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On the Aging and Precipitation of Al-Ag and Al-Zn Alloys

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Polycrystalline specimens of Al-30wt%Ag and Al-30wt%Zn alloys, which were quenched into water from the temperature of solution heat treatment, were annealed at L. T. aging temperatures or reversion temperatures so as to make them contain zones of nearly equal radii for each alloy and various concentrations of solute element in zones. These specimens were cold rolled exactly to 50%, and then annealed at L. T. aging temperatures for varying time. The state of zones and precipitates were investigated by X-ray small-angle scattering photographs. The results obtained were as follows: (1) The precipitation of γ'-phase began earlier in the specimens of Al-Ag alloy annealed at L. T. aging temperature before cold rolling than in those specimens annealed at reversion temperatures before cold rolling when annealed at L. T. aging temperatures after cold rolling. (2) The rate of precipitation of Zn solid solution in Al-Zn alloy did not depend upon the annealing temperature before cold rolling when cold rolled specimens were annealed at L. T. aging temperature. (3) In Al-Ag alloy, the rate of disappearance of G. P. zones at L. T. aging temperature depends mainly upon the annealing temperature before cold rolling. On the other hand, in Al-Zn alloy, the rate of disappearance of G. P. zones at L. T. aging temperature does not depened upon the annealing temperature before cold rolling. (4) These results may be explained without contradiction considering the relation of structures between matrix and precipitates and the deformation stacking faults.

§ 1. Introduction

There are many works on the aging and precipitation of Al alloys. In some alloys solute rich regions, G. P. zones, are formed after quenching before precipitation occurs. And it is well known that the shape of G. P. zones depends upon the difference between the radius of solvent atom and that of solute atom. Spherical zones are formed when the difference of atomic radii is small. G. P. zones which are formed in Al-Ag and Al-Zn alloys are spherical. G. P. zones whose shapes are platelet or stringlet disappear when annealed for a short time at temperatures higher than reversion temperature. But spherical G. P. zones do not disappear. In general, it is considered that G. P. zones do not change directly to precipitates and disappear when precipitation occurs. However, the behaviour of these spherical zones in the latter stage of low temperature aging is not so clear. Large zones concentrated in solute atoms and true precipitates are observed at the same time by electron microscope.

For the precipitation to occur, nucleus of precipitate must be formed. Some authors[(1)] pointed out that nucleation in G. P. zones may be possible, and G. P. zones become true precipitates in these cases.

In the present paper, some special examples on the behaviour of G. P. zones will be shown.

§ 2. Experimental Procedure

1. *Alloys*

Al-30wt%Ag and Al-30wt%Zn alloys were used. Al, Ag, and Zn used in making alloys were of high purity, the aluminium being 99.99%, the silver 99.95%, the zinc 99.99%.

Al-30wt%Ag alloy was made by melting together the proper amount of pure metals in high alumina crucibles under the cover of a flux consisting of $MgCl_2$ 60%, KCl 20%, and NaCl 20%. Al-30wt%Zn alloys were made by melting the aluminium first under the cover of the flux, then proper amounts of zinc were added lowering the temperature of molten alloy. The molten alloys were cast into a metallic mold, 3cm in diameter. The ingot of the Al-Ag alloy was homogenized at 550°C for 24 hours and then cut into a sheet 4mm thick. The ingot of the Al-Zn alloy was homogenized at 430°C for 50 hours and then cut into a sheet 4mm thick. Specimens between 0.07 to 0.10mm thick were made from these sheets by cold rolling with proper intermediate annealing at homogeniging temperatures for about 15 min.

2. *Experimental Equipments*

A camera for small angle scattering of X-rays with a monochrometer of a curved cystal of quartz(2) was used with CuKα radiation.

§ 3. Results

Strips about 0.1mm thick were first quenched from a temperature of homogeneous solid solution, and then annealed at temperatures lower or higher than reversion temperature. Annealing time was determined in order that mean radius of G. P. zones were nearly equal for various annealing temperature. Then the thickness was reduced 50% by cold rolling. In this stage, spherical G. P. zones became ellipsoid(2). Cold rolled specimens were then annealed at temperatures of L. T. aging. After various period of annealing, small angle scattering of CuKα radiation from each specimen was inspected.

1. *Al-30%Ag Alloy*

Results obtained are summarized in Table 1 and 2.

Table 1. Precipitation of γ'-phase after cold rolling.

Heat treatment before cold rolling	Annealing at 150°C after 50% cold rolling				
	15 min.	30 min.	60 min.	90 min.	180 min.
(A) 150°C 140 min.	None	1 or 2 streaks	Several streaks	Many streaks	
(A1) 190°C 18 min. +150°C 150 min.	Several streaks	Numerous streaks	Numerous streaks		
(B) 190°C 18 min.	None	None	1 or 2 diffuse streaks	1 or 2 streaks	Numerous streaks
(B1) 150₀C 150 min +190°C 18 min.	None	1 or 2 diffuse streaks	Several streaks	Numerous streaks	Numerous streaks

Table 2. Changes of central diffuse scattering (zones).

Heat treatment before cold rolling	Annealing at 150°C after 50% cold rolling				
	15 min.	30 min.	60 min.	90 min.	180 min.
(A) 150°C 140 min.	Not changed 33.3 Å	Weakened	Very weakened	Not observed	
(A) 190°C 18 min. +1150°C 150 min.	Weakened	Very weakened	Not observed		
(B) 190°C 18 min	Not changed 49.1 Å	Not changed 51.1 Å	Not changed	Not changed	Weakened
(B) 150°C 150 min +190°C 18 min.	Not changed 46.8 Å	Not changed	Not changed	Not changed	Not observed

From these results, it may be concluded that:

(1) γ'-phase is formed more easily by annealing at 150°C before cold rolling.

(2) γ'-phase appears a little later by annealing at 150°C in those specimens which were annealed at 190°C before cold rolling.

(3) G. P. zones disappear quickely by annealing at 150°C in those specimens which were annealed at 150°C before cold rolling.

(4) G. P. zones remain fairly long time when annealed at 150°C after 190°C annealing and 50% cold rolling.

Several photographs of this alloy are shown in Photo. 1 and 2.

2. *Al-30wt%Zn Alloy*

In this alloy, the rate of precipitation of Zn solid solution did not depend upon the annealing temperatures before cold rolling. Some examples of X-ray photographs are shown in Photo. 3. As seen in these photographs, scattering of precipitates is observed after 20 min. annealing at 120°C for both case, that is, (1) 190°C 1 min. annealing → 105°C 1 hour annealing and then 50% cold rolling, and (2) 105°C 1 hour annealing → 190°C 1 min. annealing and then 50% cold rolling.

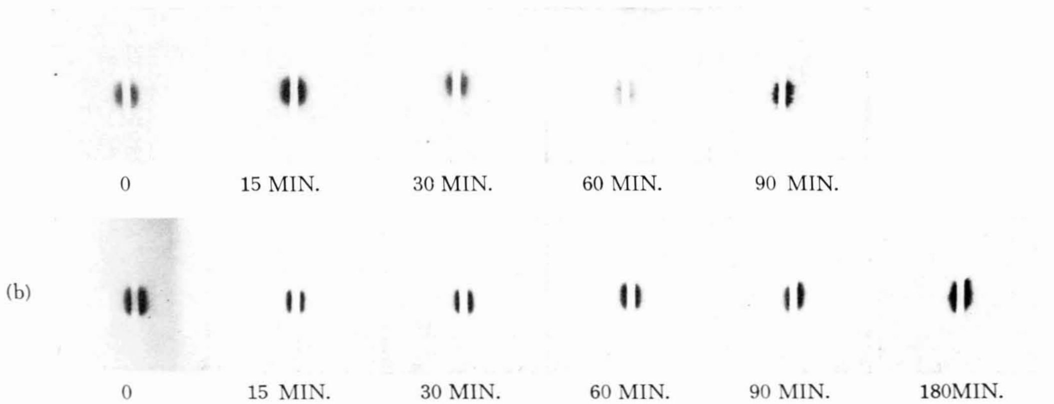

Photo 1. Small angle scattering of CuKα radiation from Al-30wt%Ag alloys. (a) Annealed at 150°C for 2 hours 20 minutes before 50% cold rolling, then annealed at 150°C for various time. (b) Annealed at 190°C for 18 minutes before 50% cold rolling, then annealed at 150°C for various time.

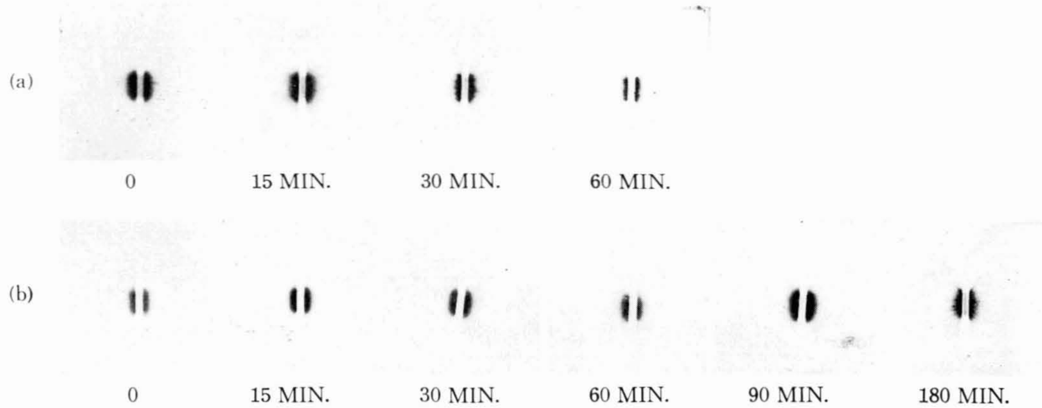

Photo. 2. Small angle scattering of CuKα radiation from Al-30wt%Ag alloys. (a) annealed at 190°C for 18 minutes then at 150°C for 2 hours 30 minutes beforc 50% cold rolling, then annealed at 150°C for various time. (b) Annealed at 150°C for 2 hours 30 minutes then at 190°C for 18 minutes before 50% cold rolling, then annealed at 150°C for various time.

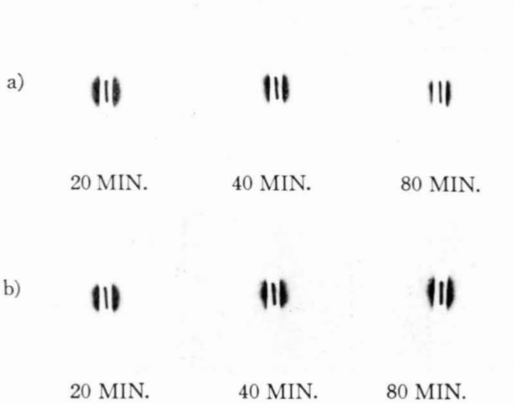

Photo. 3. Small angle scattering of CuKα radiation from Al-30wt%Zn alloys. (a) Annealed at 190°C for one minute then at 105°C for oue hour before 50% cold rolling, and then annealed at 120°C for various time. (b) Annealed at 105°C for one hour then at 190°C for one minute before 50% cold rolling, and then annealed at 120°C for various time.

§ 4. Discussion

As previously reported[2], it is considered that the concentration of solute in G. P. zones which were formed and growed by low temperature aging is larger than that in G. P. zones formed by annealing at temperatures which are higher than reversion temperature. Furthermore, these zones are deformed by cold rolling.

In Al-Ag alloys, precipitation sequence is as follows ;

G. P. zones → (γ''-phase) → γ'-phase → γ-phsae.

γ''-phase was first observed by Fukano and Ogawa[3]. The structure of this phase is close packed hexagonal, and its axial ratio is 1.633. That is, both arrangement of atoms in (001) planes and their interplaner distance are same as those in (111) planes in face centered cubic crystal (G. P. zone). The structures of γ' and

γ-phases are also close packed hexagonal and their axial ratio are 1.612 and 1.588, respectively. In γ'-phase, arrangements of atoms in (001) plane are same as those in (111) plane in f. c. c., but interplaner distance is a little smaler than that in f. c. c. Furthermore, image of stacking fault was observed with electron-microscope in this alloy(4), and it was assumed that these stacking faults are formed in such a position where concentration of silver is high as a result of fluctution. Therefore, it might be possible to assume that γ'-phase is formed at those sites where stacking faults are formed in G. P. zones by cold rolling.

On the other hand precipitation sequence of Al-rich Al-Zn alloys is;

G. P. zones → Zn solid solution (stable precipipitates).

And it seems that there is no report on the formation of stacking faults. The structure of Zn solid solution is also close packed haxagonal, but a=2.65Å, c=4.93Å, and c/a=1.860. This phase is, therefore, fairly different from f. c. c. and it is difficult to assume that Zn solid solution is formed from f. c. c. solid solution as a result of stacking faults.

It is considered generally that a state of solid solution containing G. P. zones is a metastable one, and they can not change to true precipitates. However, experimental results and considerations mentioned above might be considered to suggest that G. P. zones could change to precipitates or other stable or metastable phase when some structural conditions were filled and nucleus of new phase could be formed in G. P. zones. In the cases of Al-Ag alloy, if deformation stacking faults could be formed in G. P. zones (and truely stacking faults were observed in Al-Ag alloys(4)), these parts could be considered as γ''-phase. Furthermore, γ'-phase is very similar to γ''-phase (or deformation stacking fault in Ag-rich G.P. zones). Therefore, when G. P. zones more concentrated in Ag were deformed, they might easily change γ''-or γ'-phase. And when G. P. zones were not so rich in Ag, they could not change to γ''- or γ'-phase so easily even if they were deformed.

On the other hand, in the case of Al-Zn alloy, structural conditions and conditions for nucleus formations in G. P. zones are both unfilled. And concentration of solute in G. P. zones does not affect to the rate of formation of precipitates. Results obtained on Al-Zn alloy might be considered to support the suggestion on the role of structural relation and stacking faults.

References

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