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THERMAL TREATMENT OF ALUMINUM BASE ALLOY PRODUCTS

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This invention is concerned with improving the strength and resistance to corrosion of certain copper-free aluminum base alloy products by means of a novel sequence of thermal treatments. The invention more particularly relates to the thermal treatment of products of aluminum base alloys containing zinc and magnesium within limited ranges and which are free from copper except as an impurity.

Aluminum base alloys containing substantial amounts of zinc and magnesium have been known for many years and it has also been recognized that these alloys can develop high strength when solution heat treated and age hardened. However, it has been observed that not all respond to the same treatment in the same way, and that the resistance to corrosion can be adversely affected by improper thermal treatment. Another factor which exerts a strong influence upon the properties of this type of alloy is the presence of other alloying elements. Among the elements frequently used in combination with zinc and magnesium is copper, this addition commonly being used to effect an increase in strength. While the copper is beneficial in that respect, it alters the behavior of the alloys in a corrosive environment and special practices are often needed to offset any adverse effect.

Although much attention has been given to producing stronger and stronger aluminum base alloys there is still a demand for alloys having a moderate range of strength and which can be readily worked by any of the conventional processes, such as rolling, forging, extrusion, and the like. We have found that a combination of the desired properties can be achieved to a maximum extent in wrought products by a sequence of thermal treatments applied to bodies of aluminum-zinc-magnesium alloys containing closely controlled proportions of zinc and magnesium, the treatments, in some cases, starting with the ingot or other stock from which the wrought products are made.

It is an object of this invention to provide a method of treating wrought products of certain copper-free aluminum-zinc-magnesium alloys which will serve to increase their resistance to corrosion without any sacrifice in strength. A particular object is to increase both the strength and resistance to stress corrosion cracking of the foregoing alloy products above that normally obtained by age hardening at but one temperature. Another object is to provide a method of treating hot worked products of certain copper-free aluminum-zinc-magnesium alloys whereby both their strength and resistance to stress corrosion cracking are improved.

Our invention is predicated upon the discovery that a copper-free aluminum base alloy consisting essentially of 3.5 to 6% by weight of zinc, 0.75 to 4.3% by weight of magnesium, 0.05 to 0.75% by weight of manganese, 0.05 to 0.3% by weight of chromium and balance aluminum plus impurities, wherein the zinc content is not less than the magnesium content, responds in a peculiar manner to a sequence of thermal treatments to yield a product having an unusual combination of properties. In particular, the strength developed as a result of the treatments is greater than that produced by the conventional commercial single step aging treatments and the product

is substantially immune to stress corrosion cracking. Contrary to general experience with aluminum-zinc-magnesium type alloys we have found that the alloys referred to above achieve high resistance to stress corrosion cracking without over-aging. Briefly, the treatments consist of a solution heat treatment, that may be followed by a hot working operation, performed within the solution heat treating temperature range, a retarded cooling to room temperature, storage at room temperature for at least 72 hours and finally age hardening in two steps. Through the use of these treatments in sequence it has been found that the tensile and yield strengths of products can be increased 2000 p.s.i. and more as compared to the values obtained by conventional single aging temperature treatment, thus demonstrating the absence of over-aging. Resistance to stress corrosion cracking has also been found to be superior to that of wrought commercial aluminum-zinc-magnesium-copper alloys of the past which have received the conventional solution heat treatment and age hardening treatment as well as being superior to that of products of the copper-free alloys which have received but a single aging treatment.

The alloys employed in making the wrought products must have zinc and magnesium within the following limits in order to develop the desired properties through thermal treatment. At least 3.5% and not over 6% zinc must be present while the magnesium content must fall within the range of 0.75 to 4.3% by weight and the magnesium content should not exceed that of zinc. If smaller amounts of zinc and magnesium are present, the products fail to develop the strength or resistance to corrosion while on the other hand larger amounts introduce problems in fabrication as well as a deficiency in one or more of the desired properties.

Although zinc and magnesium are the principal added alloying components it has been found that relatively small quantities of manganese and chromium must likewise be present. These elements are beneficial in the casting and working of the alloys as well as contributing to the improvement in resistance to corrosion. Smaller amounts than those specified above are not helpful and larger quantities introduce casting and fabricating problems. To improve the welding characteristics of the product, 0.05 to 0.30% zirconium may be added to the alloy. For grain size control it may be desirable to add 0.01 to 0.15% titanium, or 0.0005 to 0.02% boron, or both elements.

The usual impurities, iron and silicon, are found in the alloy products, but the total should not exceed 0.6%. Copper may be present as an impurity but the amount should not exceed 0.10%. For this reason the alloys are referred to as being "copper-free."

The alloys can be melted, cast and worked according to customary practices for aluminum base alloys of this type. In cases where the alloy body is to be shaped by hot working the body can be given a solution heat treatment immediately prior to the hot working operation, the body shaped at a temperature within the solution heat treating temperature range and the hot worked product then cooled to room temperature at a slow rate as defined hereinbelow. In other cases the wrought product is given a solution heat treatment and at the conclusion of the treatment cooled to room temperature at a rate below the maximum indicated below. In any case the alloy body should be heated to a temperature between 700 and 970° F., but not above the temperature of incipient fusion of any of the alloy phases, and held within that temperature range for at least a long enough time to permit substantially complete solution of the zinc and magnesium components. The length of time required to effect solution will depend upon the thickness of the body, the size

of the load being treated and of course the temperature of treatment. For treating sheet, for example, the period may be as short as 3 or 4 minutes whereas the treatment of an ingot or large wrought product requires a longer time, usually a soaking at the desired temperature of 1 to 8 hours, which means that the stock to be worked is held within the furnace or other heating means for a longer time. As a general rule, longer periods are required to treat alloy bodies in the lower portion of the temperature range than in the upper portion of the range. To obtain the best results it is preferred to use a solution heat treating temperature range of 750 to 870° F.

Where the solution heat treated alloy body is to be hot worked, the hot body can be transferred to the metal working apparatus and then worked, it being necessary to maintain the temperature above 700° F., the minimum solution heat treating temperature. As an alternative, the solution heat treated alloy body can be cooled to room temperature and later reheated for working within the above-mentioned heat treating range, care being taken to insure solution of the zinc and magnesium. The hot working may involve rolling, extrusion, forging, pressing and the like or combinations of these processes. It will be appreciated that under the foregoing conditions the alloy body may be held within the solution temperature range for a longer time than required to effect solution of the zinc and magnesium, but this is not harmful. It is important, in any case, that solution be effected before the step of cooling to room temperature is initiated.

At the conclusion of the solution heat treatment or completion of the hot working operation the product is cooled to at least 250° F. at a relatively slow rate, not exceeding an average of 200° F. per second. This rate is slow with respect to that which exists during quenching in cold water, for example, where the average rate is 2000° F. per second. In the case of an extrusion or hot rolled article, the product can be progressively cooled as it issues from the die or rolls. In the case of a forging, the worked article is cooled upon removal from the forging apparatus. Faster rates than 200° F. per second have been found to have an adverse effect upon the resistance to stress corrosion cracking. On the other hand, the cooling is not to be retarded beyond a practicable time in the plant, usually a matter of minutes when handling individual or small groups of products, but longer times may be required to cool a large batch of products or products of heavy cross section. The cooling medium used can vary according to the mass of the products being cooled. For light sections quenched directly from the solution heat treating temperature, hot or boiling water may be appropriate but for heavy sections a more drastic cooling medium can be used because of the slow transfer of heat from the product. Where the hot worked product is being cooled, an air blast or water spray may be sufficient to provide the retarded cooling rate. Rates as slow as 4° F. per second have been found to give satisfactory results.

The retarded cooling of the solution heat treated product, whether hot worked or not, appears to create a particular internal structure which is necessary to the success of the two step age hardening treatment. Although we are not able to define the precise character of this structure, there seems to be ample evidence that a condition is developed which is closely related to the subsequent age hardening process and obtaining high resistance to stress corrosion cracking. A rapidly cooled product does not appear to have the requisite structure or internal condition.

Following the cooling to room temperature the product should be held at that temperature for a period of at least 72 hours before proceeding with the two step treatment of age hardening. The products can be stored for longer periods of time to accommodate plant schedules or shipment but no benefit is gained by extending the time in respect to the properties of the final product. Without this storage period the proper condition does not exist for

response to the two step treatment and unless the period extends for at least 72 hours, the desired strength is not attained in the final product. Some spontaneous age hardening seems to occur during this period as judged by an increase in strength which takes place. In any event the increase in strength falls far short of that of the finally treated product. From a theoretical viewpoint it can be assumed that any age hardening which occurs establishes a pattern of precipitate and that this controls or guides subsequent precipitation. Whether such an explanation is correct or not, we have found, nevertheless, that the storage at room temperature is a prerequisite to the next and last age hardening treatment.

Before proceeding to the age hardening treatment it may be desirable to straighten the wrought products or minimize residual stresses by a slight amount of cold work, less than 5%. This amount of cold work has no adverse effect upon the properties of the final product.

The two step age hardening treatment comprises heating the stored product to a temperature between 200 and 250° F. and holding for a period of 4 to 24 hours. The choice of a particular temperature and period of time is determined by factors akin to those which affect solution heat treatment. The range of temperature and time are important for at lower temperatures and shorter periods of time the necessary age hardening does not occur. On the other hand, higher temperatures and longer periods of time induce over-aging, a condition which must be avoided.

At the conclusion of the first step, the product may be cooled to room temperature and reheated for the second step or the product can be immediately heated to the higher temperature. In any case the product is heated to a temperature between 280 and 320° F. and held within that range for a period of 8 to 24 hours. These temperatures and times are critical with respect to attaining a high strength and substantial immunity to stress corrosion cracking without over-aging.

It will be appreciated that the final properties are influenced by the type of working operation to which the alloy has been subjected and the direction within the product in which the properties are determined whether longitudinal, i.e., parallel to direction of working, or transverse thereto. With respect to mechanical properties we have found that the minimum tensile strength which characterizes the final product is on the order of 42,000 p.s.i. and the minimum yield strength is 35,000 p.s.i.

The treatment of the alloy products described above results in an improved resistance to stress corrosion cracking as compared to that of conventionally treated wrought products. This property is usually determined in an accelerated corrosion test where specimens are stressed while being exposed to a corroding medium. In the present case two methods of stressing were used to determine susceptibility to stress corrosion, in one, the specimen was placed under a stress equivalent to 75% of its yield strength and in the other sheet specimens in the form of strips were bent around a mandrel to produce a U-shaped bulge. In the latter test the strips were sprung into place to place them in a roughly arcuate shape. This test is referred to as being of the constant deflection type and is more fully described in an article in the American Society for Testing Materials Special Technical Publication No. 64 (1944), pages 255 to 272. In both types of tests the specimens are alternately immersed in and raised from an aqueous 3½% NaCl solution. If all of the specimens of a group survive a period of 40 days in the test without failure they are considered to possess substantial immunity to stress corrosion cracking.

Another accelerated corrosion test which has been successfully used to determine susceptibility to stress corrosion is one wherein the specimen is placed under a stress equivalent to 75% of the yield strength and immersed in an aqueous solution containing 300 g. NaCl per liter and 20 g. Na₂CrO₄ per liter, the water used for

making up the solution being distilled water. Also immersed in the solution is a suitable cathode, for example, one of platinum screen wire. An external current is impressed on the system whereby the stressed specimen is made anodic under a potential of 100 mv. If the specimen survives a 24 hour exposure without cracking it is considered to be highly resistant to stress corrosion cracking.

The improvement gained through our invention is illustrated in the following comparative examples wherein sheet specimens 0.064 inch in thickness were given various thermal treatments and subsequently tested. The tensile properties were determined on standard specimens and the specimens for the corrosion tests were cold formed as described above before exposure to the corroding medium. The two alloys used had the following nominal compositions: (A) 4% zinc, 2% magnesium, 0.3% manganese, 0.1% chromium and balance aluminum; (B) 4% zinc, 3% magnesium, 0.5% manganese, 0.1% chromium and balance aluminum. The schedule of thermal treatments is given in the following table.

TABLE I

Thermal treatment schedule

Alloy	Treatment No.	Solution Heat Treatment		Cooling Medium	Storage at Room Temp.	Aging Treatment			
		Temp., ° F.	Hours			Temp., ° F.	Hours	Temp., ° F.	Hours
A	1	860	1	Cold Water	Yes	250	48		
	2	860	1	Boiling Water	Yes	225	8	300	16
B	3	920	1	Still Air	No	250	8		
	4	920	1	do.	Yes	225	48		
	5	750	1	Cold Water	No	250	8	300	16
	6	750	1	Boiling Water	Yes	225	8	300	16

The average cooling rate of sheet in cold water was considered to be 2000° F. per second, in boiling water, not over 40° F. per second, and in still air about 4° F. per second. The storage at room temperature covered a period of 72 hours or longer.

The average tensile properties of the specimens treated according to the foregoing schedule are given in Table II below.

TABLE II

Tensile properties

Alloy	Treatment No.	Tensile Strength, p.s.i.	Yield Strength, p.s.i.	Percent Elongation
A	1	57,000	50,200	13
	2	59,400	52,700	14
B	3	63,000	51,000	14
	4	66,000	56,000	13
	5	67,000	59,000	13
	6	69,000	61,000	13

It is evident in each case that the two step treatment improved the tensile properties. It is also to be observed that in the case of air cooling, the storage at room temperature was beneficial to the tensile and yield strengths.

In the series of corrosion tests, the specimens from treatment groups 1 and 2 of alloy A and treatment groups 3 and 4 of alloy B were bent for a constant deflection type of test while treatment groups 5 and 6 of alloy B were stressed to 75% of their yield strength while being exposed to the corroding medium. The results of these tests are given in Table III below.

TABLE III

Stress corrosion test results

Alloy	Treatment No.	Days to Failure
A	1	3 in 3 days.
A	2	1 in 97 days, 1 in 112 days, 1 still in test.
B	3	1 in 19 days, 1 in 91 days, 1 in 140 days.
B	4	No failures in 5 months.
B	5	3 in 34 to 39 days.
B	6	No failures in 5 months.

The beneficial effect of the various steps in the thermal treatment is apparent from the foregoing results and when considered along with the improved strength, it is evident that one of the properties need not be sacrificed to gain an improvement in the other in treating alloy products of the composition set forth above.

In another test an alloy was employed having the following composition: 3.90% zinc, 2.87% magnesium,

0.25% manganese, 0.18% chromium, 0.02% titanium, 0.04% copper, 0.11% iron, 0.06% silicon and balance substantially all aluminum. Two plates of the alloy, 3" in thickness were solution heat treated at 860° F., hot rolled to a thickness of 2 3/8" and cooled in one case by quenching in cold water and in the other by immersing in a bath of water maintained at a temperature of 180° F. The latter cooling was considered to provide a cooling rate of about 10° F. per second. The plate which was quenched in cold water was aged by heating it 48 hours at 250° F. while the other one was aged in two steps, 8 hours at 225° F. followed by 16 hours at 300° F. The mechanical properties of the cold water quenched plate were found to be 57,500 p.s.i. tensile strength, 45,000 p.s.i. yield strength and 6% elongation. The other plate had a tensile strength of 60,000 p.s.i., a yield strength of 49,500 p.s.i. and 7% elongation. Specimens from the two plates were subjected to the electrolytic accelerated stress corrosion test. Those from the cold water quenched plate failed in 12 1/2 hours whereas those from the other plate had not failed after a 24 hour exposure, thus demonstrating the benefit of the slow cooling and two step aging treatment.

This is a continuation-in-part of United States application Serial No. 259,382, now abandoned, filed February 18, 1963.

Having thus described our invention, we claim:

1. The method of improving the strength and resistance to stress corrosion of wrought products composed of a copper-free aluminum base alloy consisting essentially of 3.5 to 6% zinc, 0.75 to 4.3% magnesium, 0.05 to 0.75% manganese, 0.05 to 0.30% chromium and balance aluminum plus impurities, said method comprising subjecting a body of said alloy to a solution heat treatment within the temperature range of 700 to 970° F., but below the

temperature of incipient fusion of any alloy phase, and holding the body within said temperature range for at least a long enough period to permit substantially complete solution of the zinc and magnesium, cooling the solution treated product to room temperature at a rate not exceeding 200° F. per second, holding the cooled product at room temperature for a period of at least 72 hours and thereafter aging said product in two steps comprising first heating it to 200 to 250° F. and holding within said range for a period of 4 to 24 hours and in the second step heating the partially aged product to 280 to 320° F. and holding within said range for a period of 8 to 24 hours, and finally cooling to room temperature.

2. The method according to claim 1 wherein the solution heat treating temperature is between 750 and 870° F.

3. The method according to claim 1 wherein the alloy body is held within the solution heat treating temperature range for a period of 3 minutes to 8 hours.

4. The method according to claim 1 wherein the alloy also contains 0.05 to 0.30% zirconium.

5. The method according to claim 1 wherein the alloy also contains at least one grain refining element of the group composed of 0.01 to 0.15% titanium and 0.0005 to 0.02% boron.

6. The method of improving the strength and resistance to stress corrosion of wrought products composed of a copper-free aluminum base alloy consisting essentially of 3.5 to 6% zinc, 0.75 to 4.3% magnesium, 0.05 to 0.75% manganese, 0.05 to 0.3% chromium and balance aluminum plus impurities, said method comprising subjecting a body of said alloy to a solution heat treatment within the temperature range of 700 to 970° F., but below the temperature of incipient fusion of any alloy phase, and holding the body within said temperature range for at least a long enough time to permit substantially complete

solution of the zinc and magnesium, hot working said body within said temperature range, cooling the hot worked product to room temperature at a rate not exceeding 200° F. per second, holding said product at room temperature for a period of at least 72 hours and thereafter aging said product in two steps comprising first heating it to 200 to 250° F. and holding within said range for a period of 4 to 24 hours and in the second step heating the partially aged product to 280 to 320° F. and holding within said range for a period of 8 to 24 hours, and finally cooling to room temperature.

7. The method according to claim 6 wherein the alloy body is held within the solution heat treating temperature range for a period of 3 minutes to 8 hours.

8. The method according to claim 6 wherein the alloy also contains 0.05 to 0.30% zirconium.

9. The method according to claim 6 wherein the alloy also contains at least one grain refining element of the group composed of 0.01 to 0.15% titanium and 0.0005 to 0.02% boron.

References Cited in the file of this patent

UNITED STATES PATENTS

1,858,092	Hybinette	May 10, 1932
1,945,297	Rainer	Jan. 30, 1934
2,083,576	Nock	June 15, 1937
2,403,037	Zeigler et al.	July 2, 1946
2,993,783	Martin	July 25, 1961

FOREIGN PATENTS

544,439	Great Britain	Apr. 14, 1942
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OTHER REFERENCES

35	Metals Handbook (1948 ed.), pub. by the A.S.M., page 770 relied upon.
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Dedication

3,171,760.—*William D. Vernam*, New Kensington, and *William A. Anderson*, Verona, Pa. THERMAL TREATMENT OF ALUMINUM BASE ALLOY PRODUCTS. Patent dated Mar. 2, 1965. Dedication filed Apr. 14, 1969, by the assignee, *Aluminum Company of America*.

Hereby dedicates said patent to the Public.

[*Official Gazette January 13, 1970.*]