United States Patent [19]
Staley et al.

[11] **3,881,966**
[45] **May 6, 1975**

[54] **METHOD FOR MAKING ALUMINUM ALLOY PRODUCT**

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[22] Filed: **June 14, 1973**

[21] Appl. No.: **370,159**

Related U.S. Application Data

[60] Continuation of Ser. No. 121,056, March 4, 1971, abandoned, which is a division of Ser. No. 60,343, Aug. 3, 1970, abandoned.

[52] **U.S. Cl.** **148/12.7**
[51] **Int. Cl.** **C22f 1/04**
[58] **Field of Search** 148/12.7, 159

[56] **References Cited**

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[57] **ABSTRACT**

An aluminum base alloy containing zinc, copper and magnesium together with zirconium or both zirconium and manganese and with specially controlled composition limits exhibits very high strength when thermally treated to a condition having high resistance to stress corrosion cracking. Improved products of the alloy also exhibit low quench sensitivity and, accordingly, high strength even in very thick sections. A special aging treatment produces the optimum combination of strength and resistance to stress corrosion cracking properties.

8 Claims, 4 Drawing Figures

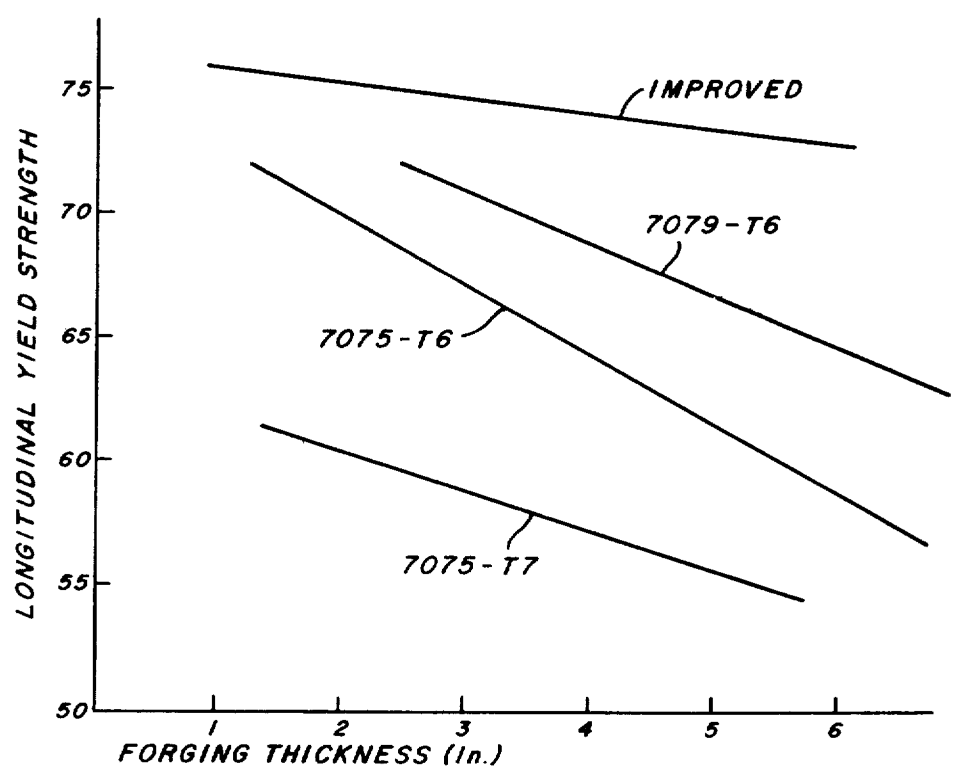

FIG. 1.

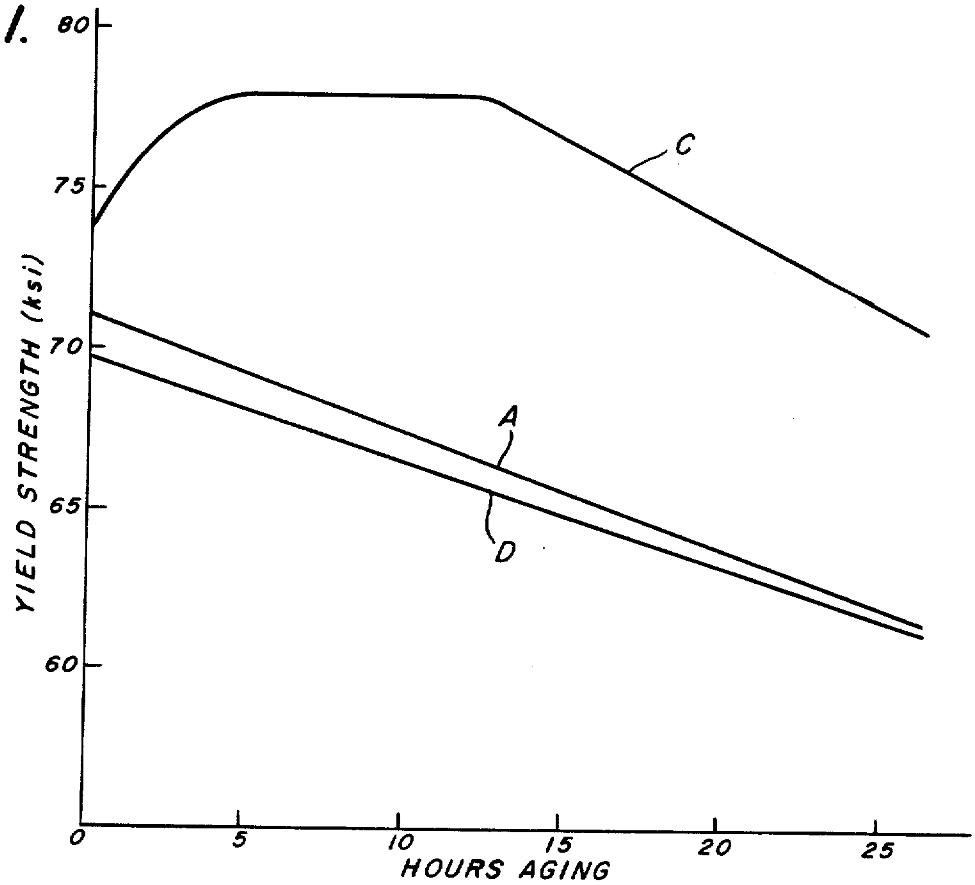

FIG. 2.

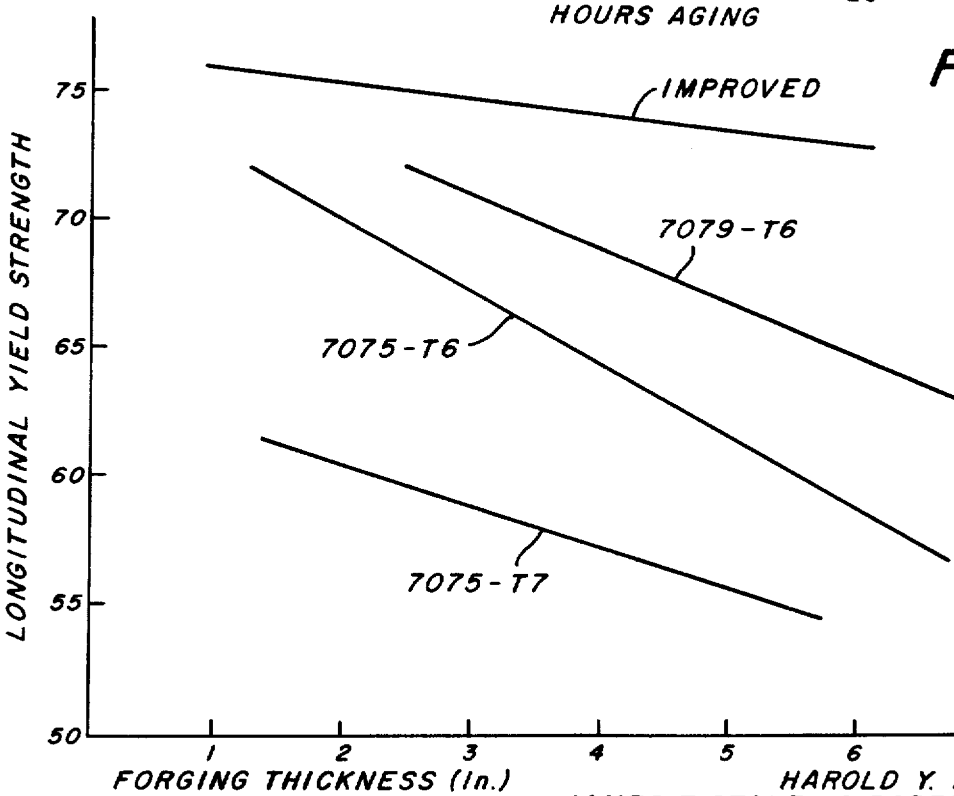

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FIG. 3.

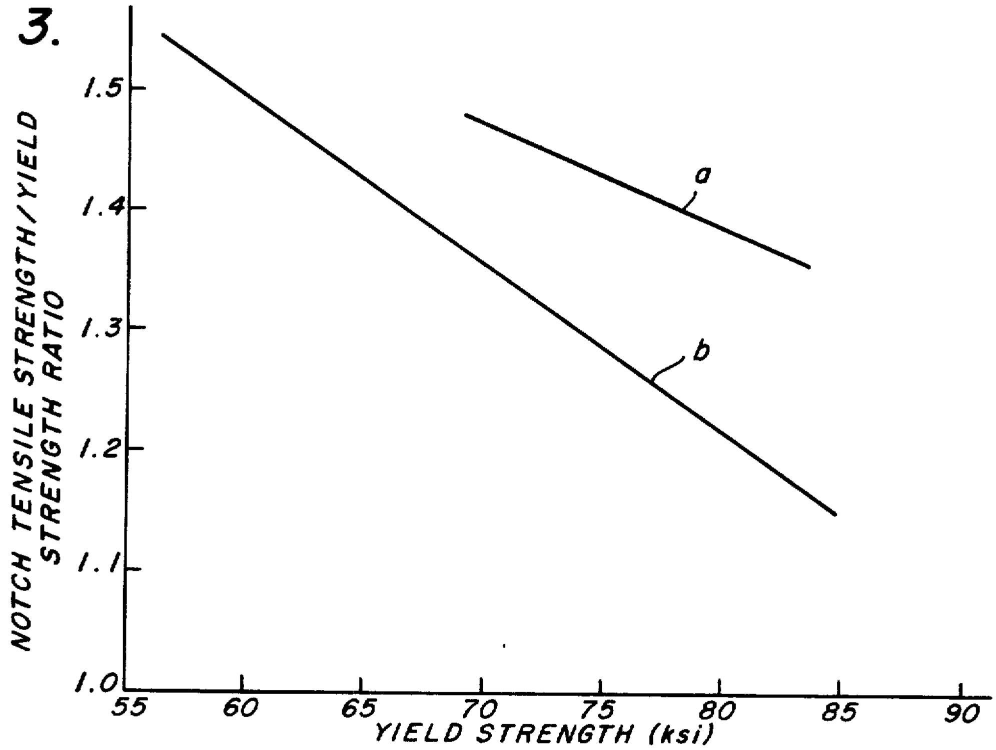
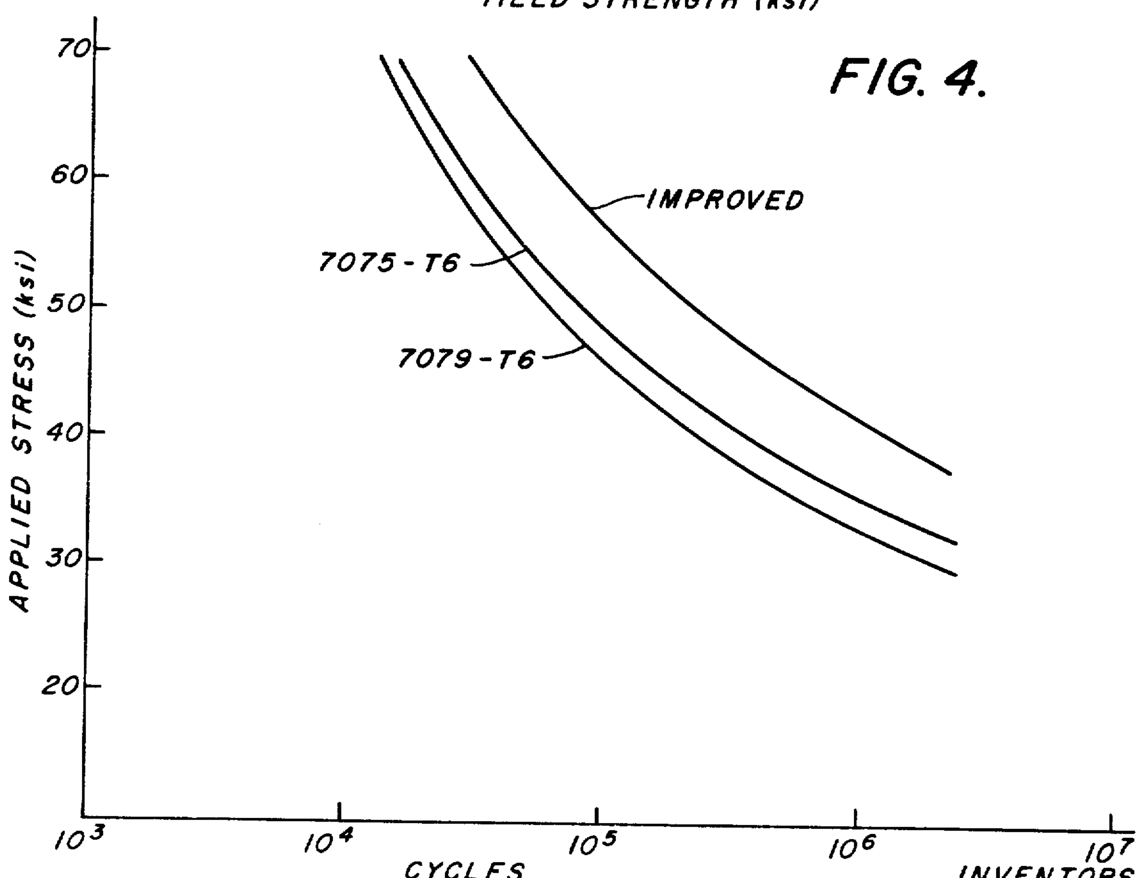


FIG. 4.



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METHOD FOR MAKING ALUMINUM ALLOY PRODUCT

This invention relates to improved wrought products and to a method of their production. This is a continuation of application Ser. No. 121,056, filed Mar. 4, 1971, now abandoned, which, in turn, was a divisional of application Ser. No. 60,343, filed Aug. 3, 1970, now abandoned. The invention herein described was made in the course of or under a contract or subcontract thereunder with the Department of the Navy.

BACKGROUND OF THE INVENTION

Aluminum alloys containing 3 to 8 percent Zn, 1.5 to 4 percent Mh and 0.75 to 2.5 percent Cu are known for their high strength to weight ratio which renders them highly suited for use in applications such as structural components for aircraft. Alloy 7075 is an example of this type of alloy and has achieved wide spread use in aircraft because of its very high strength and other desirable properties. Alloy 7075 contains 5.1 to 6.1 percent Zn, 2.1 to 2.9 percent Mg, 1.2 to 2 percent Cu, 0.18 to 0.40 percent Cr, the balance being aluminum together with incidental elements and impurities. In relatively thick members such as forgings a few inches thick, 7075 develops typical tensile and yield strength levels of, respectively, 80 and 68 ksi when artificially aged to its highest strength, which aging treatment usually contemplates an extended period of 20 hours or more at a relatively low aging temperature of about 225°F. In this temper which is often referred to as a T6 temper, however, alloy 7075 and similar alloys are sometimes objectionable because of susceptibility to stress corrosion cracking which is improved by a two-step aging cycle as described in U.S. Pat. No. 3,198,676 where, in addition to the lower temperature aging treatment the members are subjected to a second treatment at a higher temperature of about **350°** but for a comparatively short time which is usually under **15 hours**. This treatment, which produces what can be termed a T7 type temper, markedly improves resistance to stress corrosion cracking but results in a 15 percent loss in strength which, for many applications, is acceptable. This loss in strength is due to the fact that during the second, higher temperature, aging treatment while resistance to stress corrosion cracking is increasing up to the desired level, the strength is being diminished at a substantial rate as the second step proceeds. Attempts to optimize the strength and resistance to stress corrosion cracking by the most exacting controls during the second aging step have met with varying degrees of success. Guarantying the best strength levels together with high resistance to stress corrosion cracking often involves very high rejection rates which are obviously objectionable and which equally obviously increase the cost of the acceptable products.

The foregoing disadvantages of existing **7000** series alloys are overcome by the practice of the invention wherein special composition controls together with a higher temperature aging treatment which may or may not be preceded by a lower temperature aging treatment combine to produce very high resistance to stress corrosion cracking together with a very high strength level. In fact the improved products in accordance with the invention exhibit their maximum strength levels at the same temper at which they demonstrate high resistance to stress corrosion cracking which is a unique property in 7000 series alloys.

DESCRIPTION

In this description reference is made to the drawings which are all graphs plotting various properties for the improved and for comparison products, and specifically in which:

FIG. **1** is a graph of aging time versus strength;

FIG. **2** is a graph of forging thickness versus longitudinal yield strength;

FIG. **3** is a graph of yield strength versus notch tensile strength/yield strength ratio; and

FIG. **4** is a graph of cycles to fatigue failure versus applied stress.

In practicing the invention the desired combination of properties is achieved by carefully controlling the composition of the aluminum alloy which consists essentially of, by weight, 4..5 to 8 percent Zn, 1.7 to 3.25 percent Cu, 1.4 to 2.6 percent Mg, the balance being aluminum and impurities and incidental elements. The copper to magnesium ratio must be at least 0.85 and preferably at least 1.0. The alloying elements are somewhat interrelated and the following further limits also apply thereto. The weight percent of Mg plus Cu should not exceed 5.4 percent and Mg plus 0.2 times Cu is at least 2. The total of all three principal alloying elements, Zn, Cu and Mg, is between 8.75 percent and 12.25 percent. In addition to the foregoing, the alloy contains 0.05 to 0.25 percent Zr. The invention also contemplates additions of both Zr and Mn. In this latter case the maximum for Zr is 0.20 percent and the Mn range is 0.15 to 0.5 percent. It is important in practicing the invention that chromium be carefully controlled and be present only in amounts of up to but not to exceed 0.04 percent. Impurities are preferably limited as follows: 0.35 percent Fe, 0.25 percent Si, 0.06 percent Ti and 0.02 percent V. The foregoing alloy surprisingly develops its maximum strength during relatively high temperature artificial aging treatments needed to develop high resistance to stress corrosion cracking in direct contrast to other commercial 7000 series type alloys of high strength which have their high strength levels diminished considerably during that thermal treatment.

The improved alloy is especially useful in the form of forgings, which may be of the hand or die forged type, rolled products such as sheet or plate or in the form of extruded products. The improved material exhibits a surprising lack of yield strength sensitivity to quench rate which enables the realization in members of substantial thickness of the same general strength levels achieved in members of relatively thin cross section. This is in contrast with other 7000 series alloy materials which exhibit substantial decreases in yield strength with increasing thickness in section.

In fabricating improved products there are no especially cumbersome or intricate procedures required. A body of the desired composition is provided which may be a continuously direct chilled cast ingot. The ingot is subjected to an elevated temperature of about 860°F for a period sufficient to homogenize its internal structure and provide an essentially uniform distribution of the alloying elements. The alloy body is then subjected to hot working and, if desired, cold working operations to produce the desired product. As mentioned above these working operations may include forging, rolling, extrusion and other known metal working procedures useful in producing aluminum alloy products. Of course the conventional intermediate annealing or reheating operations can be employed if they facilitate ease of fabrication. The products may be of relatively thick cross section, for example, two to four inches or more in thickness, or they may have relatively thin sections of less than ¼ inch. Irrespective of thickness the members will exhibit a uniformity of high yield strength foreign to other 7000 series alloy products where strength diminishes considerably with increasing thickness which strength loss is attributed to the quench sensitivity of these alloys.

The product is typically solution heat treated at a temperature of 860°F or higher for a sufficient time for solution effects to approach equilibrium and then quenched. Quenching may be accomplished in a number of ways in view of the surprising lack of quench sensitivity possessed by the improved products. For instance, the products can be quenched by spraying with cold water, immersion in room temperature water or immersion in relatively hot water of, for instance, 180°F or even boiling water.

The solution heat treated and quenched product is then aged to develop its strength and other properties. Aging is accomplished by heating to a temperature of between 300° and 380°F for a period of at least one hour but preferably not over 70 hours. To develop the best combination of properties, mechanical and stress corrosion performance, the minimum aging time is determined in accordance with the equation shown below although the minimum time never is less than one hour.

$$\text{Log } t = 11.9 \times \frac{10^3}{T + 450} - 14.6$$

where t = time in hours and

T = temperature, °F

While the invention contemplates a relatively high temperature aging treatment, this treatment may or may not be preceded by a lower temperature treatment at a temperature of, typically, between 200° and 270°F. This is a two-step aging treatment of the type described in U.S. Pat. No. 3,198,676 may be employed provided the second aging step is in accordance with the above set forth equation with respect to time and temperature. However, the earlier aging step is not necessary and, surprisingly, the improved product can be aged to its optimum properties in a single aging step of relatively modest time which results in obvious economies in furnace utilization.

To illustrate the benefits of the invention and the importance of the herein described careful composition control and aging treatment the following examples proceed.

EXAMPLE 1

Two-inch thick plates of varying alloy composition were produced by casting large ingots which were hot rolled to produce the two-inch plate products. Before rolling, the ingots were homogenized at a temperature of about 880°F and after rolling, the plates were solution heat treated at temperature around 890°F and then quenched by immersion in room temperature water. The plates were first aged for 24 hours at 250°F and then subjected to a second aging step at a temperature of 325°F for varying amounts of time. The compositions of the materials tested are listed in Table I and the long transverse yield strength values are plotted versus the aging time at 325°F in FIG. 1. The curve identifications in FIG. 1 correspond to the composition designations in Table I.

TABLE I

Material	Zn	Mg	Cu	Zr	Mn	Cr
A	5.52	2.52	2.47	—	0.01	0.21
C	5.96	2.45	2.49	0.11	0.01	—
D	5.55	2.52	1.61	—	0.01	0.21

Referring to Table I and FIG. 1, material D is conventional 7075 alloy and it can be seen that the highest yield strength occurs with no aging time at 325°F. As the 7075 plate is exposed to the higher temperature aging treatment its strength decreases at a considerable rate. Material A would be in accordance with the invention except that it contains excessive chromium and it too exhibits a decrease in yield strength during the higher temperature aging treatment with its maximum strength level being realized before any higher temperature aging treatment. Material C, on the other hand, is in accordance with the invention and, it is readily apparent from curve C in FIG. 1 that maximum strength values are achieved and maintained between 5 or 6 and 12 hours in the 325° elevated temperature aging treatment, with quite high strength levels being maintained up to 24 hours and longer. This corresponds to the equation which indicates a minimum aging time of 5.6 hours for the 325°F treatment to achieve the best combination of properties. It is during this higher temperature aging treatment that high resistance to stress corrosion resistance is achieved in all the materials listed in Table I although, it is quite clear, that this property must be traded off against strength for materials A and D, which are similar in this respect to the prior art, but not for material which is representative of the invention.

EXAMPLE 2

2-½ inch thick plate was produced in the general manner described in Example 1 and aged for 24 hours at 250°F plus 18 hours at 325°F. The alloy compositions tested and the long transverse and short transverse yield strength, Y.S., properties together with the results of stress corrosion cracking tests are listed in Table II. In the stress corrosion tests, samples were tested at stress levels of 25, 30 and 35 ksi by alternate immersion in a 3.5 percent aqueous solution of NaCl. The stress level at which failure occurred after 84 days is shown in the Table. Sustaining a stress level of approximately one half yield strength was considered as indicative of high resistance to stress corrosion cracking. From Table II it can be seen that material E in accordance with the invention exhibits a very high strength level together with no failures at approximately 50 percent yield strength stress levels in stress corrosion testing whereas material F, not in accordance with the invention, exhibits considerably less strength and cannot sustain the alternate immersion testing at the 35 ksi stress level. Material F falls outside the invention on two counts, the Cu content and its ratio to the Mg content together with an excessive amount of Cr. The performance of material F correlates with previous experience, especially with alloy 7075, where it was considered absolutely essential to include substantial amounts of Cr to improve resistance to stress corrosion cracking.

TABLE II

Material	Composition						Transverse YS, ksi		Stress Corr.
	Zn	Mg	Cu	Zr	Cr	Cu/Mg	long	short	
E	5.96	2.30	2.37	0.12	—	1.03	75	71	None at 35 ksi
F	6.35	2.39	1.63	—	0.17	0.68	66	63	Fail at 30 ksi

EXAMPLE 3

Hot rolled plate ranging in thickness from 2 to 2-½ inches was fabricated from several alloy compositions in accordance with the general procedure, including solution heat treating and quenching, as outlined in Example 1. The plate was artifically aged for 24 hours at 250°F plus 18 hours at 325°F. As in Example **2** the various materials were tested for longitudinal and short transverse yield strength together with resistance to stress corrosion cracking by the alternate immersion technique. In this latter test short transverse specimens were tested at a stress level of 35 ksi, about 50 percent yield strength. The compositions tested and the test results are shown below in Table III together with the data for material E taken from Table II for comparison purposes. In Table III comparing materials E, G, and J versus H illustrates that materials E, G and J in accordance with the invention all exhibit good strength and demonstrate no failures in stress corrosion tests. Material H is below the defined limit for the Cu:Mg ratio and exhibits rapid failure in stress corrosion tests. Materials K, L and M are all in accordance with the invention and verify that the advantages according to the invention are realized throughout a comparatively broad range of zinc content.

TABLE III

Material	Composition					Transverse YS, ksi		Stress Corr.
	Zn	Mg	Cu	Zr	Cu/Mg	long	short	
E	5.96	2.30	2.37	0.12	1.03	75	71	None (30 days)
G	5.76	2.32	2.96	0.11	1.28	75	73	None (30 days)
H	5.77	2.30	1.94	0.11	0.84	74	72	Fail (8 days)
J	5.54	1.99	1.95	0.11	0.98	70	69	None (30 days)
K	4.60	2.26	2.42	0.11	1.07	72	68	None (30 days)
L	5.67	2.25	2.27	0.10	1.01	72	69	None (30 days)
M	6.53	2.10	2.46	0.11	1.17	72	72	None (30 days)

EXAMPLE 4

To illustrate the effect of quench rate, several alloy compositions in accordance with the invention were fabricated into thick plate and were aged for 24 hours at 250°F plus **18** hours at 325°F. Prior to aging some of the members were quenched by immersion in water at room temperature, CWQ, whereas others were quenched in hot water at 175°F, HWQ. Table IV sets forth the compositions tested together with the yield strength and long transverse percent elongation for each quench condition. In viewing the table the surprising improvement in elongation accompanied by minimal decrease in strength achieved with hot water quenching appears to be peculiar and unique to the improved product. This contrasts with the usual behavior of high strength aluminum alloys which with hot water quenching show either no improvement in elongation or an improvement only if accompanied by a marked loss in strength, typically 25 percent or more.

TABLE IV

Composition				Yield Strength ksi		% Elongation	
Zn	Mg	Cu	Zr	CWQ	WQ	WQ	HWO
5.54	1.99	1.95	0.11	72	70	9	12
5.67	2.25	2.27	0.10	72	71	5	10.5
5.76	2.32	2.96	0.11	74	71	3.5	10

To illustrate the low quench sensitivity with respect to yield strength exhibited by the improved products, reference is made to FIG. **2** where average strength levels for forgings are plotted against forging thickness for the improved and for two commercial materials. The comparison materials are alloys registered with the Aluminum Association and their nominal compositions are set forth in Table V.

TABLE V

Alloy	Zn	Mg	Cu	Cr	Mn
7075	5.6	2.5	1.6	0.30	—
7079	4.3	3.3	0.6	0.20	0.20

FIG. **2** includes properties for 7075 alloy in two tempers, the higher strength of T6 type and the more stress corrosion resistant or T7 type. From the figure it can be seen that the improved products exhibit strikingly less sensitivity to quenching as revealed by the highest strength levels in the thickest sections.

Thus, the improved material exhibits a minimum detriment in strength properties with a decreasing quench rate which can be termed a lack of quench sensitivity in strength properties. Moreover as the quench rate is reduced the improved product exhibits an improvement in elongation which is highly useful and unique characteristic and the invention contemplates in one embodiment the utilization of this inherent property wherein the improved material is quenched at a slow rate commensurate with immersion in hot water, such as water at a temperature of at least 150°F, to achieve significantly improved elongation. The quench rates contemplated in this embodiment are normally not over 10°F per second while the metal temperature exceeds 550°F.

EXAMPLE 5

Another property of substantial importance in the more critical applications for aluminum material is that of toughness or resistance to stress in the presence of a notch or stress raiser. FIG. **3** is a plot of longitudinal yield strength versus notch tensile strength to yield strength ratio. Notch tensile strength is the breaking stress of notched tensile specimen and the ratio plotted is a measure of a material's ability to deform plastically in the presence of a stress raiser. In FIG. **3,** line *a* typifies the improved material and is representative of a number of tests on specimens removed from one-inch and two-inch thick plate. Line *b* typifies the properties for a number of commercial alloys, including alloys 7075 and 7079 the nominal compositions of which are set forth in Table V in Example 4 together with alloy 7178 containing nominally 6.8 percent Zn, 2.7 percent Mg, 2.0 percent Cu and 0.30 percent Cr. Line *b* should be considered as representing the median property level as individual property levels vary with temper and other factors. It can be seen from FIG. **3** that in the important notch toughness property the improved material exceeds the performance of the previous materials especially at the higher strength levels.

EXAMPLE 6

Still another characteristic of importance in the more critical applications for aluminum materials is that of fatigue properties under cyclic stress application. FIG. **4** is a plot comparing the improved plate material with alloys 7075 and 7079 plate both in the T6 temper where maximum strength properties are exhibited. The composition of the improved material tested was 6.23 percent Zn, 2.40 percent Mg, 2.24 percent Cu, 0.13 percent Zr, the balance being aluminum and incidental elements and impurities and it was, of course, in the stress corrosion resistant temper having been aged at 250°F for 4 hours followed by 325°F for 9 hours. The particular type of fatigue test employed was of the tension type where a specimen is subjected to an initial or applied tension load which is relaxed to a level of one-fourth the initial load to constitute one cycle. In FIG. **4** the number of cycles to failure is plotted versus the value of the initial or applied stress. From FIG. **4** it becomes apparent that the fatigue properties of the improved material are significantly higher than those of the comparison materials. For instance, at an applied stress level of 60 ksi where each cycle constitutes an applied load at 60 ksi followed by a relaxed load at 15 ksi, alloy 7079 can withstand approximately 25,000 cycles and alloy 7075, about 32,000 cycles. The improved material on the other hand withstands 70,000 cycles, more than twice the best of the comparison materials. This two to one life applies to stress levels of about 55 ksi and higher. Because of the shape of the curves at lower stress levels the life differential becomes even greater.

From all of the foregoing it can be seen that the improved material exhibits superior properties in a number of areas. It has tensile properties which equal or exceed other high strength aluminum materials in thinner sections. It exhibits low yield stength quench sensitivity and accordingly exhibits much better strength levels in thicker sections than other high strength aluminum materials. The improved material can be aged to its highest strength in a single step treatment where it also achieves resistance to stress corrosion cracking. This assures a yield strength which substantially always exceeds 65 ksi and more typically a yield strength in excess of 70 ksi. Other high strength materials containing aluminum, zinc, magnesium and copper generally require a two-step aging treatment in order to achieve high resistance to stress corrosion cracking. This, however, significantly decreases the strength of these materials which must be traded off to achieve high resistance to stress corrosion cracking. The improved material exhibits higher toughness and higher fatigue properties than existing high strength commercial aluminum materials. It thus becomes apparent that the improved material is unique among high strength aluminum alloys and it is very surprising that within the narrow ranges defining the improved material's composition such a unique combination of properties can be achieved.

What is claimed is:

1. A method of producing an improved aluminum alloy product comprising

1. providing a body composed of an alloy consisting essentially of 4.5 to 8 percent Zn, 1.7 to 3.25 percent Cu, 1.4 to 2.6 percent Mg, the total of Zn + Cu + Mg being from 8.75 percent to 12.25 percent, Cu + Mg being 5.4 percent maximum with 0.2 Cu + Mg being 2 percent minimum, the Cu/Mg ratio being at least 0.85, and 0.05 to 0.25 percent Zr, chromium not to exceed 0.04 percent, the balance being aluminum and impurities and incidental elements,
2. working said body to produce said product,
3. solution heat treating said product,
4. quenching said product,
5. subjecting such product to an artificial aging treatment which includes an exposure at an elevated metal temperature to develop resistance to stress corrosion cracking.

2. The method according to claim **1** wherein the said alloy contains 0.05 to 0.2 percent Zr and, additionally, 0.15 to 0.5 percent Mn.

3. In the method of producing a solution heat treated, quenched and artificially aged aluminum alloy wrought product in an aluminum alloy of the type containing zinc, magnesium and copper as the major alloying additions wherein the alloy is worked to a wrought condition, solution heat treated, quenched and artificially aged, the improvement wherein said alloy is provided as a composition consisting essentially of 4.5 to 8 percent Zn, 1.7 to 3.25 percent Cu, 1.4 to 2.6 percent Mg, the total of Zn + Cu + Mg being from 8.75 percent to 12.25 percent, Cu + Mg being 5.4 percent maximum with 0.2 Cu + Mg being 2 percent minimum, the Cu/Mg ratio being at least 0.85, and 0.05 to 0.25 percent Zr, chromium not to exceed 0.04 percent, the balance being aluminum and impurities and incidental elements, said improvement imparting to the wrought product so produced the ability to achieve high resistance to stress corrosion cracking substantially in the condition of maximum strength and low sensitivity in strength to quench rate and good toughness.

4. In the method according to claim **3**, the further improvement wherein the artificial aging treatment includes exposing said alloy to a temperature of between

300° and 380°F for at least one hour, the minimum time being further determined by the following equation:

$$\text{Log } t = 11.9 \times \frac{10^3}{T + 450°} - 14.6$$

where t = time in hours and

T = temperature in °F

5. In the method according to claim 3 wherein the alloy composition is further controlled such that Fe does not exceed 0.35 percent, Si does not exceed 0.25 percent, V does not exceed 0.02 percent and Ti does not exceed 0.06 percent.

6. In the method according to claim 3 wherein the alloy composition is further controlled such that Zr range from 0.05 to 0.2 percent and Mn is included in

amounts of 0.15 to 0.5 percent.

7. In the method according to claim 3 wherein the alloy composition is controlled such that the ratio Cu/Mg is equal to at least 1.

8. The method according to claim 1 wherein said artificial aging treatment exposure is at a metal temperature of between 300° and 380°F and for a time of at least one hour the minimum time being further determined by the following equation:

$$\text{Log } t = 11.9 \times \frac{10^3}{T + 450°} - 14.6$$

where t = time in hours and

T = temperature in °F.

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