# Heat Treating Characteristics of High Strength Al-Zn-Mg-Cu Alloys With and Without Silver Additions

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Effects of the addition of 0.35 pct Ag on tensile properties of commercially-fabricated 2 in. thick plate were investigated with two 7075-type alloys and similar chromium-free compositions containing 0.35 pct Mn. Both rates of cooling during the quench from the solution heat treatment and rates of heating to precipitation heat-treating temperatures strongly affected relative strengths of the alloys. Alloys containing silver developed substantially higher strengths than the control alloys without silver when 0.125 in. (3.2 mm) thick specimens from the plate were rapidly quenched and rapidly heated to precipitation temperatures above 200°F (92°C) and isothermally precipitated. When the rapid quench was followed by slower heating to the precipitation temperature, however, both silver-free and silver-containing alloys developed comparable high strengths. When the full thickness plate was heat treated employing cooling and heating rates established by section size and standard commercial processing, silver had relatively little effect on the mechanical properties. With lower quenching rates, alloys without silver developed higher strengths than their counterparts with silver.

EFFECTS of silver additions to Al-Zn-Mg-Cu alloys were examined at Alcoa Research Laboratories as early as 1947 as part of extensive investigations of effects of alloying elements on properties of aluminum. In early experiments, tensile properties of 7075 and related alloys in the form of sheet were compared with those of similar sheet containing additionally 0.5 to 1.6 pct Ag. After conventional isothermal and step-precipitation heat treatments, alloys containing silver generally developed strengths comparable to those of the control alloys, but in some instances they developed strengths up to 10 pct lower.

After Polmear[1] reported in 1960 that 0.3 to 1 pct Ag additions substantially increased strengths of Al-Zn-Mg-Cu alloys isothermally precipitation-heat-treated above 250°F (121°C) additional experiments were initiated at the Alcoa Research Laboratories. Effects of time at room temperature prior to elevated temperature isothermal precipitation heat treatment on tensile properties of 7075 and 7079 sheet and of comparable sheet containing 0.4 to 0.6 pct Ag were evaluated. Silver-free alloys and alloys containing silver developed equally high strengths after precipitation heat treatments at 250°F (121°C) or lower. Alloys containing silver precipitation-heat-treated above 250°F (121°C) after a short time at room temperature, however, developed substantially higher strengths than identically processed silver-free control alloys. Strength of the silver-free alloys substantially increased when precipitation heat treatment was preceded by natural aging intervals of several days but strength of the alloys containing silver was almost unaffected. The effect of natural aging interval was also reported by Rosenkranz.[2] Because silver additions provided no strength advantage and because resistance to stress-corrosion cracking of sheet in the highest strength temper was adequate, no further work with sheet was indicated.

Additional work with thick sections was indicated, however, because silver additions appeared to provide their maximum strength advantage after precipitation heat treatment at temperatures which promote a high degree of resistance to stress-corrosion cracking in the critical short-transverse direction of Al-Zn-Mg-Cu alloy products. To determine whether silver additions were beneficial in commercially processed material, silver-free and silver-containing alloys were fabricated to plate and evaluated. This paper presents heat treating characteristics; a companion paper presents stress-corrosion performances.

## RESULTS

### Material Heat Treated as 2-in. (51 mm) Thick Plate (Cold Water Quench)

Material used in this investigation was 2-in. (51 mm) thick plate produced in the plant from 12 by 30 by 120 in. (305 by 760 by 3050 mm) DC (direct-chilled) ingot, using 7075 practices. Chemical analyses are presented in Table I.

Some of the plate was heat treated at the plant using precipitation heat treatments that have been used to produce 7075-T651 [24 hr at 250°F (121°C)] and 7075-T7351 [6 hr at 225°F (107°C) followed by 24 hr at 325°F (162°C)]. Other portions of the plate were solution heat treated and stretched at the plant and precipitation heat treated at the laboratory using 7075-T651 and 7075-T7351 practices in addition to isothermal precipitation treatments of 8 hr at 315°F (157°C) (recommended by Rosenkranz) and 16 hr at 270°F (132°C) (recommended by Polmear). Additional portions of the plate were solution heat treated and quenched at the laboratory, then precipitation heat treated by the two-step and isothermal practices described previously. Precipitation heat treatments at 315°F (157°C) and 270°F (132°C) were started immediately after quenching. In addition, a piece of the plate that was heat treated to the T651

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Table I. Analyses of Al-Zn-Mg-Cu Alloy Plate

| Alloy Type | Zn | Mg | Cu | Cr | Zr | Mn | Ag | Fe | Si | Ti | B | Be |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7075 | 5.82 | 2.18 | 1.54 | 0.20 | 0.00 | 0.01 | 0.00 | 0.30 | 0.09 | 0.03 | 0.000 | 0 000 |
| 7075 + Ag | 5.89 | 2.34 | 1.49 | 0.21 | 0.01 | 0.02 | 0.37 | 0 24 | 0.09 | 0.04 | 0.000 | 0.001 |
| Hi Zn | 6.56 | 2.31 | 1.39 | 0.21 | 0.00 | 0.02 | 0.00 | 0.24 | 0.07 | 0.03 | 0.000 | 0.001 |
| Hi Zn + Ag | 6.59 | 2.44 | 1.44 | 0.20 | 0.03 | 0.04 | 0.39 | 0.25 | 0.09 | 0.04 | 0.000 | 0.001 |
| Zr | 5.80 | 2.20 | 1.25 | 0.01 | 0.12 | 0.01 | 0.00 | 0.25 | 0.09 | 0.03 | 0.000 | 0 001 |
| Zr + Ag | 5.76 | 2.29 | 1.47 | 0.00 | 0.14 | 0.01 | 0.35 | 0.28 | 0.07 | 0.04 | 0.000 | 0.001 |
| Mn | 5.72 | 2.21 | 1.52 | 0.03 | 0.01 | 0 34 | 0.01 | 0 20 | 0 07 | 0.04 | 0.000 | 0.001 |
| Mn + Ag | 5.71 | 2.29 | 1.49 | 0.03 | 0.01 | 0.34 | 0.38 | 0.20 | 0 07 | 0.05 | 0.000 | 0 000 |

Table II. Heat Treating Conditions

| | | | Precipitation Heat Treatment | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | First Elevated Temperature Step | | | Second Elevated Temperature Step | | |
| Code | Solution Treatment Location | Time at Room Temperature | Heating Time | Soak Time | Soak Temperature | Heating Time | Soak Time | Soak Temperature |
| 3 | Lab | 4 days | 2 hr | 24 hr | 250°F (121°C) | – | – | – |
| 7 | Plant | 3 weeks | 2 hr | 24 hr | 250°F (121°C) | – | – | – |
| 10 | Plant | 3 days | 28 hr | 24 hr | 250°F (121°C) | – | – | – |
| 1 | Lab | None | 2 hr | 16 hr | 270°F (132°C) | – | – | – |
| 5 | Plant | 3 weeks | 2 hr | 16 hr | 270°F (132°C) | – | – | – |
| 2 | Lab | None | 3 hr | 8 hr | 315°F (157°C) | – | – | – |
| 6 | Plant | 3 weeks | 3 hr | 8 hr | 315°F (157°C) | – | – | – |
| 4 | Lab | 4 days | 2 hr | 6 hr | 225°F (107°C) | 2 hr* | 24 hr | 325°F (162°C) |
| 8 | Plant | 3 weeks | 2 hr | 6 hr | 225°F (107°C) | 2 hr* | 24 hr | 325°F (162°C) |
| 9 | Plant | 3 days | 15 hr | 6 hr | 225°F (107°C) | 14 hr* | 24 hr | 325°F (162°C) |
| 11 | Plant | 3 days | 28 hr | 24 hr | 250°F (121°C) | 3 hr | 24 hr | 325°F (162°C) |
| | | | All solution treated at 880°F (472°C) | | | | | |

* = Time from 225°F (107°C) to soak temperature minus 10°F (6°C). All other times are times from room temperature to soak temperature minus 10°F (6°C) Soak time is time at soak temperature minus 10°F (6°C) to time of removal from furnace.

Material spray quencyed by cold water at plant as 2 in. by 30 in. by $L$ (51 mm by 760 mm by $L$) pieces, stretched 2.5 pct within 1 hr. Material immersion quenched in cold water at laboratory 2 in. by 7 in. by 7 in. (51 by 178 by 178mm) pieces, not stretched. Both quench rates estimated to be 67°F per sec ± 5°F per sec (33°C per sec ± 3°C per sec) between 750°F (395°C) and 550°F (290°C).

temper in the plant was precipitation heat treated an additional 24 hr at 325°F (162°C) in the laboratory. A summary of the heat treating conditions is presented in Table II.

Tensile properties were determined using duplicate standard long-transverse and short-transverse orientation specimens taken from the midplane. Long-transverse direction yield strengths (0.2 pct offset) are presented in Table III. These data reveal that the alloy containing 6.6 pct Zn and 0.39 pct Ag developed slightly lower strength than its silver-free counterpart while the alloy containing 1.25 pct Cu and 0. 12 pct Zr developed slightly lower strength than the alloy containing 1.47 pct Cu, 0.14 pct Zr and 0.35 pct Ag. Strengths of the other alloy pairs were similar.

Conventional transmission electron microscopic examinations also revealed that after identical heat treatments the microstructures of the silver-free alloys were comparable to those of the alloys containing silver. The microstructure of the standard alloy 7075 solution heat treated in the plant and aged 8 hr at 315°F (157°C) in the laboratory (Code 6) is presented in Fig. 1(*a*). The large particles are Al-Mg-Cr precipitates which are insoluble at the solution temperature. The fine structure is composed of G.P. zones which appear to be transforming to the crystalline $Mg(Zn, Cu)_2$ precipitate. The microstructure of a comparable alloy containing silver is presented in Fig. 1(*b*). The structure is similar to that of the silver-free alloy, including the narrow precipitate-free zone (PFZ) at the grain boundaries.

The similarity between strengths of the silver-free alloys and the strengths of the alloys containing silver, particularly those of the materials isothermally precipitation heat treated above 250°F (121°C) immediately after quenching, was unexpected so additional work was performed to account for this behavior.

## Material Heat Treated as Thin Slices

Quenching rate from the solution temperature and heating rate to the precipitation temperature appeared to be the main differences between experimental procedures reported by other investigators and those employed during heat treatment of the 2-in. (51 mm) thick plate. Consequently, the effects of these variables were evaluated. In the initial experiment, 0.125-in. (3.2 mm) thick long-transverse orientation slices were prepared from 7075 plate and from comparable plate which contained silver. Slices were solution treated at 890°F (475°C), quenched into water at room temperature, and after $\frac{1}{2}$ hr were heated to 315°F (157°C) at various rates and held for 8 hr.

Average yield strengths of duplicate specimens ma-

Table III. Long-Transverse Yield Strengths 2 in. Thick Plate

| Code | | 7075 | 7075 + Ag | Hi Zn | Hi Zn + Ag | Zr | Zr + Ag | Mn | Mn + Ag |
|---|---|---|---|---|---|---|---|---|---|
| 3 | ksi | 67.6 | 67.7 | 73.3 | 68.7 | 71.0 | 72.0 | 71.2 | 69.6 |
| | kg/mn$^2$ | 47.5 | 47.6 | 51.5 | 48.3 | 49.9 | 50.6 | 50.0 | 48.9 |
| 7 | ksi | 69.3 | 69.8 | 74.5 | 72.2 | 71.5 | 73.7 | 72.6 | 71.9 |
| | kg/mm$^2$ | 48.6 | 49.0 | 52.3 | 50.7 | 50.2 | 51.8 | 51.0 | 50.5 |
| 10 | ksi | 71.8 | 72.3 | 77.7 | 74.4 | 73.7 | 76.6 | 74.1 | 75.2 |
| | kg/mm$^2$ | 50.4 | 50.8 | 54.6 | 52.2 | 51.8 | 53.8 | 52.0 | 52.8 |
| 1 | ksi | 69.8 | 69.3 | 73.9 | 70.7 | 72.5 | 73.1 | 72.6 | 71.3 |
| | kg/mm$^2$ | 49.0 | 48.6 | 51.8 | 49.6 | 50.9 | 51.4 | 51.0 | 50.0 |
| 5 | ksi | 69.5 | 69.2 | 74.7 | 72.3 | 72.7 | 74.3 | 72.6 | 73.2 |
| | kg/mm$^2$ | 48.8 | 48.6 | 52.5 | 50.7 | 51.0 | 52.1 | 51.0 | 51.4 |
| 2 | ksi | 69.4 | 69.0 | 72.4 | 69.2 | 73.6 | 76.0 | 76.0 | 75.9 |
| | kg/mm$^2$ | 48.7 | 48.5 | 50.8 | 48.6 | 51.7 | 53.4 | 53.4 | 53.3 |
| 6 | ksi | 68.5 | 68.2 | 74.0 | 70.3 | 72.7 | 76.2 | 75.1 | 76.1 |
| | kg/mm$^2$ | 48.1 | 47.9 | 52.0 | 49.3 | 51.1 | 53.5 | 52.8 | 53.5 |
| 4 | ksi | 63.0 | 61.6 | 62.7 | 57.4 | 67.7 | 69.9 | 71.4 | 69.9 |
| | kg/mm$^2$ | 44.2 | 43.3 | 44.0 | 40.3 | 47.6 | 49.1 | 50.1 | 49.1 |
| 8 | ksi | 64.3 | 60.8 | 67.1 | 63.6 | 65.8 | 68.7 | 70.9 | 68.8 |
| | kg/mm$^2$ | 45.1 | 42.7 | 47.1 | 44.7 | 46.2 | 48.2 | 49.8 | 48.3 |
| 9 | ksi | 56.2 | 56.7 | 57.7 | 56.5 | 60.7 | 65.0 | 64.2 | 65.7 |
| | kg/mm$^2$ | 39.4 | 39.8 | 40.5 | 39 7 | 42.6 | 45.7 | 45.1 | 46.2 |
| 11 | ksi | 65.0 | 66.0 | 68.7 | 67.1 | 68.6 | 72.3 | 72.4 | 71.6 |
| | kg/mm$^2$ | 45.6 | 46.4 | 48.3 | 47.2 | 48.2 | 50.8 | 50.8 | 50.3 |

chined from these slices are plotted vs average heating rate in Fig. 2. High strength of the alloy containing silver was not affected by heating rate, but strength of alloy 7075 appreciably decreased with increasing heating rate above 250°F per hr (140°C per hr). Similar effect of heating rate to 325°F (162°C) on precipitation behavior of 7075 was recently reported.[3]

Transmission electron microscopic examinations of the specimens heated at the lowest and the highest rates revealed structural differences which could be related to the strengths. The structures are illustrated in Fig. 3. Matrix structures of alloy containing silver which was heated at either rate were similar. They consisted of small, closely spaced G.P. zones. The slightly angular appearance of some of the zones suggests that they were beginning to transform into crystalline $Mg(Zn, Cu)_2$ precipitate. On the other hand, structures of the 7075 specimens which were heated at the two rates were markedly different from each other. While the matrix structure of the specimen which was heated at 42°F per hr (23°C per hr) was similar to that of the specimens containing silver, the structure of the specimen which was heated at 80,000°F per hr (44,000°C per hr) contained a Widmanstätten precipitate of the $Mg(Zn, Cu)_2$ phase.

Examination also revealed differences in the width of the PFZ. This region was substantially narrower in the material containing silver than it was in 7075.

Additional work explored effects of quench rate from solution temperature, heating rate to precipitation temperature, and precipitation treatment time and temperature on tensile properties of 7075, a similar alloy which contained 0.3 pct Mn and less than 0.05 pct Cr, and comparable alloys which contained 0.3 to 0.4 pct Ag. Long-transverse orientation slices 0.125-in. (3.2 mm) thick were solution treated at 890°F (475°C) and were quenched into water at either room temperature or the boiling point. Average quenching rates between 750°F (395°C) and 550°F (290°C) are estimated to be 2000°F per sec (1100°C per sec) and 20°F per sec (11°C per sec), respectively. The lower quench rate approximates the rate at the midplane of 3-in. (76 mm) thick plate quenched in cold water. These slices were heated to precipitation treatment temperatures of 200°F (94°C) through 350°F (177°C) within 1 hr after quenching at average heating rates of either 75°F per hr (42°C per hr) or 80,000°F per hr (44,000°C per hr). They were removed after exposures of $\frac{1}{2}$ to 192 hr, and duplicate 1-in. gage length tension specimens were machined and tested after several weeks.

Maximum yield strengths developed at each precipitation treatment temperature were used as the criterion of response to heat treatment. Strengths of the alloys containing chromium which were rapidly quenched and rapidly heated are presented in Fig. 4. These data essentially duplicate the effect originally reported by Polmear.[1] The silver-free alloy developed strengths up to 30 ksi (21 kg per sq mm) lower after it was precipitation heat treated above 270°F (132°C) than it did after it was precipitation heat treated at lower temperatures. In contrast, the alloy containing silver developed strengths after precipitation treatment above 270°F (132°C) which were at most 10 ksi (7 kg per sq mm) below strengths developed at lower temperatures. Maximum strength developed by the alloy containing silver was three ksi (2 kg per sq mm) higher than that developed by the silver-free alloy.

Strengths of the alloys containing manganese which were comparably heat treated are presented in Fig. 5. The alloy containing silver developed substantially higher strengths than its silver-free counterpart after precipitation heat treatments above 270°F (132°C), and it developed a maximum strength that was two ksi (1.5 kg per sq mm) higher than that developed by the silver-free alloy.

Strengths of the specimens quenched at the high rate and heated at the low rate are presented in Figs. 6 and 7. Decreasing heating rate increased strengths of the

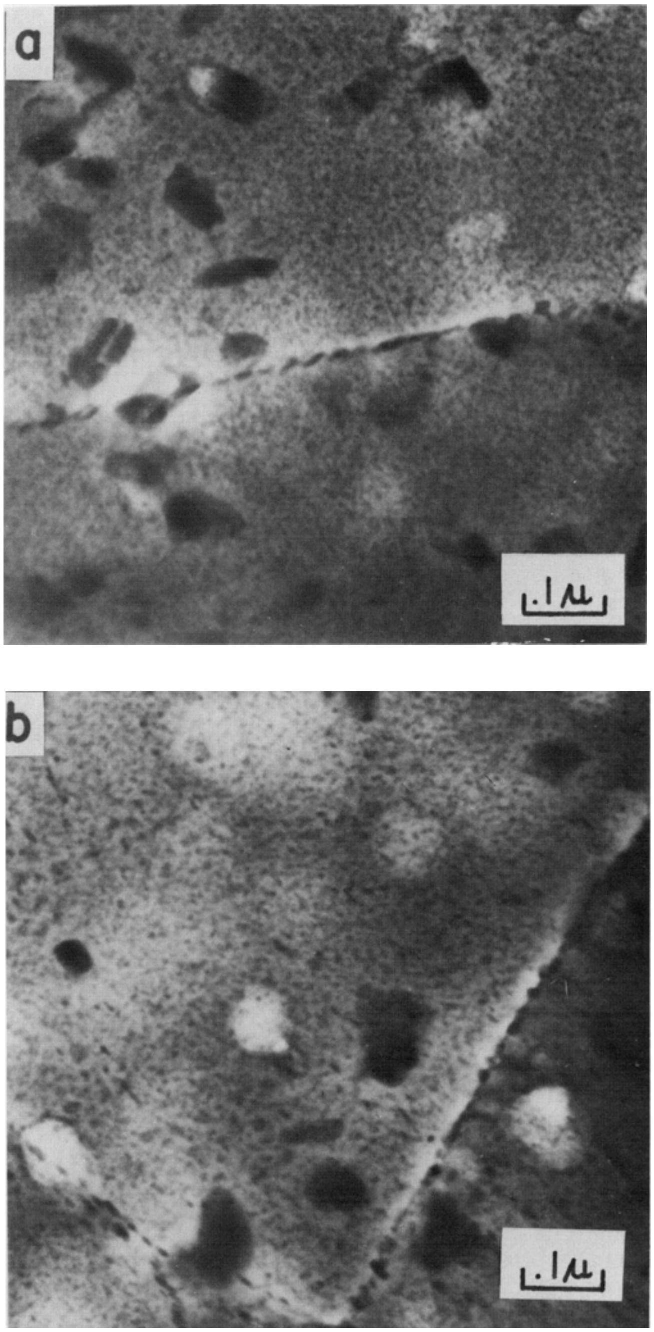


Fig. 1—Structures of 2-in. (51 mm) thick plate of 7075 (*a*), and of a similar alloy containing 0.37 pct Ag (*b*) quenched in cold water from the solution temperature, stretched 2.5 pct, precipitation heat treated 8 hr at 315°F (157°C) after 2 weeks at room temperature.

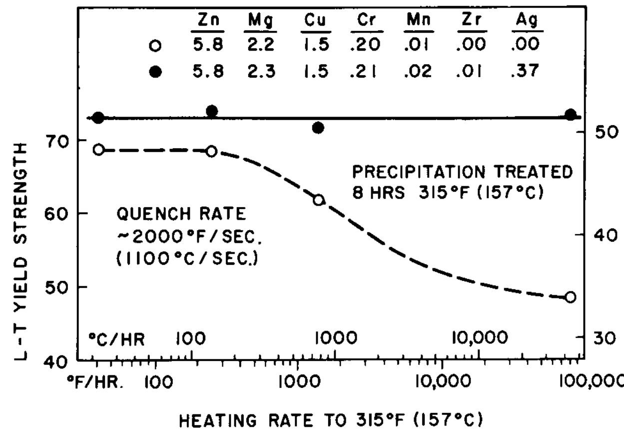


Fig. 2—Effects of heating rate to the precipitation heat treatment temperature on strength of 7075 and a similar alloy containing 0.37 pct Ag.

silver-free materials precipitation heat treated above 270°F (132°C), but had little effect on strength of the alloy containing silver. Consequently, maximum strength advantage of the alloys containing silver in this higher temperature range significantly decreased. Maximum strengths of the alloys containing manganese were almost totally unaffected by precipitation treatment temperature.

Strength of the materials both quenched and heated at the low rates are presented in Figs. 8 and 9. In contrast to the behavior of the alloys containing chromium when quenched and heated at high rates, the silver-free alloy of this pair developed strengths approximately five ksi (3.5 kg per sq mm) higher than those developed by the alloy containing silver. Under these same conditions strengths of the two manganese alloys were almost identical.

To illustrate the effect of increasing time between quenching and elevated temperature precipitation heat treatment, specimen blanks were prepared from material that had been solution treated, quenched, and stretched in the plant $1\frac{1}{2}$ years previously. Effects of the high heating rate only were determined. Strengths of the materials precipitation heat treated after the $1\frac{1}{2}$ year interval are presented in Figs. 10 and 11. Under these conditions the silver-free alloys developed strengths only slightly lower than those of the alloys containing silver although they were heated to precipitation treatment temperature at a high rate.

To completely eliminate the effect of heating rate to precipitation heat treatment temperature, specimen blanks taken from 7075 and 7075 + Ag similar to those previously described were solution treated at 890°F (475°C) and quenched in a Wood's metal bath directly to precipitation treatment temperatures. They were removed after periods of $\frac{1}{2}$ to 96 hr and were quenched in water at room temperature. Duplicate tension specimens were subsequently machined and tested. Data were analyzed by plotting precipitation heat treatment temperature vs time at temperature with yield strength as the parameter. Time-Temperature-Yield Strength plots are presented in Figs. 12 and 13. Alloy 7075 developed its maximum strength of 72 ksi (51 kg per sq mm) at 250°F (121°C), and did not develop strength higher than 60 ksi (42 kg per sq mm) at precipitation temperatures above 325°F (162°C). In contrast, the silver-bearing alloy developed its maximum strength of 76 ksi (54 kg per sq mm) near 275°F (135°C) and developed almost 70 ksi (49 kg per sq mm) during precipitation heat treatment at 350°F (175°C). The alloy containing silver also developed a given strength level in a shorter time, but this trend diminished with decreasing precipitation heat treatment temperature.

To determine if the alloy containing silver developed strength at a higher rate than the silver-free alloy during precipitation at room temperature, similar specimens of 7075 and 7075 plus silver were solution treated, quenched in water at room temperature and tested after

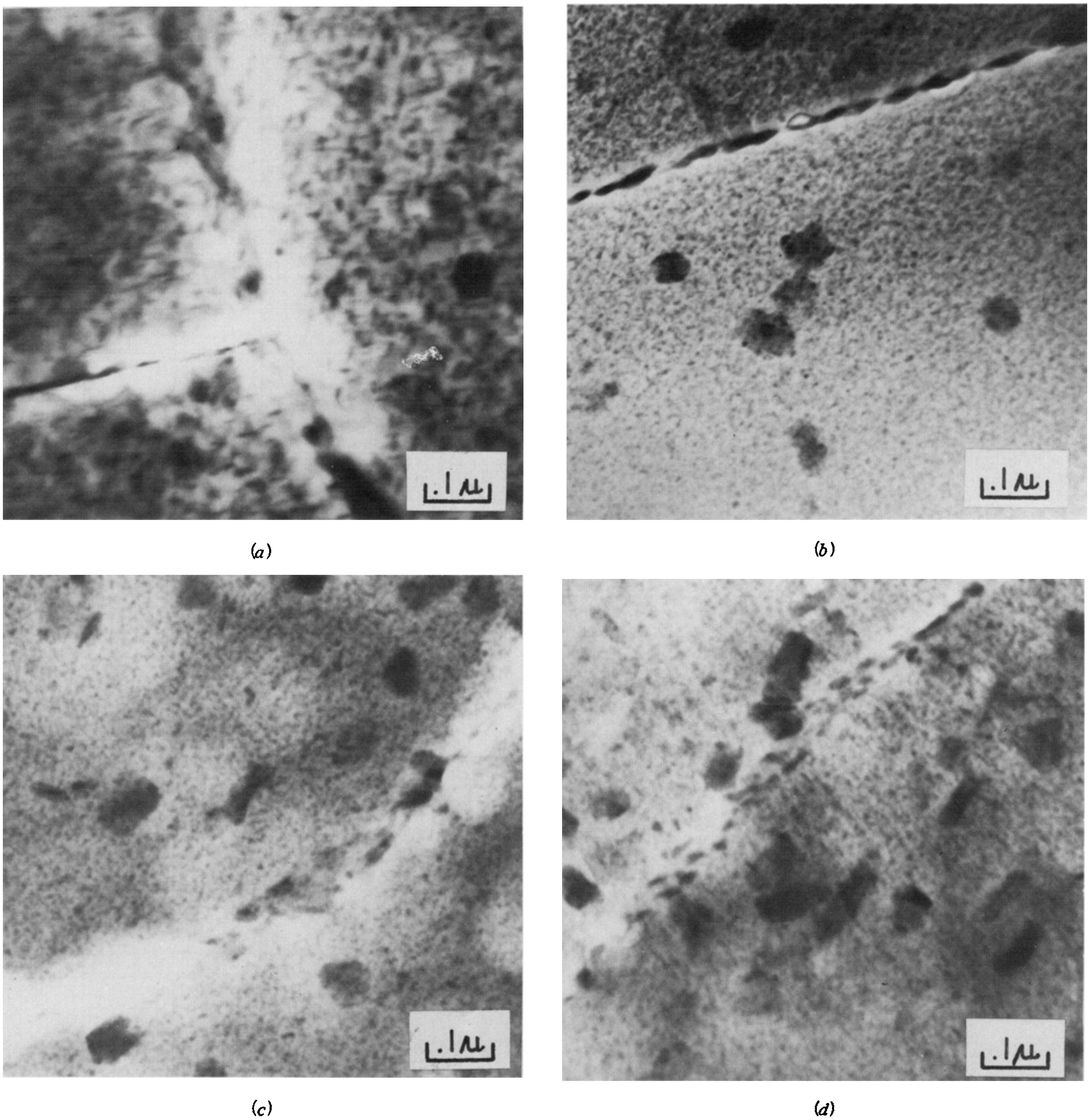


Fig. 3—Effects of heating rate on structures of rapidly quenched specimens of 7075 and of a similar alloy containing 0.37 pct Ag precipitation heat treated 8 hr at 315°F (157°C). (*a*) 7075, slow heating; (*b*) 7075 + Ag, slow heating; (*c*) 7075, rapid heating; (*d*) 7075 + Ag, rapid heating.

times of $\frac{1}{2}$ hr to several months. Strengths of both alloys were virtually identical after comparable intervals.

### Material Heat Treated as 2-in. Thick Plate (Quenched in Boiling Water)

To determine the combined effect of quenching under conditions designed to reduce residual stress and of precipitation heat treating under commercial conditions, additional experiments were conducted. Portions of 2-in. (51 mm) thick plate in the alloys which contained either 0.2 pct Cr or 0.3 pct Mn were solution heat treated at 890°F (475°C) and quenched in water at the boiling point. After four days they were precipitation heat treated 24 hr at 250°F (121°C) (2 hr to temperature), cooled to room temperature, then precipitation heat treated 24 hr at 325°F (162°C) (24 hr to temperature). Average yield strengths of duplicate long-transverse orientation tension specimens are presented in Fig. 14. Alloys containing silver developed strengths 9 to 18 pct lower than those of the comparable silver-free alloys.

## DISCUSSION

Some of the differences in structure and strength of these alloys can be explained using Nicholson's[4-7] and Pashley's[8,9] theories of precipitation. Although these

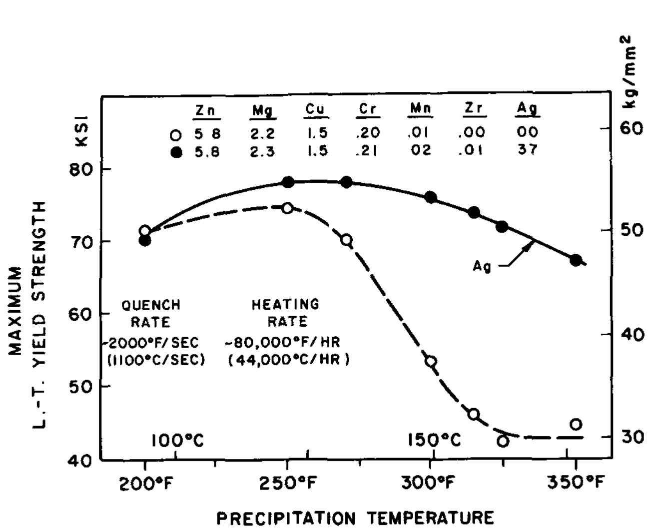


Fig. 4—Effect of a silver addition and heat treatment conditions on strength of an Al-Zn-Mg-Cu-Cr alloy (rapid quench from solution treatment temperature and rapid heating to the precipitation treatment temperature).

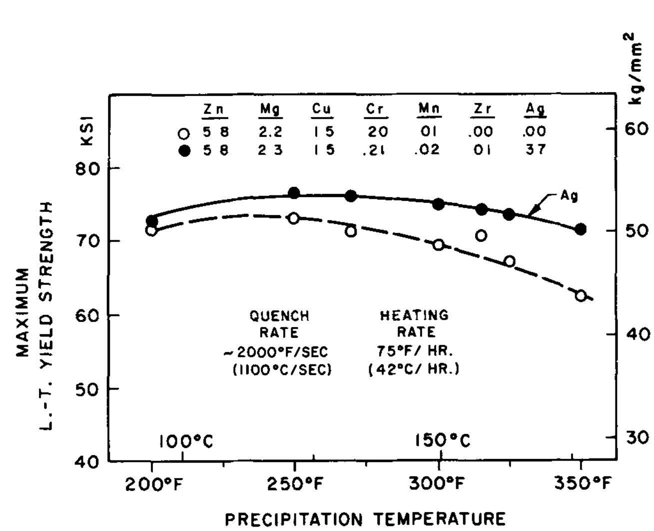


Fig. 6—Effect of a silver addition and heat treatment conditions on strength of an Al-Zn-Mg-Cu-Cr alloy (rapid quench from the solution treatment temperature and slow heating to the precipitation treatment temperature).

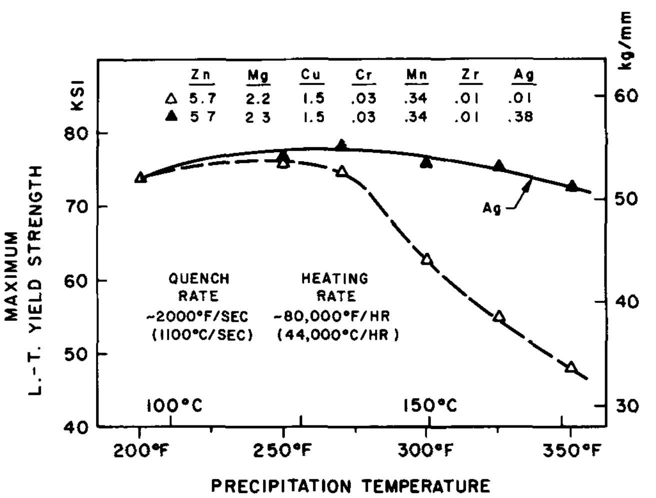


Fig. 5—Effect of a silver addition and heat treatment conditions on strength of an Al-Zn-Mg-Cu-Mn alloy (rapid quench from the solution treatment temperature and rapid heating to the precipitation treatment temperature).

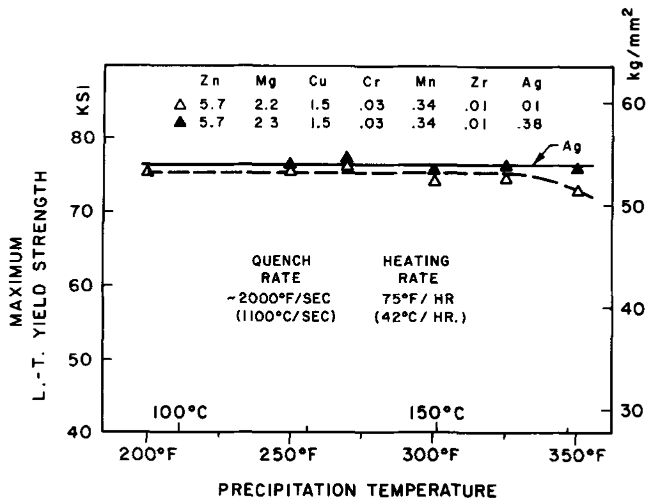


Fig. 7—Effects of a silver addition and heat treatment conditions on strength of an Al-Zn-Mg-Cu-Mn alloy (rapid quench from the solution treatment temperature and slow heating to the precipitation treatment temperature).

authors used different terminology, both considered existence of a temperature above which homogeneous nucleation is impossible because of decreased solute supersaturation. The decrease of G.P. zone size with decreasing precipitation temperature below this critical temperature is attributed to higher supersaturation of solute allowing smaller nuclei to be stable. Both theories also consider that G.P. zones formed at a low temperature will dissolve on heating to a higher temperature if they are smaller than a critical size but will transform to the intermediate precipitate with increasing time at higher temperature if they are larger than a critical size.

Vacancies play the same role in both theories and their concentration must be considered. Presence of excess vacancies at precipitation temperature increases the temperature at which homogeneous nucleation can occur, and increases the rate of nucleation by increasing diffusion rate. Because of the increased nucleation rate, increasing excess vacancy concentration increases density of the G.P. zones formed at a given precipitation treatment temperature.

Using these concepts, the coarse structure and low strengths of the silver-free materials either quenched to room temperature and rapidly heated above 250°F (121°C) or quenched directly to aging temperatures above 250°F (121°C) are readily explained by the decrease in supersaturation with increasing temperature. Either decreasing heating rate or increasing time at room temperature before precipitation heat treating above 250°F (121°C) increases strength by promoting copious nucleation of G.P. zones and allowing them to grow until most of them develop into the intermediate precipitate after heating above 250°F (121°C) rather than dissolve.

Differences in widths of the precipitate-free zones of 7075 alloy are also explained using these theories. Because of a vacancy concentration gradient near grain boundaries, G.P. zones near grain boundaries will grow at a lower rate than those away from the boundaries.

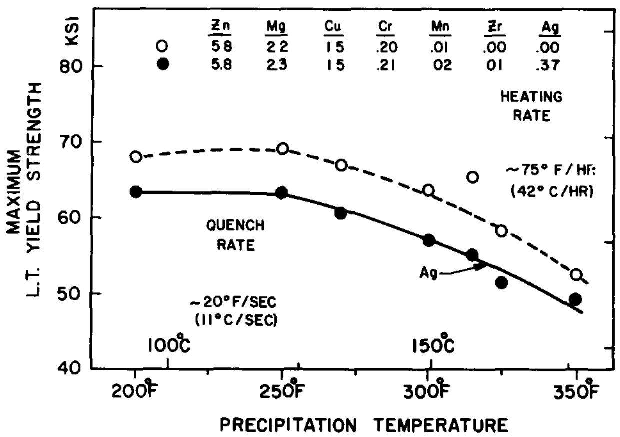


Fig. 8—Effects of a silver addition and heat treating conditions on strength of an Al-Zn-Mg-Cu-Cr alloy (slow quench from the solution treatment temperature and slow heating to the precipitation treatment temperature).

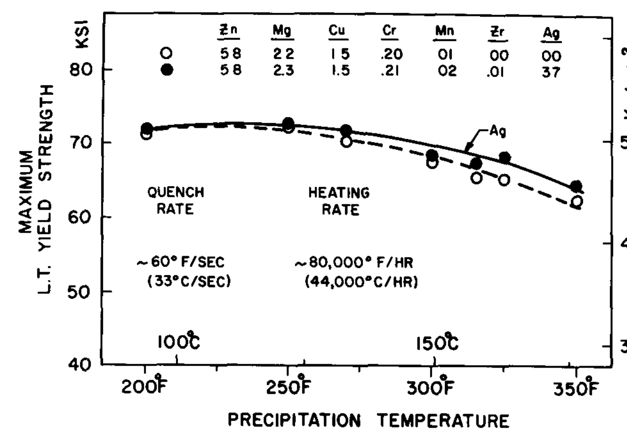


Fig. 10—Effects of silver and heat treatment conditions on strength of an Al-Zn-Mg-Cu-Cr alloy ($1\frac{1}{2}$ year interval between quench from solution treatment temperature and elevated temperature precipitation heat treatment).

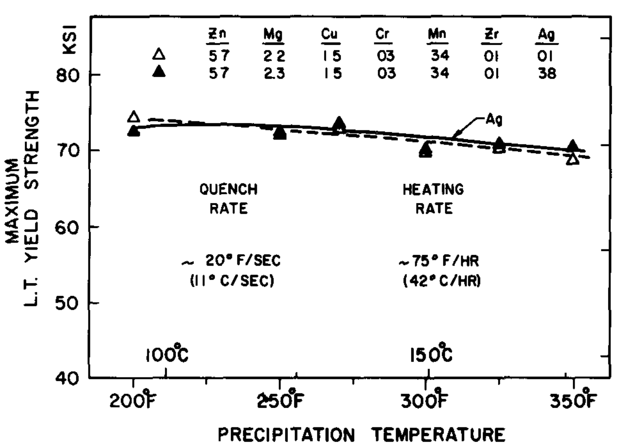


Fig. 9—Effects of a silver addition and heat treating conditions on strength of an Al-Zn-Mg-Cu-Mn alloy (slow quench from the solution treatment temperature and slow heating to the precipitation treatment temperature).

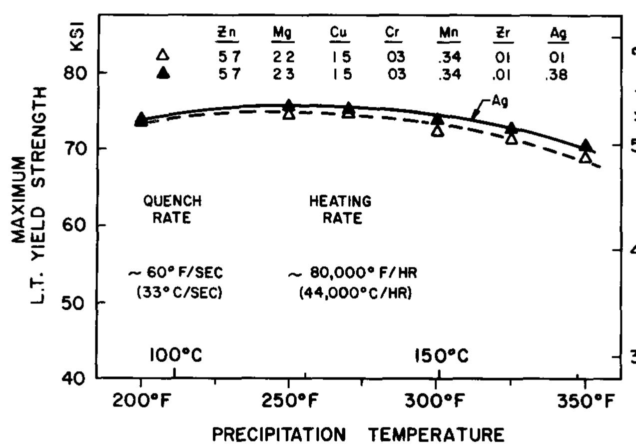


Fig. 11—Effects of silver and heat treatment conditions on strength of an Al-Zn-Mg-Cu-Mn alloy ($1\frac{1}{2}$ year interval between quench from solution treatment temperature and elevated temperature precipitation heat treatment).

Consequently, average G.P. zone size will increase with increasing distance from the grain boundary until vacancy concentration becomes constant. After a short time at room temperature, G.P. zone size near the grain boundaries would be small. Consequently, G.P. zones would dissolve on subsequent heating to 315°F (157°C) leaving a relatively wide PFZ. With increased natural aging interval, however, zone size near the boundaries would increase until it was above the critical size which would not dissolve at 315°F (157°C).

The critical G.P. zone size is unknown, but it cannot be resolved with the electron microscope. No zones were detected in 7075-W plate which was examined 1.5 years after solution treatment, but specimens of this material developed high strengths even though they were rapidly heated to precipitation treatment temperatures.

Reasons for the effects of silver on structure and strength of these alloys are more speculative. One possible explanation would be that silver traps vacancies during the quench, thus increasing the temperature at which homogeneous nucleation occurs and increasing nucleation rate. This explanation is unlikely, however, because the silver addition to 7075 had no effect on natural aging characteristics.

A more probable explanation is offered based on the work described and on three other observations. These observations are: 1) silver clusters readily in aluminum alloys,[10] 2) silver increases precipitation rate in Al-Mg alloys,[11] 3) silver dissolves in $\beta$ (Zn-Mg precipitate.[12] The proffered explanation is that silver atom-vacancy complexes decrease critical G.P. zone size possibly by lowering volume free energy. Reducing critical zone size decreases the PFZ width and increases strength by permitting smaller zones to transform to intermediate precipitate rather than to dissolve.

The concept of silver atom-vacancy complexes also can be used to explain the significantly lower strength of alloys containing silver when slowly quenched. One explanation for the well-known quench sensitivity of Al-Zn-Mg-Cu alloys containing either chromium or manganese is that An, Mg, and Cu atoms precipitate preferentially by deposition on undissolved $Al_{12}Mg_2Cr$ or $Al_{12}Mn_{20}Cu$ particles, thus decreasing the amount of solute that is available for subsequent coherent precipitation.[13,14] Precipitation nucleated by such particles has been observed by transmission electron microscopy.[14,15] If this explanation is correct, the effect of silver on further increasing quench sensitivity may be

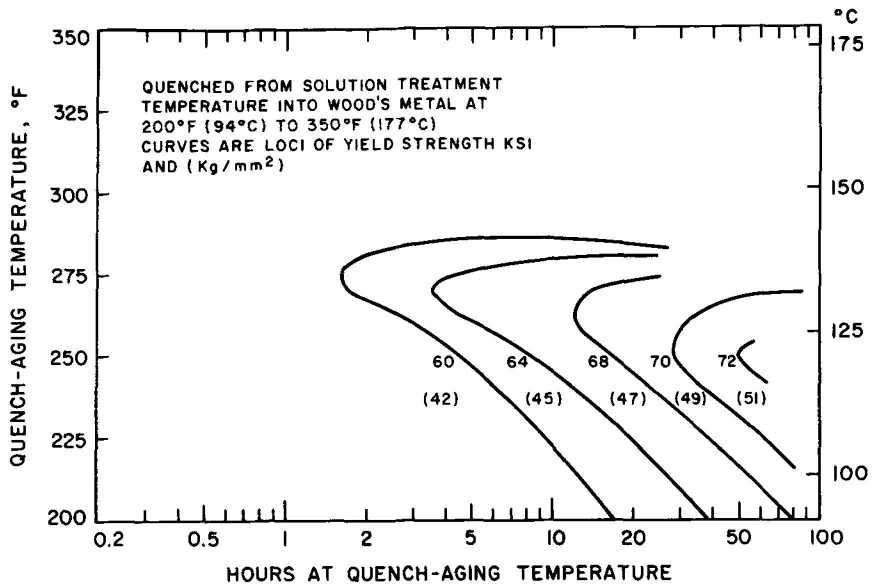


Fig. 12—Effects of precipitation treatment time and temperature on strength of 7075 plate quenched directly to the precipitation treatment temperature.

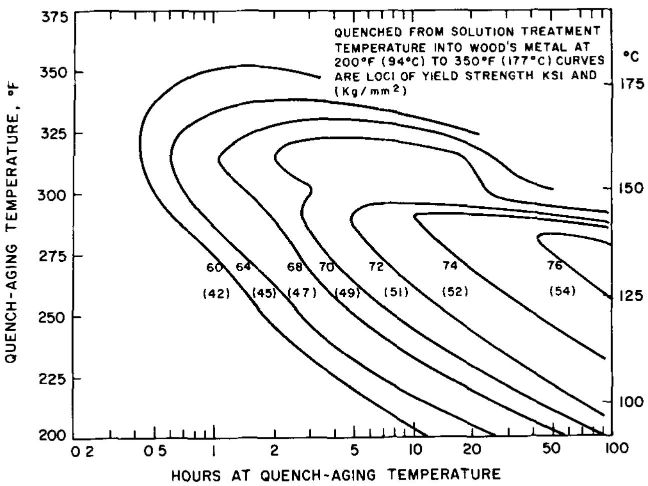


Fig. 13—Effects of precipitation treatment time and temperature on strength of 7075 + Ag plate quenched directly to the precipitation treatment temperature.

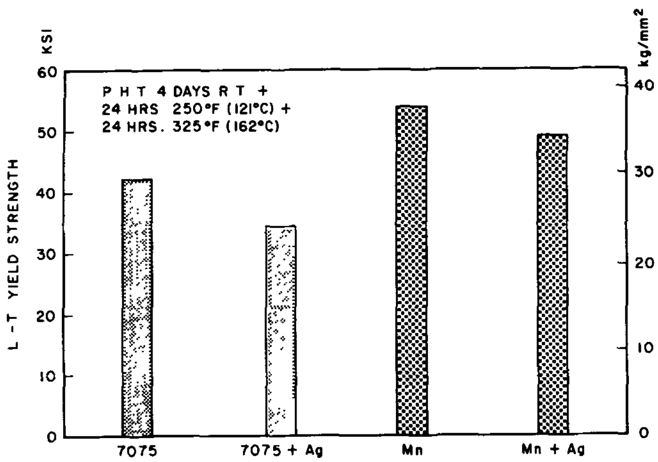


Fig. 14—Strength of 2-in. thick plate quenched in boiling water and precipitation heat treated by a two-step practice.

attributed to silver atom-vacancy complexes which facilitate precipitation onto particles containing either chromium or manganese. It is possible, however, that this mechanism is not the only factor and that amounts of chromium or manganese remaining in solid solution also alter precipitation kinetics through vacancy-solute atom-silver atom interactions.

## SUMMARY

Silver-free Al-Zn-Mg-Cu alloys develop progressively lower strengths with increasing precipitation heat treatment temperatures above 250°F (121°C) when they are quenched directly to precipitation treatment temperature or are heated to precipitation treatment temperature at a high rate shortly after quenching. The low strengths are attributed to a relatively coarse dispersion of the hardening precipitate. Extending natural aging, heating at a low rate, or preaging near 200°F (94°C) increases strength by allowing G.P. zones to grow to a stable size which will transform into fine, closely-spaced crystalline precipitate at higher precipitation temperatures. Necessary exposure time near 200°F (94°C) is short enough in 7075-type alloys that it can be attained during heating to precipitation temperatures that are normally observed in heat treating thick section products under commercial conditions.

Al-Zn-Mg-Cu alloys containing silver develop high strength even when quenched directly to precipitation treatment temperatures above 250°F (121°C). This behavior is tentatively ascribed to silver-atom vacancy complexes which effectively decrease the size of the stable G.P. zone. Silver additions are of no commercial advantage in 7075-type alloys, however, because mill heating rates are low enough to allow stable G.P. zones to form before precipitation temperature is attained. Furthermore, when alloys containing silver plus either 0.2 pct Cr or 0.35 pct Mn are quenched at rates approximating those at the midplane of 3-in. (76 mm) thick or thicker plate, they develop lower strengths than similar silver-free alloys. Silver atom-vacancy complexes may be responsible for quench sensitivity by promoting precipitation during the quench on particles containing either chromium or manganese.

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