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PROCESS FOR IMPROVING STRESS-CORROSION RESISTANCE
OF AGE-HARDENABLE ALLOYS

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2 Sheets-Sheet 1

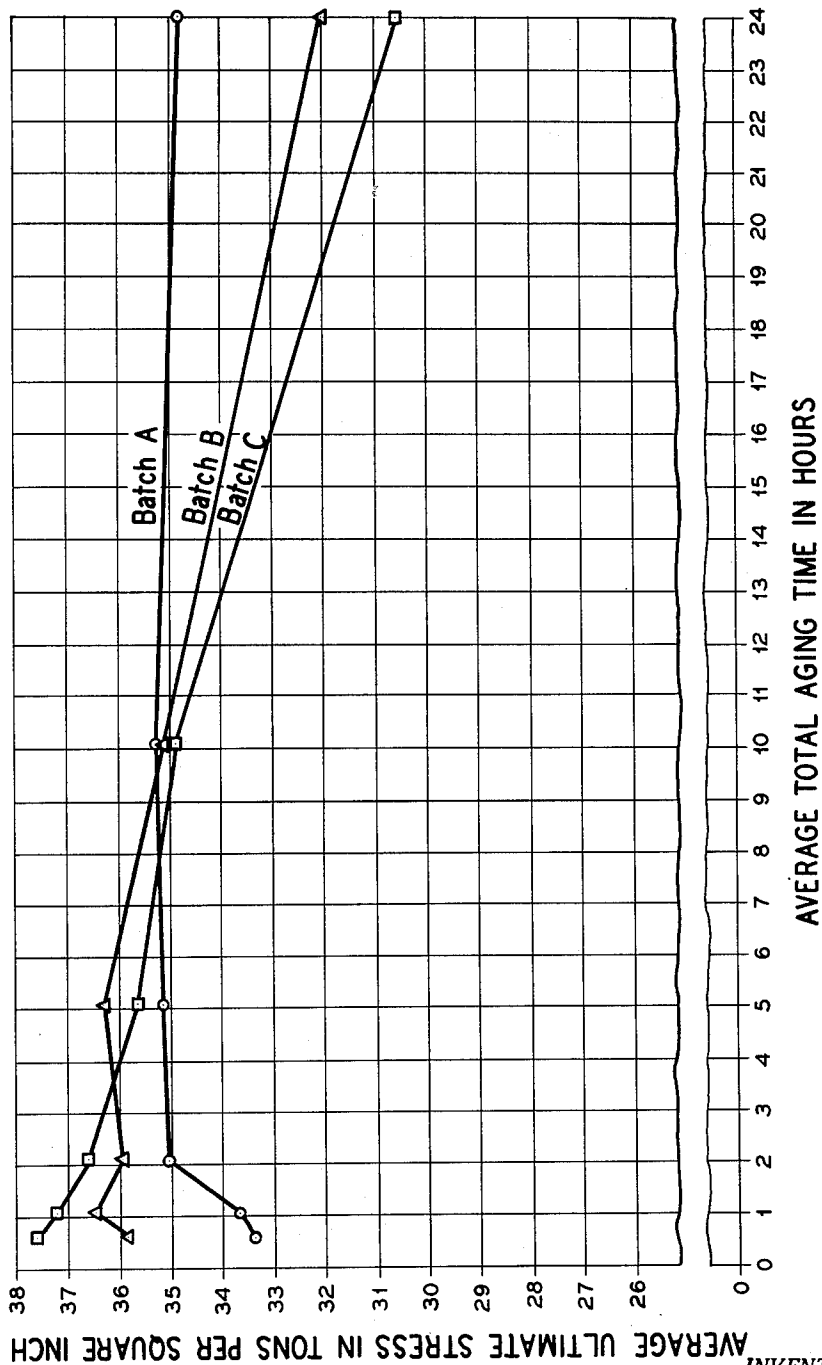


Fig. 1.

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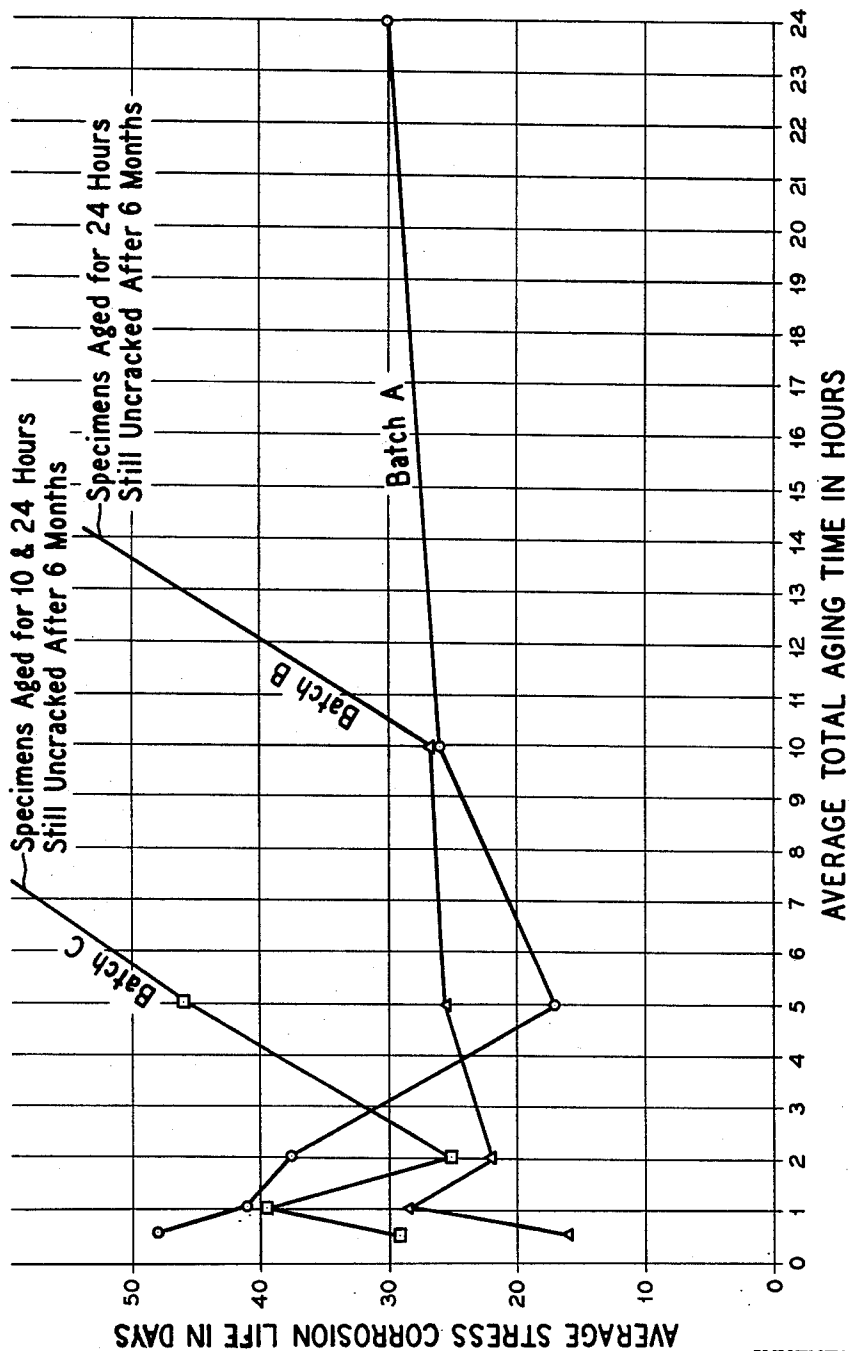


Fig. 2.

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PROCESS FOR IMPROVING STRESS-CORROSION RESISTANCE OF AGE-HARDENABLE ALLOYS

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5 Claims. (Cl. 148—12.7)

The present invention relates to a process for improving the stress-corrosion resistance of age-hardenable alloys and, more particularly, to a process for improving the stress-corrosion resistance of age-hardenable alloys based on the aluminum-zinc-magnesium system. Stress-corrosion concerns the behavior of metals under the combined action of corrosive environment and high tensile stresses, and refers to both the acceleration of corrosion by stress and stress-corrosion cracking.

As used herein, the term "alloys based on the aluminum-zinc-magnesium system" refers to alloys consisting essentially of zinc in an amount between about two and about ten percent by weight, magnesium in an amount between about one and about four percent by weight, and the balance aluminum with or without minor additions of copper (less than one percent by weight), manganese (less than 0.5 percent by weight), chromium (less than 0.2 percent by weight, etc. and/or impurities such as iron (less than 0.3 percent by weight), silicon (less than 0.2 percent by weight), titanium (less than 0.1 percent by weight), etc.

Heretofore, it has been shown that the mechanical strength of the light alloys based on the aluminum-zinc-magnesium system can be increased by subjecting the alloys to solution heat treatment and subsequent aging. Solution heat treatment is a process wherein an alloy is heated sufficiently to effect a solution of the soluble alloying elements and then cooled rapidly to hold the elements in solution. When solution heat treated alloys are allowed to stand or age, their strength and hardness usually continue to increase beyond the values existing immediately after the solution heat treatment. If this gradual change in the physical properties of the alloy takes place at room temperature, it is called natural or spontaneous aging; if it takes place at temperatures above room temperature, it is termed artificial aging or precipitation heat treatment.

Although solution heat treated and aged alloys based on the aluminum-zinc-magnesium system have the highest available mechanical strength of all the age-hardenable aluminum-base alloys, they are extremely susceptible to stress-corrosion, i.e., they have a low stress-corrosion resistance. Various alloying elements, such as copper, manganese, and chromium, have been added to these ternary alloys in an attempt to improve their resistance to stress-corrosion, but the resulting alloys are still not acceptable for many applications where a relatively high-stress-corrosion resistance is required.

It is, therefore, the main object of the present invention to provide a process for improving the stress-corrosion resistance of age-hardenable alloys based on the aluminum-zinc-magnesium system.

It is another object of the invention to provide such a process which will not detract from the mechanical strength of the alloys.

It is a further object of the invention to provide such a process wherein precipitate-free regions next to grain

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boundaries are eliminated or modified in order to prevent intercrystalline embrittlement and preferential chemical attack.

Other aims and advantages of the invention will be apparent from the following description and appended claims.

In the drawings:

FIG. 1 is a graph showing the average ultimate tensile strength (as a function of aging time) of samples of an aluminum-zinc-magnesium alloy treated by the inventive process and samples of the same alloy treated by a conventional aging process; and

FIG. 2 is a graph showing the average stress-corrosion life (as a function of aging time) of the alloy samples of FIG. 1.

In accordance with the present invention, there is provided a process for improving the stress-corrosion resistance of an age-hardenable alloy based on the aluminum-zinc-magnesium system comprising partially aging said alloy, cold working said alloy more than five per cent, and completing the aging of said alloy.

The problem of stress-corrosion cracking generally arises in alloys which have been solution heat treated and then aged to produce maximum tensile strength, where there is an absence of precipitates in the regions next to the grain boundaries. The inventive process eliminates or modifies these precipitate-free regions, thereby preventing intercrystalline embrittlement and improving stress-corrosion resistance.

The alloy to be treated by the inventive process is first subjected to a conventional solution heat treatment. In general, the heat treating temperature is made as high as possible without melting any of the eutectic material present in the alloy. The preferred temperature range for the aluminum-zinc-magnesium alloys to be treated by the present process is about 465° C. ($\pm 5^\circ$ C.). The alloy is held at the high temperature long enough for solution and diffusion to take place and produce, as nearly as practicable, a homogeneous solid solution. The alloy is then rapidly cooled or quenched so that there is not time for the hardening elements to precipitate from solid solution during the cooling period, in accordance with their lower solubility at lower temperatures. With the ternary alloys to be treated by the present process, it is preferable to quench into hot water (about 80° C.). The solution heat treatment increases all the mechanical properties of the alloy.

The solution heat treatment may be carried out in a molten salt bath, such as fused sodium nitrate, or in an air furnace. The furnace may be heated electrically or by gas, oil, or radiant tubes. For best results, artificial circulation should be provided. Furnaces in which products of combustion are circulated can be used satisfactorily if the atmosphere contains a sufficiently high percentage of carbon dioxide and is free from sulfur compounds and excessive moisture.

Following solution heat treatment, the dissolved alloying constituents tend to precipitate from solid solution in accordance with their true solubility. This precipitation or aging is accelerated by raising the temperature of the alloy; the preferred temperature range for the ternary alloys to be treated by the present process is from about 100° to about 160° C. The alloy is maintained at the increased temperature only long enough to initiate precipi-

tation of the dissolved alloying constituents; for example, if 150° C. is chosen as the aging temperature, the partial aging time should be less than three hours. The actual time required for this preliminary aging step depends on the particular alloy being treated and the particular temperature employed, but should always be less than the time required to produce maximum age hardening.

Both the preliminary and final aging steps can be carried out in a furnace or oven heated electrically or by gas. Provision should be made for circulating the air in order to obtain a uniform temperature throughout the furnace, as well as more rapid transfer of heat.

After the alloy has been partially aged, it is cooled to room temperature and cold worked. The inventive process introduces this intermediate deforming step into the normal aging sequence in order to allow precipitation to occur near grain boundaries during the final aging step. The cold working introduces preferential plastic flow near the grain boundaries, thus introducing excess vacancies as a result of dislocation interactions and enabling the subsequent heat treatment to effect precipitation in the previously precipitate-free regions adjacent to the grain boundaries. The alloy must be cold worked more than about five percent, but preferably less than about ten percent. Deformations above about ten percent create a condition in the alloy which tends to reduce the beneficial effect of the preliminary aging. The amount of cold working is measured by the reduction in cross-sectional area of the particular article being deformed.

Following the cold working, the alloy is again heated to a temperature high enough to permit development of the desired properties in a reasonable time, and the aging process is completed. The temperature employed in this final aging step may not be higher than that employed in the preliminary aging step. As in the first aging step, the preferred final aging temperature range for the subject aluminum-zinc-magnesium alloys is from 100° to 160° C. The period required to complete the aging process depends on the particular alloy being treated, the particular temperature employed, and the amount of aging affected by the preliminary aging step. Normally, the aging process is considered to be complete at the point of maximum strength and hardness.

In an example of the inventive process, an alloy (in sheet form) containing 5.93% zinc, 2.9% magnesium, 0.5% copper, 0.17% chromium, 0.48% elemental impurities, and the balance aluminum (all percentages by weight) was solution heat treated by quenching into water at 80° C. after a 12-hour anneal at 465° C. The solution heat treated alloy was split into three batches of specimens for further processing. The specimens in batch A were subjected to a direct heat treatment at 150° C. for various periods up to 24 hours, with no intermediate cold working. The specimens in batch B and batch C were aged at 150° C. for 30 minutes; cooled to room temperature; deformed five and ten percent, respectively, by rolling; and then further aged at 150° C. for various periods up to 23.5 hours. Each specimen was tested for ultimate tensile strength and stress-corrosion resistance. The stress-corrosion test was carried out by bending the specimen to 90% proof stress and exposing it to industrial atmosphere. The results of the tensile strength tests are shown in FIG. 1, while the results of the stress-corrosion resistance tests are shown in FIG. 2, the results of each test being plotted as a function of aging time.

Referring to FIGS. 1 and 2, it can be seen that the maximum ultimate tensile strength for the batch A specimens (no intermediate cold working) was about 35 tons per square inch, but the maximum resistance to stress-corrosion at that strength was less than 40 days. Also, the maximum average stress-corrosion resistance out of all the batch A specimens was only 48 days, which is not acceptable for certain practical applications. In the batch B specimens (5% intermediate cold working), the stress-corrosion resistance in the specimens having the maxi-

mum ultimate tensile strength was only about 25 days, but the specimens having an ultimate tensile strength of about 32 tons per square inch were still uncracked after six months in the stress-corrosion test. An ultimate tensile strength of 30 tons per square inch is adequate for many structural purposes. In batch C, the specimens having an ultimate tensile strength of about 35 tons per square inch were still uncracked after six months in the stress-corrosion test.

The curves in FIG. 1 indicate that the ultimate tensile strength of the alloy *decreased* as the amount of cold working and the aging time increased, whereas the curves in FIG. 2 indicate that the stress-corrosion life *increased* as the amount of cold working and the aging time increased. However, the rate of increase in the stress-corrosion life was much greater than the rate of decrease in the ultimate tensile strength. Thus, the inventive process can increase the stress-corrosion life considerably while sacrificing only a relatively small amount of tensile strength; by varying the total aging time and the amount of intermediate cold working in accordance with the curves illustrated in FIGS. 1 and 2, the stress-corrosion resistance of the alloy can be increased to many times that of conventionally aged alloys without substantially detracting from the mechanical strength of the alloy. Alloys treated by the present process are especially suitable for aircraft and rocket structures.

While various specific forms and preferred ranges for the present invention have been herein set forth, it is not intended to limit this invention to the embodiments herein described, but only as set forth in the appended claims.

What is claimed is:

1. A process for improving the stress-corrosion resistance of an age-hardenable alloy consisting essentially of zinc in an amount between about one and about ten percent by weight, magnesium in an amount between about one and about four percent by weight, and the balance aluminum, comprising partially aging said alloy at a temperature between about 100° and about 160° C., cold working said alloy between about 5 and about 10 percent, and completing the aging of said alloy at a temperature between about 100° C. and the temperature employed in said partial aging step.

2. A process for improving the stress-corrosion resistance of an age-hardenable alloy consisting essentially of zinc in an amount between about one and about ten percent by weight, magnesium in an amount between about one and about four percent by weight, and the balance aluminum, comprising aging said alloy at a temperature between about 100° and about 160° C. for 30 to 90 minutes, cold working said alloy between about 5 and about 10 percent, and completing the aging of said alloy at a temperature between about 100° C. and the temperature employed in the first aging step.

3. A process for improving the stress-corrosion resistance of an age-hardenable alloy consisting essentially of zinc in an amount between about one and about ten percent by weight, magnesium in an amount between about one and about four percent by weight, and the balance aluminum, comprising partially aging said alloy at a temperature between about 100° and about 160° C., cooling the partially aged alloy to room temperature, cold working said alloy between five and ten percent, and completing the aging of said alloy at a temperature between about 100° C. and the temperature employed in said partial aging step.

4. A process for improving the stress-corrosion resistance of an age-hardenable alloy consisting essentially of zinc in an amount between about one and about ten percent by weight, magnesium in an amount between about one and about four percent by weight, and the balance aluminum, comprising partially aging said alloy at a temperature between about 100° and about 160° C., cold working said alloy between about 5 and about 10 percent, and completing the aging of said alloy, the total

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aging time and the amount of cold working effected being adjusted to provide the desired stress-corrosion resistance and tensile strength in said alloy at a temperature between about 100° C. and the temperature employed in said partial aging step.

5. A process for improving the stress-corrosion resistance of an age-hardenable alloy consisting essentially of zinc in an amount between about one and about ten percent by weight, magnesium in an amount between about one and about four percent by weight, and the balance aluminum, comprising aging said alloy at a temperature between about 100° and 160° C. for 30 to 90 minutes, cold working said alloy between five and ten

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percent, and further aging said alloy at a temperature between about 100° C. and the temperature employed in the first aging step until the desired stress-corrosion resistance and tensile strength are obtained in said alloy.

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