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HEAT TREATMENT OF ALUMINUM

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This invention relates to a novel method for improving the corrosion resistance of aluminum base alloys. More particularly, the invention concerns a novel two-stage method of aging such aluminum base alloys subsequent to their solution heat treatment.

Heat-treatable aluminum base alloys, especially the aluminum-copper and the aluminum-zinc-magnesium copper alloys, are extensively employed by the aircraft and aerospace industries. In these and other applications, such alloys must meet stringent corrosion requirements. However, experience has shown that these alloys frequently exhibit a tendency toward the development of undesirable forms of corrosion, such as intergranular corrosion which results in drastic reduction of the mechanical properties of these alloys, and stress corrosion which may result in sudden and possibly catastrophic failures.

Previous attempts to alleviate this tendency to corrode have either failed to adequately improve corrosion resistance or have done so only at the expense of reducing mechanical properties. An object of the invention was, therefore, to find a way of minimizing the tendency toward intergranular and stress corrosion in the case of artificially aged aluminum base alloys; and a further object was to find an optimum aging procedure, which would change the tendency toward intergranular corrosion to a shallow, pitting type of attack when the alloy was exposed to accelerated corrosion, and which would also produce typical mechanical properties.

The conventional practices previously known may be classified in three categories: (1) "constant temperature aging treatments," in which the metal is aged at a suitable temperature which is not intentionally varied during the aging operation; (2) "interrupted aging treatments," in which the metal is aged at one temperature for a period of time, then cooled to room temperature, and thereafter is heated at a higher temperature for an additional period of time; and (3) "progressive aging treatments," in which the metal is aged at one temperature for a period of time, then is heated and held at a higher temperature for an additional period of time.

In accordance with the invention, it has been found that the tendency toward intergranular and stress corrosion of aluminum base alloys of the type which are susceptible to artificial aging can be minimized by performing the aging treatment in two stages, whereby the first stage is conducted at a higher temperature than the second stage. After the first stage the metal may be either cooled directly to the second stage temperature, or cooled to room temperature and subsequently reheated to the temperature of the second stage of the treatment, the former practice ordinarily being preferred because it reduces the overall processing time. Thus, for example, in the case of 2024 alloy, which is a copper-bearing aluminum base alloy and will serve for purposes of illustration, a typical high-low aging treatment in accordance with the invention is to maintain the alloy at about 400° F. for about three hours, followed by holding the alloy at about 300° F. for about ten hours. For comparison purposes, the conventional aging treatment normally specified for 2024 alloy (Military Specification MIL-H-6088C, October 15, 1962) consists of a constant aging temperature of 370° to 380° F. for a time of 7 to 16 hours, the aging time varying with the temper desired. Thus, the first stage aging temperature in accordance with the present inven-

tion is preferably higher than the usual constant-temperature aging practice for the alloy, and the second stage temperature is ordinarily lower than the conventional aging temperature.

By carrying out the aging practice in this high-low sequence, resistance to intergranular and stress corrosion is appreciably improved. The initial high temperature is believed to have the effect to starting a controlled precipitation of the strengthening constituents in a generally uniform manner throughout the alloy, with the result that concentration of precipitated constituents at the grain boundaries (and consequent depletion thereof in the adjoining portions) is avoided or at least minimized. The final aging at a reduced temperature completes the precipitation begun at the favorable locations, without causing the reduction in mechanical properties which ordinarily is associated with long aging times at higher temperatures.

The method of the invention is applicable to a variety of heat-treatable aluminum base alloys, including copper-bearing alloys as well as zinc-bearing alloys. The conventional solution heat treating practice for such alloys involves heating at a temperature which ranges from about 840° F. to 1050° F., followed by water quenching.

The novel process of the invention produces particularly favorable results with aluminum base alloys which are low in silicon content, preferably below about 0.5% by weight. Thus, in the copper-bearing alloy series, alloy 2024, which has a silicon content of 0.50% maximum is virtually completely protected against intergranular corrosion by the method of the invention, whereas alloy 2017, which has 0.8% maximum silicon content and ordinarily contains more silicon than 2024 alloy, responds less favorably.

In the case of alloy 2024, the most favorable high-low aging treatment comprises maintaining the alloy in a first aging step at a temperature of from about 375° F. to about 425° F. for about 3 hours, and in a second aging step, maintaining the alloy at a temperature from about 275° F. to about 325° F. for about 10 hours. The preferred treatment for alloy 2024 is a first step aging at 400° F. for 3 hours, followed by a second step aging at 300° F. for 10 hours. The time periods for the two steps can vary somewhat according to the temperature used. Thus, the aging time can be shorter for a temperature of 425° F. than the 3 hour period for 400° F.

In the case of alloy 2017, it has been found that a first aging step at 450° F. for about 2 hours, followed by a second aging step at 325° F. for about 4 hours, yielded satisfactory results. These temperatures are similarly subject to variations in range of about 25° F. upward or downward.

In the case of alloy 7075, the preferred treatment is a first aging step at about 350° F. for about 5 hours, followed by a lower temperature aging step at about 250° F. for about 10 hours. The temperature ranges for zinc-bearing alloys in general are about 325–400° F. for the initial aging step, and about 200–300° F. for the second step.

In evaluating the improvement in intergranular corrosion produced by the method of the invention, there may be employed the procedure outlined in Military Specification MIL-H-6088C, October 15, 1962. In this procedure, each sample is immersed for 1 minute in an etching solution at 200° F. to produce a uniform surface condition. The etching solution is composed of 50 ml. 70% HNO₃, 5 ml. 48% HF, balance distilled water. After this etching treatment, the sample is rinsed in distilled water, immersed for 1 minute in concentrated HNO₃ (70%) at room temperature to remove surface plated copper, rinsed in distilled water and allowed to dry. The sample is then corroded by immersion in a minimum of 30 ml. per square inch of surface area of a solution hav-

ing the composition: Sodium chloride 57 grams, hydrogen peroxide (30%) 10 ml., diluted to 1 liter with distilled water. The immersion period is six hours. At the end of the immersion period, the sample is removed, washed and dried. A cross-section specimen is cut and subjected to microscopic examination at 100 to 500 diameters magnification. The microscopic examination is made both before and after etching the specimen, using a metalurgical microscope. The etching is done by immersion for 6 to 20 seconds in a solution having the composition: 70% HNO₃, 2.5 ml., HCl (conc.) 1.5 ml., 48% HF 1 ml., distilled water 95 ml. There should be no evidence of excessive intergranular corrosion.

The heat-treated test samples are also tested for tensile strength, yield strength, and elongation properties.

The following examples illustrate the practice of the novel method of the invention, but are not to be considered as limiting:

EXAMPLE 1

High-low aging of alloy 2024

A length of (solution heat treated) 2024 alloy rod, 1 1/8 inches in diameter, was cut into tensile strength and corrosion test specimens. The corrosion specimens consisted of 3/4 inch disc, cut in half and machined along the cut face. The tensile strength specimens were standard size. The chemical analysis of the rod was Si 0.15, Fe 0.30, Cu 4.20, Mn 0.60, Mg 1.48, balance substantially Al.

Various individual specimens were subjected to aging cycles as shown in Table 1. The aged tensile strength specimens were tested for tensile strength, yield strength, and elongation, using standard tests. The corrosion specimens were subjected to the standard accelerated NaCl-H₂O₂ corrosion test, mounted, etched and examined microscopically, as described above. The results are summarized in Table 1.

TABLE 1

| Sample No. | 1st Step Aging Cycle | 2nd Step Aging Cycle | Tensile (k.s.i.) | Yield (k.s.i.) | Elongation in 2 inch |
|------------|----------------------|----------------------|------------------|----------------|----------------------|
| 1 | 400° F., 3 hrs. | 300° F., 17 hrs. | 71.7 | 65.5 | 10 |
| 2 | do | 300° F., 10 hrs. | 72.7 | 65.2 | 10 |
| 3 | 375° F., 10 hrs. | do | 71.2 | 64.7 | 9 |

Of the specimens shown in the table, No. 2 had received the optimum aging treatment. Metallographic examination showed the precipitate was finely divided throughout the matrix. The mechanical properties of all three samples were very good, and exceeded the minimum specification properties (66.0 k.s.i. tensile strength, 58 k.s.i. yield strength, and 5% elongation).

Corrosion specimens corresponding to those in Table 1 were tested, and the corrosion depth measured. The results are set forth in Table 2:

TABLE 2

| Sample No. | Depth (mils), Avg. | Depth (mils), Max. | Type of Corrosion |
|------------|--------------------|--------------------|-------------------|
| 1 | 3.4 | 6.1 | Pitting. |
| 2 | 3.4 | 5.3 | Do. |
| 3 | 3.5 | 7.5 | Do. |

EXAMPLE 2

The purpose of this example was to provide two sets of comparative corrosion tests in aging alloy 2024, the

first employing the standard aging treatment of 13 hours at 375° F., the control group, and a second series according to the preferred method of the invention, aging at 400° F. for 3 hours followed by a second aging at 300° F. for 10 hours.

Different diameter 2024 rods, ranging from 2.5" to 3.5" diameter were cut into corrosion specimens. The corrosion tests were carried out as specified previously. Average and maximum depths of corrosion and type of corrosion were determined.

The results as shown in Table 3 clearly demonstrate the superior properties imparted by the high-low aging treatment of the invention, as compared with the standard one-step aging treatment. They show that all specimens that had received the high-low aging treatment of the invention exhibited a pitting type of corrosion attack. The control specimens were more susceptible to intergranular corrosion.

TABLE 3
(Corrosion depth in mils)

| Dia. (in.) | Standard Aging | | | High-Low Aging | | |
|------------|----------------|------|---------|----------------|------|------|
| | Avg. | Max. | Type | Avg. | Max. | Type |
| 2.500 | 3.7 | 7.3 | P and I | 3.6 | 7.5 | P |
| 2.5625 | 5.1 | 6.8 | P and I | 3.2 | 4.7 | P |
| 2.8750 | 4.2 | 7.0 | P and I | 2.9 | 4.7 | P |
| 3.00 | 5.5 | 9.0 | P and I | 2.9 | 5.8 | P |
| 3.125 | 4.3 | 8.2 | P and I | 2.9 | 5.8 | P |
| 3.250 | 4.6 | 7.1 | P and I | 2.4 | 4.7 | P |
| 3.500 | 4.5 | 7.2 | P and I | 2.3 | 4.5 | P |

P, Pitting; I, Intergranular—Attack.

EXAMPLE 3

A 3/8" diameter rod of alloy 2017-T4 was cut into standard tensile and corrosion test specimens. The alloy had the chemical composition: Si 0.52, Fe 0.55, Cu 3.74, Mn 0.61, Mg 0.65, balance substantially Al.

The specimens were aged at 450° F. for 2 hours, followed by aging at 325° F. for 4 hours. The mechanical properties were tested while the corrosion specimens were subjected to the standard NaCl-H₂O₂ accelerated test described above. Average and maximum values and type of corrosion were determined.

The specimens tested typically showed a tensile strength (k.s.i.) of 58.7, a yield strength (k.s.i.) of 46.0, and elongation of 13%. The corrosion depth in mils was 3.7 average, 10.2 maximum. The corrosion was entirely of the pitting type.

EXAMPLE 4

High-low aging of alloy 7075

In order to illustrate the applicability of the high-low aging treatment to other alloy systems, samples of zinc-bearing alloy 7075 rod in solution heat treated condition were aged, and standard tensile and corrosion test specimens were tested as described previously. The high-low aging practices used and the results obtained are compared in Table 4 with the results obtained by conventional aging practice at 245-255° F. for 24 hours.

TABLE 4

| Aging Practice | Corrosion Depth (mils) | | | Properties | | |
|--|------------------------|------|------|------------|------|----|
| | Avg. | Max. | Type | TS | YS | EL |
| 250° F., 24 hrs. (Standard) | 6.1 | 9.1 | I | 79.6 | 73.4 | 11 |
| 350° F., 5 hrs., plus 275° F., 10 hrs. | 2.8 | 3.4 | P | 78.7 | 68.7 | 13 |
| 350° F., 5 hrs., plus 250° F., 10 hrs. | 4.5 | 6.7 | P | 77.5 | 66.0 | 12 |
| 350° F., 5 hrs., plus 250° F., 15 hrs. | 1.8 | 2.4 | P | 75.0 | 64.5 | 13 |

The comparison shows that high-low aging practices can be employed to substantially eliminate intergranular corrosion, with only a slight reduction in mechanical properties.

The aging practice of the present invention may follow conventional preparation of the alloy in solution heat treated condition, after which the alloy is heated from substantially ambient temperature to a suitable aging temperature for the initial aging step previously discussed. The temperature is maintained for a substantial proportion of the total aging time, not less than about one hour. The subsequent lower temperature aging step accounts for at least half (e.g. about 50-90%) of the total aging time.

The expressions "copper-bearing" and "zinc-bearing" aluminum base alloys are used herein to specify alloys which are predominantly aluminum and contain, respectively, copper and zinc as their major alloying addition, which is consistent with Aluminum Association designations for the 2000 and 7000-series alloys.

The published composition limits for various commercial alloys discussed herein are given below:

| | 2024 | 2017 | 7075 |
|--------------------|---------------|---------------|------------|
| Si..... | 0.50 max..... | 0.8 max..... | 0.50 max. |
| Fe..... | 0.50 max..... | 1.0 max..... | 0.7 max. |
| Cu..... | 3.8-4.9..... | 3.5-4.5..... | 1.2-2.0. |
| Mn..... | 0.30-0.9..... | 0.40-1.0..... | 0.30 max. |
| Mg..... | 1.2-1.8..... | 0.20-0.8..... | 2.1-2.9. |
| Cr..... | 0.10 max..... | 0.10 max..... | 0.18-0.40. |
| Zn..... | 0.25 max..... | 0.25 max..... | 5.1-6.1. |
| Ti..... | | | 0.20 max. |
| Others, each..... | .05..... | .05..... | .05. |
| Others, Total..... | 0.15..... | 0.15..... | 0.15. |
| Al..... | Balance..... | Balance..... | Balance. |

While present preferred examples of the practice of the invention have been described, it will be understood that the invention may be otherwise variously embodied and practiced within the scope of the following claims.

What is claimed is:

1. The method of treating a copper-bearing aluminum base alloy so as to reduce its tendency toward the development of intergranular corrosion in the aged condition, comprising the steps of: providing the alloy in solution heat treated condition, substantially at room temperature, heating the solution treated alloy to an aging temperature of about 400° F., maintaining said temperature for about 3 hours, cooling the alloy to a lower temperature of about 300° F., and aging the alloy at said lower temperature for about 10 hours.

2. The method of treating a copper-bearing aluminum base alloy so as to reduce its tendency toward the development of intergranular corrosion in the aged condition, comprising the steps of: providing the alloy in solution heat treated condition, substantially at room temperature, heating the solution treated alloy to an aging temperature of about 450° F., maintaining said temperature for about 2 hours, cooling the alloy to a lower temperature of about 325° F., and aging the alloy at said lower temperature for about 4 hours.

3. The method of treating a zinc-bearing aluminum base alloy so as to reduce its tendency toward the development of intergranular corrosion in the aged condition, comprising the steps of: providing the alloy in solution heat treated condition, substantially at room temperature, heating the solution treated alloy to an aging

temperature of about 350° F., maintaining said temperature for about 5 hours, cooling the alloy to a lower temperature of about 250° F., and aging the alloy at said lower temperature for about 10 hours.

4. In the treatment of aluminum alloys which are susceptible to solution heat treatment and artificial aging, the method of treating a copper-bearing or zinc-bearing aluminum base alloy of the type which exhibits a tendency toward the development of intergranular corrosion following constant-temperature aging, comprising the steps of: providing the alloy in solution heat treated condition, by heating said alloy in the temperature range from about 840 to about 1050° F. for sufficient time to dissolve the soluble constituents and thereafter quenching the alloy substantially to room temperature; heating the solution treated alloy to an aging temperature in the range from about 325° F. to about 475° F., and maintaining said temperature substantially constant in a first aging step for a period of time representing about one-third of the total aging time; and completing the aging of said alloy in a second aging step by maintaining the alloy for the remaining aging time at a lower aging temperature in the range from about 200° F. to about 350° F.

5. The method of treating an aluminum base alloy which is susceptible to solution heat treatment and artificial aging, comprising the steps of:

providing the alloy in solution heat treated condition, substantially at room temperature, including the step of quenching the alloy in water from a solution temperature in the range from about 840° F., to about 1050° F.;

heating the solution treated alloy to an aging temperature in the range from 325° F. to 475° F., and maintaining the temperature of the alloy in that range during a first aging period of at least an hour;

cooling the alloy directly to a lower temperature in the range from 200° F. to 350° F. and maintaining the temperature of the alloy in the latter range during a second aging period;

said first aging period constituting from about 10% to about 50% of the total aging time in said first and second aging periods.

6. The method of claim 5, wherein said first aging period constitutes about one-third of the total aging time.

7. The method of treating a copper-bearing aluminum base alloy in accordance with claim 5, including the steps of maintaining the alloy during said first aging period in the temperature range of about 375-475° F., and thereafter maintaining the alloy during said second aging period in the temperature range of about 275-350° F.

8. The method of treating a copper-bearing aluminum base alloy in accordance with claim 5, said alloy containing not more than 0.5% silicon, by weight, including the steps of maintaining the alloy during said first aging period for about 3 hours in the temperature range of 375-425° F., and thereafter maintaining the alloy during said second aging period for about 10 hours in the temperature range of 275-325° F.

9. The method of treating a zinc-bearing aluminum base alloy in accordance with claim 5, including the steps of maintaining the alloy during said first aging period for about 5 hours in the temperature range of 325-400° F., and thereafter maintaining the alloy during said second aging period for about 10 hours in the temperature range of 200-300° F.

10. The method of treating a zinc-bearing aluminum base alloy in accordance with claim 5, said alloy containing 5.1 to 6.1% zinc, 2.1 to 2.9% magnesium and 1.2 to 2.0% copper, by weight, including the steps of maintaining the alloy during said first aging period at about 350° F. for approximately 5 hours, and, during said second aging period, at about 250° F.

11. The method of treating a copper-bearing aluminum base alloy in accordance with claim 5, said alloy containing 3.8 to 4.9% copper, 1.2 to 1.8% magnesium and

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0.30 to 0.9% manganese, by weight, including the steps of maintaining the alloy during said first aging period at about 400° F. for approximately 3 hours, and, during said second aging period, at about 300° F.

12. The method of treating a copper-bearing aluminum base alloy in accordance with claim 5, said alloy containing 3.5 to 4.5% copper, 0.4 to 1.0% manganese and 0.20 to 0.8% magnesium, by weight, including the steps of maintaining the alloy during said first aging period at about 450° F. for approximately 2 hours, and, during said second aging period, at about 325° F.

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