streaks" in the table means the streaks running in $[100]_{Al}$ directions through {131} matrix spots. These streaks correspond to the G.P. zone (1) formed on the {100} aluminium matrix during ageing. In as-quenched specimens, the central streaks at small angles, which show the existence of the zones formed during the quenching, increase in intensity and sharpness during the course of ageing. In cold worked alloys, these changes are found to be slower. The {131} streaks in unworked specimens are not found after 12 days as in Photo. 7. After 22

Table 6. Analysis of Laue photographs of Al-1.80 wt % Cu alloys unworked or 6.3% cold worked, aged at 70°C after water quenching.

Ageing time at 70°C	Unworked		6.3% cold worked	
	Patterns, precipitates	Photo. No.	Patterns, precipitates	Photo. No.
0	No streaks	5	No streaks	6
5 hr	No streaks		No streaks	
1 day	No streaks		No streaks	
5 "	No streaks		No streaks	
12 "	No streaks	7	No streaks	
22 "	Streaks, G.P. (1)	8	No streaks	9

days ageing at 70°C, the streaks due to G.P. (1) were obtained in unworked alloys, but not in 6.3 pct cold worked materials (Photo. 8 and 9). In isothermal ageing at 110°C, the appearances of Laue patterns in unworked and 5.3 pct cold worked alloys are shown in Table 7. After 7 days ageing the weak streaks due to G.P. (1) were found in water quenched alloys, but not in 5.3 pct cold worked alloys as shown in Photo. 10 and 11. Photo. 12 shows that these streaks in quenched crystals increase in intensity in the specimen aged 18 days. On the other hand, in 5.3 pct cold worked alloys, G.P. (1) and G.P. (2) seem to be absent and weak spots due to θ' precipitate at the {131} matrix spots can be recognized in Photo. 13. The θ' precipitates were not observed in water quenched alloys after 30 days ageing at 110°C. The patterns show a weak intensity maxima due to G.P. (2). It may be concluded that in cold worked Al-1.80 wt% Cu alloys the formation of the less stable G.P. (1) and G.P. (2) is hindered, though the precipitation of the more stable θ' phase is accelerated.

With respect to Al-4.00 wt% Cu alloys, Photo. 14 is a Laue photograph of a water quenched specimen. Photo. 15 is that of the same alloy 4.5 pct elongated after

Table 7. Analysis of Laue photographs of Al-1.80 wt % Cu alloys unworked or 5.3% cold worked, aged at 110°C after water quenching.

Ageing time at 110°C	Unworked		5.3% cold worked	
	Patterns, precipitates	Photo. No.	Patterns, precipitates	Photo. No.
0	No streaks		No streaks	
15 min	No streaks		No streaks	
2 hr	No streaks		No streaks	
5 "	No streaks		No streaks	
1 day	No streaks		No streaks	
7 "	Weak streaks, G.P. (1)	10	No streaks	11
18 "	Streaks, G.P. (1)	12	θ' spots	13
30 "	Streaks, weak intensity maxima, G.P. (1), (2)		θ' spots	

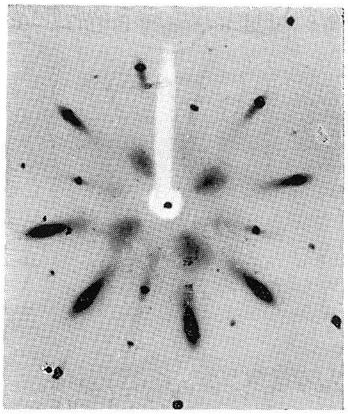

Photo. 1. Al–16.51% Ag alloy water quenched.

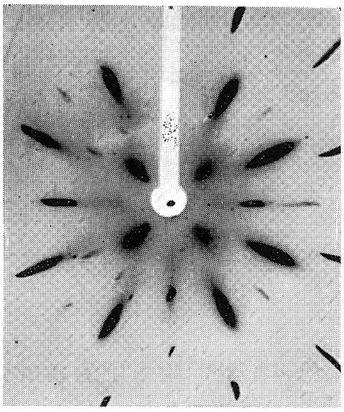

Photo. 2. Al–16.51% Ag alloy W. Q. and elongated 5.3%.

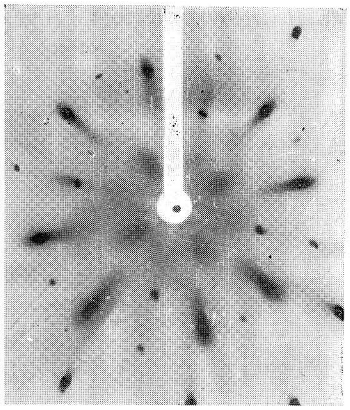

Photo. 3. Specimen shown in Photo. 1, aged 20 days at 110°C.

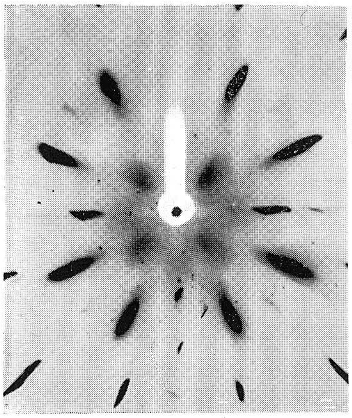

Photo. 4. Specimen shown in Photo. 2, aged 20 days at 110°C.

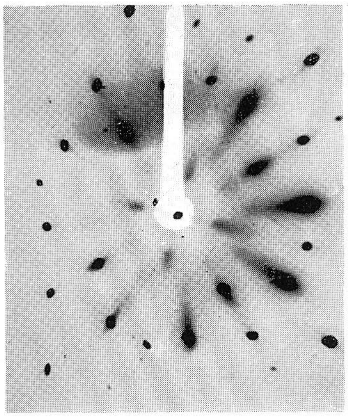

Photo. 5. Al–1.80% Cu alloy water quenched.

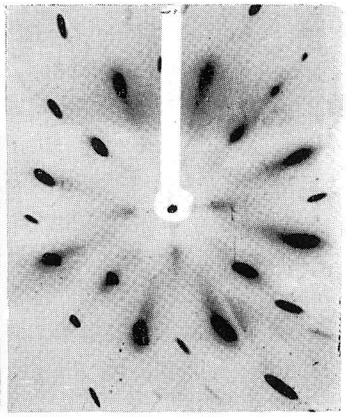

Photo. 6. Al–1.80% Cu alloy W. Q. and elongated 6.3%.

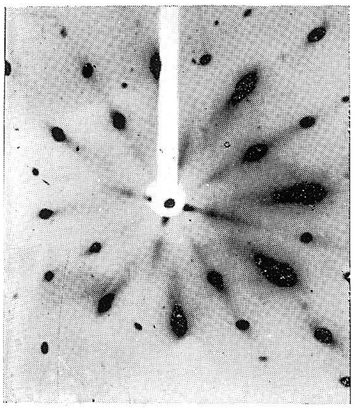

Photo. 7. Specimen shown in Photo. 5, aged 12 days at 70°C.

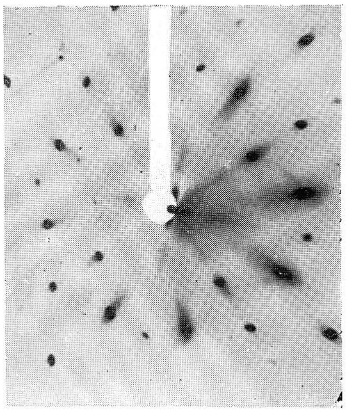

Photo. 8. Specimen shown in Photo. 5, aged 22 days at 70°C.

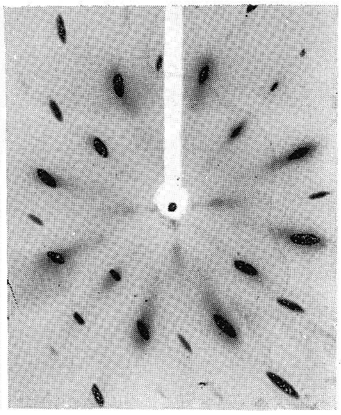

Photo. 9. Specimen shown in Photo. 6, aged 22 days at 70°C.

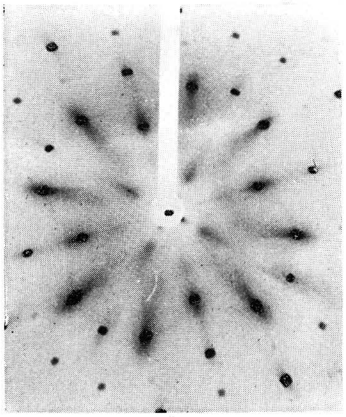

Photo. 10. Al–1.80% Cu alloy W. Q. and aged 7 days at 110°C.

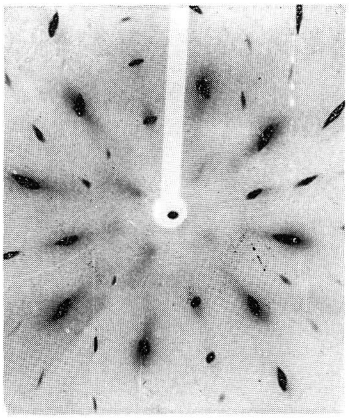

Photo. 11. Al–1.80% Cu alloy W. Q., elong. 5.3% and aged 7 days at 110°C.

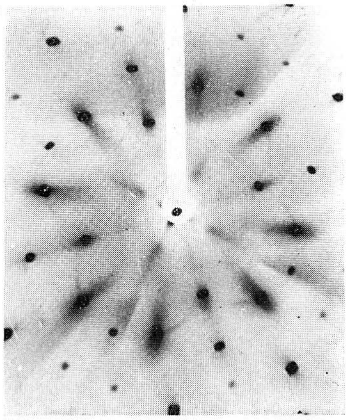

Photo. 12. Al–1.80% Cu alloy W. Q. and aged 18 days at 110°C.

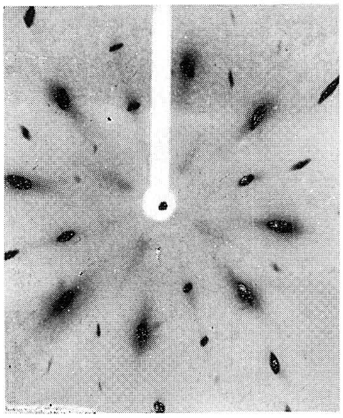

Photo. 13. Al–1.80% Cu alloy W. Q., elong. 5.3% and aged 18 days at 110°C.

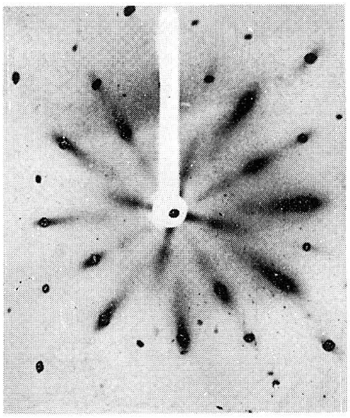

Photo. 14. Al–4.00% Cu alloy water quenched.

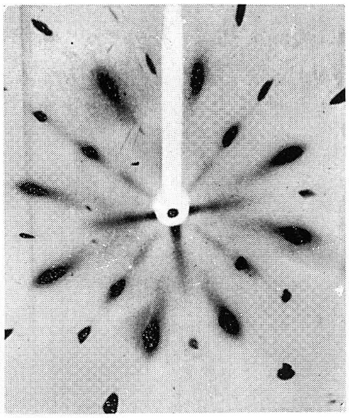

Photo. 15. Al–4.00% Cu alloy W. Q. and elong. 4.5%.

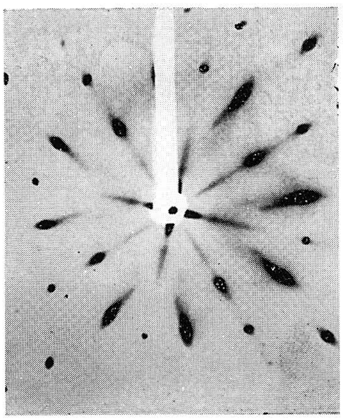

Photo. 16. Specimen shown in Photo. 14, aged 1 hr at 70°C.

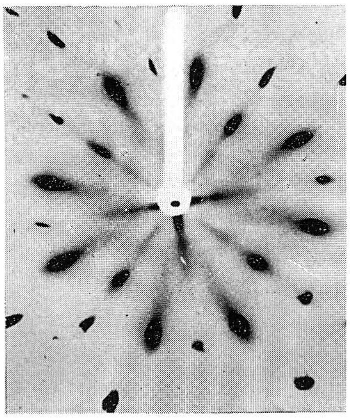

Photo. 17. Specimen shown in Photo. 15, aged 1 hr at 70°C.

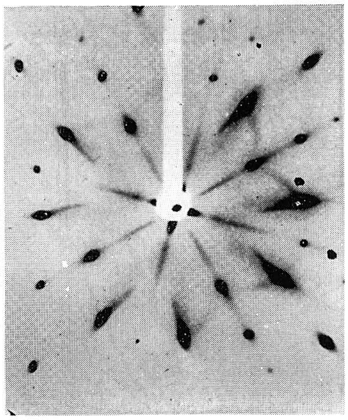

Photo. 18. Specimen shown in Photo. 14, aged 5 hr at 70°C.

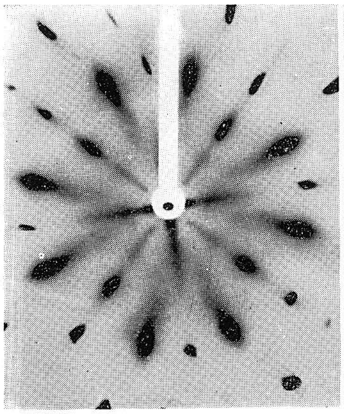

Photo. 19. Specimen shown in Photo. 15, aged 5 hr at 70°C.

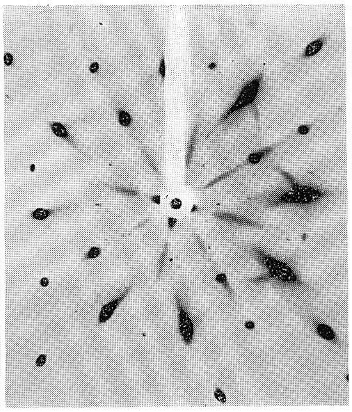

Photo. 20. Specimen shown in Photo. 14, aged 22 days at 70°C.

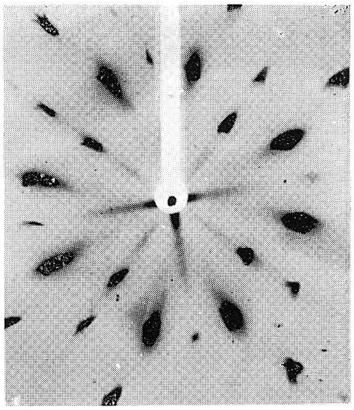

Photo. 21. Specimen shown in Photo. 15, aged 22 days at 70°C.

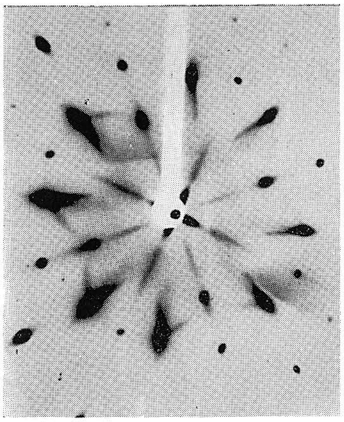

Photo. 22. Al-4.00% Cu alloy W. Q. and aged 15 min at 110°C.

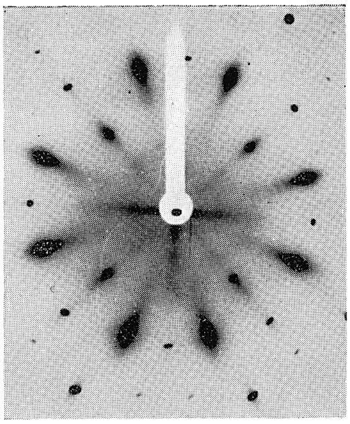

Photo. 23. Al-4.00% Cu alloy W. Q., elong. 7.5% and aged 15 min at 110°C.

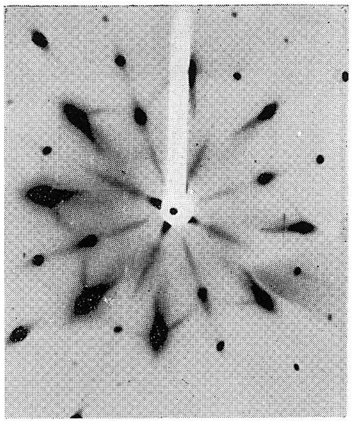

Photo. 24. Al-4.00% Cu alloy W. Q. and aged 5 hr at 110°C.

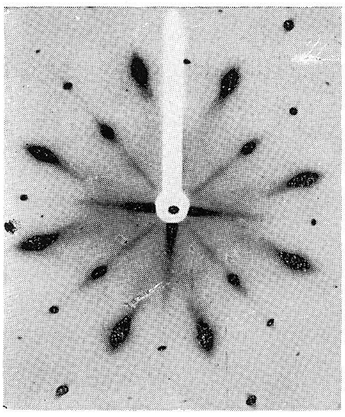

Photo. 25. Al-4.00% Cu alloy W. Q., elong. 7.5% and aged 5 hr at 110°C.

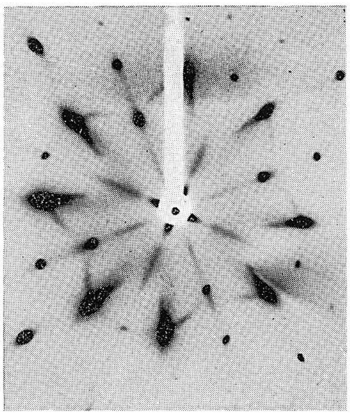

Photo. 26. Al-4.00% Cu alloy W. Q. and aged 1 day at 110°C.

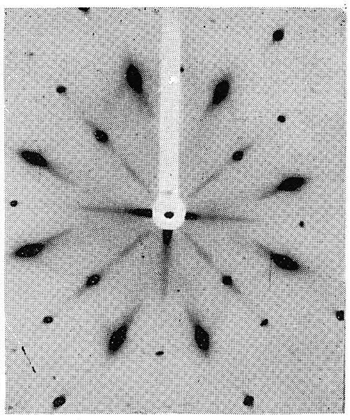

Photo. 27. Al-4.00% Cu alloy W. Q., elong. 7.5% and aged 1 day at 110°C.

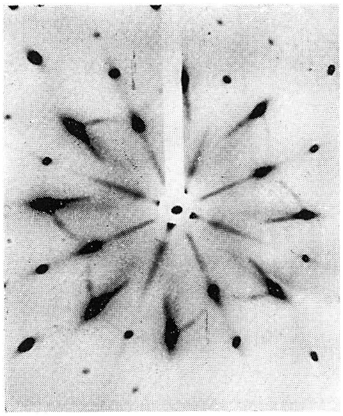

Photo. 28. Al-4.00% Cu alloy W. Q. and aged 3 days at 110°C.

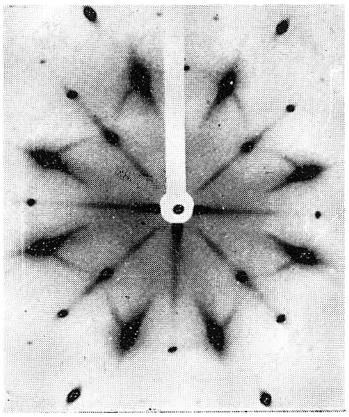

Photo. 29. Al-4.00% Cu alloy W. Q., elong. 7.5% and aged 3 days at 110°C.

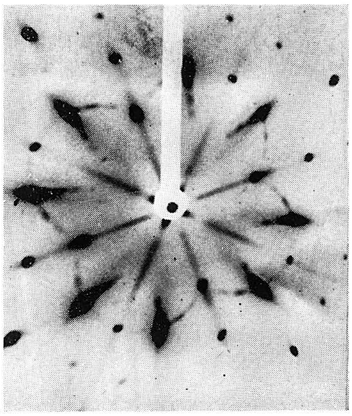

Photo. 30. Al-4.00% Cu alloy W. Q. and aged 10 days at 110°C.

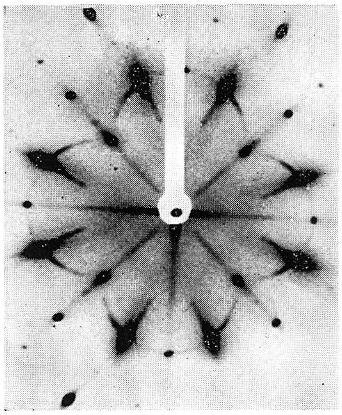

Photo. 31. Al-4.00% Cu alloy W. Q., elong. 7.5% and aged 10 days at 110°C.

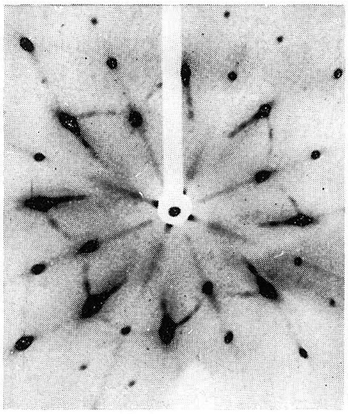

Photo. 32. Al-4.00% Cu alloy W. Q. and aged 18 days at 110°C.

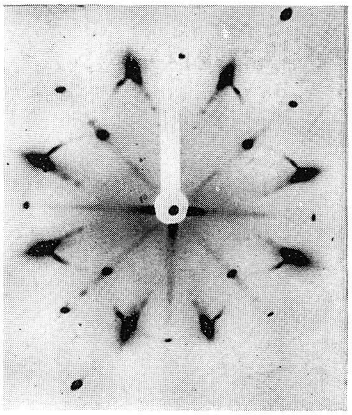

Photo. 33. Al-4.00% Cu alloy W. Q., elong. 7.5% and aged 18 days at 110°C.

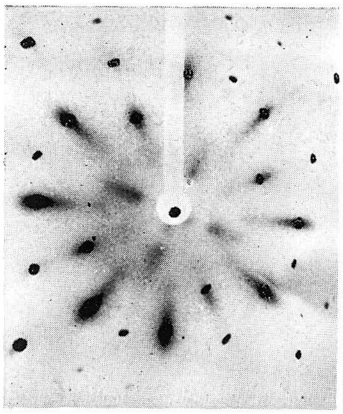

Photo. 34. Al-4.00% Cu alloy air cooled,

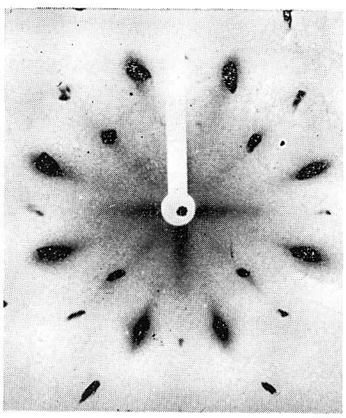

Photo. 35. Al-4.00% Cu alloy A. C. and elong. 7.5%.

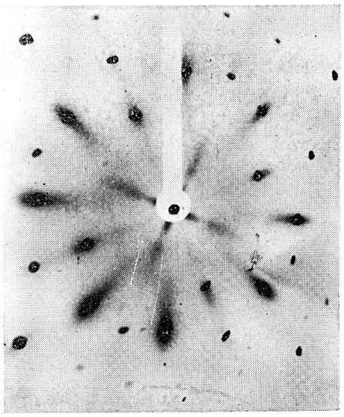

Photo. 36. Specimen shown in Photo. 34, aged 15 min at 110°C.

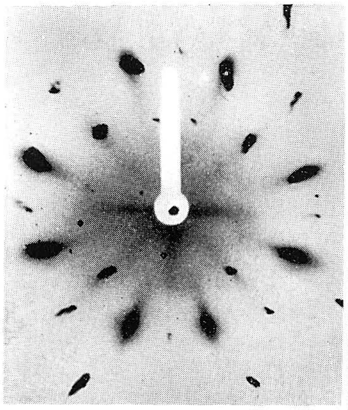

Photo. 37. Specimen shown in Photo. 35, aged 15 min at 110°C.

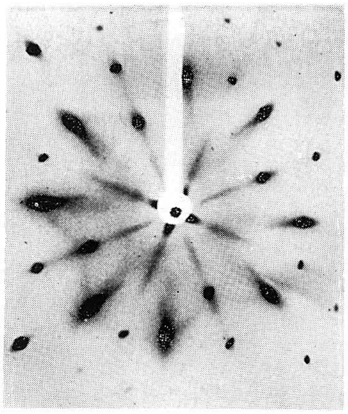

Photo. 38. Specimen shown in Photo. 34, aged 5 hr at 110°C.

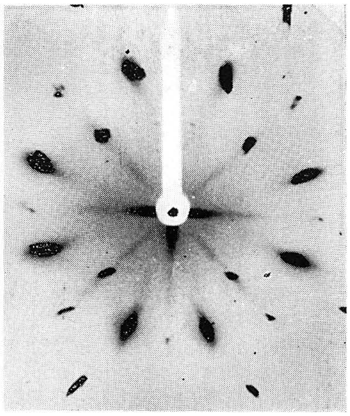

Photo. 39. Specimen shown in Photo. 35, aged 5 hr at 110°C.

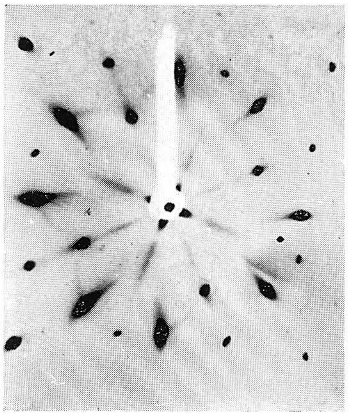

Photo. 40. Specimen shown in Photo. 34, aged 1 day at 110°C.

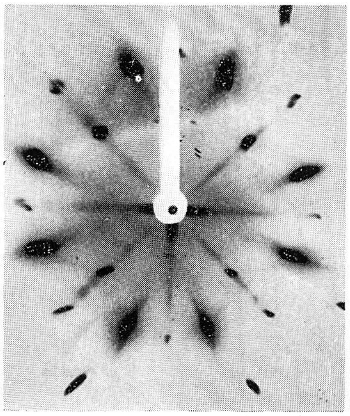

Photo. 41. Specimen shown in Photo. 35, aged 1 day at 110°C.

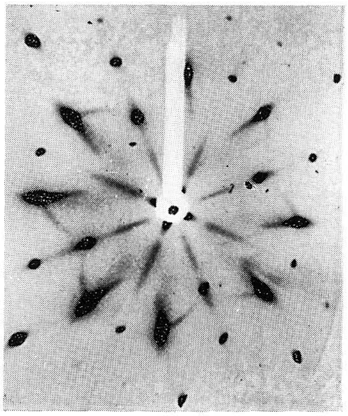

Photo. 42. Specimen shown in Photo. 34, aged 3 days at 110°C.

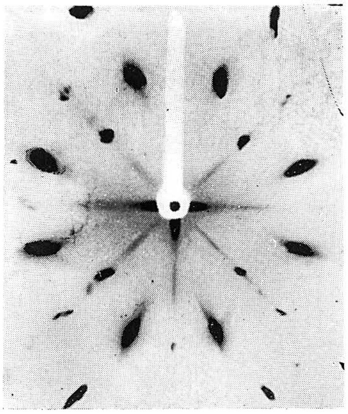

Photo. 43. Specimen shown in Photo. 35, aged 3 days at 110°C.

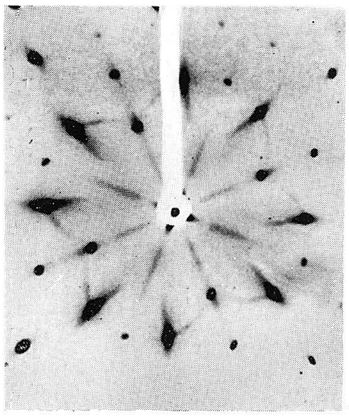

Photo. 44. Specimen shown in Photo. 34, aged 10 days at 110°C.

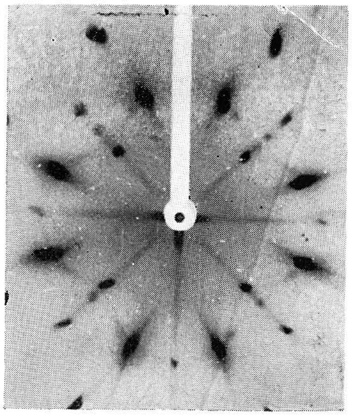

Photo. 45. Specimen shown in Photo. 35, aged 10 days at 110°C.

Photo. 46~48. Small angle scatter films of Al–16.51 wt% Ag alloys.

Photo. 46. Water quenched and aged at 110°C:
Photo. 47. Water quenched, deformed by simple extension of 5.4% and aged at 110°C:
Photo. 48. Water quenched, cold rolled by 55.6% and aged at 110°C:

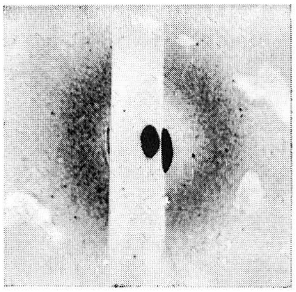

Photo. 46 (a). As quenched

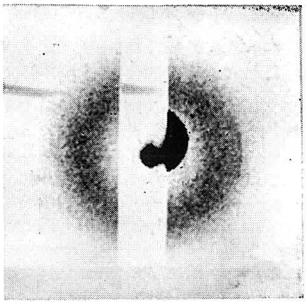

Photo. 46 (b). Aged 0.5 hr

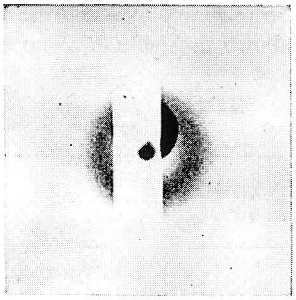

Photo. 46 (c). Aged 10 hr

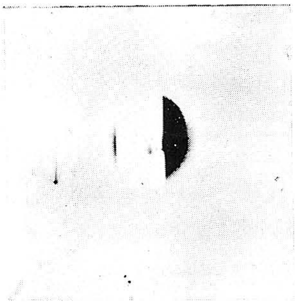

Photo. 46 (d). Aged 5 days

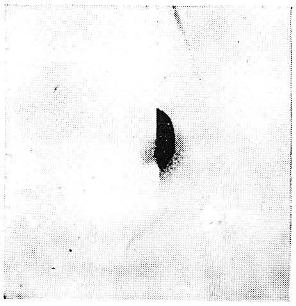

Photo. 46 (e). Aged 75 days

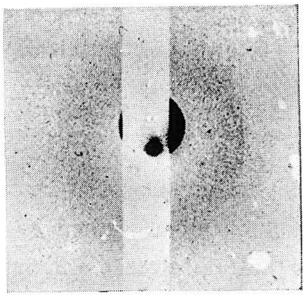

Photo. 47 (a). As deformed

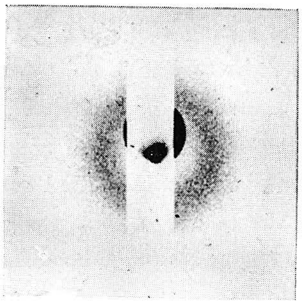

Photo. 47 (b). Aged 10 hr

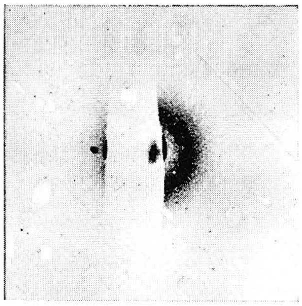

Photo. 47 (c). Aged 5 days

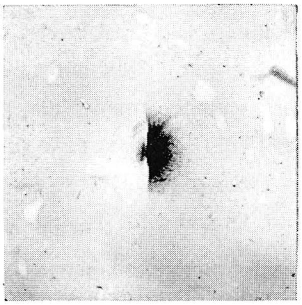

Photo. 47 (d). Aged 75 days

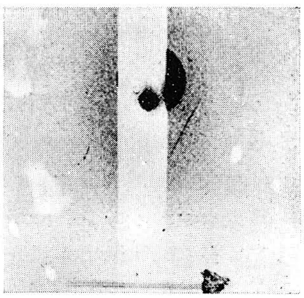

Photo. 48 (a). As rolled

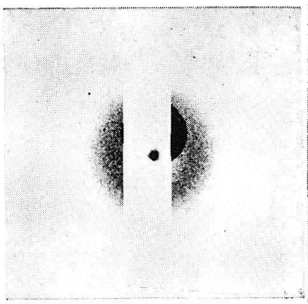

Photo. 48 (b). Aged 10 hr

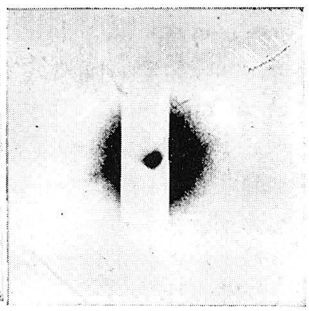

Photo. 48 (c). Aged 5 days

water quenching. In isothermal ageing at 70°C, the weak streaks due to G.P. (1) appear after 1 hr in unworked alloys as in Photo. 16, but cannot be observed in 4.5 pct worked materials even after 22 days (Photo. 17, 19 and 21). In unworked crystal, the streaks are very apparent after 5 hr ageing (Photo. 18 and 20). These changes are shown in Table 8. The suppressive effects of cold working are very remarkable

Table 8. Analysis of Laue photographs of Al-4.00 wt % Cu alloys unworked or 4.5% cold worked, aged at 70°C after water quenching.

Ageing time at 70°C	Unworked		4.5% cold worked	
	Patterns, precipitates	Photo. No.	Patterns, precipitates	Photo. No.
0	No streaks	14	No streaks	15
1 hr	Weak streaks, G.P. (1)	16	No streaks	17
5 "	Streaks, G.P. (1)	18	No streaks	19
1 day	Streaks, G.P. (1)		No streaks	
5 "	Streaks, G.P. (1)		No streaks	
12 "	Streaks, G.P. (1)		No streaks	
22 "	Streaks, G.P. (1)	20	No streaks	21

at this temperature. In regard to the isothermal ageing at 110°C, Photo. 22 is a Laue photograph of unworked alloy aged for 15 min at 110°C. This photograph shows very definite streaks through the {131} matrix spots. But these streaks were not observed in 7.5 pct cold worked alloys as shown in Photo. 23. Unworked specimens aged 5 hr at 110°C show intense streaks and weak intensity maxima due to G.P. (2) as in Photo. 24. But Photo. 25 shows that under the same ageing conditions, 7.5 pct worked crystal does not show these changes. In ageing 24 hr at 110°C, the intense streaks and the weak intensity maxima appear in the unworked alloy (Photo. 26) but only the weak streaks due to G.P. (1) are found in the worked material (Photo. 27). Even after ageing for 3 days G.P. (2) is found only in the unworked alloy (Photo. 28 and 29). In the ageing of more than 10 days, the effects of cold working are not remarkable (Photo. 30~33). In both specimens, G.P. (1) and G.P. (2) are observed. These appearances are summarized in Table 9.

In the air cooled Al-4.00 wt% Cu alloys, the effects of cold working were also examined. Photo. 34 shows a Laue photograph of an air cooled alloy. Comparing with Photo. 14, the central streaks due to G.P. zone formed during quenching are weaker in air cooled alloys. On the other hand, in Al-16.51 wt% Ag alloys the spherical Ag rich zones were larger in air cooled alloys than in rapidly quenched materials. The Laue photograph of alloys which were air cooled and 7.5 pct cold worked is shown in Photo. 35. The changes in the patterns of these alloys for ageing at 110°C are shown in Table 10. In ageing for 15 min at 110°C, the streaks due to

Table 9. Analysis of Laue photographs of Al–4.00 wt % Cu alloys unworked or 7.5% cold worked, aged at 110°C after water quenching.

Ageing time at 110°C	Unworked		7.5% cold worked	
	Patterns, precipitates	Photo. No.	Patterns, precipitates	Photo. No.
0	No streaks		No streaks	
15 min	Streaks, G.P. (1)	22	No streaks	23
2.5 hr	Intense streaks, weak intensity maxima, G.P. (1), (2)		No streaks	
5 〃	Intense streaks, weak intensity maxima, G.P. (1), (2)	24	No streaks	25
1 day	Intense streaks, intensity maxima, G.P. (1), (2)	26	Weak streaks, G.P. (1)	27
3 〃	Intense streaks, intensity maxima, G.P. (1), (2)	28	Streaks, G.P. (1)	29
10 〃	Intense streaks, sharp intensity maxima, G.P. (1), (2)	30	Intense streaks, intensity maxima, G.P. (1), (2)	31
18 〃	Streaks nearly gone, strong and sharp intensity maxima, G.P. (2)	32	Intense streaks, sharp intensith maxima, G.P. (1), (2)	33

Table 10. Analysis of Laue photographs of Al–4.00 wt % Cu alloys unworked or 7.5% cold worked, aged at 110°C after air cooling.

Ageing time at 110°C	Unworked		7.5% cold worked	
	Patterns, precipitates	Photo. No.	Patterns, precipitates	Photo. No.
0	No streaks	34	No streaks	35
15 min	No streaks	36	No streaks	37
5 hr	Weak streaks, G.P. (1)	38	No streaks	39
1 day	Streaks, G.P. (1)	40	Weak streaks, G.P. (1)	41
3 〃	Intense streaks, G.P. (1)	42	Streaks, G.P. (1)	43
10 〃	Intense streaks, intensity maxima, G.P. (1), (2)	44	Streaks, intensity maxima, G.P. (1), (2)	45
18 〃	Streaks, sharp intensity maxima, G.P. (1), (2)		Streaks, sharp intensity maxima, G.P. (1), (2)	

G.P. (1) could not be found in air cooled alloys as in Photo. 36. And the rate of formation of G.P. (2) is slower in air cooled alloys than in water quenched materials (Photo. 38, 40 and 42). After ageing for 10 days the intensity maxima appears (Photo. 44). Comparing the photographs in water quenched specimens with those in air cooled ones, it may be concluded that the excess vacancies by quenching are necessary for the formation of G.P. (1) and G.P. (2) in Al–Cu alloys. Photo. 37 and 39 show the photographs of the worked specimens, aged 15 min and 5 hr at 110°C respectively. No streaks are found in both photographs. After 1 day at 110°C, the streaks due to G.P. (1) are observed in the cold worked specimen as in Photo. 41 and 43. In ageing for more than 10 days, G.P. (1) and G.P. (2) are detected in the

Laue photographs and the effects of cold working become less marked. These changes are shown in Photo. 44 and 45. From these results in the air cooled Al-Cu alloys, it is found that the rate of formation of G.P. (1) and G.P. (2) in cold worked specimens is also slower than in unworked materials.

In Table 9 and 10, it must be emphasized that the suppressive effects of cold working are not so marked in air cooled alloys as in water quenched specimens. In other words, the rate of decomposition in unworked alloys is more rapid in water quenched specimens than in air cooled materials. But there is no difference in the rate of decomposition for cold worked alloys between water quenched and air cooled specimens.

6. *X-ray small angle scattering patterns of Al-Ag alloys*

The typical pattern for a quenched Al-Ag foil shows a diffuse ring surrounding the trace of the direct beam. This is shown in Photo. 46 (a). The diameter of the ring depends on the rate of quenching. Air cooled specimens gave rise to a ring of very small diameter. Guinier[18,19] obtained diffraction patterns which were interpreted as due to zones, roughly spherical solute rich regions surrounded by a shell-like region devoid of silver atoms. And when the same Al-Ag alloy is annealed at elevated temperatures, the ring decreases in size until finally several streaks of scattering due to γ' precipitates appear.

When the quenched specimens were annealed for various lengths of time at 110°C, the diameter of the ring of diffuse scattering diminished and the intensity increased as the zones grew. These changes are shown in Photo. 46.

In the 5.4 pct cold worked alloy, small angle scattering is somewhat anisotropic and the intensity of the pattern is weaker than in unworked specimens. The anisotropic scattering may be due to the cluster deformed by cold working. The subsequent growth of the clusters tends to make them isotropic. For ageing at 110°C, the anisotropy disappeared after 10 hr of ageing. The rate of growth of zones in 5.4 pct cold worked specimens is slower than in unworked specimens. The changes in cold worked foils are shown in Photo. 47. The streaks due to γ' precipitates are observed after 75 days as in Photo. 47 (d).

In 55.6 pct cold rolled specimens, the anisotropy of the radius of the ring was remarkable. The anisotropy of the patterns in cold worked specimens shows that an extension produces an elongation of the clusters in the direction of tensile stress[21]. The rolling direction is shown by the arrow in Photo. 48 (a). The changes in the pattern with ageing of the 55.6 pct cold rolled specimen are shown in Photo. 48. The rate of growth of zones in this specimen is slightly more rapid than in 5.4 pct elongated foils. And after 5 days of ageing the sharp streaks due to γ' phase are observed as shown in Photo. 48 (c). In this ageing condition, the streaks were not observed in unworked or 5.4 pct elongated specimens. These results show qualitatively that cold working slows down slightly the growth of zones and accelerates the precipitation of γ'.

Discussion

On the basis of this study, the effects of cold working on precipitation are not simple but complex. It seems possible that cold working actually hinders the decomposition process at lower ageing temperatures, though the effect differs considerably with the nature of the alloys.

To examine the mechanism by which ageing at low temperatures is hindered, the logarithm of the time necessary for each decrease in the electrical resistance (5 pct, 10 pct and 25 pct) in Cu-Ti alloy (Fig. 6) was plotted against the reciprocal of the absolute temperature of ageing for unworked, 15 pct and 90 pct worked specimens as shown in Fig. 18. The activation energies were calculated from the gradients of the straight line in Fig. 18 and are shown in Table 11. The value of 12.3 kcal/mol for as-quenched specimens in the early stage of decomposition is thought to be the energy for the precipitation of the intermediate phase[9]. For cold worked alloys, this value 12.3 kcal/mol is absent from the table and the other larger values are thought to correspond to the activation energies for diffusion of titanium in copper. From this result in Cu-Ti alloys, it is considered that the formation of the less stable intermediate phase may actually be hindered by cold working at lower ageing temperatures at which the hardness change is not so marked.

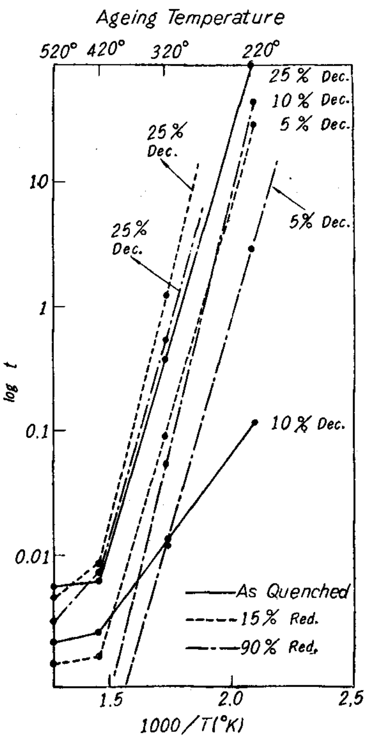

Fig. 18. Logarithms of the time required for decreases of electrical resistance (5%, 10% and 25%) in Fig. 6 vs. the reciprocal of the absolute temperature for each degree of cold working in Cu-Ti alloys.

It is probably generally accepted that at lower ageing temperatures lattice defects, such as dis-

Table 11. Activation energies (kcal/mol) for the precipitation of Cu-Ti alloys calculated from the electrical resistance measurements.

Degree of work / Dec. of Resis.	As-quenched	15% Red.	30% Red.	90% Red.
5%	—	31.5	31.7	32.6
10%	12.3	—	32.3	35.8
25%	31.6	34.3	35.1	35.8

locations introduced by plastic deformation, are so stable that the solute atoms make a special distribution around the defects by the interaction between the solute atom and the lattice defect and therefore the formation of a new phase will be hindered. The interactions between solute atoms and dislocations were discussed by A. H. Cottrell[22]. Stationary or moving dislocations interact elastically or electrically with solute atoms in a dilute solution. A solute atom which distorts the lattice equally in all directions interacts with the hydrostatic components of a stress field provided by an edge dislocation. For copper solid solution, the elastic interaction is about $-2\cdot\mathcal{E}$ electron volts, where $\mathcal{E}=(1/a)\cdot(da/dc)$ is the degree of misfit of the solute atom, a being the lattice parameter and c the concentration.

In the dilatation field of an edge dislocation in a metal the Fermi energy and the ground state of the conduction electrons are both altered. To preserve a constant level of the Fermi surface everywhere, a charge shift occurs from a redistribution of the electrons and an electrical dipole is formed at the dislocation. A. H. Cottrell, S. C. Hunter and F. R. N. Nabarro[23], using Mott's estimate of the effective charge on a solute atom in copper, calculated the electrical interaction of an atom with an edge dislocation, the electrical interaction energy for a z-valent solute atom amounting to about $-0.02\,(z-1)$ electron volts. The authors have calculated the approximate interaction energies between solute atoms and edge dislocations in copper. Goldschmidt's atomic radius was used for the calculation. These results are shown in Table 12.

To compare the calculated values of the interaction energies with the retardation effects due to cold working as clarified in the present experiments, the degree of retardation was expressed as follows: $(1-\Delta R_c/\Delta R_w)\times 100(\%)$ where ΔR_w and ΔR_c are the decreases in the electric resistance after 10 days ageing at 175°C in the water quenched and the cold worked specimens respectively.

Table 12. Interaction energy between solute atoms and dislocations in copper and degree of retardation by cold working in water quenched alloys.

Solute element	Goldschmidt's atomic radius		Valency difference with Cu	Interaction energy (eV)	Degree of retardation by cold working	
	Å	Difference with Cu (%)			15% Red.	50% Red.
Fe	2.54	− 0.39	0	0.008	11.8	−37.5
Co	2.50	− 1.96	0	0.040	56.4	32.5
Cr	2.57	+ 0.78	+5	0.104	45.3	21.6
Ag	2.88	+12.94	0	0.229	71.6	58.8
Be	2.25	−11.76	+1	0.284	—	—
Ti	2.93	+14.90	+3	0.310	88.5	83.0
Mg	3.20	+25.49	+1	0.424	—	—
Sn	3.16	+23.92	+3	0.437	—	—

In Cu-Fe, Cu-Co, Cu-Cr, Cu-Ag and Cu-Ti alloys as shown in Fig. 9 and 10, the degree of retardation by 15 pct and 50 pct cold working are shown in Table 12. The minus sign in 50 pct cold worked Cu-Fe alloys indicates the acceleration due to cold working. In Cu-Be, Cu-Mg and Cu-Sn alloys (Fig. 11), unworked specimens show substantial resistance increases for ageing at 175°C. Therefore, the degree of retardation could not be calculated for these alloys. For Cu-Be alloys, it was reported[3] on the basis of X-ray studies that the tendency to form the intermediate γ' precipitate as the first decomposition product was reduced by cold working even though the γ precipitate did not occur until ageing times greater than that required to produce γ' in the absence of cold working. Fig. 19 shows the relation between the degree of retardation and the interaction energies in Table 12. In Cu-Ti, Cu-Cr alloys, the degrees of retardation calculated with ageing for 10 days at 220°, 320° and 420°C (Fig. 6 and 7) were also plotted in Fig. 19.

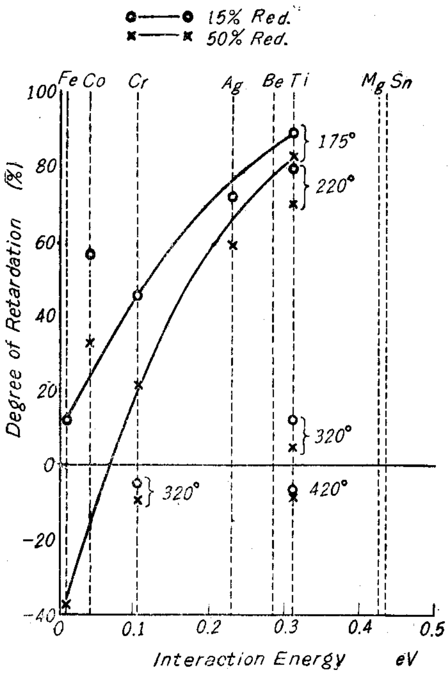

Fig. 19. Degree of retardation by cold working (15 pct and 50 pct reduction) with interaction energies shown in Table 12.

It must be that an ordinary dislocation in a close packed plane in the face centered cubic lattice splits into a pair of half-dislocations, that the latter are jointed by a stacking fault and that there is chemical interaction between solute atoms and dislocations. But it may be almost quantitatively certain that the suppressive effects of cold working at lower ageing temperatures are due to the interactions between solute atoms and lattice defects. Moreover, as shown in Fig. 19, the suppressive effect due to cold working is more marked for lower degrees of cold working and lower ageing temperatures.

From the above experiments, the effect of cold working is to accelerate the rate of formation of the more stable precipitates: θ' in Al-Cu, γ' in Al-Ag alloys, while the formation of the less stable phases, such as G.P. zones, is actually hindered.

In air cooled or directly quenched alloys, the rate of precipitation is slower than in water quenched materials. This fact indicates that the increased rate in water quenched alloys is due to the fact that a greater than equilibrium number of lattice vacancies are retained in quenching. When the interaction between solute atoms and vacancies, such as in Al–Mg alloys, is larger, excess vacancies facilitate diffusion of solute atoms[24]. The activation energy for low temperature clustering in Al–Ag and Al–Cu alloys is about 12 kcal/mol which is near that for the annealing out of the quenched-in point defects in pure metals[25,26]. In Cu–Ti alloys, the value of 12.3 kcal/mol, which is thought to be the activation energy for the formation of the intermediate phase, is near that of vacancy recovery. There is little doubt that the quenched-in vacancies play a great role in the ageing process. The quenched-in vacancies accelerate the low temperature ageing in unworked alloys but not in cold worked specimens. In air cooled alloys the suppressive effects of cold working were found to be not so remarkable as in water quenched specimens by measurements of electrical resistance and Laue photographs.

These results indicate that the mechanism by which the ageing at lower temperature is retarded by cold working is due to two effects:

(1) The excess vacancies retained in quenching, which are necessary for solute diffusion, are swept out by the motion of jogs in dislocations during plastic deformation.

(2) At lower ageing temperatures, lattice defects, such as dislocations introduced by cold working, are so stable that solute atoms make a special distribution around the lattice defects by the interactions between solute atoms and lattice defects. The smaller clusters may hinder the formation of larger precipitates.

Summary

The effects of cold working on precipitation were studied in age-hardenable alloys by measurements of electrical resistance, micro-hardess and thermo-electromotive force, Laue photographs and small angle scatter method. It may be concluded that:

(1) In copper alloys, at lower ageing temperatures the decomposition process is retarded by cold working and at elevated temperatures, cold work accelerates the process. In Al–Ag alloys, the rate of growth of zones is retarded and the formation of the more stable intermediate γ' phases is accelerated by cold working. In Al–Cu alloys, the formation of the less stable G.P. (1) and G.P. (2) is hindered, though the precipitation of the more stable θ' phases is accelerated.

(2) The suppressive effect due to cold working is also found in alloys such as Cu–Cr alloys in which the precipitation sequence is simple. Therefore, the effect is thought to be a general phenomenon in age-hardenable alloys.

(3) The rate of precipitation is more rapid in water quenched specimens than in air cooled or directly quenched materials. The increased rate is due to the fact that a greater than equilibrium number of lattice vacancies are retained in quenching. On the other hand, in air cooled alloys the suppressive effects of cold working were found to a smaller degree than in water quenched specimens.

(4) The mechanism by which the rate of ageing is retarded at lower ageing temperatures is due to two effects: one is the sweeping out of the quenched-in vacancies, which are necessary for solute diffusion, by the motion of jogs in dislocations during plastic deformation; and the other is the formation of many smaller enriched clusters of solute atoms which were formed by the stronger binding interaction energies between solute atoms and lattice defects introduced by cold working.

(5) In Al–Cu alloys containing small quantities of cadmium, cold working immediately after water quenching weakens the suppressive effect of cadmium addition for the formation of G.P. zones. This is due to the binding interaction between large cadmium atoms and dislocations.

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