

IN THE UNITED STATES DISTRICT COURT
FOR THE NORTHERN DISTRICT OF ILLINOIS
EASTERN DIVISION

MCCOOK METALS, L.L.C. an Illinois limited liability corporation)

Plaintiff,)

v.)

ALCOA, Inc., a Pennsylvania corporation)

Defendants.)

DOCKETED
OCT 31 2000

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FILED OCT 30 2000
CLERK
U.S. DISTRICT COURT

No. 00 C — JUDGE ANDERSEN

Judge _____

Magistrate Judge _____

MAGISTRATE JUDGE LEVIN

Jury Demanded

COMPLAINT

Plaintiff McCook Metals, L.L.C. ("McCook"), by and for its Complaint for declaratory, injunctive and other relief against Alcoa, Inc. ("Alcoa"), states as follows:

THE PARTIES

1. McCook is a limited liability company organized and existing under the laws of the State of Illinois, with its principal place of business in McCook, Illinois.
2. McCook is a manufacturer of cast aluminum alloy plate and sheet products.
3. Alcoa, Inc. ("Alcoa") is a Pennsylvania corporation, organized and existing under the laws of the State of Pennsylvania, with its principal place of business in Pittsburgh, Pennsylvania.
4. Alcoa is the world's largest aluminum company and is an integrated producer of alumina, primary aluminum, and aluminum alloy plate and sheet products.

H

JURISDICTION

5. Pursuant to 28 U.S.C. § 1332, this Court has federal diversity jurisdiction to hear McCook's claims because the parties are of diverse citizenship and the matter in controversy exceeds, exclusive of interest and costs, \$75,000.00.

6. Pursuant to 28 U.S.C. §§ 1331, 1338(a), and 2201 this Court has federal question jurisdiction over McCook's declaratory judgment claims (arising under 35 U.S.C. §§ 101 *et seq.*), and its Lanham Act claims (arising under 15 U.S.C. § 1125).

7. Pursuant to 28 U.S.C. §§ 1338(b) and 1367, this Court has supplemental jurisdiction over McCook's common-law tortious interference claims and trade disparagement claims, and its claims under the Illinois Uniform Deceptive Trade Practices Act (815 ILCS §§ 510/1 *et seq.*).

VENUE

8. Because Alcoa is subject to personal jurisdiction in this district it is deemed to reside in this District, and therefore venue is proper in the Northern District of Illinois pursuant to 28 U.S.C. § 1391(c) and (b)(1), and 28 U.S.C. § 1400(b).

9. Venue is also proper in the Northern District of Illinois pursuant to 28 U.S.C. §§ 1391(b)(2) and 1400(b), because a substantial part of the events or omissions giving rise to McCook's claims occurred in this District, or a substantial part of property that is the subject of the action is situated in this District.

COMMON ALLEGATIONS

The Production of Cast and Machined Wingskins.

10. Both McCook and Alcoa are manufacturers of cast aluminum alloy plate and sheet products for the aeronautic and aerospace industries, and they vigorously compete with one another as suppliers to these industries.

11. One of the products that both parties manufacture and sell is airplane wingskins, which are aluminum alloy plates that serve as the exterior surface of airplane wings.

12. Whereas McCook casts and machines wingskins into the finished product, Alcoa can cast but not machine wingskins; Alcoa must therefore ship its wingskins to a third party for machining before they can be used in an aircraft.

13. The production of wingskins for large commercial and military aircraft requires special equipment, a large capital investment, and a highly trained work force.

14. In addition, before a manufacturer can produce such wingskins it must undertake and pass a series of qualification tests prescribed by the purchaser, or, in the case of federal procurement programs, the federal government.

15. The qualification process is lengthy, time-consuming, resource intensive and expensive.

The C-17 Procurement Program.

16. The Department of the Air Force awarded the Boeing Corporation ("Boeing") the prime contract for the military's C-17 transport jet on or before 1990.

17. The C-17 is the largest military transport jet in production in the United States, and it requires upper wingskins of cast aluminum plate in a size and irregular shape that only a few manufacturers in the world – including McCook and Alcoa – are capable of producing.

18. Each C-17 aircraft requires one shipset of machined upper wingskins, consisting of one wingskin for the left wing and one for the right wing.

19. At the inception of the C-17 procurement program, it was envisioned and expected that the Department of the Air Force would ultimately purchase 120 aircraft from Boeing, but because of the manner in which the federal procurement and appropriations processes work, the Department of the Air Force could not immediately place one order for all 120 aircraft, but instead issued a prime contract to Boeing based on its estimated need for approximately 120 aircraft.

20. The Department of the Air Force has subsequently placed successive orders for C-17 aircraft in smaller lots, as funds were appropriated and authorized for the acquisition of the aircraft, and, on information and belief, the Air Force will continue to do so until all 120 aircraft have been procured.

McCook's "Life of Program" Subcontract with Boeing for C-17 Wingskins.

21. In 1990, Boeing awarded McCook's predecessor in interest, the Reynolds Metals Company ("Reynolds"), the subcontract for the production of machined upper wingskins for the C-17 aircraft, and McCook succeeded to Reynolds' rights under that subcontract when it purchased Reynolds' McCook, Illinois plant.

22. McCook's subcontract with Boeing is a "life of program" (i.e., requirements) contract, meaning that McCook is to be the exclusive supplier of upper wingskins to Boeing for the duration of the C-17 procurement program.

23. The C-17 wingskins McCook supplies pursuant to its subcontract with Boeing must meet certain materials specifications (e.g., fracture toughness, corrosion resistance, etc.), as well as certain design specifications (e.g., machining of the wingskins to certain shapes and within certain size tolerances, etc.).

24. To produce wingskins that meet the prescribed materials specifications, the cast aluminum plate from which wingskins are machined must be alloyed, tempered, stretched, and treated in certain ways.

25. McCook's production process in this regard is based on a two-step tempering process that was developed and patented by its predecessor in interest, the Reynolds Metals Company, in the 1960s, and McCook has used and will continue to use this proprietary process to manufacture all of its wingskins for the C-17 aircraft. To cast and machine wingskins into the specifications required takes between six and eight weeks, and to incorporate the wingskins into aircraft suitable for delivery takes approximately one year.

26. When each lot of airplanes is ordered by the Department of the Air Force, McCook and Boeing, pursuant to their subcontract and consistent with their longstanding practice and custom, have negotiated the specifications, price, and delivery terms for the shipsets of wingskins that are required for the C-17 aircraft in that lot.

27. The subcontract between McCook and Boeing runs through April, 2003, and McCook and/or Reynolds have already manufactured, delivered and sold approximately 80 shipsets of C-17 wingskins to Boeing pursuant to the subcontract.

28. These wingskins have been incorporated by Boeing into C-17 aircraft that have been or will soon be sold to the Department of the Air Force for military purposes.

29. McCook is currently manufacturing shipsets of C-17 wingskins for Boeing, and, but for the tortious and illegal actions of Alcoa described below, McCook had every reasonable expectation of continuing to produce wingskins for Boeing for the life of the C-17 procurement program, based on its "life of program" subcontract with Boeing, the parties' course of dealing, and the past and current business relationships that McCook enjoys with Boeing.

Alcoa's Groundless Threats of Litigation Based on McCook's Allegedly Infringing Wingskins.

30. On information and belief, Alcoa currently contends, and for much if not all of the life of the C-17 procurement it has contended, that the tempering process employed by McCook to cast upper wingskins for the C-17 infringes a patented tempering technology that Alcoa owns, which is hereafter referred to as the T-77 temper technologies.

31. Alcoa has made known these patent infringement contentions to Boeing in the past, but Alcoa has never confronted McCook (or, on information and belief, Reynolds) with them, Alcoa has never contacted McCook to demand that McCook refrain from infringing the T-77 temper technologies, and Alcoa has never sought reasonable royalties from the federal government for McCook's allegedly infringing production of wingskins – as Alcoa would be entitled to do under applicable federal law and regulations (1) if its patents were valid and (2) if McCook's production of wingskins infringed Alcoa's patents.

32. Boeing representatives have apprised McCook that Alcoa has threatened Boeing, claiming that Alcoa will sue to enjoin Boeing from completing any authorized sales of C-17 aircraft to domestic civilian purchasers or any authorized sales direct to certain foreign governments if those aircraft contain wingskins manufactured by McCook's allegedly infringing processes.

Boeing's Plans to Produce 60 More C-17 Aircraft.

33. Boeing is currently contemplating the production of an additional sixty (60) C-17 aircraft for the Department of the Air Force, beyond the 120 aircraft currently envisioned for the program.

34. On information and belief, this additional production of aircraft could normally be accomplished by an extension of the prime contract and subcontracts for the C-17, and thus McCook would reasonably expect under normal circumstances to continue as Boeing's subcontractor for the C-17 wingskins pursuant to its "life of program" subcontract.

35. Indeed, Boeing has asked for and received proposals from McCook for the production of the sixty (60) additional shipsets of wingskins.

36. On information and belief, McCook's production of these additional wingskins would not commence until the expiration of its existing subcontract in 2003 and the delivery to Boeing of the 120th shipset ordered thereunder, and in no event would such production of the sixty (60) additional shipsets of C-17 wingskins commence before November 1, 2001.

37. Boeing, however, has also expressed an interest in maintaining the flexibility to sell or lease at least some of the 60 additional C-17s it manufactures to foreign governments or domestic commercial customers, should the Air Force not need them and/or authorize such sales or leases.

38. If, however, any of these additional aircraft are sold to such a customer, then any patented processes employed by Boeing's subcontractors must be owned, licensed, or assigned to the subcontractor, and may not be licensed against the will of the licensor merely by payment of a reasonable royalty, as is the case when the federal government is the purchaser.

39. Boeing representatives have therefore stated to McCook that while Boeing would prefer to purchase machined wingskins from McCook for the additional sixty (60) C-17 aircraft currently being contemplated – because, *inter alia*, McCook’s C-17 wingskins are of superior quality, McCook can both cast and machine the wingskins, and McCook has a superior record of responsiveness to Boeing’s delivery and other requirements – as a direct result of Alcoa’s threatened patent infringement suit, Boeing has, on information and belief, entered into a Memorandum of Understanding with Alcoa for the supply of the upper wingskins for the additional sixty (60) C-17 aircraft.

40. Thus, Boeing has stated that but for Alcoa’s threats of injunction, it would continue to purchase the C-17 wingskins from McCook, including those to be incorporated into the additional sixty (60) C-17 aircraft whose production is currently under active consideration.

41. Alcoa’s groundless assertions of infringement and invalid, expiring, and/or unenforceable patents have harmed McCook’s business reputation with Boeing and have unfairly and groundlessly called into question the quality of McCook’s C-17 upper wingskins and the legality of its production processes.

42. The damage to McCook’s business and product reputations, and the damage to McCook’s business relationships with Boeing, that has been and will be caused by Alcoa’s groundless assertions of infringement of invalid, expiring and/or unenforceable patents it is difficult to measure and quantify, and it constitutes irreparable harm.

43. McCook has no adequate and complete remedy at law for Alcoa’s tortious interference, disparagement, deceptive business practices, and false advertising.

44. The balance of harms and public interests in this case favors an award of preliminary and permanent injunctive relief to McCook.

COUNT I
Declaratory Judgment

45. McCook repeats and incorporates by reference paragraphs 10 through 44 of its Complaint.

46. On information, Alcoa currently owns, and at all relevant times has owned, all right, title, and interest in and to four United States patents: US 4,477,292 (the “292 patent”); US 4,832,758 (the “758 patent”); US 4,863,528 (the “528 patent”); and US 5,108,520 (the “520 patent”). These four patents are collectively referred to herein as “the patents in suit,” and copies of the patents in suit are attached hereto as Exhibits 1-4, respectively.

47. McCook believes that the patents in suit are the patents that Alcoa contends McCook has, is, and would be infringing by its past, current, and future production of upper wingskins for the C-17 aircraft.

48. McCook denies that its production of wingskins for the C-17 aircraft has in the past infringed, or is currently infringing, or in the future will infringe, any of the patents in suit. As set forth above, McCook’s two-step tempering process for the production of C-17 wingskins was pioneered and patented by its predecessor in interest, the Reynolds Metals Company, and that process does not infringe the patents in suit.

49. On information and belief, Alcoa is aware that McCook’s production of wingskins for the C-17 aircraft does not infringe the patents in suit, and for that reason Alcoa has not sought

payment of a reasonable royalty from the federal government for McCook's allegedly infringing production of such wineskins.

50. The '292, '528, and '758 patents will expire on or about October 16, 2001, and therefore McCook's production of wingskins for the C-17 aircraft after October 16, 2001 could not infringe those patents.

51. On information and belief, Alcoa knows or should know that the '292, '528, and '758 patents will expire before production of the wingskins for the sixty (60) additional C-17 aircraft commences, but Alcoa has nonetheless asserted the future infringement of these patents after their expiration in bad faith and with the intent to harm McCook, dissuade Boeing from honoring its "life of program" subcontract with McCook, and/or to frustrate McCook's reasonable expectation of receiving the orders for the sixty (60) shipsets of wingskins required for the additional C-17 aircraft currently under contemplation.

52. On information and belief, each of the patents in suit is invalid under 35 U.S.C. § 102, because each was anticipated; and/or each of the patents in suit is invalid under 35 U.S.C. § 103, because, in light of prior art, the subject matter of the patent as a whole would have been obvious at the time the invention was made to one of ordinary skill in the relevant field.

53. Alcoa knowingly withheld from the patent examiners who examined the patents in suit relevant prior art respecting the claimed invention, with the purpose and intent of misleading the United States Patent Office as to the patentability of the claimed inventions, and as a result of this inequitable conduct, the patents in suit are unenforceable.

54. Alcoa's attempted misuse of the '292, '528, and '758 patents, by, *inter alia*, asserting their validity after their expiration date, also renders those patents unenforceable.

55. The patents in suit are also unenforceable by reason of laches, estoppel, and/or acquiescence.

56. On information and belief, Alcoa is aware that each of the patents in suit is invalid and/or unenforceable, but Alcoa has nonetheless asserted the infringement of these invalid and unenforceable patents in bad faith and with the intent to harm McCook, dissuade Boeing from honoring its "life of program" subcontract with McCook, and/or to frustrate McCook's reasonable expectation of receiving the orders for the sixty (60) shipsets of wingskins required for the additional C-17 aircraft currently under contemplation.

57. On information and belief, Alcoa has been aware of the alleged infringement of the patents in suit since on or about 1990.

58. Alcoa's delay in pursuing McCook's alleged infringement of the patents in suit is manifestly unreasonable, on information and belief that delay exceeds six years, and McCook (and its predecessor in interest) have reasonably relied on the non-infringing nature and legality of McCook's wingskin production processes in investing in capital improvements, seeking further work from Boeing, and in other ways.

59. A present and actual controversy exists between Alcoa and McCook with respect to the infringement, validity, and enforceability of the patents in suit.

60. A declaratory judgment determining these issues will greatly facilitate resolution of the parties' current disputes respecting who can be the supplier of upper wingskins for the sixty (60) additional C-17 aircraft currently being contemplated.

WHEREFORE, the plaintiff, McCook Metals L.L.C., respectfully prays that the Court award McCook declaratory relief pursuant to 28 U.S.C. § 2201 as follows:

- A. A declaration that McCook's production of upper wingskins for the C-17 aircraft does not infringe the patents in suit;
- B. A declaration that the '292, '528, and '758 patents expire on or about October 16, 2001, and therefore McCook's production of wingskins for the C-17 aircraft after October 16, 2001 would not and could not infringe these patents.
- C. A declaration that each of the patents in suit is invalid under 35 U.S.C. §§ 102 and/or 103;
- D. A declaration that each of the patents in suit is unenforceable by reason of Alcoa's inequitable conduct, patent misuse, or by operation of laches, equitable estoppel, and/or acquiescence;
- E. Attorneys fees and costs, as provided for under the federal patent laws for exceptional cases like this one, i.e., 35 U.S.C. § 285; and
- F. Such other and further relief as the Court may deem just and proper, including costs and attorneys fees associated with the prosecution of this action.

COUNT II
Tortious Interference with Contract

61. McCook repeats and incorporates by reference paragraphs 10 through 60 of its Complaint.

62. The subcontract between McCook and Boeing constitutes a valid and enforceable contract.

63. At all relevant times, Alcoa was aware of McCook's subcontract with Boeing for the production and supply of machined upper wingskins for the C-17 aircraft.

64. With such knowledge, and without justification, defendant Alcoa has wrongfully and intentionally interfered with Boeing's performance under its subcontract with McCook by Alcoa's knowing and bad-faith assertions of McCook's infringement of the patents in suit and by Alcoa's knowing and bad-faith assertions of invalid and/or expiring patents.

65. On information and belief, Alcoa has engaged in willful, wanton, bad faith, and/or reckless conduct simply to harm McCook, or at the very least Alcoa has undertaken such conduct with callous disregard and indifference to McCook's existing contractual relationship with Boeing.

66. Defendant Alcoa's continued interference with the Boeing-McCook subcontract for C-17 wingskins has and will continue to deprive McCook of the benefits of its "life or program" subcontract with Boeing.

67. Despite the invalidity and unenforceability of the patents in suit and the baselessness of Alcoa's assertions respecting McCook's infringement of the patents in suit, Alcoa has intentionally interfered with McCook's existing contract with Boeing for the supply of C-17 upper wingskins by:

- (a) asserting the validity of Alcoa's patents for the T-77 process; and
- (b) contacting Boeing and informing it that McCook's process for producing C-17 wingskins infringes those patents.

68. Alcoa's tortious interference with McCook's contractual relationship with Boeing has directly and proximately caused McCook to sustain substantial damages, and threatens to force the termination of McCook's agreement with Boeing for the ongoing supply of upper wingskins during the C-17 program.

69. McCook's current and future business relationships with Boeing have been seriously and perhaps irretrievably harmed by Alcoa's tortious and bad faith assertion of invalid, expiring and unenforceable patents in suit and by Alcoa's bad faith and groundless assertions of McCook's infringement of the patents, and Alcoa's continued assertions of McCook's infringement of the patents in suit and continued contentions that the patents in suit are valid, will not expire, and are enforceable threaten to irreparably harm McCook's current and future business relationships with Boeing.

70. As a direct and proximate result of ALCOA's intentional interference with McCook's reasonable business expectations, McCook has suffered substantial damages and will suffer even greater damages in the future.

71. McCook has no adequate remedy at law for the injuries Alcoa's baseless assertions of infringement and invocation of invalid and/or expiring patents is having on McCook's current and expected business relationships with Boeing.

WHEREFORE, the plaintiff, McCook Metals L.L.C., respectfully requests:

A. Entry of a judgment in its favor and against Alcoa for damages sustained by McCook as a result of Alcoa's actions;

B. Entry of a preliminary and permanent injunction enjoining Alcoa, its officers, agents, servants, employees, and attorneys, and those persons in active concert or participation with them who receive actual notice thereof, from

(1) continuing to engage in the intentional tortious interference alleged herein or similar interference;

(2) proceeding with any further contract negotiations with Boeing respecting the supply of C-17 wingskins;

(3) taking any action to enforce or assert its rights under the Memorandum of Understanding between Alcoa and Boeing respecting the supply of C-17 wingskins; and

C. Such other and further relief as the Court may deem just and proper, including costs and attorneys fees associated with the prosecution of this action.

COUNT III

Tortious Interference with Current and Prospective Business Relationships with Boeing

72. McCook repeats and incorporates by reference paragraphs 10 through 71 of its Complaint.

73. Based upon McCook's well-established commercial relationship with Boeing, Boeing's invitation for McCook to submit a proposal for the sixty (60) shipsets of wingskins for the additional C-17s currently being contemplated, Boeing's prior course of dealing with McCook, and Boeing's statements that but for Alcoa's threatened infringement actions it would have used McCook as its supplier for the additional C-17 wingskins, McCook has and had a reasonable expectancy of

entering into an extension of its subcontract with Boeing for the production of the additional 60 shipsets of C-17 wingskins.

74. Alcoa knew or should have known of McCook's reasonable expectancy of entering into an extension of its subcontract with Boeing respecting the purchase and sale of C-17 upper wingskins.

75. Alcoa also knew or should have known of McCook's prior dealings with Boeing with respect to the C-17.

76. Alcoa also knew that Boeing had a long-standing relationship with McCook and that McCook had a reasonable expectation of making C-17 wingskin sales to Boeing in the future.

77. Alcoa intentionally and in bad faith interfered with McCook's relationships with Boeing to prevent McCook from selling C-17 wingskins to Boeing in the future.

78. Alcoa intentionally induced Boeing's breach of the McCook's "life of program" subcontract to prevent McCook from selling C-17 wingskins to Boeing in the future.

79. On information and belief, Alcoa contacted Boeing to inform it that Alcoa's patents for the T-77 process were valid and were being infringed by McCook's production of C-17 upper wingskins for Boeing.

80. By falsely and in bad faith asserting the validity and infringement of its patents, Alcoa intentionally, and without justification or privilege, interfered with and frustrated McCook's reasonable business expectancy, and induced or caused Boeing to fail to extend the subcontract with McCook for future sales of C-17 wingskins and to instead enter into a Memorandum of Understanding with Alcoa for such sales.

81. On information and belief, on or after McCook's completion of the 120th shipset, and as reflected in the Boeing-Alcoa Memorandum of Understanding, Boeing intends to purchase unmachined wingskins from Alcoa for the sixty (60) additional C-17 aircraft whose production is currently contemplated.

82. Alcoa's conduct has been and is willful, wanton, and reckless and undertaken in bad faith and with callous disregard and indifference to McCook's contractual relationships with Boeing.

83. McCook has been damaged and will continue to be damaged by Alcoa's ongoing interference with McCook's expected business relationship with Boeing.

84. McCook has lost its advantageous relationship with Boeing and is now potentially subject to being unable to assure its future business relationship with Boeing, except on terms less favorable than those previously available to McCook.

85. McCook's current and future business relationships with Boeing have been seriously and perhaps irretrievably harmed by Alcoa's tortious and bad faith assertion of invalid patents and infringement of such patents, and Alcoa's continued assertions of McCook's infringement of the patents in suit and continued contentions that the patents in suit are valid and enforceable threaten to irreparably harm McCook's current and future business relationships with Boeing.

86. As a direct and proximate result of Alcoa's intentional interference with McCook's reasonable business expectations, McCook has suffered substantial damages and will suffer even greater damages in the future.

87. McCook has no adequate remedy at law for the injuries Alcoa's baseless assertions of infringement and invocation of invalid and/or expiring patents is having on McCook's current and expected business relationships with Boeing.

WHEREFORE, the plaintiff, McCook Metals L.L.C., respectfully requests:

- A. Entry of a judgment in its favor and against Alcoa for damages sustained by McCook as a result of Alcoa's actions; or
- B. Entry of a preliminary and permanent injunction in its favor and against Alcoa enjoining Alcoa, its officers, agents, servants, employees, and attorneys, and those persons in active concert or participation with them who receive actual notice thereof, from
 - (1) continuing to engage in the intentional tortious interference alleged herein or similar interference;
 - (2) proceeding with any further contract negotiations with Boeing respecting the supply of C-17 wingskins;
 - (3) taking any action to enforce or assert its rights under the Memorandum of Understanding between Alcoa and Boeing respecting the supply of C-17 wingskins; and
- C. Such other and further relief as the Court may deem just and proper, including costs and attorneys fees associated with the prosecution of this action.

COUNT IV
Common Law Trade Disparagement

88. McCook repeats and incorporates by reference paragraphs 10 through 87 of its Complaint.

89. On information and belief, Alcoa's unfounded and bad faith assertions that McCook has infringed the patents in suit and that those patents are valid and enforceable has damaged McCook's reputation with Boeing and deterred Boeing from broadening and/or continuing its commercial relations with McCook at the same level.

90. On information and belief, Alcoa's unfounded and bad faith assertions that McCook has infringed the patents in suit and that those patents are valid and enforceable has harmed both McCook's existing sales of wingskins to Boeing and its prospective sales or wingskins to Boeing – the sole customer for this product.

91. Alcoa's unfounded and bad faith assertions that McCook has infringed the patents in suit and that those patents are valid and enforceable has damaged McCook's business relationship with Boeing and will irretrievably damage that relationship if Alcoa is permitted to continue asserting its unfounded claims of infringement and invalid and unenforceable patents.

92. Alcoa's statements respecting McCook's alleged infringement of the patents in suit and respecting the alleged validity and enforceability of those statements are false, and Alcoa knew or should have known that they were false when it made them.

93. Alcoa's statements to Boeing in this regard were unprivileged and published to a third party, Boeing.

94. McCook has been and continues to be directly and proximately damaged by Alcoa's disparagement of McCook's non-infringing C-17 wingskins, including, among other things, McCook's failure to secure an extension of its subcontract for the production of C-17 wingskins for the additional sixty (60) aircraft whose production is currently contemplated.

WHEREFORE, the plaintiff, McCook Metals L.L.C., respectfully requests:

- A. Entry of a judgment in its favor and against Alcoa for damages sustained by McCook as a result of Alcoa's disparagement;
- B. Entry of a preliminary and permanent injunction in its favor and against Alcoa enjoining Alcoa, its officers, agents, servants, employees, and attorneys, and those persons in active concert or participation with them who receive actual notice thereof, from
 - (1) continuing to engage in the common law disparagement alleged herein or similar disparagement;
 - (2) proceeding with any further contract negotiations with Boeing respecting the supply of C-17 wingskins;
 - (3) taking any action to enforce or assert its rights under the Memorandum of Understanding between Alcoa and Boeing respecting the supply of C-17 wingskins; and
- C. Such other and further relief as the Court may deem just and proper, including costs and attorneys fees associated with the prosecution of this action.

COUNT V
Uniform Deceptive Trade Practices Act Claim

95. McCook repeats and incorporates by reference paragraphs 10 through 94 of its Complaint.

96. Alcoa's bad-faith disparagement of McCook's C-17 wingskins as infringing its invalid and expiring patents, as set forth above, wrongly implies to Boeing (and the federal government) that McCook is dishonest or untrustworthy in its business operations and relations and that McCook's wingskins are of inferior quality and/or are unsuitable for use in C-17s that are subsequently sold to authorized domestic and foreign purchasers.

97. Alcoa's disparagement of McCook and bad-faith assertion of McCook's infringement of Alcoa's expiring and invalid patents constitutes a deceptive trade practice under Section 2(8) of the Illinois Uniform Deceptive Trade Practices Act, codified as amended at 815 ILCS 510/2.

98. Alcoa's bad-faith assertion of McCook's infringement of expiring and invalid patents is knowing, wilful, false, and misleading.

99. Alcoa's trade practices have damaged and are likely to continue damaging McCook's business reputation and sale of C-17 wingskins.

WHEREFORE, the plaintiff, McCook Metals L.L.C., respectfully requests:

A. Pursuant to 815 ILCS 510/3, entry of a preliminary and permanent injunction in its favor and against Alcoa enjoining Alcoa, its officers, agents, servants, employees, and attorneys, and those persons in active concert or participation with them who receive actual notice thereof, from

(1) continuing to engage in the deceptive trade practices alleged herein, or similar practices;

(2) proceeding with any further contract negotiations with Boeing respecting the supply of C-17 wingskins;

(3) taking any action to enforce or assert its rights under the Memorandum of Understanding between Alcoa and Boeing respecting the supply of C-17 wingskins; and

B. Entry of an award of attorneys fees and costs in its favor and against Alcoa, as provided for by 815 ILCS 510/3; and

C. Such other and further relief as the Court may deem just and proper.

COUNT VI
Lanham Act Claim

100. McCook repeats and incorporates by reference paragraphs 10 through 99 of its Complaint.

101. Alcoa's disparagement of McCook before Boeing and assertions to Boeing that McCook's production of C-17 wingskins infringed Alcoa's invalid and expiring patents were made in bad faith.

102. On information and belief, Alcoa made some or all of its false and misleading statements about the infringing nature of McCook's C-17 wingskins while promoting to Boeing Alcoa's own wingskins.

103. On information and belief, Alcoa's false and misleading statements have deceived and/or are likely to deceive Boeing, Alcoa's intended audience for these statements and sole purchaser of C-17 wingskins.

104. On information and belief, Alcoa's false and misleading statements were material to Boeing's decision to enter into the Memorandum of Understanding with Alcoa for the provision of wingskins for the sixty (60) additional C-17 aircraft whose production is currently contemplated and persuaded Boeing to enter into the Memorandum of Understanding with Alcoa instead of extending its subcontract with McCook.

105. On information and belief, Alcoa used the instrumentalities of interstate commerce and communication to make its false and misleading statements respecting McCook's allegedly infringing production processes known to Boeing, either in whole or in part.

106. Alcoa's false and misleading statements have injured McCook and will continue to injure McCook by depriving it of an extension of its subcontract for the upper wingskins required for the sixty (60) additional C-17 aircraft whose production is currently contemplated.

107. The above actions of Alcoa violate § 43(a) of the Lanham Act, codified as amended at 15 U.S.C. § 1125(a), and entitle McCook to relief thereunder.

WHEREFORE, the plaintiff, McCook Metals L.L.C., respectfully requests:

A. Entry of a judgment in its favor and against Alcoa for damages sustained by McCook as a result of Alcoa's violations of the Lanham Act;

B. Entry of a preliminary and permanent injunction in its favor and against Alcoa enjoining Alcoa, its officers, agents, servants, employees, and attorneys, and those persons in active concert or participation with them who receive actual notice thereof, from

(1) continuing to engage in the false and deceptive advertising alleged herein, or similar practices;

(2) proceeding with any further contract negotiations with Boeing respecting the supply of C-17 wingskins;

(3) taking any action to enforce or assert its rights under the Memorandum of Understanding between Alcoa and Boeing respecting the supply of C-17 wingskins; and

C. Such other and further relief as the Court may deem just and proper, including costs and attorneys fees associated with the prosecution of this action.

Dated: October 30, 2000

MCCOOK METALS L.L.C.
Plaintiff

By:

One of its attorneys.

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EXHIBIT 1

United States Patent [19]
Brown

[11] **Patent Number:** 4,477,292
 [45] **Date of Patent:** Oct. 16, 1984

- [54] **THREE-STEP AGING TO OBTAIN HIGH STRENGTH AND CORROSION RESISTANCE IN AL-ZN-MG-CU ALLOYS**
- [75] **Inventor:** Melvin H. Brown, Freeport, Pa.
- [73] **Assignee:** Aluminum Company of America, Pittsburgh, Pa.
- [21] **Appl. No.:** 311,552
- [22] **Filed:** Oct. 15, 1981

Related U.S. Application Data

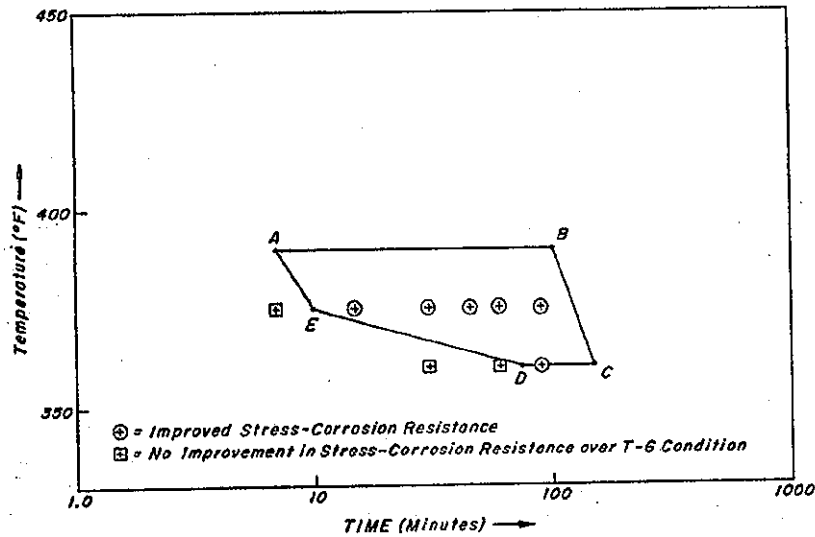
- [63] Continuation-in-part of Ser. No. 142,541, Apr. 21, 1980, which is a continuation of Ser. No. 410,109, Oct. 26, 1973, abandoned.
- [51] **Int. Cl.³** C22F 1/04
- [52] **U.S. Cl.** 148/20; 148/20.6; 148/159; 148/417
- [58] **Field of Search** 148/159, 12.7 A, 32.5, 148/20, 20.6

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U.S. PATENT DOCUMENTS
 3,856,584 12/1974 Cina 148/159

Primary Examiner—R. Dean
Attorney, Agent, or Firm—Glenn E. Klepac

[57] **ABSTRACT**
 A three-step thermal aging method for improving the strength and corrosion resistance of an article comprising a solution heat treated aluminum alloy containing zinc, magnesium, copper and at least one element selected from the group consisting of chromium, manganese and zirconium. The article is precipitation hardened at about 175° to 325° F., heat treated for from several minutes to a few hours at a temperature of about 360° to 390° F. and again precipitation hardened at about 175° to 325° F. In a preferred embodiment the article treated comprises aluminum alloy 7075 in the T6 condition. The method of the invention is easier to control and is suitable for treating articles of greater thickness than other comparable methods.

13 Claims, 1 Drawing Figure

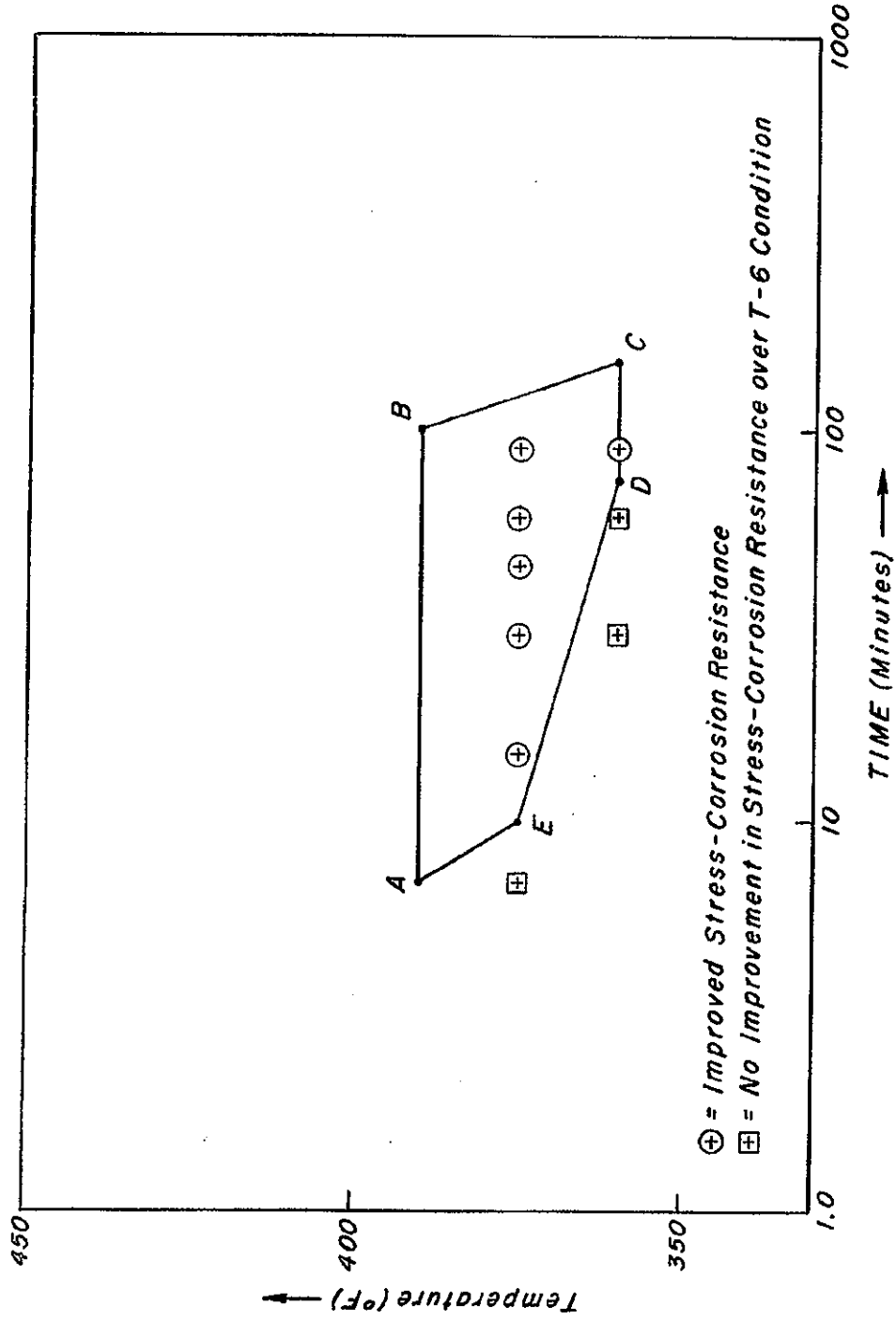


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FIG. 1.



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THREE-STEP AGING TO OBTAIN HIGH STRENGTH AND CORROSION RESISTANCE IN AL-ZN-MG-CU ALLOYS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. application Ser. No. 142,541, filed Apr. 21, 1980, which application is a continuation of U.S. application Ser. No. 410,109, filed Oct. 26, 1973, abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a method for thermally treating articles containing an alloy based on aluminum.

Various methods have been developed in the prior art for improving the resistance to corrosion under certain service conditions of the precipitation hardened condition of aluminum alloy 7075. This condition is referred to as the T6 condition of alloy 7075. However, none of these prior art methods is completely suitable for its intended purpose.

For example, Sprowls et al U.S. Pat. No. 3,198,676 describes a two-step method for improving the resistance of precipitation hardened 7075 alloy to stress-corrosion cracking. Aluminum alloy treated according to the method of the Sprowls et al patent is in a condition that is referred to as the T73 temper. Aluminum 7075 alloy in the T73 temper has improved resistance to stress-corrosion cracking although the T73 temper decreases tensile strength significantly compared with the T6 condition.

Specimens of commercially prepared aluminum 7075 alloy in the T73 temper have sometimes been subjected to a third aging step in order to increase tensile strength and yield strength. For example, a 7075 specimen subjected to precipitation hardening for six hours at 225° F. and heat treatment for eight hours at 350° F. had a tensile strength of 72 ksi (kilopounds per square inch) and a yield strength of 61 ksi. Further precipitation hardening for 48 hours at 250° F. increased tensile strength to 76 ksi and yield strength to 66 ksi. Resistance to stress-corrosion cracking was retained. Although the time of the heat treatment step has been varied between six hours and nine hours in this procedure, applicant is not aware of any prior art three-step aging process wherein the times and temperatures for the second (heat treatment) step correspond to the times and temperatures for the second step of the three-step process described and claimed herein.

Another prior art two-step method for heat treating aluminum alloys is disclosed in Nock et al U.S. Pat. No. 2,248,185. The times and heat treating temperatures described for both of the steps of the Nock et al method are comparable to the times and temperatures employed in the first two steps of the method of the present invention. However, the Nock et al patent does not suggest addition of a third, precipitation hardening step.

Cina U.S. Pat. No. 3,856,584 describes a method that is claimed to reduce the susceptibility to stress-corrosion cracking of 7000 series aluminum alloys. Alloys are successively subjected to a solution heat treatment, an age hardening step at a lower temperature than the heat treatment step, a "retrogression" heat treatment for a few seconds to a few minutes at a temperature of 200° to 260° C. and a reaging heat treatment at a temperature of 115° to 125° C. The thermal aging method of the present

invention differs from the method claimed by Cina in that Cina's "retrogression" heat treatment is carried out at higher temperatures than are preferred herein. The present method has the advantages of being easier to control and being suitable for treatment of articles having greater thicknesses than Cina's method.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a new heat treating method to produce an aluminum alloy in a unique heat treated condition providing favorable resistance to corrosion combined with high tensile strength.

It is a related object of the invention to provide a method for heat treating aluminum alloy that is easier to control than comparable prior art methods.

A further object of the invention is to provide a method for heat treating aluminum alloy that is suitable for treating articles of greater thickness than other comparable methods.

The foregoing objects are achieved according to the present invention by thermally treating an article comprising a solution heat treated alloy of the 7000 series, said alloy containing aluminum, zinc, magnesium, copper and at least one element selected from the group consisting of chromium, manganese and zirconium. The method comprises the steps of precipitation hardening the article at about 175° to 325° F., heat treating the article for from several minutes to a few hours at about 360° to 390° F. and again precipitation hardening the article at about 175° to 325° F. In a preferred embodiment, the heat treating step is carried out at a time and temperature within the perimeter of ABCDE in FIG. 1.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph showing some preferred times and temperatures for the heat treating step of the method of the invention.

DESCRIPTION OF A PREFERRED EMBODIMENT

Alloys treated by the method of the present invention contain aluminum, zinc, magnesium, copper and at least one other element selected from the group consisting of chromium, manganese and zirconium. Some composition ranges for these 7000 series aluminum alloys are as follows: 4 to 8% zinc; 1.5 to 3.5% magnesium; 1 to 2.5% copper; at least one element selected from the group made up of 0.05 to 0.3% chromium, 0.1 to 0.5% manganese and 0.05 to 0.3% zirconium; balance aluminum.

Alloys designated 7075 by the aluminum industry are preferred for the present invention and have a composition containing 5.1 to 6.1% zinc, 2.1 to 2.9% magnesium, 1.2 to 2.0% copper, 0.18 to 0.35% chromium, 0.30% maximum manganese, 0.40% maximum silicon, 0.50% maximum iron, 0.20% maximum titanium, others each 0.05% maximum and others total 0.15% maximum, balance aluminum.

The alloys used in the present invention may also contain one or more of the group of grain refining elements including titanium at 0.01 to 0.2% and boron at 0.0005 to 0.002%. These elements serve to produce a fine grain size in the cast form of the alloy. This is generally advantageous to mechanical properties.

In addition, it may be helpful to add 0.001 to 0.005% beryllium for the purpose of minimizing oxidation at times when the alloy is molten.

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Iron and silicon are generally present as impurities. Up to 0.5% iron can be tolerated, and the silicon content should not exceed 0.4% in order to avoid the formation of any substantial amount of the intermetallic compound Mg₂Si.

A preferred heat treatment according to the present invention for obtaining improved stress-corrosion resistance is to immerse aluminum alloy, as above defined, in the precipitation hardened, T6 condition into molten metal for a time and temperature within the perimeter of the outline ABCDE in FIG. 1, then precipitation harden again.

In its broader aspects, a T6 condition may be obtained by precipitation hardening solution heat treated alloy at 175° to 325° F. Typical conditions may be:

- (a) For alloys containing less than 7.5% zinc, heating a solution heat treated article to 200° to 275° F. and holding for a period of 5 to 30 hours;
- (b) For alloys containing more than 7.5% zinc, heating a solution heat treated article to 175° to 275° F. and holding for a period of 3 to 30 hours.

A usual practice for obtaining the T6 condition is to heat a specimen for 24 hours at 250° F. in a circulatory air furnace.

In accordance with the present invention, an article comprising a solution heat treated aluminum alloy of the 7000 series is precipitation hardened at about 175° to 325° F., then subjected to a temperature and time within the perimeter of the outline ABCDE in FIG. 1, and then again precipitation hardened at about 175° to 325° F.

In a particularly preferred embodiment, the initial precipitation hardening step is carried out for a period of 24 hours at about 250° F. The heat treatment step is preferably conducted for about 45 to 90 minutes at a temperature of about 375° F. The final precipitation hardening step is preferably carried out for about 6 to 12 hours at a temperature of about 275° to 300° F.

It is an advantage of the present invention that the thermal aging method described herein is suitable for use with specimens having greater maximum thicknesses than previously published thermal aging methods having a heat treating step conducted at higher temperatures. The following equation, derived from heat transfer theory, describes the maximum suitable thickness in inches for an article having a heat treating step performed in accordance with the invention:

$$L = 0.2 + 0.54 \left[\frac{480 - T}{100} \right]^{3.75} [t_T]^{0.56}$$

In the above equation, L is the thickness of the article in inches, T is the temperature in degrees Fahrenheit of the heat treating medium and h_T is the coefficient of heat transfer between the heat treating medium and the article in BTU/(hr)(sq.ft.)(deg.F.). Gurney-Lurie charts (reprinted in W. H. McAdams, *Heat Transmission*, 1st Edition 1933, pp. 30-35) were used to develop this equation for combinations of thickness, temperature and heat transfer that would allow enough time to heat and cool aluminum 7075 alloy articles within the time and temperature constraints shown in FIG. 1.

Applying the above equation to the condition wherein the heat treating medium is air and the article is composed of aluminum 7075 alloy, the article may have a maximum thickness of about 1.5 inches at 390° F., about 2.2 inches at 380° F., about 3.0 inches at 370° F.

and about 4.1 inches at 360° F. Air is the preferred heat treating medium for commercial applications although molten metal or mineral oil may be used for more precise temperature control. When the heat treating medium is a molten metal and the article is composed of aluminum 7075 alloy, the article may have a maximum thickness of about 17.9 inches at a heat treating temperature of 390° F., about 26.5 inches at 380° F., about 37.8 inches at 370° F. and about 52.3 inches at 360° F. When the heat treating medium is mineral oil and the article is composed of aluminum 7075 alloy, the article may have a maximum thickness of about 5.0 inches at a heat treating temperature of 390° F., about 7.4 inches at 380° F., about 10.5 inches at 370° F. and about 14.5 inches at 360° F. Heat treatment of articles having maximum thicknesses in excess of those allowed by the above equation is likely to result in either insufficient heat treatment for a central portion of the article or excessive heat treatment for outer portions of the article which might result in diminished strength.

EXAMPLES

Specimens of aluminum alloy 7075 in the T6 condition were treated by the method of the invention and tested for stress-corrosion resistance. All specimens tested had the composition shown in Table 1.

TABLE 1

Composition of Specimens	
Element	Proportion in Wt. %
Cu	1.63
Fe	.30
Si	.12
Mn	.07
Mg	2.48
Zn	5.68
Cr	.19
Ti	.05
Be	.001
Al	Remainder

To determine stress-corrosion resistance, short-transverse 1/8-inch (3.2 mm) diameter specimens were stressed in constant strain fixtures. The fixtures are described in ASTM Special Technical Publication No. 425, *Stress Corrosion Testing*, July 1966, Stress-Corrosion Testing Methods, Report of Task Group I, pp. 3-20. Specimens in the T6 condition were used as controls. Both the control and test specimens were exposed by an alternate immersion test comprising ten minutes immersion in 3.5% aqueous NaCl solution and a 30-minute drying cycle. Stresses were maintained constant at 42 ksi (kilopounds per square inch) throughout the tests. Test results are summarized in Tables 2 and 3.

TABLE 2

t ₁ hr	T ₁ °F.	t ₂ min	T ₂ °F.	t ₃ hr	T ₃ °F.	T.S. ksi ⁽²⁾	Y.S. ksi ⁽³⁾	Y.S. Y.S.T6 ⁽⁴⁾	Days to Failure ⁽⁵⁾
24	250 ⁽¹⁾	—	—	—	—	72.2	64.5	1.00	2
24	250	7	375	24	250	71.8	63.5	0.98	3
24	250	15	375	24	250	71.8	63.7	0.99	37
24	250	30	375	24	250	70.3	63.2	0.98	45
24	250	45	375	24	250	67.1	58.4	0.91	80
24	250	60	375	24	250	68.2	60.7	0.94	54
24	250	90	375	24	250	67.1	58.1	0.90	66
24	250	30	360	24	250	72.7	64.4	1.00	2
24	250	60	360	24	250	71.4	62.9	0.98	2
24	250	90	360	24	250	70.0	61.4	0.95	59
24	250	120	360	24	250	69.2	61.6	0.96	52

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TABLE 2-continued

t ₁ hr	T ₁ °F.	t ₂ min	T ₂ °F.	t ₃ hr	T ₃ °F.	T.S. ksi ⁽²⁾	Y.S. ksi ⁽³⁾	Y.S. Y.S.T6 ⁽⁴⁾	Days to Fail- ure ⁽⁵⁾
24	250	150	360	24	250	67.1	59.5	0.92	81

⁽¹⁾T6 temper
⁽²⁾Tensile strength, kilopounds per square inch
⁽³⁾Yield strength, kilopounds per square inch
⁽⁴⁾Ratio of yield strength of test specimen to yield strength of specimen with T6 temper
⁽⁵⁾Specimens exposed by alternate immersion in 3.5% NaCl solution and stressed to 42 ksi

Results of the tests of Table 2 are illustrated in FIG. 1. Specimens subjected to a preferred heat treating step in accordance with the present invention exhibit increased stress-corrosion resistance. The time and temperature relationships of such preferred heat treating step are within the perimeter of outline ABCDE in FIG. 1. Time and temperature relationships for the heat treating step outside the perimeter of outline ABCDE resulted in no significant increase in stress-corrosion resistance compared with the T6 condition.

TABLE 3

t ₁ hr	T ₁ °F.	t ₂ min	T ₂ °F.	t ₃ hr	T ₃ °F.	T.S. ksi ⁽¹⁾	Y.S. ksi ⁽²⁾	Y.S. Y.S.T6 ⁽³⁾	Days to Fail- ure ⁽⁴⁾
24	250	60	375	6	275	75.3	71.8	1.11	11
24	250	60	375	6	300	74.2	69.9	1.08	10
24	250	60	375	12	275	73.4	69.1	1.07	8
12	275	60	375	12	275	72.2	68.5	1.06	11
6	275	60	375	24	250	72.3	68.4	1.06	14
4	300	60	375	4	300	70.8	65.9	1.02	21
2	300	60	375	2	300	69.2	64.7	1.00	58
24	250	60	375	24	250	78.4	64.2	1.00	48
6	300	60	375	6	300	69.4	63.3	0.98	40
6	300	60	375	24	250	68.2	62.5	0.97	56
18	275	60	375	18	275	68.9	62.5	0.97	47
12	275	60	375	24	250	69.0	61.6	0.96	9
4	300	60	375	8	300	67.7	61.5	0.96	54
24	250	60	375	24	250	69.8	60.7	0.94	73
8	300	60	375	4	300	67.7	60.6	0.94	36
24	250	90	375	6	275	71.9	66.4	1.03	40
6	275	90	375	24	250	69.6	63.7	0.99	45
12	275	90	375	12	275	69.1	63.4	0.98	42
6	275	90	375	6	275	68.3	61.4	0.95	38
24	250	90	375	24	250	67.1	58.1	0.90	66

⁽¹⁾Tensile strength, kilopounds per square inch
⁽²⁾Yield strength, kilopounds per square inch
⁽³⁾Ratio of yield strength of test specimen to yield strength of specimen with T6 temper
⁽⁴⁾Specimens exposed by alternate immersion in 3.5% NaCl solution and stressed to 42 ksi

The test results in Table 3 are arranged in order of decreasing yield strength for second-step (heat treating) aging of 60 and 90 minutes at 375° F. with conditions of the first and third (precipitation hardening) steps being varied. These data indicate that highest yield strengths were obtained by treating the specimens for 24 hours at 250° F. in the first step and for 6 to 12 hours at 275° to 300° F. in the third step.

While the foregoing description of my invention has been made with respect to a preferred embodiment, persons skilled in the art will understand that numerous changes and modifications may be made therein without departing from the spirit and scope of the following claims.

What is claimed is:

1. In a method for heat treating an article comprising a solution heat treated aluminum alloy of the 7000 series, said alloy containing aluminum, zinc, magnesium, copper and at least one element selected from the group

consisting of chromium, manganese and zirconium, said method comprising the steps of

- (a) precipitation hardening the article at about 175° to 325° F.;
- (b) heat treating the article by immersing it in a heat treating medium; and
- (c) precipitation hardening the article at about 175° to 325° F.;

the improvement wherein step (b) is carried out for about 10 minutes to a few hours at a temperature of about 360° to 375° F., said method thereby being suitable for treatment of articles having greater maximum thickness than methods in which step (b) is carried out at greater than 390° F.

2. The method of claim 1 wherein step (b) is carried out at a time and temperature within the perimeter of ABCDE of FIG. 1 and consistent with the limitations of claim 1.

3. The method of claim 2 wherein step (b) is carried out at a temperature of about 375° F. for about 45 to 90 minutes.

4. The method of claim 1 wherein step (b) is carried out for about 10 to 150 minutes.

5. The method of claim 1 wherein step (a) is carried out for about 24 hours at a temperature of about 250° F.

6. The method of claim 5 wherein step (c) is carried out for about 6 to 12 hours at a temperature of about 275° to 300° F.

7. The method of claim 1 wherein steps (a) and (c) are each carried out for about 2 to 30 hours.

8. The method of claim 1 wherein the maximum thickness of said article in inches is given by the formula

$$0.2 + 0.54 \left[\frac{480 - T}{100} \right]^{3.75} (h_T)^{0.56}$$

wherein T is the temperature in degrees Fahrenheit of the heat treating medium, and h_T is the coefficient of heat transfer between the heat treating medium and the article in BTU/(hr)(sq.ft.)(deg.F.).

9. The method of claim 8 wherein the heat treating medium is air, and at least a portion of the article has a maximum thickness of about 3.0 inches at 370° F. and about 4.1 inches at 360° F.

10. The method of claim 8 wherein the heat treating medium is mineral oil, and at least a portion of the article has a maximum thickness of about 10.5 inches at 370° F. and about 14.5 inches at 360° F.

11. The method of claim 8 wherein the heat treating medium is a molten metal, and at least a portion of the article has a maximum thickness of about 37.8 inches at 370° F. and about 52.3 inches at 360° F.

12. In a method for heat treating an article comprising a solution heat treated aluminum 7075 alloy, said method comprising the steps of

- (a) precipitation hardening the article for about 24 hours at about 250° F.;
- (b) heat treating the article by immersing it in a heat treating medium; and
- (c) precipitation hardening the article for about 6 to 12 hours at about 275° to 300° F.;

the improvement wherein step (b) is carried out for about 45 to 90 minutes at about 375° F., said method thereby being suitable for treatment of articles having greater maximum thickness than methods in which step (b) is carried out at greater than 390° F.

13. The method of claim 1 wherein said article comprises an aluminum 7075 alloy.

* * * * *

EXHIBIT 2

United States Patent [19]

[11] Patent Number: **4,832,758**

Brown

[45] Date of Patent: * **May 23, 1989**

[54] **PRODUCING COMBINED HIGH STRENGTH AND HIGH CORROSION RESISTANCE IN AL-ZN-MG-CU ALLOYS**

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 1480351 7/1977 United Kingdom .

[75] Inventor: **Melvin H. Brown, Leechburg, Pa.**

[73] Assignee: **Aluminum Company of America, Pittsburgh, Pa.**

[*] Notice: The portion of the term of this patent subsequent to Oct. 16, 2001 has been disclaimed.

[21] Appl. No.: **82,414**

[22] Filed: **Aug. 6, 1987**

Related U.S. Application Data

[63] Continuation of Ser. No. 142,541, Apr. 21, 1980, abandoned, which is a continuation of Ser. No. 410,109, Oct. 26, 1973, abandoned.

[51] Int. Cl.⁴ **C22F 1/04**

[52] U.S. Cl. **148/12.7 A; 148/159; 148/417**

[58] Field of Search **148/159, 12.7 A, 415-418**

[56]

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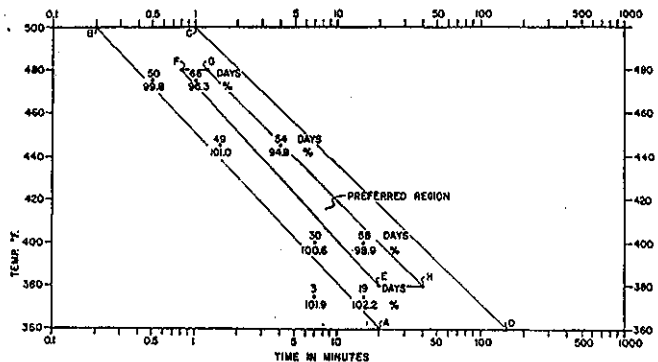
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Primary Examiner—R. Dean
 Attorney, Agent, or Firm—Carl R. Lippert; Daniel A. Sullivan, Jr.; Gary P. Topolosky

[57] **ABSTRACT**

The method of thermally treating an article composed of an alloy consisting essentially of aluminum, 4 to 8% zinc, 1.5 to 3.5% magnesium, 1 to 2.5% copper, and at least one element selected from the group consisting of 0.05 to 0.3% chromium, 0.1 to 0.5 manganese, and 0.05 to 0.3% zirconium, which method includes the steps of solution heat treating the article, then precipitation hardening the article at 173° to 325° F., then subjecting the article to a time and temperature within the perimeter ABCD of FIG. 4, and then again precipitation hardening at 175° to 325° F.

75 Claims, 2 Drawing Sheets



U.S. Patent

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Sheet 1 of 2

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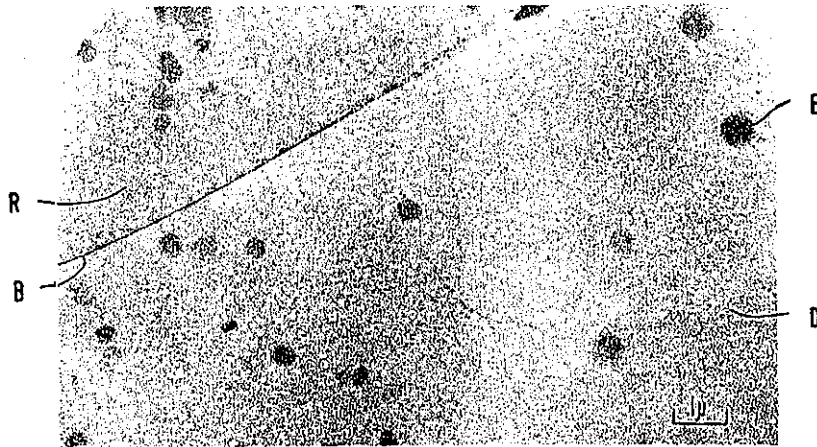


FIG. 1 (PRIOR ART)

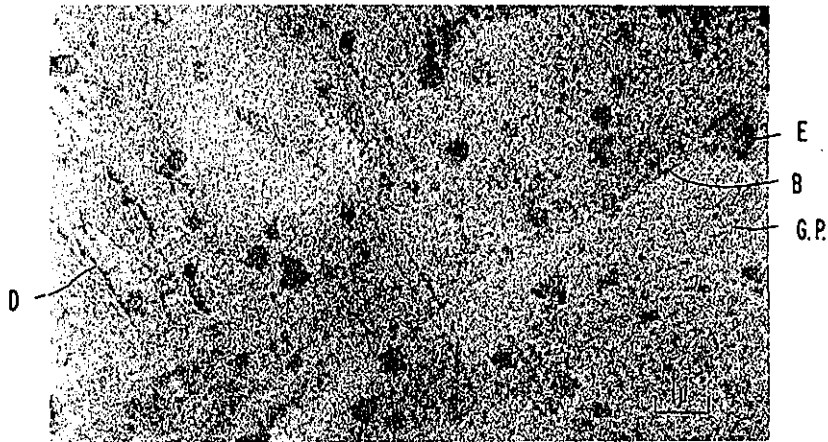


FIG. 2 (PRIOR ART)

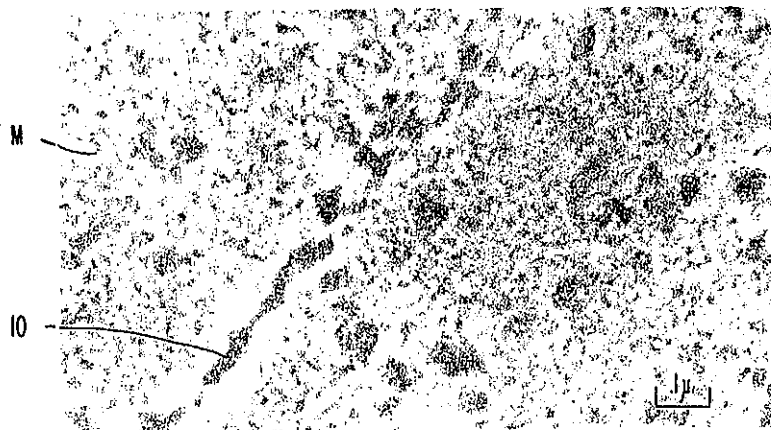


FIG. 3 (PRIOR ART)

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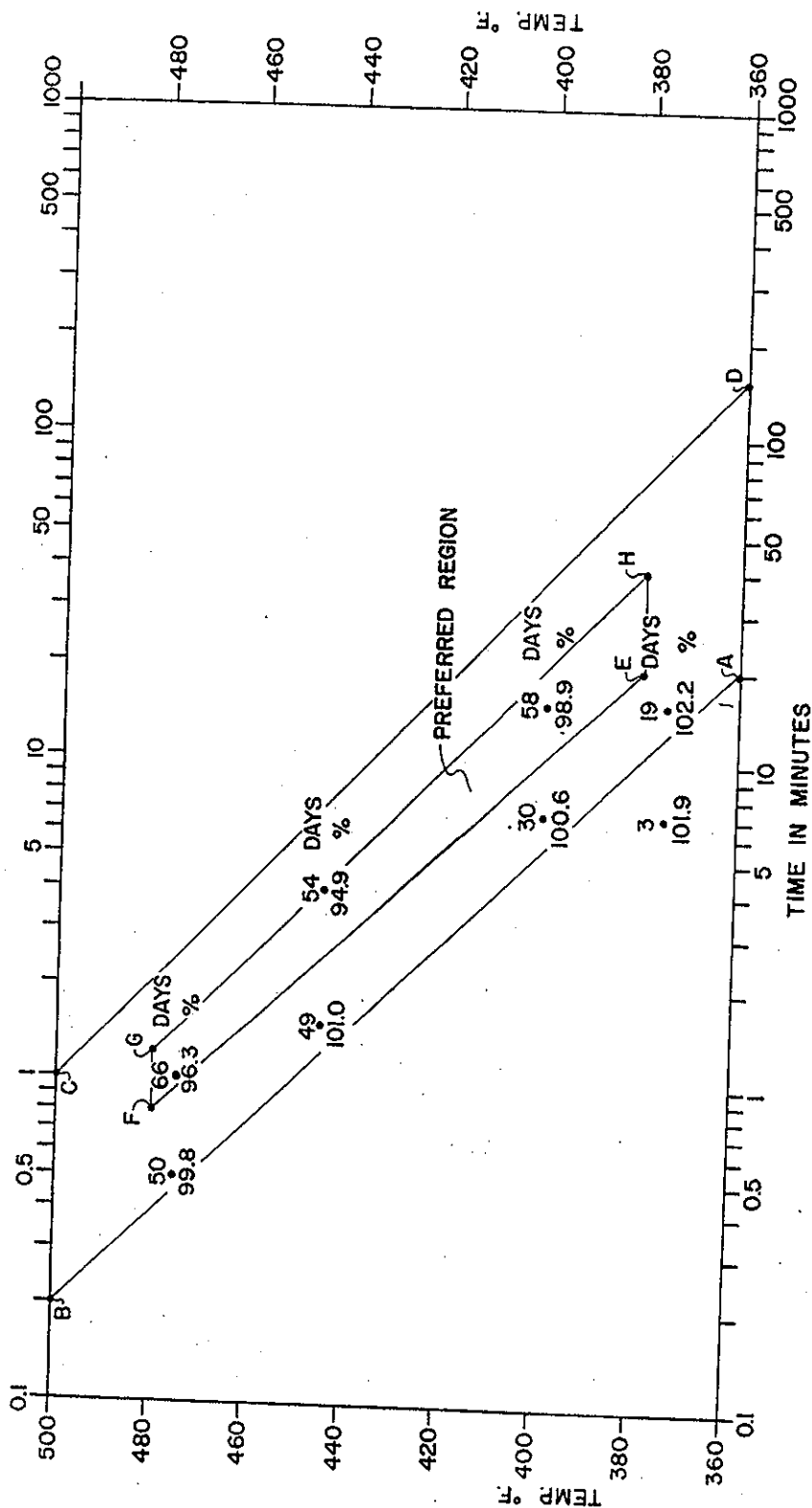


FIG. 4

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**PRODUCING COMBINED HIGH STRENGTH AND
HIGH CORROSION RESISTANCE IN
AL-ZN-MG-CU ALLOYS**

This application is a continuation, of application Ser. No. 142,541, filed Apr. 21, 1980, which is a continuation of Ser. No. 410,109, now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a method of thermally treating particles containing an alloy based on aluminum.

The precipitation hardened condition of aluminum alloy 7075, referred to as the T6 condition of alloy 7075, has not given sufficient resistance to corrosion under certain service conditions. The T73 temper improves the resistance of precipitation hardened 7075 alloy to stress corrosion cracking, although it decreases strength significantly vis-a-vis the T76 condition.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a new heat treating method to produce an aluminum alloy in a unique heat treated condition for providing favorable resistance to corrosion combined with high strength.

Another object is to provide a new method for providing resistance to stress corrosion cracking in 7075 aluminum alloy.

These as well as other objects which will become apparent in the discussion which follows are achieved, according to the present invention, by the method of thermally treating an article composed of an alloy consisting essentially of aluminum, 4 to 8% zinc, 1.5 to 3.5% magnesium, 1 to 2.5% copper, and at least one element selected from the group consisting of 0.05 to 0.3% chromium, 0.1 to 0.5% manganese, and 0.05 to 0.3% zirconium, which method includes the steps of solution heat treating the article, then precipitation hardening the article at 175° to 325° F., then subjecting the article to a time and temperature within the perimeter ABCD of FIG. 4, and then again precipitation hardening at 175 to 325° F.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1-3 are transmission electron micrographs of sections in a plate of aluminum alloy 7075. The distance equivalent to 0.1 micron is indicated on the micrographs. The metal surfaces reproduced in the micrographs all were perpendicular to the direction of rolling of the plate.

FIG. 1 shows a prior art solution heat treated and stress relieved condition referred to as the W51 condition.

FIG. 2 shows the prior art precipitation hardened condition referred to as the T6 condition.

FIG. 3 shows the prior art stress corrosion cracking resistant condition referred to as the T73 condition.

FIG. 4 is a graph showing characteristics of the invention.

**DESCRIPTION OF THE PREFERRED
EMBODIMENTS**

The alloys in the present invention have a composition containing 4 to 8% zinc, 1.5 to 3.5% magnesium, 1 to 2.5% copper, and at least one element selected from the group made up by chromium at 0.05 to 0.3%, man-

gane at 0.1 to 0.5%, and zirconium at 0.05 to 0.3%. The balance of the composition is essentially aluminum.

Alloys designated 7075 by the aluminum industry are preferred for the present invention and have a composition containing 5.1 to 6.1% zinc, 2.1 to 2.9% magnesium, 1.2 to 2.0% copper, 0.18 to 0.35% chromium, 0.30% maximum manganese, 0.40% maximum silicon, 0.50% maximum iron, 0.20% maximum titanium, others each 0.05% maximum and others total 0.15% maximum, balance aluminum.

The alloys used in the present invention may also contain one or more of the group of grain refining elements including titanium at 0.01 to 0.2% and boron at 0.0005 to 0.002%. These elements serve to produce a fine grain size in the cast form of the alloy. This is generally advantageous to mechanical properties.

In addition, it may be helpful to add 0.001 to 0.005% beryllium for the purpose of minimizing oxidation at times when the alloy is molten.

Iron and silicon are generally present as impurities. Up to 0.5% iron can be tolerated, and the silicon content should not exceed 0.4%, in order to avoid the formation of any substantial amount of the intermetallic compound Mg₂Si.

A preferred heat treatment according to the present invention for obtaining improved stress-corrosion resistance is to immerse alloy, as above defined, in the precipitation hardened, T6 condition into molten metal for a time and temperature within the perimeter of the quadrilateral EFGH in FIG. 4, then precipitation harden again.

In its broader aspects, a T6 condition may be obtained by precipitation hardening solution heat treated alloy at 175° to 325° F. Typical conditions may be:

- For alloys containing less than 7.5% zinc, heating a solution heat treated article to 200° to 275° F. and holding for a period of 5 to 30 hours;
- For alloys containing more than 7.5% zinc, heating a solution heat treated article to 175° to 275° F. and holding for a period of 3 to 30 hours.

A usual practical for obtaining the T6 condition is obtained by heating a specimen for 24 hours at 250° F. in a circulatory-air furnace.

According to another preferred embodiment of the invention, the alloy is solution heat treated, then precipitation hardened at a temperature of 175° to 325° F., then subjected to a time and temperature within the perimeter ABCD, more preferably EFGH, and then again precipitation hardened for a time of 2 to 30 hours at a temperature of 270° to 320° F.

The article of J. T. Staley et al. entitled "Heat Treating Characteristics of High Strength Al-Zn-Mg-Cu Alloys With and Without Silver Additions" appearing at pages 191 to 199 in the January, 1972 issue of *Metalurgical Transactions*, published by ASM/AIME, shows that solution heat treat quench rate, the lapse of time between the solution heat treat quench and the beginning of heating for precipitation hardening, and the heating rate for precipitation hardening may effect the maximum yield strength obtainable in 7075 aluminum alloys. It is intended that, within the concepts of the present invention, the teachings of Staley et al. be used in the present invention for optimizing results. Thus, it may be advantageous for increasing strength to immerse specimens, which have had their solution heat treatment quench, for example, 1½ years ago, into molten Wood's metal according to the invention.

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Referring now to FIGS. 1 to 3, transmission electron micrographs of various microstructures important for consideration of the present invention are presented. All of FIGS. 1 to 3 were taken from a single $\frac{1}{8}$ -inch thick 7075 aluminum alloy plate of composition A in Table I. FIGS. 1 to 3 are microstructures of prior art conditions of 7075 aluminum. In FIG. 1, an example of the W51 solution heat treated condition is given. A W51 solution heat treated microstructure is obtained in 7075 aluminum alloy plate by heating to 900° F. and then quenching in water at room temperature. The plate material is then stretched to from 1½ to 3% permanent set for stress relief. This gives the microstructure shown in FIG. 1, including E-phase particles of Al-Mg-Cr precipitate, matrix regions R of single phase aluminum solid-solution material, grain boundaries B and dislocations D. The mottling effect appearing in the matrix region of FIG. 1 is an artifact of the action of the thinning solution used in preparing thinned material for transition electron microscopy.

TABLE I

Element	Composition of Alloys, in Weight-%.	
	Alloy	
	A	B
Cu	1.45	1.63
Fe	0.19	0.30
Si	0.09	0.12
Mn	0.02	0.07
Mg	2.40	2.48
Zn	5.92	5.68
Ni	0.00	0.00
Cr	0.18	0.19
Ti	0.02	0.05
Be	0.001	0.001

FIG. 2 shows the 7075 alloy material of FIG. 1 after it has been brought to the T6, in particular the T651, temper by heating W51 material in a circulatory-air furnace for 24 hours at 250° F. E-phase remains substantially unchanged. Dislocations D and a grain boundary B are shown. Now in the matrix there has appeared many small black dots; these are referred to as G.P. zones and are clusterings of magnesium and zinc atoms generally in the ratio two zinc atoms for each magnesium atom.

FIG. 3 shows a specimen taken from the same plate of FIGS. 1 and 2 in the T73 condition, which is produced from W51 material by heating in circulatory-air furnaces for, first, 24 hours at 250° F. and, second, 8 hours at 350° F. Grain boundary precipitate 10 has appeared, and the G.P. zones have grown to greater size. The G.P. zones have begun to exhibit crystallinity by giving rise to X-ray diffraction patterns and are referred to by those in the art as M' and M phase. Solution potential studies indicate that the M' and M phases contain some copper atoms. It is believed that the G.P. zones progress toward crystallinity by becoming first M' phase, which is still partially coherent with the matrix crystal structure. The M' phase then changes to M phase, which has a crystal structure different from the matrix. It is believed also that the progression through the M' phase to the M phase makes the original G.P. zones increasingly anodic with respect to the matrix and that the resulting anodic particulate matter in the matrix protects against stress-corrosion cracking.

Further illustrative of the present invention are the following examples.

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EXAMPLES 1 to 8

For each example, two tensile blanks of dimensions $\frac{3}{8}$ inch by $\frac{1}{2}$ inch by $2\frac{1}{2}$ inches were cut from a single lot of $2\frac{1}{2}$ inch thick 7075-T651 (metallurgical history as described for FIG. 2) alloy plate such that their lengths were in the short-transverse direction, i.e., in the direction perpendicular to the surface of the plate.

TABLE II

Example No., or Point	Times and Temperatures in Wood's Metal for Examples 1 to 8 and the Coordinates of Points A to H.	
	Time, min.	Temperature, °F.
1	0.5	475
2	1.0	475
3	1.5	445
4	4.0	445
5	7.0	400
6	15.0	400
7	7.0	375
8	15.0	375
A	20.0	360
B	0.2	500
C	1.0	500
D	150.0	360
E	20.0	380
F	0.8	480
G	1.2	480
H	40.0	380

The chemical composition of the alloy is as presented for alloy B in Table I. The tensile blanks for each example were immersed in molten Wood's metal of composition 50% bismuth, 25% lead, 12.5% tin and 12.5% cadmium. The immersion temperatures and times are presented in tubular form in Table II and are plotted in FIG. 4. Following immersion in the molten Wood's metal, the cooled specimens were then precipitation hardened by heating them in a circulatory-air furnace for a time of 24 hours at 250° F. In each of Examples 1 to 8, a tensile blank was machined to a 0.125 inch diameter tensile bar for exposure to 3½% sodium chloride solution by alternate immersion at a stress level of 42 ksi according to Military Specification MIL-A-22771B. The specimens were held until failure with successive immersions for 10 minutes in the salt solution followed by 50 minutes in air. The number of days until failure under such treatment is provided in FIG. 4 above time-temperature point for each Example. The remaining blank of each example was tested for yield strength. The yield strength data for Examples 1 to 8 are presented in FIG. 4, below the time-temperature points, in terms of percentage of a yield strength of 62.3 ksi for the T651 condition.

Further illustrative of the preferred embodiment of the invention wherein the second precipitation hardening step is carried out for 2 to 30 hours at a temperature of 270 and 320° F. are the following examples:

EXAMPLES 9 TO 14

Procedure was as described for Examples 1 to 8, except that all examples utilized an immersion in molten Wood's metal for 90 seconds at 445° F., before the second precipitation hardening. Other parameters and results were as presented in Table III. Examples 9 to 11 form one group of comparative examples characterized by 3 hours at temperature in the second precipitation hardening step, with Examples 12 to 14 forming a second group characterized by 24 hours at temperature in

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the second precipitation hardening step. The superior strength and corrosion resistance obtained when the second precipitation hardening was done for 2 to 30 hours at 270° to 320° F. will be apparent from comparison of the examples within the groups.

TABLE III

Parameters and Data for Examples 9 to 14, Involving Immersing Aluminum Alloy 7075-T651 in Molten Wood's Metal for 90 seconds At 445° F., Followed by a Second Precipitation Hardening Step.

Example No.	Time (Hours) & Temperature (°F.) of Second Precipitation Hardening	Tensile Strength, ksi	Yield Strength, ksi	Days to Fail	
				42 ksi load	level
9	3 hrs./250° F.	67.2	58.5	27	74
10	3 hrs./275° F.	68.8	58.8	43	62
11	3 hrs./300° F.	66.8	58.1	60	84
12	24 hrs./250° F.	70.5	62.9	49	50
13	24 hrs./275° F.	69.5	61.0	47	61
14	24 hrs./300° F.	69.6	61.4	56	63

The following definitions hold herein:

- The term "ksi" is equivalent to kilopounds per square inch.
- Wherever percentages are given, reference is to % by weight, unless indicated otherwise.
- The initials "G.P." stand for Guinier-Preston.

It will be understood that the above description of the present invention is susceptible to various modifications, changes and adaptations, and the same are intended to be comprehended within the meaning and range of equivalents of the appended claims.

What is claimed is:

- A method for thermally treating an alloy consisting essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and at least one element selected from the group consisting of: about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities, said method comprising: (a) solution heat treating the alloy; (b) precipitation hardening the alloy in a first temperature range above room temperature; (c) subjecting the alloy to treatment within a second temperature range above the first temperature range and sufficient to improve corrosion resistance; (d) precipitation hardening the alloy in a third temperature range above room temperature but below the second temperature range to improve the relative strength of said alloy; and (e) the cumulative time in said second temperature range being greater than 3 minutes and sufficient to improve corrosion resistance but not so long as to prevent imparting a substantial strength increase in said recitation (d), said method imparting improved combinations of strength and corrosion resistance properties to the alloy.
- The method as claimed in claim 1 wherein the first temperature range includes temperatures within about 175° F. to 325° F.
- The method as claimed in claim 1 wherein the first temperature range is substantially the same as the third temperature range.
- The method as claimed in claim 1 wherein the first and third temperature ranges include temperatures within about 175°-325° F.
- The method as claimed in claim 1 wherein the second temperature range is about 360 to about 500° F. and said cumulative time in said temperature range is about four minutes or more.

6. The method as claimed in claim 1 wherein the second temperature range is about 360° F. to about 430° F. and said cumulative time in said second temperature range is about four minutes or more.

7. The method as claimed in claim 1 wherein the second temperature range is about 360° to about 410° F. and said cumulative time in said second temperature range is about five minutes more.

8. The method as claimed in claim 1 wherein said treatment according to recitation (c) extends for about five minutes or more and corresponds to time-temperature equivalence substantially within ABCD of FIG. 4.

9. The method as claimed in claim 1 wherein said treatment according to recitation (c) extends for about seven minutes or more and corresponds to time-temperature equivalence substantially within ABCD of FIG. 4.

10. The method as claimed in claim 1 wherein the second temperature range is about 380° F. to about 480° F. and corresponds to time-temperature equivalence substantially within EFGH of FIG. 4.

11. The method as claimed in claim 1 wherein the resulting alloy has corrosion resistance properties greater than the T6 condition and a relative strength greater than the T7 condition.

12. The method as claimed in claim 11 wherein the resulting alloy has a relative strength greater than the T73 condition.

13. The method as claimed in claim 1 which includes: working the alloy into a wrought condition.

14. A method for thermally treating a 7XXX aluminum alloy containing about 4% or more zinc, about 1.5% or more magnesium, about 1% or more copper and one or more of: chromium, manganese and zirconium, said method comprising: (a) providing the alloy in a precipitation hardenable condition; (b) precipitation hardening the alloy including treating within about 175°-325° F.; (c) subjecting the alloy to treatment for more than three minutes at one or more temperatures sufficient for improving the corrosion resistance of said alloy and achieving a cumulative time-temperature equivalence substantially within the perimeter ABCD of FIG. 4; and (d) precipitation hardening the alloy including treating within about 175°-325° F. to improve its strength, said method imparting improved combinations of strength and corrosion resistance properties to the alloy.

15. The method as claimed in claim 14 wherein recitation (c) includes subjecting the alloy to one or more temperatures within about 360° F. to about 500° F. for a cumulative time within 360° F. to 500° F. of about four minutes or more.

16. The method as claimed in claim 14 wherein recitation (c) includes subjecting the alloy to one or more temperatures within about 360° F. to about 500° F. for a cumulative time within 360° F. to 500° F. of about five minutes or more.

17. The method as claimed in claim 14 wherein recitation (c) includes subjecting the alloy to treatment within about 360° to about 420° F. for a cumulative time of five minutes or more and within the perimeter ABCD of FIG. 4.

18. A method for treating an aluminum 7XXX alloy containing about 4% or more zinc, about 1.5% or more magnesium and about 1% or more copper, said method comprising:

- providing the alloy in a wrought precipitation-hardenable condition;

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- (b) subjecting the alloy to one or more precipitation-hardening temperatures above room temperature to effect some precipitation therein;
- (c) treating the alloy for a cumulative time of about four minutes or more at one or more elevated temperatures sufficient to improve the corrosion resistance thereof, said treating imparting thereto cumulative time-temperature effect substantially within ABCD of FIG. 4;
- (d) subjecting said alloy to one or more precipitation-hardening temperatures above room temperature to impart a significant strength increase to said alloy;
19. The method according to claim 18 wherein either or both of said recitations (b) and (d) includes subjecting said alloy to one or more temperatures within about 175° F. to 325° F.
20. The method according to claim 18 wherein said alloy consists essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities.
21. The method according to claim 18 wherein recitation (c) includes subjecting said alloy to one or more temperatures within about 360° to 500° F.
22. A method for treating an aluminum 7XXX alloy containing zinc, magnesium and copper comprising:
- (a) providing the alloy in a precipitation-hardenable condition;
- (b) subjecting the alloy to one or more precipitation hardening temperatures above room temperature to effect some precipitation therein;
- (c) subjecting the alloy to treatment at one or more temperatures sufficient to improve the corrosion resistance thereof;
- (d) subjecting the alloy to one or more precipitation-hardening temperatures above room temperature to significantly increase the strength of said alloy;
- (e) the cumulative time at temperatures sufficient to improve corrosion resistance in said recitation (c) being about 5 minutes or more and sufficient to improve corrosion resistance but not so long as to prevent a significant strength increase in said recitation (d).
23. The method according to claim 22 wherein said alloy consists essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities.
24. The method according to claim 22 wherein either or both of said recitations (b) and (d) includes subjecting said alloy to one or more temperatures within about 175° to 325° F.
25. The method according to claim 22 wherein said recitation (c) produces time-temperature equivalence substantially within ABCD of FIG. 4.
26. The method according to claim 22 wherein the cumulative time in recitation (e) is from about 6 minutes to about two and one-half hours.
27. The method according to claim 22 wherein the cumulative time in recitation (e) is from about 7 minutes to about two and one-half hours.
28. The method for treating an aluminum alloy consisting essentially of about 4 to 8% zinc, about 1.5 to

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- 3.5% magnesium, about 1 to 2.5% copper, and one or more of the group of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities, comprising:
- (a) providing said alloy in wrought precipitation-hardenable condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. to effect some precipitation therein;
- (c) subjecting the alloy to treatment at one or more temperatures within about 360° to 500° F. ;
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. to significantly increase the strength of said alloy;
- (e) the cumulative time at temperatures within about 360° to about 500° F. in said recitation (c) being from about 4 minutes to about two-and-one-half hours and sufficient to improve corrosion resistance but not so long as to prevent a significant strength increase in said recitation (d).
29. The method according to claim 28 wherein either or both of said recitations (b) and (d) includes subjecting the alloy to one or more temperatures within about 175° to 325° for about two hours or more.
30. The method according to claim 28 wherein said recitation (c) produces time-temperature equivalence substantially within ABCD of FIG. 4.
31. The method according to claim 28 wherein said cumulative time in said recitation (e) is about 5 minutes or more.
32. A method for treating a 7XXX aluminum alloy containing zinc, magnesium and copper, comprising:
- (a) providing said alloy in a wrought precipitation-hardenable condition;
- (b) subjecting said alloy to one or more temperatures within about 175° to 325° F. to effect some precipitation therein;
- (c) increasing the temperature of said alloy to one or more temperatures within about 360° to about 500° F. and subjecting said alloy to treatment at temperatures within said 360° to 500° F. for cumulative time within 360° to 500° of about 4 minutes to about two-and-one-half hours, said treatment substantially corresponding to time-temperature equivalence substantially within ABCD of FIG. 4 and improving the corrosion resistance of said alloy;
- (d) subjecting said alloy to one or more temperatures within about 175° to 325° F. to significantly increase the strength of said alloy.
33. The method according to claim 32 wherein said alloy consists essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of the group of about 0.5 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities.
34. The method according to claim 32 wherein recitation (c) includes subjecting said alloy to one or more temperatures within about 360° to 440° F. for a cumulative time within about 360° to 440° of about 5 minutes or more.
35. A method for treating an aluminum alloy consisting essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance

aluminum and incidental elements and impurities, comprising:

- (a) providing said alloy in a wrought precipitation-hardenable condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. to impart some precipitation therein;
- (c) subjecting the alloy to treatment within a temperature range of about 360° to 480° F. for a cumulative time within said range of about 4 minutes to about two-and-one-half hours, said treatment substantially corresponding to time-temperature equivalence substantially within ABCD of FIG. 4;
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. to significantly increase the strength of said alloy.
36. A method for treating a 7XXX aluminum alloy containing about 4% or more zinc, about 1.5% or more magnesium and about 1% or more copper to improve strength and corrosion resistance property combinations comprising:
- (a) providing said alloy in a solution heat treated condition;
- (b) subjecting said alloy to one or more temperatures within about 175° to 325° F. for a substantial cumulative time within about 175° to 325° F.;
- (c) subjecting the alloy to one or more temperatures within about 360° to 500° F. for a cumulative time within 360° to 500° F. of about four minutes to about two and one-half hours;
- (d) subjecting said alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. sufficient to significantly strengthen the alloy;
- (e) said subjecting in said recitation (c) not being excessive to obtaining a significant strength increase in said recitation (d).
37. The method according to claim 36 wherein said cumulative time in recitation (b) is about 3 hours or more within 175° to 325° F.
38. The method according to claim 36 wherein said cumulative time in recitation (d) is about 2 hours or more within 175° to 325° F.
39. The method according to claim 36 wherein recitation (c) includes subjecting the alloy to one or more temperatures within about 370° to 430° F.
40. The method according to claim 36 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within ABCD of FIG. 4.
41. The method according to claim 36 wherein said alloy consists essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities.
42. The method according to claim 36 wherein recitation (c) includes subjecting the alloy to one or more temperatures within about 360° to 450° F.
43. A method for treating a 7XXX aluminum alloy containing zinc, magnesium and copper comprising:
- (a) providing said alloy in a solution heat treated condition;
- (b) subjecting said alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. of about three hours or more;
- (c) subjecting the alloy to one or more temperatures within about 360° to 480° F. for a cumulative time within 360° to 480° F. of about four minutes to about two and one-half hours to impart to said alloy time-temperature equivalence substantially within ABCD of FIG. 4;
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within 175° to 325° F. of about 2 hours or more to significantly strengthen the alloy.
44. The method according to claim 43 wherein said alloy consists essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities.
45. The method according to claim 43 wherein recitation (c) includes subjecting the alloy to one or more temperatures within about 370° to 430° F.
46. A method for treating a 7XXX aluminum alloy containing about 4% or more zinc, about 1.5% or more magnesium and about 1% or more copper, said method comprising:
- (a) providing said alloy in solution heat treated condition;
- (b) subjecting said alloy to one or more temperatures within about 175° to 325° F. for a substantial cumulative time within about 175° to 325° F.;
- (c) subjecting said alloy to one or more temperatures within about 360° to 490° F. for a cumulative time within 360° to 490° F. of about four minutes to about two and one-half hours;
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. sufficient to increase the strength thereof;
- (e) said subjecting in said recitation (c) not being excessive to obtaining a significant strength increase in said recitation (d).
47. The method according to claim 46 wherein said cumulative time in recitation (b) is about 3 hours or more within 175° to 325° F.
48. The method according to claim 46 wherein said cumulative time in recitation (d) is about 2 hours or more within about 175° to 325° F.
49. The method according to claim 46 wherein recitation (c) includes subjecting the alloy to one or more temperatures within about 370° to 430° F.
50. The method according to claim 46 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within ABCD of FIG. 4.
51. The method according to claim 46 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within EFGH of FIGS. 4.
52. The method according to claim 46 wherein said alloy consists essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities.
53. A method for treating an aluminum alloy consisting essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, and one or more of about 0.05 to 0.3% chromium, about 0.1 to 0.5% manganese, and about 0.05 to 0.3% zirconium, the balance

aluminum and incidental elements and impurities, said method comprising:

- (a) providing said alloy in a wrought precipitation-hardenable condition;
- (b) subjecting said alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. of about 3 hours or more;
- (c) increasing the temperatures of said alloy and subjecting said alloy to one or more temperatures within about 360° to 500° F. for a cumulative time within about 360° to 500° F. of about 4 minutes to about two and one-half hours to impart to said alloy time-temperature equivalence substantially within ABCD of FIG. 4;
- (d) subjecting said alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. of about two hours or more to significantly increase the strength thereof.

54. The method according to claim 53 wherein recitation (c) includes subjecting the alloy to one or more temperatures within about 370° to 430° F.

55. The method according to claim 53 wherein said recitation (c) includes subjecting the alloy to one or more temperatures within about 360° to 450° F.

56. The method for treating a 7XXX aluminum alloy containing zinc, magnesium and copper, said method comprising:

- (a) providing said alloy in a wrought precipitation-hardenable condition;
- (b) subjecting said alloy to one or more temperatures in the range of about 175° to 325° F. for a cumulative time of about 3 hours or more in said range;
- (c) subjecting the alloy to one or more temperatures within about 360° to 460° F. for a cumulative time within about 360° to 460° F. of about 5 minutes or more and imparting thereto a cumulative time-temperature effect substantially within ABCD of FIG. 4;
- (d) subjecting said alloy to one or more temperatures within about 175° to 325° F. for a cumulative time of about 2 hours or more within 175° to 325° F. to impart a significant strength increase to said alloy.

57. The method according to claim 18 wherein recitation (c) includes subjecting said alloy to one or more temperatures within about 360° to 460° F.

58. The method according to claim 57 wherein the cumulative time in recitation (c) is about 5 minutes or more.

59. The method for imparting improved combinations of strength and corrosion resistance to a solution heat treated alloy consisting essentially of about 4 to 8% zinc, about 1.5 to 3.5% magnesium, about 1 to 2.5% copper, about 0.05 to 0.3% zirconium, the balance aluminum and incidental elements and impurities, said method comprising: (a) treating the alloy at more than one elevated temperature to: (i) form hardening precipitates therein; and (ii) improve its corrosion resistance, said treatment including heating within about 360°-500° F. for substantially more than three minutes to impart a cumulative time-temperature effect substantially within ABCD of FIG. 4; and (b) precipitation hardening the alloy including treating at one or more temperatures between about 175°-325° F. to increase its strength.

60. The method as claimed in claim 59 wherein (i) of recitation (a) includes treating the alloy for at least about two hours between about 175°-325° F. to form hardening precipitates before heating the alloy for said cumulative-temperature effect.

61. The method as claimed in claim 60 wherein said cumulative time-temperature effect in (ii) of recitation (a) is greater than or equal to about five minutes and within the perimeter ABCD of FIG. 4.

- 62. The product produced by the method of claim 1.
- 63. The product produced by the method of claim 14.
- 64. The product produced by the method of claim 18.
- 65. The product produced by the method of claim 22.
- 66. The product produced by the method of claim 35.
- 67. The product produced by the method of claim 36.
- 68. The product produced by the method of claim 43.
- 69. The product produced by the method of claim 46.
- 70. The product produced by the method of claim 53.

71. The method according to claim 35 wherein said cumulative time in said recitation (c) is 5 minutes or more.

72. The method according to claim 36 wherein said cumulative time in said recitation (c) is 5 minutes or more.

73. The method according to claim 43 wherein said cumulative time in said recitation (c) is 5 minutes or more.

74. The method according to claim 46 wherein said cumulative time in said recitation (c) is 5 minutes or more.

75. The method according to claim 53 wherein said cumulative time in said recitation (c) is 5 minutes or more.

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EXHIBIT 3

United States Patent [19]

Brown et al.

[11] Patent Number: **4,863,528**

[45] Date of Patent: * **Sep. 5, 1989**

[54] **ALUMINUM ALLOY PRODUCT HAVING IMPROVED COMBINATIONS OF STRENGTH AND CORROSION RESISTANCE PROPERTIES AND METHOD FOR PRODUCING THE SAME**

[75] Inventors: **Melvin H. Brown, Morning Sun, Iowa; James T. Staley, Murrysville, Pa.; John Liu, Lower Burrell, Pa.; Sootae Lee, Export, Pa.**

[73] Assignee: **Aluminum Company of America, Pittsburgh, Pa.**

[*] Notice: **The portion of the term of this patent subsequent to Oct. 16, 2001 has been disclaimed.**

[21] Appl. No.: **99,445**

[22] Filed: **Sep. 21, 1987**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 142,541, Apr. 21, 1980, abandoned, which is a continuation of Ser. No. 410,109, Oct. 26, 1973, abandoned.

[51] Int. Cl.⁴ **C22F 1/04**

[52] U.S. Cl. **148/12.7 A; 148/159; 148/417; 148/418; 148/439**

[58] Field of Search **148/159, 2, 3, 11.5 A, 148/12.7 A, 415-418, 437-440**

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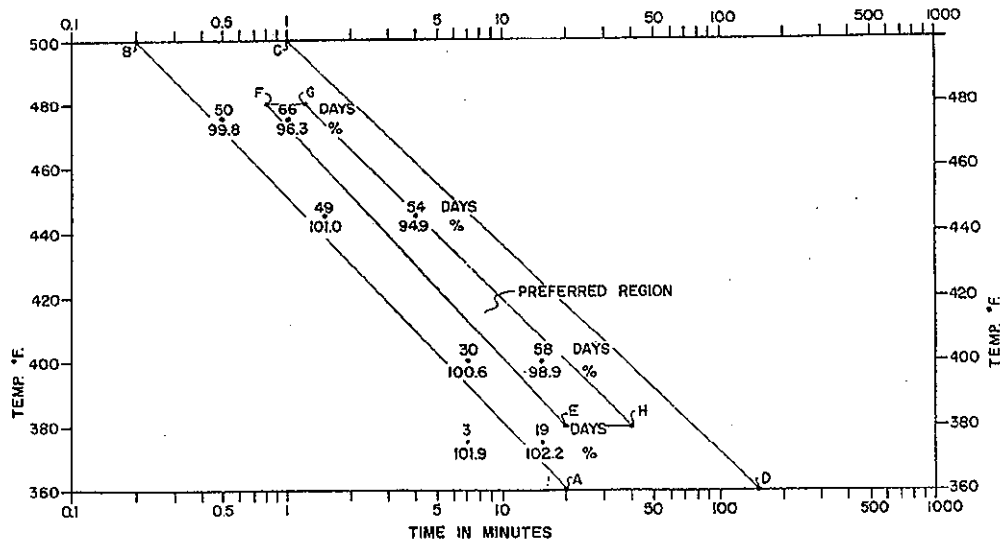
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Primary Examiner—R. Dean
 Attorney, Agent, or Firm—Carl R. Lippert; Daniel A. Sullivan, Jr.; Gary P. Topolosky

[57] **ABSTRACT**

There is disclosed a method for producing an aluminum alloy product and the resulting product having improved combinations of strength and corrosion resistance. The method includes providing an alloy consisting essentially of about 6-16% zinc, about 1.5-4.5% magnesium, about 1-3% copper, one or more elements selected from zirconium, chromium, manganese, titanium, vanadium and hafnium, the total of said elements not exceeding about 1%, the balance aluminum and incidental impurities. The alloy is then solution heat treated; precipitation hardened to increase its strength to a level exceeding the as-solution heat treated strength level by at least about 30% of the difference between as-solution heat treated strength and peak strength; subjected to treatment at a sufficient temperature or temperatures for improving its corrosion resistance properties; and again precipitation hardened to raise its yield strength and produce a high strength, highly corrosion resistant alloy product.

133 Claims, 4 Drawing Sheets



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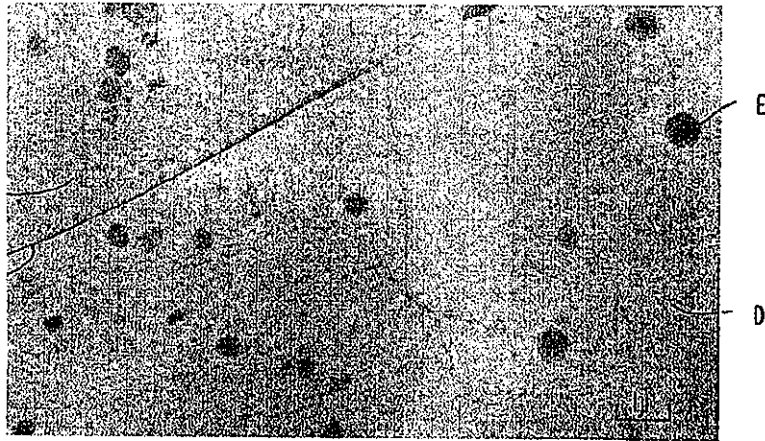


FIG. 1 (PRIOR ART)

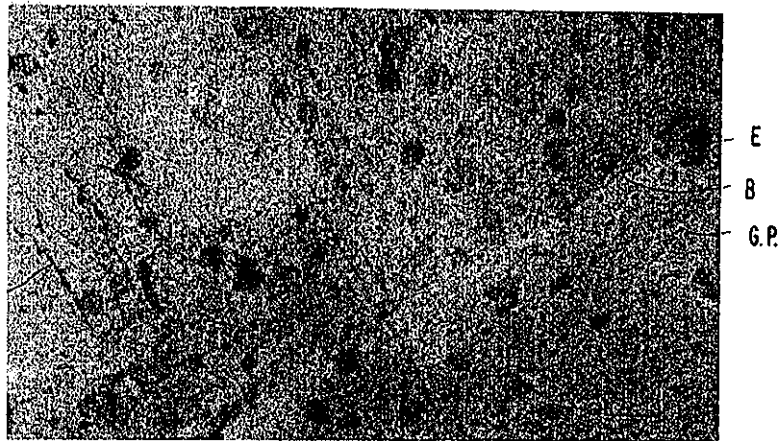


FIG. 2 (PRIOR ART)

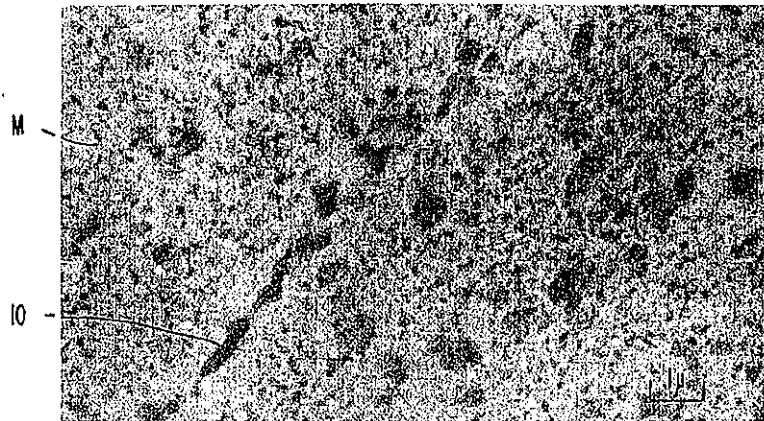


FIG. 3 (PRIOR ART)

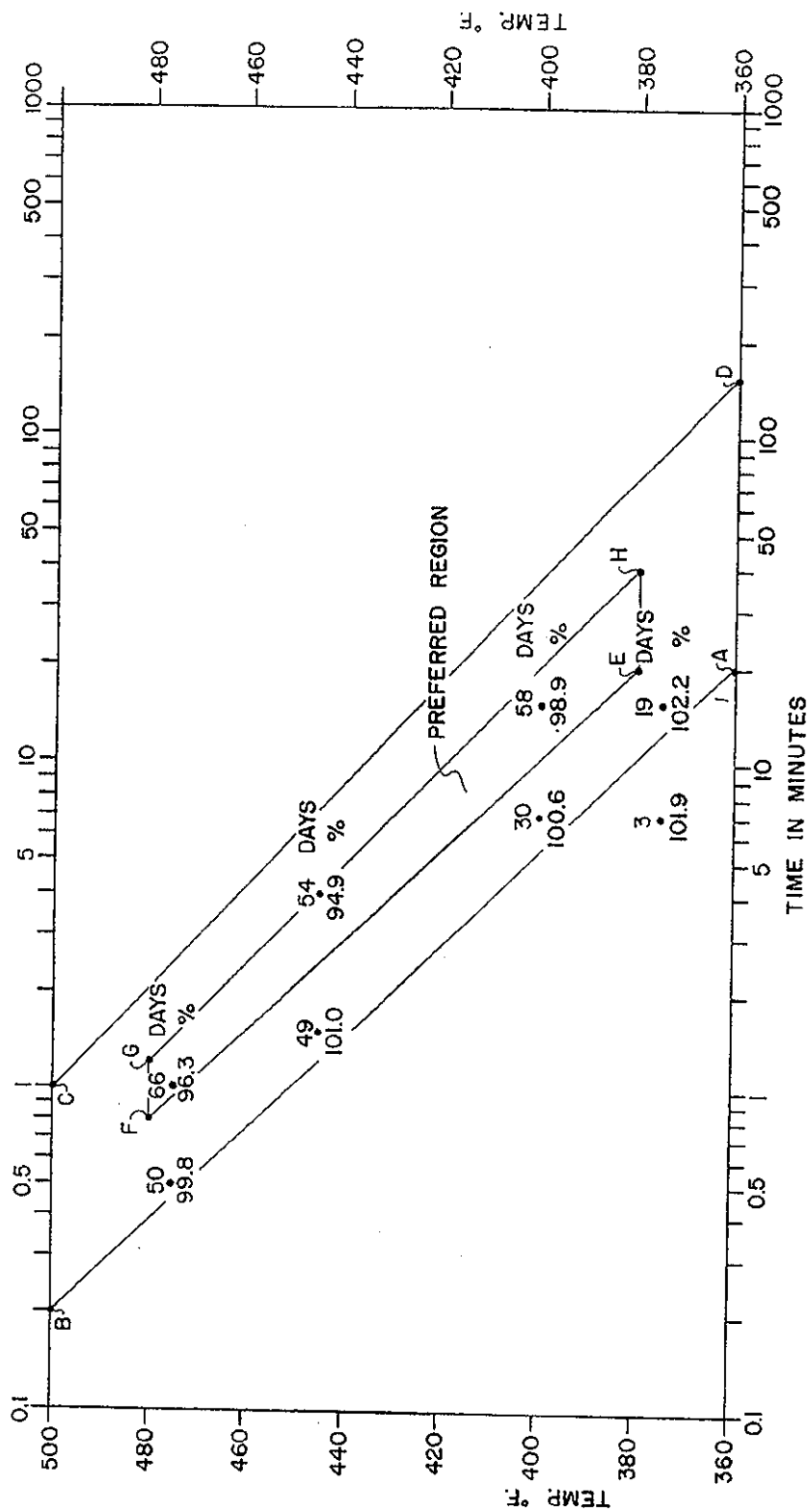


FIG. 4

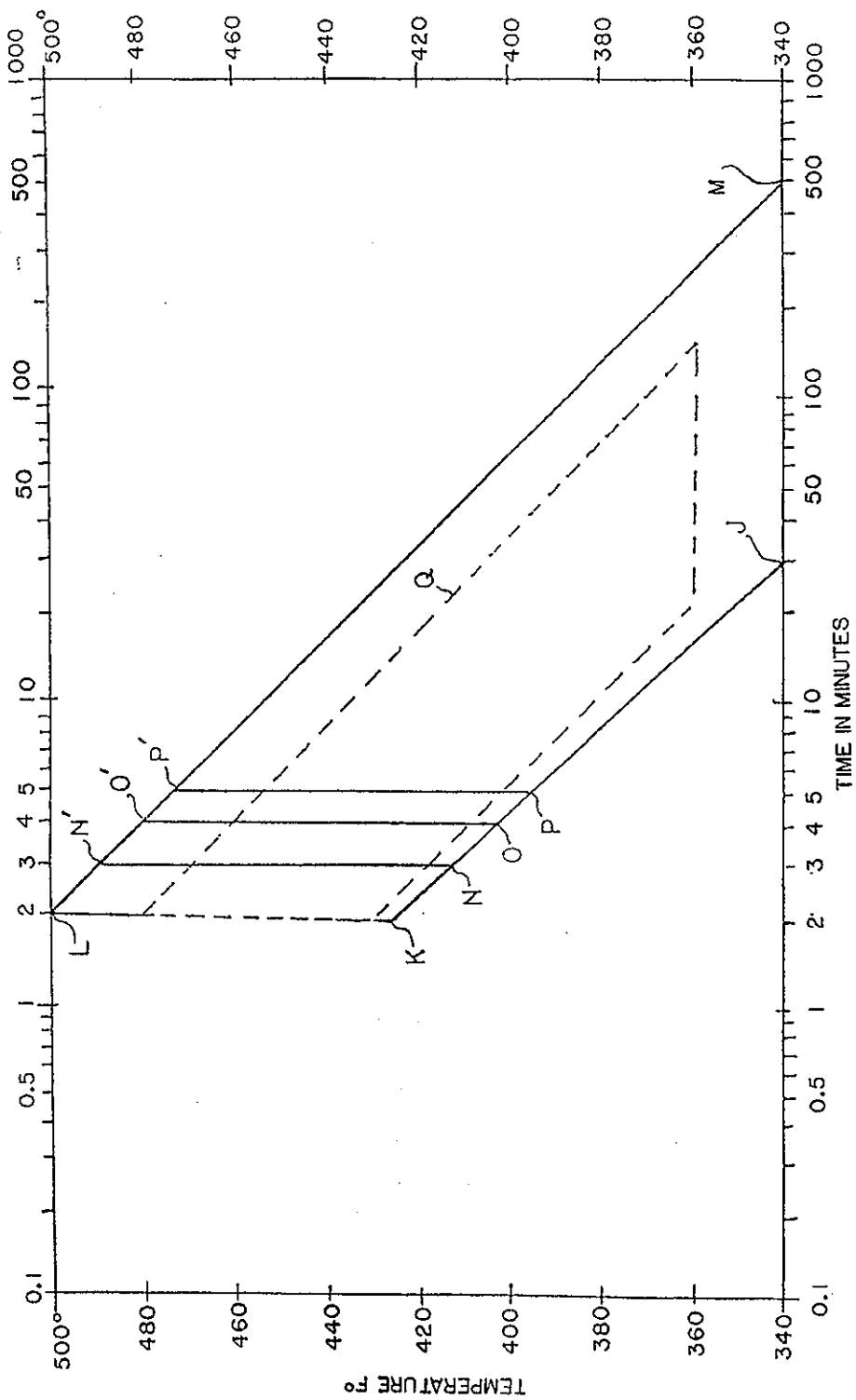


FIG. 5

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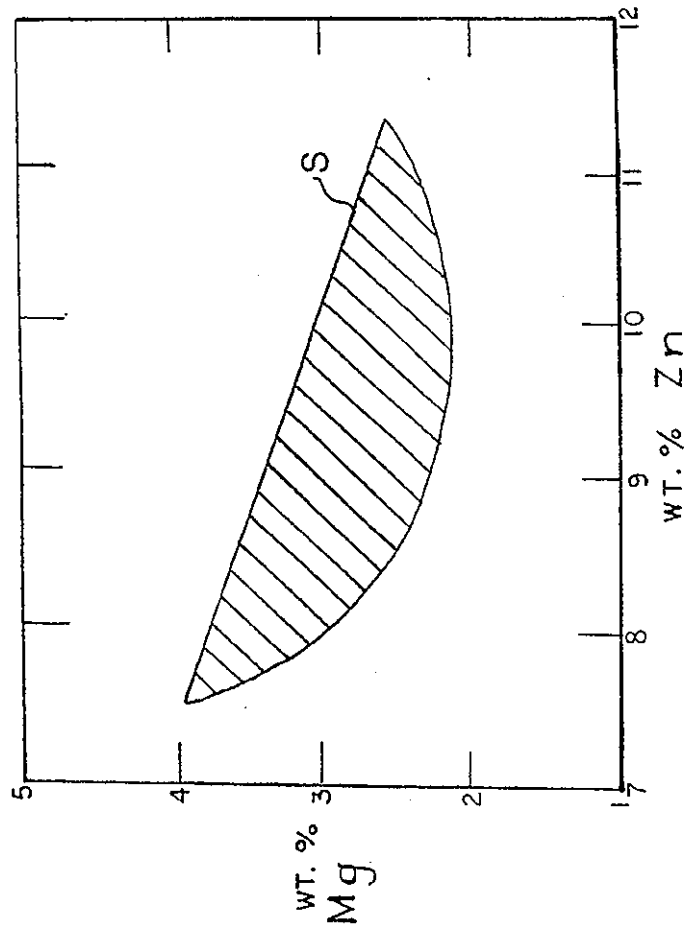


FIG. 6

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**ALUMINUM ALLOY PRODUCT HAVING
IMPROVED COMBINATIONS OF STRENGTH
AND CORROSION RESISTANCE PROPERTIES
AND METHOD FOR PRODUCING THE SAME**

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

This is a continuation-in-part of pending U.S. applica-
tion Ser. No. 142,541, filed on Apr. 21, 1980, which is a
continuation of U.S. application Ser. No. 410,109, now
abandoned, the disclosures of which are fully incorpo-
rated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to a method for ther-
mally treating articles containing an alloy based on
aluminum and to improved alloy products produced by
this method.

The precipitation-hardened aluminum alloy 7075, and
other 7XXX alloys, in the T6 temper have not given
sufficient resistance to corrosion under certain service
conditions. The T7-type tempers improve the resistance
of these alloys to stress corrosion cracking, but decrease
strength significantly vis-a-vis the T6 condition.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a new
heat treating method to produce an aluminum alloy in a
unique heat treated condition for providing favorable
resistance to corrosion combined with high strength.

Another object is to provide an aluminum-based alloy
product having at least about 5% greater yield strength
than a similarly sized 7X50 alloy product in the T6
condition in combination with corrosion resistance prop-
erties which meet or exceed those of 7X50 alloy in a
T7-type temper, for instance the T76 condition.

These objects, as well as other objects which will
become apparent in the discussion which follows, are
achieved according to the present invention by the
herein-described method of thermally treating an article
composed of an alloy consisting essentially of alumi-
num, about 4 or 6 to 16% zinc, about 1.5 to 4.5% mag-
nesium, about 1 to 3% copper, and one or more ele-
ments selected from the group consisting of up to about
0.2% zirconium, up to about 0.25% chromium, up to
about 0.8% manganese, up to about 0.2% vanadium and
up to about 0.5% hafnium. All composition percentages
herein are by weight percent unless indicated other-
wise. Improved products in accordance with the inven-
tion exhibit very high strength combined with good
exfoliation corrosion and stress corrosion cracking re-
sistance. The method includes the steps of solution heat
treating the article, then precipitation hardening the
article at 175° to 325° F., then subjecting the article to a
time and temperature within the perimeter ABCD of
FIG. 4 or JKLM of FIG. 5, and then again Precipita-
tion hardening at 175° to 325° F.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1-3 are transmission electron micrographs of
sections in a plate of aluminum alloy 7075. The distance
equivalent to 0.1 micron is indicated on the micro-
graphs. The metal surfaces reproduced in the micro-
graphs all were perpendicular to the direction of rolling
of the plate.

FIG. 1 shows a prior art solution heat treated and
stress relieved condition referred to as the W51 condi-
tion.

FIG. 2 shows the Prior art Precipitation-hardened
condition referred to as the T6 condition.

FIG. 3 shows the Prior art stress corrosion cracking
resistant condition referred to as the T73 condition.

FIG. 4 is a graph showing characteristics of the in-
vention.

FIG. 5 is a graph showing characteristics of another
embodiment for other 7000 Series aluminum alloy prod-
ucts.

FIG. 6 is a graph showing preferred zinc and magne-
sium composition ranges for an improved aluminum
alloy product containing about 1.5 to 2.5 wt. % copper.

**DESCRIPTION OF THE PREFERRED
EMBODIMENTS**

Alloys in the present invention have a composition
containing 4 to 8% zinc, 1.5 to 3.5% magnesium, 1 to
2.5% copper, and at least one element selected from the
group made up by chromium at 0.05 to 0.3%, manga-
nese at 0.1 to 0.5%, and zirconium at 0.05 to 0.3%. The
balance of the composition is essentially aluminum.

Alloys designated 7075 by the aluminum industry are
preferred for one embodiment of the present invention
and have a composition containing 5.1 to 6.1% zinc, 2.1
to 2.9% magnesium, 1.2 to 2.0% copper, 0.18 to 0.35%
chromium, 0.30% maximum manganese, 0.40% maxi-
mum silicon, 0.50% maximum iron, 0.20% maximum
titanium, others each 0.05% maximum and others total
0.15% maximum, balance aluminum.

The alloys used in the present invention may also
contain one or more of the group of grain refining ele-
ments including titanium at 0.01 to 0.2% and boron at
0.0005 to 0.002%. These elements serve to produce a
fine grain size in the cast form of the alloy. This is gen-
erally advantageous to mechanical properties.

In addition, it may be helpful to add 0.001 to 0.005%
beryllium for the purpose of minimizing oxidation at
times when the alloy is molten.

Iron and silicon are generally present as impurities.
Up to 0.5% iron can be tolerated, and the silicon con-
tent should not exceed 0.4%, in order to avoid the for-
mation of any substantial amount of the intermetallic
compound Mg₂Si.

A preferred heat treatment according to the present
invention for obtaining improved stress-corrosion resis-
tance is to immerse the alloy, as above defined, in the
precipitation-hardened, T6 condition into molten metal
for a time and temperature within the perimeter of the
quadrilateral EFGH in FIG. 4, then precipitation
harden again.

In its broader aspects, a T6 condition may be obtained
by Precipitation hardening solution heat treated alloy at
175° to 325° F. Typical conditions may be:

- a. For alloys containing less than 7.5% zinc, heating
a solution heat treated article to 200° to 275° F. and
holding for a period of 5 to 30 hours;
- b. For alloys containing more than 7.5% zinc, heating
a solution heat treated article to 175° to 275° F. and
holding for a period of 3 to 30 hours.

A usual practice for obtaining the T6 condition is
obtained by heating a specimen for 24 hours at 250° F.
in a circulatory-air furnace.

According to another preferred embodiment of the
invention, the alloy is solution heat treated, then precip-
itation hardened at a temperature of 175° to 325° F.,

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then subjected to a time and temperature within the perimeter ABCD, more preferably EFGH, and then again precipitation hardened for a time of 2 to 30 hours at a temperature of 270° to 320° F.

The article of J. T. Staley et al. entitled "Heat Treating Characteristics of High Strength Al-Zn-Mg-Cu Alloys With and Without Silver Additions" appearing at pages 191 to 199 in the January 1972 issue of *Metallurgical Transactions*, published by ASM/AIME, shows that solution heat treat quench rate, the lapse of time between the solution heat treat quench and the beginning of heating for precipitation hardening, and the heating rate for precipitation hardening may affect the maximum yield strength obtainable in 7075 aluminum alloys. It is intended that, within the concepts of the present invention, the teachings of Staley et al be used in the present invention for optimizing results. Thus, it may be advantageous for increasing strength to immerse specimens, which have had their solution heat treatment quench, for example, 1½ years ago, into molten Wood's metal according to the invention.

Referring now to FIGS. 1 to 3, transmission electron micrographs of various microstructures important for consideration of the present invention are presented. All of FIGS. 1 to 3 were taken from a single ¼-inch thick 7075 aluminum alloy plate of composition A in Table I. FIGS. 1 to 3 are microstructures of prior art conditions of 7075 aluminum. In FIG. 1, an example of the W51 solution heat treated condition is given. A W51 solution heat treated microstructure is obtained in 7075 aluminum alloy plate by heating to 900° F. and then quenching in water at room temperature. The plate material is then stretched to from 1½ to 3% permanent set for stress relief. This gives the microstructure shown in FIG. 1, including E-phase particles of Al-Mg-Cr precipitate, matrix regions R of single phase aluminum solid-solution material, grain boundaries B and dislocations D. The mottling effect appearing in the matrix region of FIG. 1 is an artifact of the action of the thinning solution used in preparing thinned material for transition electron microscopy.

TABLE I

Element	Composition of Alloys, in Weight %	
	Alloy	
	A	B
Cu	1.45	1.63
Fe	0.19	0.30
Si	0.09	0.12
Mn	0.02	0.07
Mg	2.40	2.48
Zn	5.92	5.68
Ni	0.00	0.00
Cr	0.18	0.19
Ti	0.02	0.05
Be	0.001	0.001

FIG. 2 shows the 7075 alloy material of FIG. 1 after it has been brought to the T6, in particular the T651, temper by heating W51 material in a circulatory-air furnace for 24 hours at 250° F. E-phase remains substantially unchanged. Dislocations D and a grain boundary B are shown. Now in the matrix there has appeared many small black dots; these are referred to as G.P. zones and are clusterings of magnesium and zinc atoms generally in the ratio two zinc atoms for each magnesium atom.

FIG. 3 shows a specimen taken from the same plate of FIGS. 1 and 2 in the T73 condition, which is produced from W51 material by heating in circulatory-air fur-

naces for, first, 24 hours at 250° F. and, second, 8 hours at 350° F. Grain boundary precipitate 10 has appeared, and the G.P. zones have grown to greater size. The G.P. zones have begun to exhibit crystallinity by giving rise to X-ray diffraction patterns and are referred to by those in the art as M' and M-phase. Solution potential studies indicate that the M' and M-phases contain some copper atoms. It is believed that the G.P. zones progress toward crystallinity by becoming first M'-phase, which is still partially coherent with the matrix crystal structure. The M'-phase then changes to M phase, which has a crystal structure different from the matrix. It is believed also that the progression through the M'-phase to the M-phase makes the original G.P. zones increasingly anodic with respect to the matrix and that the resulting anodic particulate matter in the matrix protects against stress-corrosion cracking.

Further illustrative of the present invention are the following examples.

EXAMPLES 1 to 8

For each example, two tensile blanks of dimensions ½ inch by ½ inch by 2½ inches were cut from a single lot of 2½ inch thick 7075-T651 (metallurgical history as described for FIG. 2) alloy plate such that their lengths were in the short-transverse direction, i.e., in the direction perpendicular to the surface of the plate.

TABLE II

Times and Temperatures in Wood's Metal for Examples 1 to 8 and the Coordinates of Points A to H		
Example No., or Point	Time, min.	Temperature °F.
1	0.5	475
2	1.0	475
3	1.5	445
4	4.0	445
5	7.0	400
6	15.0	400
7	7.0	375
8	15.0	375
A	20.0	360
B	0.2	500
C	1.0	500
D	150.0	360
E	20.0	380
F	0.8	480
G	1.2	480
H	40.0	380

The chemical composition of the alloy is as presented for alloy B in Table I. The tensile blanks for each example were immersed in molten Wood's metal of composition 50% bismuth, 25% lead, 12.5% tin and 12.5% cadmium. The immersion temperatures and times are presented in tabular form in Table II and are plotted in FIG. 4. Following immersion in the molten Wood's metal, the cooled specimens were then precipitation hardened by heating them in a circulatory-air furnace for a time of 24 hours at 250° F. In each of Examples 1 to 8, a tensile blank was machined to a 0.125 inch diameter tensile bar for exposure to 3½% sodium chloride solution by alternate immersion at a stress level of 42 ksi according to Military Specification MIL-A-22771B. The specimens were held until failure with successive immersion for 10 minutes in the salt solution followed by 50 minutes in air. The number of days until failure under such treatment is provided in FIG. 4 above the time-temperature point for each example. The remaining blank of each example was tested for yield strength. The yield

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strength data for Examples 1 to 8 are presented in FIG. 4, below the time-temperature points, in terms of percentage of a yield strength of 62.3 ksi for the T651 condition.

Further illustrative of the preferred embodiment of the invention wherein the second precipitation-hardening step is carried out for 2 to 30 hours at a temperature of 270° and 320° F. are the following examples:

EXAMPLES 9 to 14

Procedure was described for Examples 1 to 8, except that all examples utilized an immersion in molten Wood's metal for 90 seconds at 445° F., before the second precipitation hardening. Other parameters and results were as presented in Table III Examples 9 to 11 form one group of comparative examples characterized by 3 hours at temperature in the second precipitation-hardening step, with Examples 12 to 14 forming a second group characterized by 24 hours at temperature in the second precipitation-hardening step. The superior strength and corrosion resistance obtained when the second precipitation-hardening was done for 2 to 30 hours at 270° to 320° F. will be apparent from comparison of the examples within the groups.

TABLE III

Parameters and Data for Examples 9 to 14, Involving Immersing Aluminum Alloy 7075-T651 in Molten Wood's Metal for 90 seconds At 445° F., Followed by a Second Precipitation Hardening Step

Example No.	Time (Hours) & Temperature (°F.) of Second Precipitation Hardening	Tensile Strength, ksi	Yield Strength, ksi	Days to Fail	
				42 ksi load level	35 ksi load level
9	3 hrs./250° F.	67.2	58.5	27	74
10	3 hrs./275° F.	68.8	58.8	43	62
11	3 hrs./300° F.	66.8	58.1	60	84
12	24 hrs./250° F.	70.5	62.9	49	50
13	24 hrs./275° F.	69.5	61.0	47	61
14	24 hrs./300° F.	69.6	61.4	56	63

The following definitions hold herein:

- The term "ksi" is equivalent to kilipounds per square inch.
- Wherever percentages are given, reference is to % by weight, unless indicated otherwise.
- The initials "G.P." stand for Guinier-Preston.
- The term "minimum strength" means the level of strength at which 99% of the alloy product is expected to conform with a confidence level of 0.95 using standard statistical methods.
- The term "ingot-derived" means solidified from liquid metal by a known or subsequently developed casting process rather than through powder metallurgy techniques. This term shall expressly include, but not be limited to, direct chill casting, electromagnetic continuous casting and any variations thereof.
- In stating a numerical range for an element of a composition or a temperature or any other matter herein, and apart from and in addition to the customary rules for rounding off numbers, such is intended to specifically designate and disclose each number, including each fraction and/or decimal, between the stated minimum and maximum for said range. (For example 6 to 8 discloses 6.1, 6.2, . . . 6.9, 7, 7.1, 7.2, . . . and so on, up to 8. Similarly, 370 to 390 discloses 371, 372, . . . and so on, up to 390.)

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The invention has been described to this point with specific reference to alloys containing 4% to 8% zinc, 1.5% to 3.5% magnesium and 1% to 2.5% copper. The invention is considered especially useful for alloys containing higher amounts of zinc such as 6% or 8% to 16% zinc, for instance 8% to 12% zinc. Alloys containing high amounts of zinc are known to exhibit high strength, but these alloys were previously considered of limited usefulness: because of corrosion problems such as exfoliation and stress corrosion cracking. The practice of the invention enables making new products of high zinc aluminum alloys having very high minimum yield strengths of at least about 83 or 85 ksi in sheet, plate or forgings, and for extruded products even higher minimum yield strength levels of about 90 si or more, in combination with good corrosion resistance.

The new products in accordance with the invention contain at least 6% zinc, preferably 8% or more zinc in order to achieve the desired high strength. Alloys containing at least 7 or 7.5% zinc are considered useful as are zinc contents of 9 or 10%. The zinc content for the improved products may be as high as 16% or possibly higher, for instance 18 or 20%. A maximum zinc of about 12% is preferred in some embodiments although maximum zinc levels up to as much as 13 or 14 or even 15% may be applied in the practice of this invention. Suitable ranges for zinc include: from about 7.5 or 8% or more up to about 9 or 9.5%; from about 8.5 or 9% up to about 10 or 10.5%, or even 11%; and from about 9.5 or 10% up to about 11.5 or 12%.

The improved aluminum alloy products contain magnesium in minimum amounts of about 1.5% although a minimum of at least 1.75 or 2% is preferred in some embodiments. The maximum amount for magnesium is about 4 or 4.25%, or possibly even 4.5% magnesium. Suitable ranges for magnesium include: from about 1.5% to about 2.5 or 3%; from about 1.7 or 2% up to about 3 or 3.5%; and from about 2% up to about 4 or 4.5%. Copper is present in an amount of at least 1 or 1.5% with the maximum copper being about 2.5 or 2.75%, or in some cases about 3%. Suitable ranges for copper include: from about 1% to about 2%; from about 1.3 or 1.5% up to about 2.5 or 2.7%, or even 3%; and from about 1% to about 2.5 or 3%. One preferred range for copper is about 1.75 or 2% to 2.5 or 2.75%. One range of alloys considered useful in practicing this invention contains from about 8% to about 11 or 11.5% zinc, from about 2% to about 3% magnesium and from about 1.75% to about 2.5% copper. The shaded area S of FIG. 6 sets out one preferred range of zinc and magnesium in accordance with the present invention for an alloy containing about 1.5 to 2.5% copper.

In practicing the invention, it is preferred, especially from the standpoint of toughness and fatigue properties, that the amount of zinc, magnesium and copper not exceed a dissolvable amount, by which is meant an amount that can be brought into solid solution during solution heat treatment such that not more than one volume percent of undissolved intermetallic phases greater than about 1 micron containing Zn, Cu and/or Mg are present after solution heat treating. Preferably, not over one-half volume percent of said intermetallic phases remains. Accordingly, it can be advantageous to limit the combined total of zinc, magnesium and copper to levels not exceeding about 16 or 17%. A preferred minimum for zinc, magnesium and copper should be at least about 12% although total contents of about 11 or 10.5% may also be sufficient. In some embodiments, the

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amount of copper present exceeds the amount of magnesium present, while in other embodiments, copper is less than or equal to the magnesium amount.

The improved alloy product should contain one or more ancillary elements selected from: up to about 0.2% zirconium, for instance about 0.03 to about 0.15% zirconium; up to about 0.25% chromium, for instance about 0.03 to about 0.2% chromium; up to about 0.2% vanadium, for instance about 0.03 to about 0.15% vanadium; up to about 0.5% hafnium, for instance about 0.03 to 0.4% hafnium; and/or up to about 0.4 or 0.5% manganese, for instance about 0.03 to about 0.35% manganese, although manganese levels up to about 0.8% or possibly 1% or 1.1 or 1.2% may impart further benefit to the improved alloy products. Preferably, the cumulative total for such elements should not exceed about 0.7 or 0.8%, or even about 1%. Where manganese is present above 0.5 or 0.6%, this total level might be as high as 1.3 or 1.4% or possibly even more. In any event, the total quantity of ancillary elements should not exceed an amount which can be maintained in supersaturated solid solution upon solidification of the molten alloy. These ancillary elements are considered to enhance the desired properties in the improved alloy products of the invention by suppressing recrystallization in products hot worked prior to solution heat treating and, in the case of recrystallized products such as some products cold worked by a substantial extent prior to solution heat treatment, controlling recrystallized grain size to fine grain sizes.

It is preferred that the iron and silicon content in the present products be less than about 0.05% each. Impurity levels of up to about 0.1% or more iron and up to about 0.1% or more silicon may also be acceptable but typically on a less preferred basis. On a still less preferred basis, the alloy can contain iron up to about 0.5% and silicon up to about 0.4%.

Some alloys considered suitable in accordance with the invention include those set forth in the following table:

TABLE IV

Alloy No.	Examples of Alloy				
	Zn	Mg	Cu	Zr	Mn
1	6-8	1-2.5	1-2.5	.04-.15	—
2	7.5-9	2-3	1.5-2.5	.04-.15	—
3	8-9.5	2-3	1.5-2.5	.04-.15	—
4	7.5-9	2.2-3.4	1.2-2.2	.04-.15	—
5	8.5-10	2.1-3.2	1.2-2.2	.04-.15	—
6	8-10	1.5-2.5	2-3	.04-.15	—
7	8-11	2-3	1.5-2.5	.04-.15	—
8	9-11.5	2-3	1.5-2.75	.04-.15	—
9	9-11	2-3	1.7-2.6	.04-.15	—
10	10-11.5	2-3	1.7-2.6	.04-.15	—
11	8.5-10	1.5-2.5	1-2	—	.5-.8
12	10.5-12	1.8-2.8	1-2	—	.5-.8
13	9-11.5	1.7-2.6	1-2	.04-.15	.3-.8

Products in accordance with this invention may be formed various techniques for producing aluminum alloy products such as rolling, forging, extruding or any other metal working operations. Accordingly, the alloy products produced may include sheet, plate, extrusions, forgings or rods, bars or any other shapes. In some embodiments, it is preferred to have products including thicknesses from about 0.3 or 0.35 inch to about 1.5 or 2 inches, although the invention is considered suitable for producing products having or including other thicknesses in sections thereof.

The improved alloy products are produced by providing an ingot or other suitable working stock from the

herein described alloy compositions and working said stock into the desired product, shape or configuration. Prior to working, the working stock can be homogenized by heating to a suitable high temperature, typically between about 860° and 920° F. Alternatively, the alloy may be cast into final shape although wrought or worked products are preferred. After desired working or shaping, the alloy may be solution heat treated by heating to one or more elevated temperatures from about 840° or 850° F. to about 880° or 900° F., or at still higher or lower temperatures depending on alloy composition, lower temperatures being favored with higher zinc content to avoid melting. The solution heat treatment is carried out to take into solid solution substantial portions or preferably substantially all of the zinc, magnesium and copper, it being recognized that physical processes are often not perfect such that every last vestige of these alloying ingredients may not be dissolved. Nonetheless, it is preferred where toughness and fatigue properties are concerned that not more than about one volume percent, preferably 0.5 vol. % or less, of undissolved intermetallic phases over one micron in size containing Zn, Cu and/or Mg remain in the alloy product after solutionizing.

After the aforesaid heating, the alloy is rapidly cooled or quenched by immersion or other suitable treatment in a quenching medium. This usually includes immersing in water, although water sprays or even air chilling may be useful in this respect. After quenching and prior to precipitation hardening, the alloy may be cold worked such as by stretching to relieve internal stresses. The solution heat treated and quenched alloy, with or without cold working, is then considered to be in a precipitation-hardenable condition. It is to be understood that solution heat treating or solutionizing as used herein includes quenching to a suitable lower temperature or a substitute or equivalent therefor so as to render the alloy suited to subsequent treatments described herein.

The precipitation-hardenable alloy is then treated in three steps, phases or treatments, although there may not be clear lines of demarcation between steps or phases. That is, it is known that ramping up to a particular aging temperature and ramping down therefrom are in themselves precipitation treatments which can, and often need to be, taken into account by integrating them, and their precipitation-hardening effects, into the treatment. This effect is described in U.S. Pat. No. 3,645,804, which is incorporated herein by reference. Thus while the three phases of aging according to this invention can be effected in a single furnace operation, properly programmed, they are described herein for purposes of convenience as three phases or treatments. In accordance with the invention, the first phase or treatment precipitation hardens the alloy. Then the second phase treats the alloy at an elevated temperature to increase resistance to exfoliation and stress corrosion cracking (SCC). Then the third phase precipitation hardens the alloy to a high strength level.

In the first phase, the alloy is precipitation hardened to strengthen it to a point at or near peak strength, preferably less than peak strength (underaged strength), or, on a less preferred basis, at peak or slightly overaged strength. This can be effected by treating at one or more temperatures between room temperature and about 330° F., preferably between about 175° and 325° F. This treatment typically can extend a significant period of

time, typically between about 2 to 30 or more hours and can occur through a temperature ramp-up to an elevated temperature for the second treatment phase. This precipitation hardening should strengthen the alloy product substantially over the strength achieved immediately after quenching (herein referred to as the as-quenched strength or solution treated strength) by at least 30% of the difference between as-quenched strength and peak yield strength, preferably to about 40% or 50% or more, for instance 60% or 70% or more of the difference between the as-quenched strength, or solution treated strength, and peak strength (the solution-peak strength differential) for the alloy product. Putting it another way, the precipitation-hardening of the alloy entering the second phase or treatment should have carried (increased) the product's strength by at least 30% (preferably more) of the way from as-quenched or solution treated strength (low strength) toward the peak strength.

The first phase can extend until the strength reaches up to about 95% of peak strength or reaches peak strength or even run past peak strength (overaged) back down to 95% of peak strength. However, it can be advantageous in some embodiments to limit the precipitation-hardening in the first phase to an underaged condition not exceeding 95% of peak yield strength. In a preferred embodiment, the alloy contains about 1.7% or more copper and the alloy enters the second phase at a strength increased above solution treated strength by about 70% to about 90% of the strength differential referred to in the immediately preceding paragraph. It is worth noting that alloys containing this copper level can increase in strength during the second treatment phase.

The alloy in the condition just described is then subjected to the second phase or treatment at one or more temperatures above about 340° F. or 350° F., preferably at one or more temperatures within the range of about 360° F. to about 500° F., preferably for more than a few minutes. In general, temperatures of 360° F. or higher are preferred but as the zinc content increases, for instance above 9% or 10% or so, lower temperatures such as 350° F. or 340° F. or even possibly less become more useful than for lower zinc contents. The temperatures employed in the second phase normally exceed those in the first and third phases. In some preferred embodiments, the second treatment phase proceeds by subjecting the alloy to treatment within the perimeter ABCD of FIG. 4 or within the perimeter JKLM of FIG. 5, said treatment producing a cumulative time and temperature effect corresponding to a point within the aforesaid perimeter even though more than one temperature may be utilized during this phase. For instance, the effects of this treatment for a particular alloy can commence at a temperature of about 345° or 350° F. and continue as the temperatures are further increased such that "ramping up" and, or "ramping down" of temperatures between about 345°, 350° or 355° F. and higher temperatures within the aforesaid perimeter can be taken into account and integrated into determining the equivalent aging effect within the aforesaid perimeters ABCD and JKLM. This treatment may proceed for 3 or more minutes at one or more temperatures between about 360° and 490° F.; for 4 or more minutes at one or more temperatures between about 360° and 480° F.; or for 5 or more minutes at one or more temperatures between about 360° and 475° F. The 3, 4, and 5-minute marks of FIG. 5 are shown by lines N-N', O-O' and P-P', respec-

tively. The area of overlap between FIGS. 4 and 5 is shown by dotted perimeter Q in FIG. 5. When referring to heating to one or more temperatures for a time of "x" minutes, such embraces heating to any number of temperatures in the designated range but for a cumulative time of "x" above the lowest temperature in the range. For instance, heating for 5 or more minutes at one or more temperatures from about 360° to 475° F. does not require holding for 5 minutes at each of several temperatures in said range, but rather, that the cumulative time at all temperatures between 360° and 475° F. is 5 minutes or more.

The second treatment phase increases resistance to stress corrosion cracking (S.C.C.), exfoliation and other corrosion effects. Generally speaking, better properties of S.C.C. resistance are achieved when proceeding at times and temperatures closer to line C-D of FIG. 4 and line L-M of FIG. 5, and better strength with good exfoliation resistance are achieved when proceeding in that area closer to lines A-B (FIG. 4) and J-K (FIG. 5). The second phase or treatment can be carried out by immersion in hot liquid such as molten salt, hot oil or molten metal. A furnace (hot air and/or other gases) may also be used. One advantageous practice utilizes a fluidized bed for the second treatment. Suitable media for the fluidized bed include alumina particles of about 50 or 60 mesh. The fluid bed heating media can provide fairly rapid heating (faster than a hot air furnace but slower than molten salt) and uniform heating of large or complex parts while presenting easier clean-up and environmental aspects than some other approaches. Induction heaters may also be used in the practice of the invention.

As indicated elsewhere herein, heating operations can be ramped-up fairly slowly such that much or even all of the treatments, especially the precipitation-hardening treatments of the first and/or third phases, can be accomplished by or during ramping-up to and/or -down from the elevated second phase temperature or temperatures such that there may not be discrete disruptions or interruptions between phases. However, the second phase can be considered to start when the corrosion properties start to improve. This typically involves some time at temperatures of about 360° or so or more after achieving the strengthening (precipitation-hardening) described in the first phase as mentioned hereinbefore. In some embodiments, the second phase can be considered accomplished when the desired degree of corrosion resistance is achieved and the temperature is suitably lowered for third phase precipitation-hardening. However, in some cases, the corrosion resistance can improve in the third phase such that the second phase can be shortened to a level less than the desired corrosion resistance to allow for this effect.

The alloy is then precipitation hardened in the third treatment or phase typically at one or more temperatures between room temperature and about 330° F., typically from about 175° to 325° F. This precipitation-hardening step may proceed at substantially the same temperature or temperatures employed in the earlier precipitation-hardening operation. The times employed in this third phase to utilize substantial exposures, typically for several hours, at one or more temperatures substantially below the higher (or highest) temperatures used in the second phase. During this precipitation-hardening phase, the strength of the product is increased to a very high level, above that accompanying the improved

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corrosion resistance achieved in the second phase and typically to the desired final yield strength level.

As can be seen from the foregoing, either or both precipitation-hardening phases and/or the intermediate higher temperature treatment can be performed at one or more temperatures by ramping up and/or down within a particular temperature range. As is generally recognized in the art, integration of aging effects under ramp-up or ramp-down conditions is useful in determining the total aging effect as described in U.S. Pat. No. 3,645,804, the disclosure of which is incorporated herein by reference.

It is preferred that the second phase treatment not be carried for time-temperature combinations excessively exceeding the extent needed to develop the desired level of corrosion resistance properties. Use of excessive time-temperature exposure in the second phase can impede the ability of the third phase to achieve the desired high level of strength. Accordingly, preferred practices for some products can include treatments to the left of line C-D in FIG. 4, and even to the left of line G-H (and upward and downward extensions thereof). Also, it may be of advantage in some cases to rapidly cool the product after a desired amount of treatment. Such cooling can be relatively drastic, such as by water quenching (immersion or sprays), or less drastic, such as by removal from the furnace and air or forced air (fans) cooled. Some advantage to rapid cooling from the second treatment, or rapid heating at the commencement of the second phase, can arise in some cases because of improvement in control of time and temperature. Thus, while ramping-up to and/or down from a temperature (more or less gradual heat-up and cool-down) can be employed, especially if ramp-up and ramp-down effects are appropriately accounted for, nonetheless, it may be advantageous in some cases to utilize rapid heat-up and/or rapid cool-down in one or more treatment phases, for instance in the second phase.

The microstructure changes that are believed to occur through the treatment phases just discussed can be of interest in understanding the invention. In the first treatment phase there are a relatively large number of closely spaced small particles containing Mg and Zn formed. The strength rises quite substantially and the overall solution potential of the alloy drops measurably. The microstructure is similar to a T6 microstructure and includes G.P. zones and metastable eta prime (η') precipitates in the grain interior, equilibrium eta (η) (MgZn_2) precipitates at the grain boundaries, and zones normally adjacent to the grain boundaries where there is substantially no detectable precipitate (precipitate-free-zone-PFZ). The PFZ contains more Zn and Mg in solution than the matrix further away from the grain boundary. This makes the PF electrochemically different (anodic) relative to the matrix in the grain interior such that corrosion can occur preferentially in this PFZ. This gives rise to exfoliation and stress corrosion cracking (S.C.C.) along PFZ's, thereby resulting in reduced resistance to these corrosion effects.

In the second treatment phase, strength can increase or decrease depending on composition and/or the extent of strengthening in the first phase. Solution potential does increase and so does corrosion resistance. The improvement in corrosion resistance is attributed to reducing the electrochemical difference referred to just above by removing more copper from solution in the grain interior region than in the PFZ regions. This is considered to occur as follows. Some all η' (normally

copper-free) in the grain interior matrix transforms to copper-free η (MgZn_2). Dissolved copper leaves solution and converts Cu-free η to copper-bearing η ($\text{Mg}(\text{Zn}, \text{Cu}, \text{Al})$), in both the grain boundaries and the grain matrix interior although some copper may possibly otherwise leave solution. The depletion of dissolved copper is more extensive in the grain interior region than the PFZ region, thus reducing the electrochemical (anodic) differential previously referred to. This, in turn, improves corrosion resistance quite substantially.

In the third phase, more η' precipitate forms and this improves strength quite significantly.

Thus, the strength-imparting precipitation that occurs in the first phase is accompanied by an anodic differential between the PFZ's immediately adjacent the grain boundaries and the matrix within the grains, which differential causes serious corrosion problems. This anodic differential and the resulting corrosion problems are substantially relieved in the second phase, and the alloy is further strengthened in the third phase.

The alloy products produced in accordance with the invention will exhibit very high levels of minimum or guaranteeable strength, at least about 5% greater than the similarly sized and shaped 7X50 alloy product in the T6 temper. Alloy products of the invention may have minimum yield strengths about 7 or 9%, and up to 12% or more greater than 7X50-T6 counterparts while not suffering from the serious disadvantages previously associated with high zinc alloys. The improved products of the invention will exhibit T7-type levels of resistance to stress corrosion cracking, exfoliation and other corrosion effects while substantially exceeding the minimum strength levels of 7150-T6 products exemplified in Table V below, it being remembered that 7150-T6 is considered a very high strength aluminum alloy in the aerospace industry.

TABLE V

Minimum Yield Strength Levels in Tension (ksi)		
Plate: 7150-T651		
Thickness (in.)	Longitudinal (L) Strength	Long Transverse (L-T) Strength
0.500-0.749	78	77
0.750-1.000	78	78
1.001-1.500	78	77
Extrusion: 7150-T651X Registered by Boeing		
Thickness (in.)	Longitudinal (L) Strength	
0.250-0.499	78	
0.500-0.749	78	
0.750-2.000	78	
Alcoa-modified 7150-T651		
0.250-0.499	82	
0.500-0.749	83	
0.750-2.000	84	

Strength comparisons herein refer to minimum strength, by which is meant the strength level that normal statistical methods would show at 95% confidence that 99% of the samples would equal or exceed. This guaranteeable or design-useful strength is referred to rather than typical values which are higher but not normally used for design purposes. When compared for typical strength, the improved products would show substantially the same levels of improvement (5% or 10% or more over 7X50-T6) as for minimum or guaranteeable values. Improved plate products of the invention will exhibit minimum yield strengths which meet or

exceed about 83 ksi, for instance greater than about 85 ksi, 87 ksi or more. Minimum yield strength values of about 90 ksi or more may also be achieved for plate products made according to this invention without suffering unacceptable levels of stress corrosion cracking, exfoliation or other corrosion effects. For improved extruded alloy products of the invention, minimum yield strengths of at least about 87 ksi to 88.5 ksi are achievable depending upon final alloy composition and overall product thickness. It is further considered practical to achieve minimum yield strength levels of about 90 ksi, 93 ksi or 95 ksi or more for thicker extruded shapes at acceptable levels of corrosion resistance. Minimum yield strengths in the neighborhood of about 100 ksi or higher may also be achieved without sacrificing acceptable corrosion resistance.

The improved products can exhibit corrosion resistance properties which meet or exceed those of 7X50 alloy products in T7-type tempers, for instance the T76 condition. This means that the improved products will be capable of surviving 20 days or more of alternate immersion testing in a 3.5% NaCl solution without cracking while under a constant stress of about 25 ksi or more. The practice of the invention may provide certain alloy products having stress corrosion cracking resistance levels which will survive 20 or more days of alternate immersion testing at stresses of about 35 ksi or more without cracking (the T74 temper). The resulting alloy product will further possess exfoliation resistances which meet or exceed those of the T76 and, more preferably, the T74 conditions listed in Table VI.

In Table VI, commercial corrosion resistance performance standards for T73, T74 and T76 tempers are set forth. Any product designated T76 must be capable of passing the T76 tests, and so on. The SCC test is based on the stress level that the product can sustain in a 20-day SCC test conducted by alternate immersion in accordance with ASTM Standard G44-75, incorporated herein by reference. In this test, short transverse specimens 1/8 inch (3.2 mm) in diameter are stressed in constant strain fixtures. The test specimens are then alternately exposed to 10 minutes immersion in a 3.5% aqueous NaCl solution and a 50-minute drying cycle while under a constant stress value (ksi). The test is carried out for 20 days (less if the specimen fails in less than 20 days). The exfoliation test is the EXCO test, ASTM Standard G34-72, -79, incorporated herein by reference.

TABLE VI

Temper	Corrosion Resistance Standards	
	SCC Test Stress (ksi)	Exfoliation Requirement EXCO Test
T73	42	P - pitting; little or no exfoliation
T74	35	EA - slight or superficial exfoliation
T76	25	EB - Moderate - more exfoliation than EA but still acceptable

As can be seen, T73 is the most corrosion resistant temper in Table VI, with T74 and T76 being progressively less resistant but progressively stronger. The T6 temper normally fails all of these tests and is not considered well suited where stress corrosion cracking is a concern or where exfoliation corrosion could present a problem. Alloy 7050 (U.S. Pat. No. 3,881,966) is often sold in T74 and T76 tempers, whereas substantially

identical alloy 7150 is typically sold in T6-type tempers because of its higher strength.

The present invention will enable achieving a substantial increase in strength over 7150 and 7050 products at equivalent levels of corrosion resistance. The invention can produce strength levels as much as 5 or 7% and more, such as increases of 9 or 10%, or even 12% or more greater than 7X50-T6. Moreover, T76-type corrosion resistance, or better, combined with such strength increases over the high strength levels of 7150-T651 will also be achievable in practicing the invention. Such combinations of high strength together with T76 corrosion resistance are extremely valuable in aerospace and other high strength aluminum alloy applications.

Having described the presently preferred embodiments, it is to be understood that the invention may be otherwise embodied within the scope of the appended claims which are intended to embrace all equivalents and all embodiments within the spirit of the invention.

What is claimed is:

1. A method for producing an aluminum alloy product having improved combinations of strength and corrosion resistance properties, said method comprising:

- (a) providing an alloy consisting essentially of about 6-16% zinc, about 1.5-4.5% magnesium, about 1-3% copper, one or more elements selected from zirconium, chromium, manganese, titanium, vanadium and hafnium, the total of said elements not exceeding about 1%, the balance aluminum and incidental elements and impurities;
 - (b) solution heat treating the alloy;
 - (c) precipitation hardening the alloy above room temperature to increase its strength to a level exceeding as-solution heat treated strength by at least about 30% of the difference between as-solution heat treated strength and peak strength;
 - (d) subjecting the alloy to treatment at one or more temperatures sufficient for improving the corrosion resistance properties of said alloy for a cumulative time at said temperatures of more than about three minutes; and
 - (e) precipitation hardening the alloy above room temperature.
2. The method of claim 1 wherein the alloy contains about 7.5 to about 12% zinc.
 3. The method of claim 2 wherein the alloy contains about 9 to about 11% zinc.
 4. The method of claim 1 wherein the alloy contains about 2 to about 4% magnesium.
 5. The method of claim 1 wherein the alloy contains about 1.5 to about 2.5% copper.
 6. The method of claim 1 wherein the alloy contains about 0.3 to about 0.8% manganese.
 7. The method of claim 1 wherein the alloy further contains up to about 0.1% impurities including iron and silicon.
 8. The method of claim 1 wherein the alloy contains more magnesium than copper.
 9. The method of claim 1 wherein the alloy contains more copper than magnesium.
 10. The method of claim 1 wherein (c) includes heating the alloy to one or more temperatures below about 340° F.
 11. The method of claim 10 wherein recitation (c) includes precipitation hardening the alloy at one or more temperatures between room temperature and about 330° F.

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12. The method of claim 1 wherein recitations (c) and (e) include subjecting the alloy to one or more temperatures within about 175° to 325° F.

13. The method of claim 1 wherein recitation (d) includes subjecting the alloy to one or more temperatures within about 350° to 500° F.

14. The method of claim 1 wherein recitation (d) includes subjecting the alloy to treatment for a cumulative time-temperature effect substantially within ABCD of FIG. 4, said treatment extending for a cumulative time of four or more minutes at temperatures between about 360° and 480° F.

15. The method of claim 14 wherein more than one temperature is used in recitation (d).

16. The method of claim 1 wherein recitation (d) includes subjecting the alloy to one or more temperatures within about 360° to 475° F. for a cumulative time within 360° to 475° F. of about five or more minutes.

17. The method of claim 1 wherein recitation (d) includes subjecting the alloy to treatment for cumulative time temperature effect substantially within JKLM of FIG. 5.

18. The method according to claim 17 wherein more than one temperature is used in recitation (d).

19. The method of claim 1 is capable of producing an improved alloy product wherein the alloy product produced has at least about 5% greater yield strength than a similarly-sized 7X50-T6 alloy product and has corrosion resistance properties which meet or exceed those of a 7X50-T76 alloy product.

20. The method of claim 1 wherein the alloy product produced: (i) has about 7% or more greater yield strength than a similarly-sized 7X50-T6 alloy product; (ii) is capable of surviving at least about 20 days of alternate immersion testing in a 3.5% NaCl solution without cracking under a stress of about 25 ksi or more; and (iii) has an exfoliation resistance level of "EB" or better.

21. A method for improving the strength, toughness and corrosive resistance properties of a solution heat treated 7XXX aluminum alloy containing about 7 to about 12% zinc; about 1.5 to about 2.7% magnesium; about 1 to about 3% copper; the total zinc, magnesium and copper content not exceeding an amount which will cause more than one volume percent of undissolved intermetallic phases containing said elements to remain after solution heat treating, said alloy further containing one or more elements selected from: up to about 0.2% zirconium, up to about 0.25% chromium, up to about 0.8% manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, said method comprising:

(a) precipitation hardening the alloy at one or more temperature above room temperature but below about 340° F.;

(b) subjecting the alloy to treatment at one or more temperatures above about 340° F. for a cumulative time at temperatures above 340° F. of more than three minutes; and

(c) precipitation hardening the alloy at one or more temperatures above room temperature but below about 340.

22. The method of claim 21 wherein the alloy contains about 7.5 to about 11.5% zinc, about 1.7 to about 2.3% magnesium and about 1.2 to about 3% copper.

23. The method of claim 21 wherein the alloy further contains up to about 0.08% iron and up to about 0.08% silicon.

24. The method of claim 21 wherein recitations (a) and (c) include heating the alloy at one or more temperatures between about 175° and 325° F.

25. The method of claim 21 wherein recitation (b) includes heating the alloy at one or more temperatures from about 360° F. to about 500° F.

26. The method of claim 21 wherein recitation (b) includes heating the alloy for a time-temperature equivalence substantially within JKLM of FIG. 5.

27. A method for producing aluminum alloy product having a minimum yield strength at least about 5% greater than the minimum yield strength for a similarly-sized 7X50-T6 alloy product and having corrosion resistance properties which meet or exceed those of a 7X50-T6 alloy product, said method comprising:

(a) providing an alloy consisting essentially of about 7 to about 12% zinc, about 1.5 to about 2.7% magnesium, about 1 to about 3% copper, the total zinc, magnesium and copper content not exceeding an amount which will substantially enter into solid solution during solution heat treatment, said alloy further including one or more elements selected from: up to about 0.2% zirconium, up to about 0.25% chromium, up to about 0.8% manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, the balance aluminum and incidental elements and impurities;

(b) working said alloy into wrought condition;

(c) solution heat treating the alloy;

(d) precipitation hardening the alloy for about 2 or more hours in a first elevated temperature range to increase its strength;

(e) subjecting the alloy to one or more temperatures within about 340° C. to 500° F. for a cumulative time at temperatures within 340° to 500° F. of four minutes or more to impact to said alloy time temperature equivalence substantially within the perimeter JKLM of FIG. 5; and

(f) precipitation hardening the alloy in the first temperature range to further improve its strength, said method imparting to the alloy improved combinations of strength and corrosion resistance properties.

28. The method of claim 27 wherein the alloy contains about 0.3 to about 0.8% manganese.

29. The method of claim 27 wherein the alloy further contains up to about 0.1% impurities including iron and silicon.

30. The method of claim 27 wherein the first temperature range is between about 175° and 325° F.

31. An improved alloy product consisting essentially of about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, one or more elements selected from zirconium, chromium, manganese, vanadium and hafnium, the total of said elements not exceeding about 1%, the balance aluminum and incidental elements and impurities, said alloy product having at least about 5% greater yield strength than a similarly-sized 7X50-T6 product and having corrosion resistance properties which meet or exceed those of a 7X50-T6 product.

32. The alloy product of claim 31 which contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.05 to 0.2% zirconium.

33. The alloy product of claim 31 which contains about 9.5 to 1.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.05 to 0.2% zirconium.

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34. The alloy product of claim 31 which contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.05 to 0.2% zirconium.

35. The alloy product of claim 31 which contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.05 to 0.2% zirconium.

36. The alloy product of claim 31 which contains about 0.3 to 0.8% manganese.

37. The alloy product of claim 31 which is plate having at least about 83 ksi yield strength.

38. The alloy plate product of claim 37 wherein the yield strength is about 85 ksi or more.

39. The alloy product of claim 31 which is an extrusion having at least about 87 ksi yield strength.

40. The alloy extrusion product of claim 39 the yield strength is about 90 ksi or more.

41. The alloy product of claim 31 which is capable of surviving at least about 20 days of alternate immersion testing in a 3.5% NaCl solution without cracking under a stress of about 25 ksi or more, said alloy product having an exfoliation resistance level of "EB" or better.

42. An ingot-derived alloy product which consists essentially of about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, one or more elements selected for zirconium, chromium, manganese, vanadium and hafnium, the total of said elements not exceeding about 1%, the balance aluminum and incidental elements and impurities, said alloy product having at least about 83 ksi yield strength and having an exfoliation resistance level of "EB" or better and good toughness.

43. The alloy product of claim 42 which contains one or more of: 0.05 to 0.2% zirconium, 0.03 to 0.2% vanadium and 0.03 to 0.5% hafnium.

44. The alloy product of claim 42 which has at least about 7% greater yield strength than a similarly-sized 7X50-T6 alloy product.

45. The alloy product of claim 44 which has at least about 9% greater yield strength than the 7X50-T6 alloy product.

46. The alloy product of claim 42 which is capable of surviving at least about 20 days of alternate immersion testing in a 3.5% NaCl solution without cracking under a stress of about 25 ksi or more.

47. The alloy product of claim 42 which is capable of surviving at least about 20 days of alternate immersion testing in a 3.5% NaCl solution without cracking under a stress of about 35 ksi or more, said alloy product having an exfoliation resistance level of "EA" or better.

48. An aluminum alloy product characterized by improved strength, toughness and corrosion resistance properties, said alloy product comprising an alloy consisting essentially of about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, the total weight of zinc, magnesium and copper not exceeding about 15%, one or more elements selected from: up to about 0.2% zirconium, up to about 0.25% chromium, up to about 0.8% manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, the balance aluminum and incidental elements and impurities, said alloy product having been solution heat treated and:

- (a) precipitation hardened at one or more elevated temperatures to increase its relative strength;
- (b) subjected to treatment for four or more minutes at one or more temperatures sufficient to improve its corrosion resistance properties; and

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(c) precipitation hardened to raise its yield strength to a level at least about 5% greater than that for a similarly-sized 7X50-T6 alloy product.

49. The alloy product of claim 48 which is plate having about 83 ksi minimum yield strength and an exfoliation resistance level of "EB" or better.

50. The alloy plate product of claim 49 wherein the minimum yield strength is about 85 ksi or more.

51. The alloy product of claim 48 which is an extrusion having about 87 ksi minimum yield strength and an exfoliation resistance level of "EB" or better.

52. The alloy extrusion product of claim 51 wherein the minimum yield strength is about 90 ksi or more.

53. A method for thermally treating an alloy product consisting essentially of about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper and up to about 0.2% zirconium, the balance aluminum and incidental elements and impurities, said method including: (a) solution heat treating the alloy product; (b) precipitation hardening the alloy product in a first temperature range above room temperature and below about 330° F.; (c) subjecting the alloy product to treatment in a second temperature range above the first temperature range for greater than three minutes but not so long as to prevent imparting a substantial strength increase to the alloy product during subsequent treatment; and (d) precipitation hardening the alloy product in a third temperature range above room temperature and below the second temperature range.

54. The method as claimed in claim 53 wherein the first and third temperature ranges are between about 175°-325° F.

55. The method as claimed in claim 53 wherein recitation (c) extends for about five or more minutes and corresponds to time-temperature equivalence substantially within ABCD of FIG. 4.

56. The method as claimed in claim 53 wherein recitation (c) corresponds to time-temperature equivalence substantially within JKLM of FIG. 5.

57. A method for thermally treating a wrought aluminum alloy consisting essentially of about 7.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1.2 to 3% copper and up to about 0.2% zirconium, said method comprising: (a) providing the alloy in a precipitation-hardenable condition; (b) precipitation hardening the alloy including heating within about 175°-325° F.; (c) subjecting the alloy to treatment for more than three minutes at one or more temperatures sufficient for improving its corrosion resistance properties, said treatment imparting a cumulative time-temperature equivalence substantially within JKLM of FIG. 5; and (d) precipitation hardening the alloy including heating within about 175°-325° F. to raise its relative strength.

58. The method as claimed in claim 57 wherein recitation (c) includes heating the alloy to one or more temperatures within about 360° to 500° F. for a cumulative time within 360° to 500° F. of about four minutes or more.

59. The method as claimed in claim 57 wherein recitation (c) includes heating the alloy to one or more temperatures within about 340° to 500° F. for a cumulative time within 340° to 500° F. of about four minutes or more.

60. A method for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, up to about 0.2% zirconium, up to about 0.25% chromium, up to about 0.8%

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manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, said method comprising:

- (a) providing the alloy in a wrought precipitation-hardenable condition;
 - (b) subjecting the alloy to one or more precipitation-hardening temperatures above room temperature to effect some precipitation therein;
 - (c) treating the alloy for a cumulative time of about four or more minutes at one or more elevated temperatures sufficient to improve the corrosion resistance of said alloy, said treatment imparting to the alloy time-temperature equivalence substantially within ABCD of FIG. 4; and
 - (d) subjecting the alloy to one or more precipitation-hardening temperatures above room temperature to improve the strength of said alloy.
61. The method according to claim 60 wherein either or both of recitations (b) and (d) include subjecting said alloy to one or more temperatures within about 175° and 325° F.
62. The method according to claim 60 wherein recitation (c) includes heating the alloy to one or more temperatures within 340° to 500° F. for a cumulative time within 340° to 500° F. of five minutes or more.
63. The method according to claim 60 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.
64. The method according to claim 60 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.
65. The method according to claim 60 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.
66. The method according to claim 60 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.
67. A method for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, up to about 0.2% zirconium, up to about 0.25% chromium, up to about 0.8% manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, said method comprising:
- (a) providing the alloy in a precipitation-hardenable condition;
 - (b) subjecting the alloy to one or more precipitation-hardening temperatures above room temperature to effect some precipitation therein;
 - (c) subjecting the alloy to treatment at one or more temperatures sufficient to improve the corrosion resistance thereof;
 - (d) subjecting the alloy to one or more precipitation-hardening temperatures above room temperature to significantly increase the strength of said alloy;
 - (e) the cumulative time at temperatures sufficient to improve corrosion resistance in recitation (c) being about four minutes or more but not so long as to prevent imparting a strength increase to the alloy in recitation (d).
68. The method according to claim 67 either or both recitations (b) and (d) include subjecting said alloy to one or more temperatures within about 175° to 325° F.
69. The method according to claim 67 wherein recitation (c) produces time-temperature equivalence substantially within ABCD of FIG. 4.

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70. The method according to claim 67 wherein the cumulative time in recitation (e) is from about 5 minutes to about two and one-half hours.

71. The method according to claim 67 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.

72. The method according to claim 67 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

73. The method according to claim 67 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.

74. The method according to claim 67 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

75. A method for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, up to about 0.2% zirconium, up to about 0.25% chromium, up to about 0.8% manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, the balance aluminum and incidental elements and impurities, said method comprising:

- (a) providing the alloy in a wrought precipitation-hardenable condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. to effect some precipitation therein;
- (c) subjecting the alloy to treatment at one or more temperatures within about 360° to 500° F.; and
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. to increase the strength of said alloy;
- (e) the cumulative time spent at temperatures within about 360° to 500° F. in recitation (c) being from about 4 minutes to about two-and-one-half hours but not so long as to prevent imparting a strength increase in said recitation (d).

76. The method according to claim 75 wherein recitation (c) imparts to the alloy time-temperature equivalence substantially within ABCD of FIG. 4.

77. The method according to claim 75 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.

78. The method according to claim 75 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

79. The method according to claim 75 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.

80. The method according to claim 75 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

81. A method for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, up to about 0.25% chromium, up to about 0.8% manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, said method comprising:

- (a) providing said alloy in a wrought precipitation-hardenable condition;

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- (b) subjecting said alloy to one or more temperatures within about 175° to 325° F. to effect some precipitation therein;
- (c) increasing the temperature of said a to one or more temperatures within about 360° to 500° F. for subjecting it to treatment for a cumulative time within about 360° to 500° F. from about 4 minutes to about two-and-one-half hours, said treatment corresponding to time-temperature equivalence substantially within ABCD of FIG. 4; and
- (d) subjecting said alloy to one or more temperatures within about 175° to 325° F. to improve its strength.
82. The method according to claim 81 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.
83. The method according to claim 81 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.
84. The method according to claim 81 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.
85. The method according to claim 81 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.
86. A method-for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, up to about 0.2% zirconium, up to about 0.25% chromium, up to about 0.8% manganese, up to about 0.2% vanadium and up to about 0.5% hafnium, the balance aluminum and incidental elements and impurities, said method comprising:
- (a) providing the alloy in a wrought precipitation-hardenable condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within 175° to 325° F. of about two hours or more to impart some precipitation therein;
- (c) subjecting the alloy to treatment within a range of about 340° to 500° F. for a cumulative time within said range from about 5 minutes to about two-and-one-half hours, said treatment corresponding to time-temperature equivalence substantially within ABCD of and
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within 175° to 325° F. of about two hours or more to significantly increase its relative strength.
87. The method according to claim 86 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.
88. The method according to claim 86 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.
89. The method according to claim 86 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.
90. The method according to claim 86 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

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91. A method for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper and one or more elements selected from zirconium, chromium, manganese, vanadium and hafnium, the total of said elements not exceeding about 1%, comprising:
- (a) providing the alloy in a solution heat treated condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a substantial cumulative time within about 175° to 325° F.;
- (c) subjecting the alloy to one or more temperatures within about 340° to 500° F. for a cumulative time within about 340° to 500° F. from about four minutes to about two and one-half hours; and
- (d) subjecting the alloy to one or more within about 175° to 325° F. for a cumulative time within about 175° to 325° F. sufficient to increase the strength of said alloy;
- (e) said subjecting in recitation (c) being excessive to obtaining a strength increase in recitation (d).
92. The method according to claim 91 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within ABCD of FIG. 4.
93. The method according to claim 91 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within JKLM of FIG. 5.
94. The method according to claim 91 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.
95. The method according to claim 91 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.
96. The method according to claim 91 the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.
97. The method according to claim 91 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.
98. A method for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, and up to about 1% of one or more elements selected from zirconium, chromium, manganese, vanadium and hafnium, said method comprising:
- (a) providing the alloy in a solution heat treated condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. of about three hours or more;
- (c) subjecting the alloy to one or more temperatures within about 360° to 500° F. for a cumulative time within about 360° to 500° F. from about 4 minutes or more to about two and one-half hours for imparting to the alloy time-temperature equivalence substantially within ABCD of FIG. 4; and
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. of about 2 hours or more.
99. The method according to claim 98 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5%

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magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.

100. The method according to claim 98 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

101. The method according to claim 98 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.

102. The method according to claim 98 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

103. A method for treating a 7XXX aluminum alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, and up to about 1% of one or more elements selected from zirconium, chromium, manganese, vanadium and hafnium, said method comprising:

- (a) providing the alloy in a solution heat treated condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a substantial cumulative time within about 175° to 325° F.;
- (c) increasing the temperature of said alloy and subjecting it to one or more temperatures within about 340° to 500° F. for a cumulative time within 340° to 500° F. from about four minutes or more to about two and one-half hours; and
- (d) subjecting the alloy to one or more cumulative time within about 175° to 325° F.;
- (e) said subjecting in recitation (c) not being excessive to imparting a significant strength increase to the alloy in recitation (d).

104. The method according to claim 103 wherein said substantial cumulative time within about 175° to 325° F. in recitation (b) is about 3 hours or more.

105. The method according to claim 103 wherein said cumulative time within about 175° to 325° F. in recitation (d) is about 2 hours or more.

106. The method according to claim 103 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within ABCD of FIG. 4.

107. The method according to claim 103 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within EFGH of FIG. 4.

108. The method according to claim 103 wherein said subjecting in recitation (c) imparts time-temperature equivalence substantially within JKLM of FIG. 5.

109. The method according to claim 103 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.

110. The method according to claim 103 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

111. The method according to claim 103 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.

112. The method according to claim 103 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

113. A method for treating a 7XXX alloy containing about 7 to 12% zinc, about 1.5 to 2.7% magnesium,

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about 1 to 3% copper, up to about 1% of one or more elements selected from zirconium, chromium, manganese, vanadium and hafnium, the balance aluminum and incidental elements and impurities, said method comprising:

- (a) providing the alloy in a wrought precipitation-hardenable condition;
- (b) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. of about 3 hours or more;
- (c) increasing the temperature of said alloy and subjecting it to one or more temperatures within about 340° to 500° F. for a cumulative time within 340° to 500° F. from about 5 minutes to about two and one-half hours to impart to said alloy time-temperature equivalence substantially within JKLM of FIG. 5; and
- (d) subjecting the alloy to one or more temperatures within about 175° to 325° F. for a cumulative time within about 175° to 325° F. of about two hours or more.

114. The method according to claim 113 wherein the alloy contains about 7 to 9.5% zinc, about 1.5 to 2.5% magnesium, about 1.8 to 3% copper and about 0.03 to 0.2% zirconium.

115. The method according to claim 113 wherein the alloy contains about 9.5 to 11.5% zinc, about 1.5 to 2.5% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

116. The method according to claim 113 wherein the alloy contains about 8 to 10% zinc, about 1.5 to 2.5% magnesium, about 2 to 3% copper and about 0.03 to 0.2% zirconium.

117. The method according to claim 113 wherein the alloy contains about 10.5 to 12% zinc, about 1.8 to 2.8% magnesium, about 1 to 2% copper and about 0.03 to 0.2% zirconium.

118. A method for imparting improved combinations of strength, toughness and corrosion resistance to a solution-heat-treated alloy product consisting essentially of about 7 to 12% zinc, about 1.5 to 2.7% magnesium, about 1 to 3% copper, and up to about 1% of one or more elements selected from zirconium, chromium, manganese, vanadium and hafnium, the balance aluminum and incidental elements and impurities, said method comprising: (a) treating the alloy product at more than one elevated temperature to: (i) form hardening precipitates; and (ii) improve its corrosion resistance, said treatment including heating within about 360°-500° F. for greater than three minutes to impart a cumulative time-temperature effect substantially within JKLM of FIG. 5; and (b) precipitation hardening the alloy product including heating at one or more temperatures between about 175°-325° F. to increase its strength.

119. The method as claimed in claim 118 wherein recitation (a)(i) includes treating the alloy product for at least about two hours between about 175°-325° F. to form hardening precipitates before heating for said cumulative time-temperature effect.

120. The product produced by the method of claim 1.

121. The product produced by the method of claim 21.

122. The product produced by the method of claim 27.

123. The product produced by the method of claim 53.

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- 124. The product produced by the method of claim 57.
- 125. The product produced by the method of claim 69.
- 126. The product produced by the method of claim 75.
- 127. The product produced by the method of claim 86.
- 128. The product produced by the method of claim 91.
- 129. The product produced by the method of claim 98.
- 130. The product produced by the method of claim 103.
- 131. The product produced by the method of claim 113.
- 132. The product produced by the method of claim 118.
- 133. The product produced by the method of claim 123.

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EXHIBIT 4



United States Patent [19]

Liu et al.

[11] Patent Number: **5,108,520**

[45] Date of Patent: **Apr. 28, 1992**

[54] HEAT TREATMENT OF PRECIPITATION HARDENING ALLOYS

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Michael M. Kersker, Beverly, Mass.

[73] Assignee: Aluminum Company of America,
Pittsburgh, Pa.

[21] Appl. No.: 365,442

[22] Filed: Jun. 13, 1989

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Primary Examiner—R. Dean

Assistant Examiner—Robert R. Koehler

Attorney, Agent, or Firm—Daniel A. Sullivan, Jr.

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 19,995, Feb. 27, 1980, abandoned.

[51] Int. Cl. 3 C22F 1/04

[52] U.S. Cl. 148/12.7 R; 148/159;
148/405; 148/417

[58] Field of Search 148/159, 12.7 R, 417,
148/405

[56] References Cited

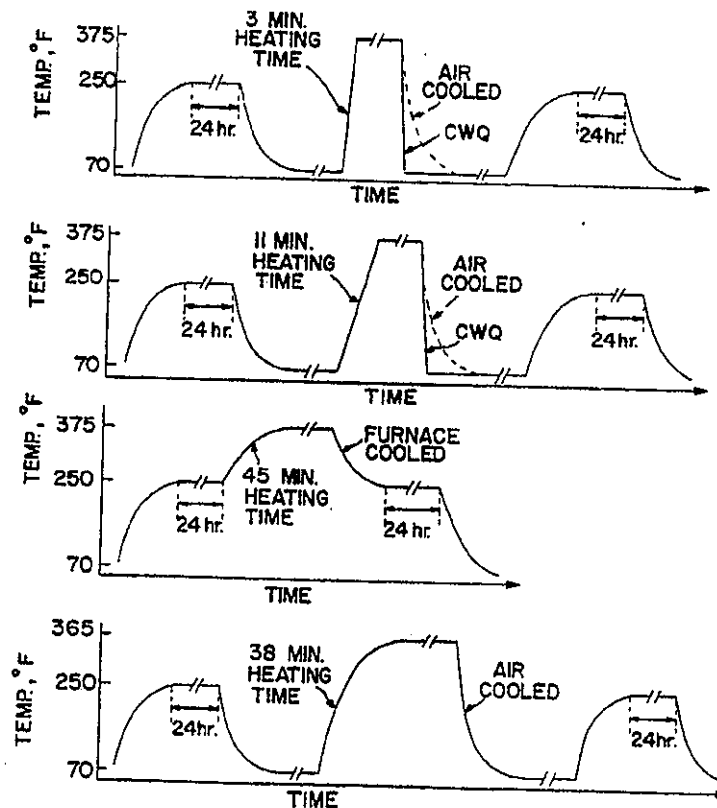
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[57] ABSTRACT

An aging process for solution-heat-treated, precipitation hardening metal alloy includes first underaging the alloy, such that a yield strength below peak yield strength is obtained, followed by higher aging for improving the corrosion resistance of the alloy, followed by lower temperature aging to strength increased over that achieved initially.

54 Claims, 11 Drawing Sheets



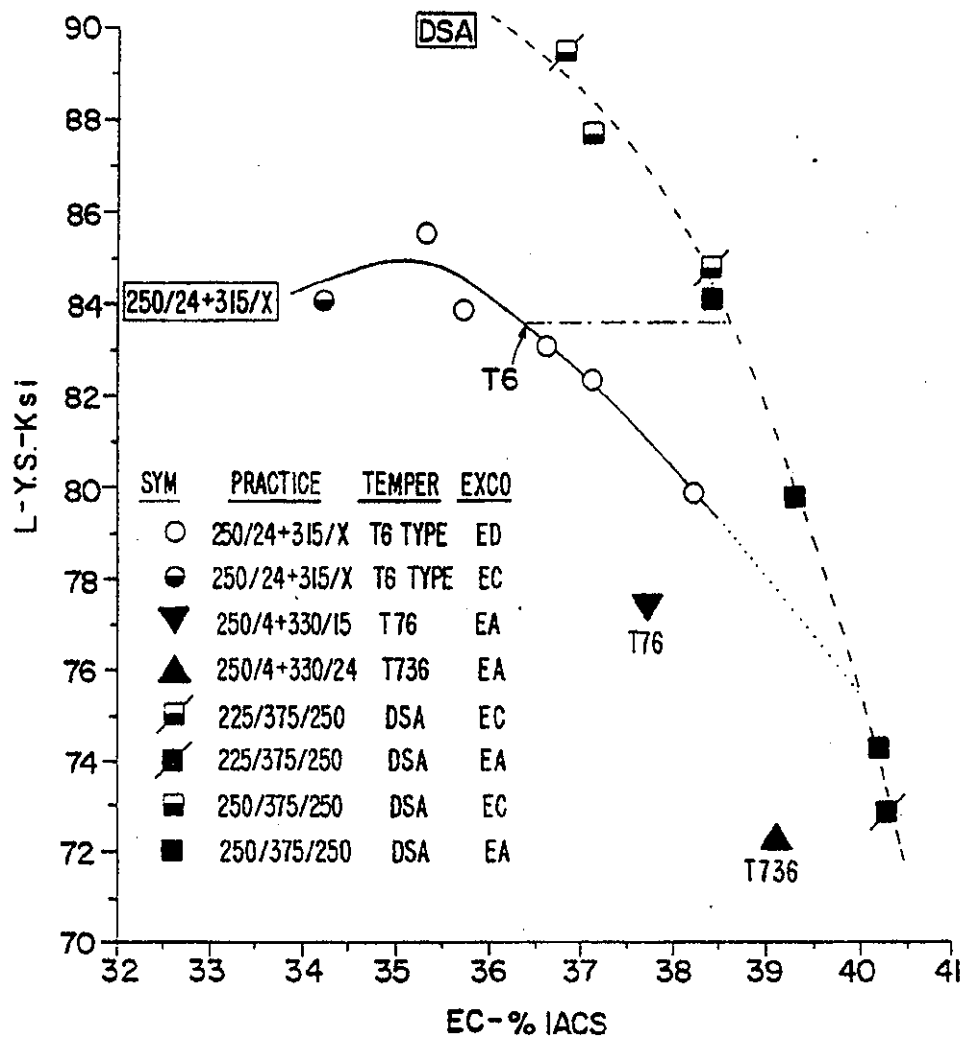
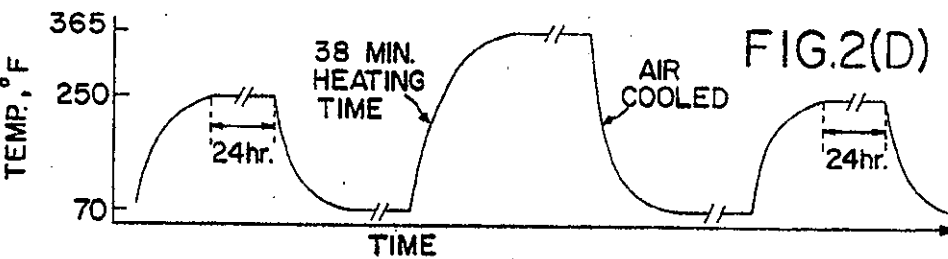
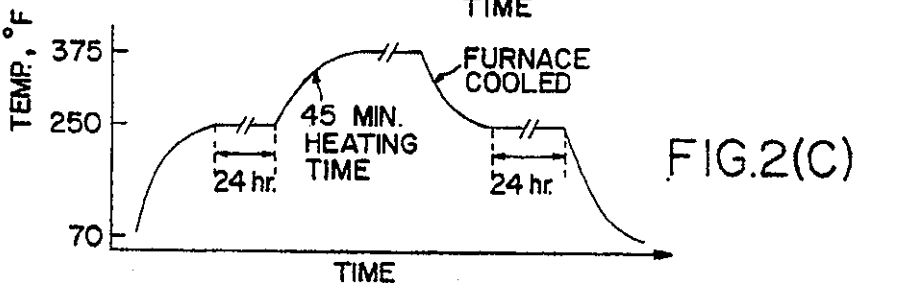
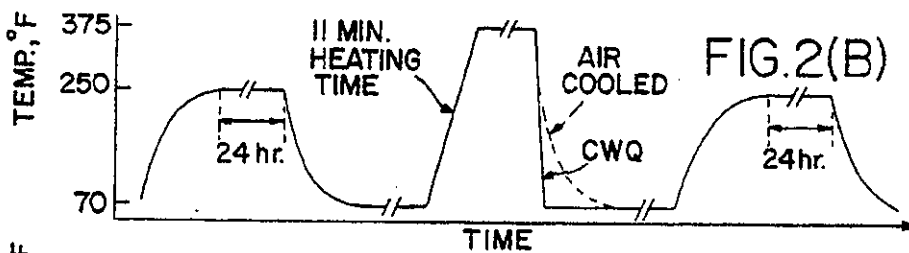
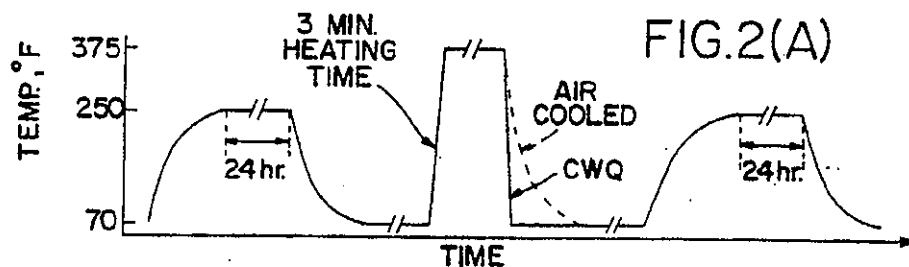


FIG.1



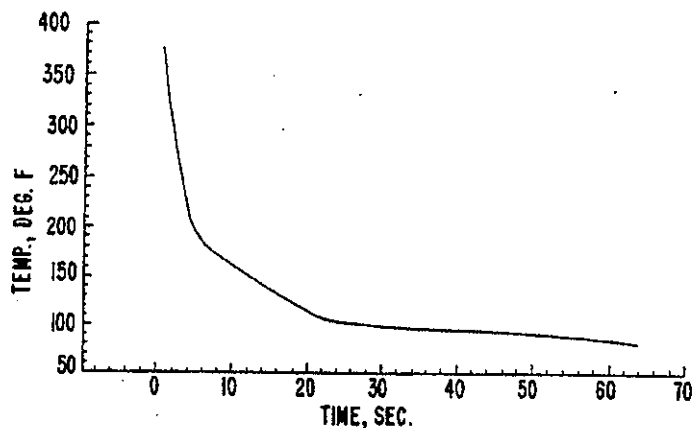


FIG.3(A)

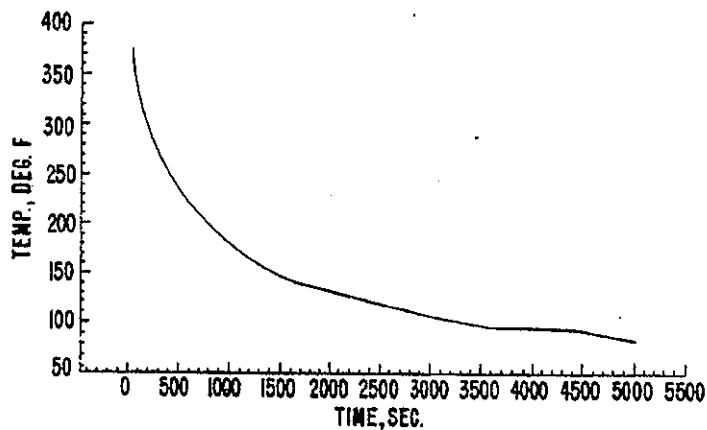


FIG.3(B)

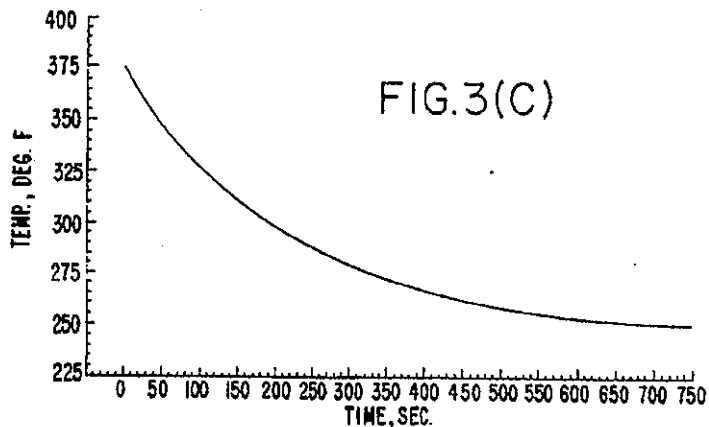


FIG.3(C)

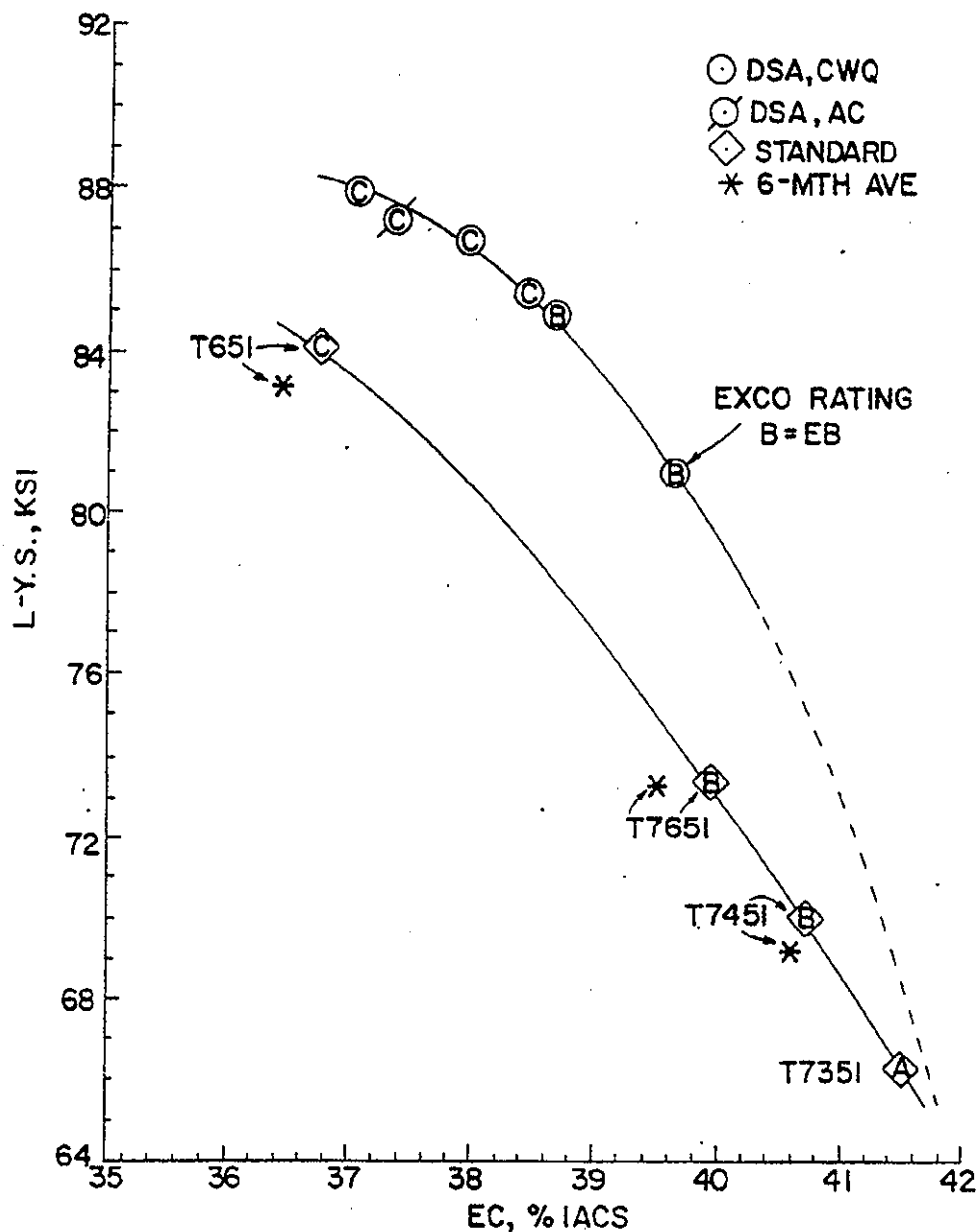


FIG.4

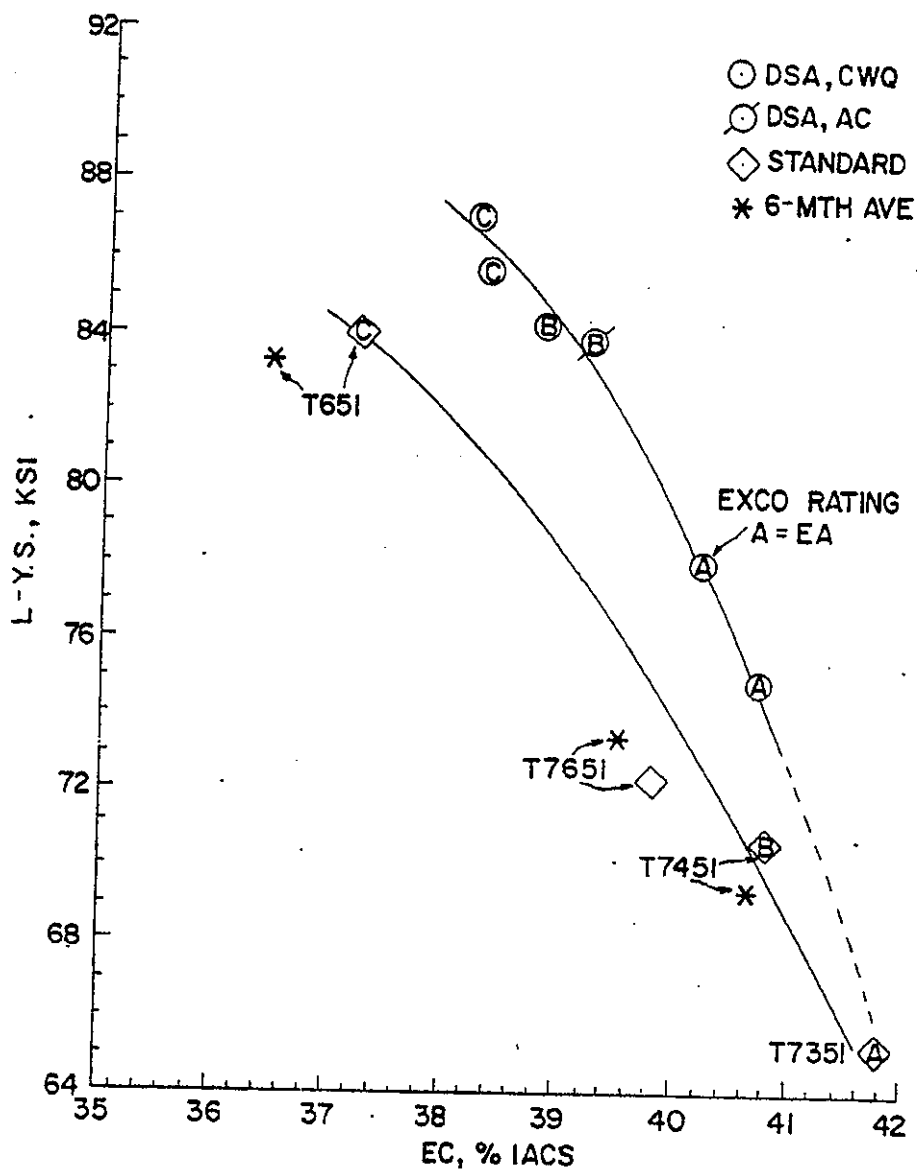


FIG.5

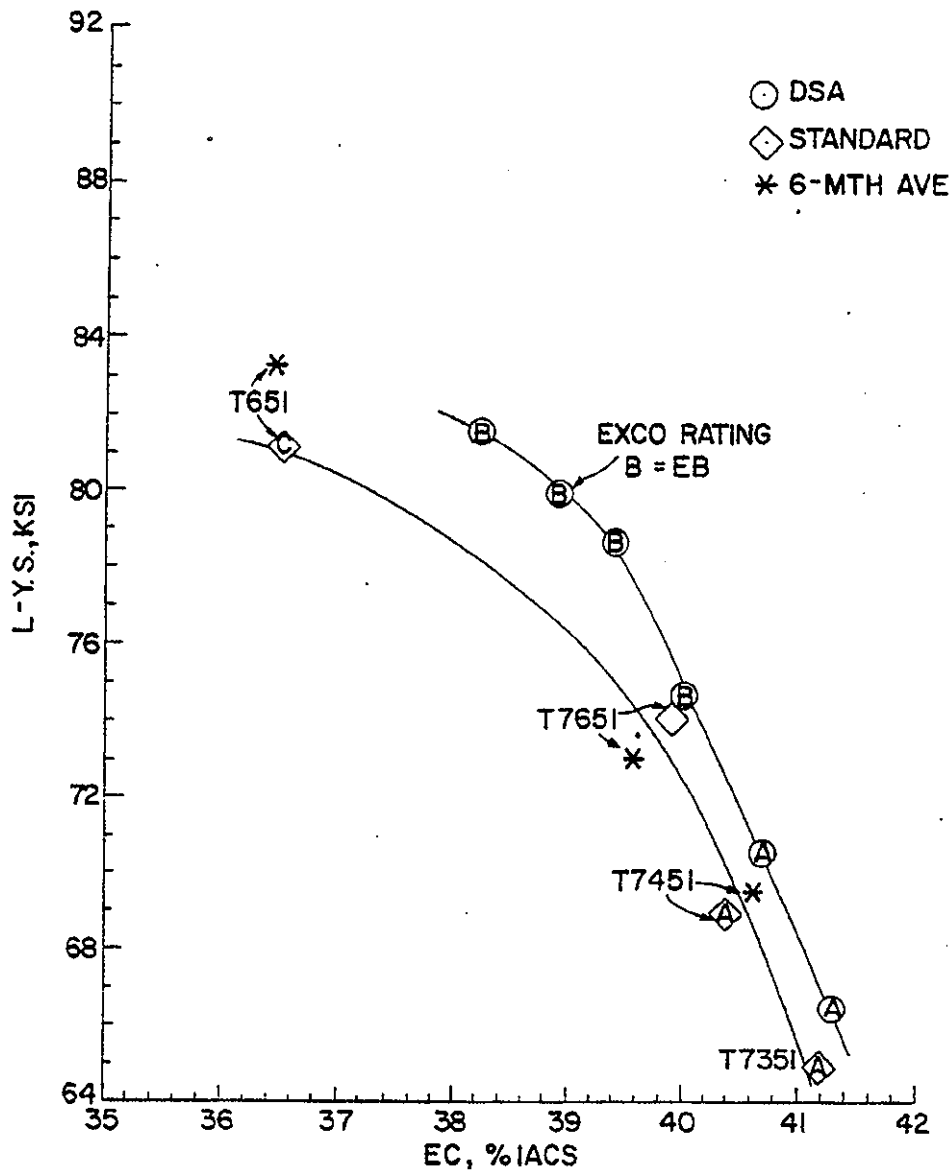


FIG.6

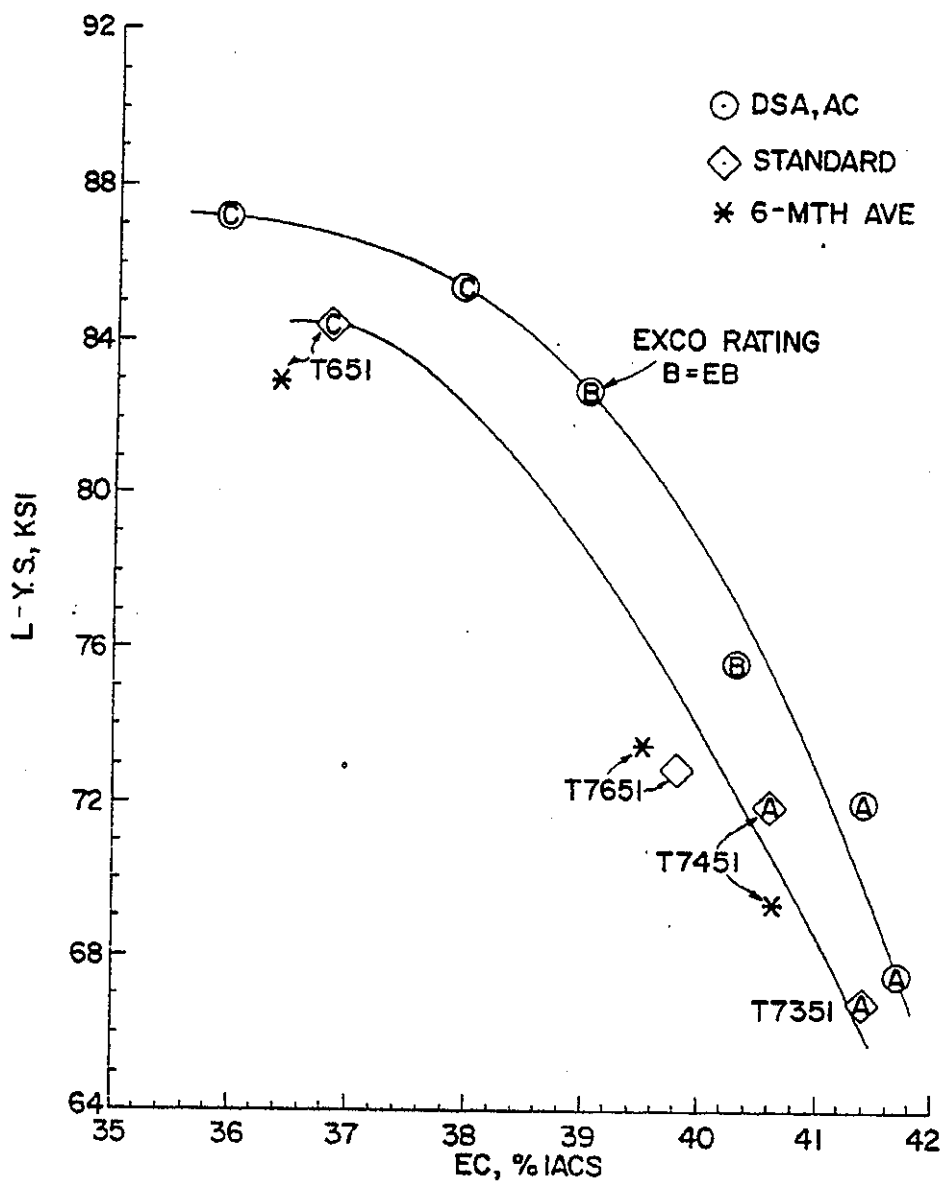


FIG. 7

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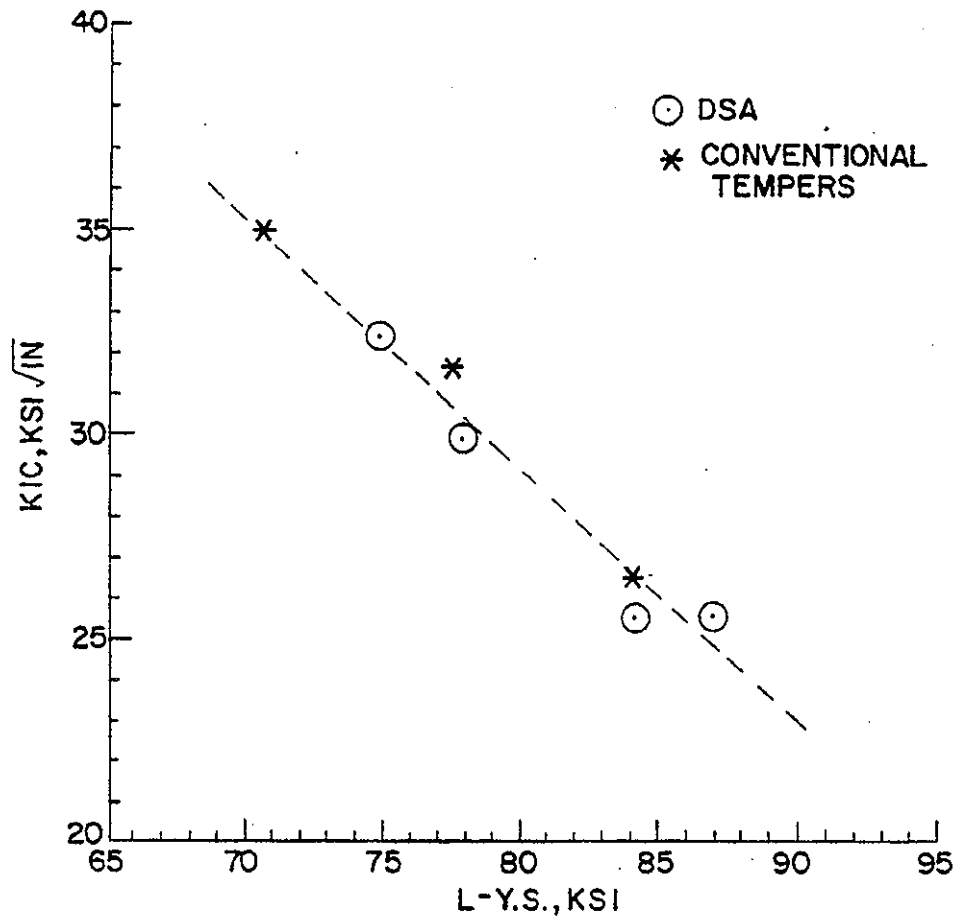


FIG.8

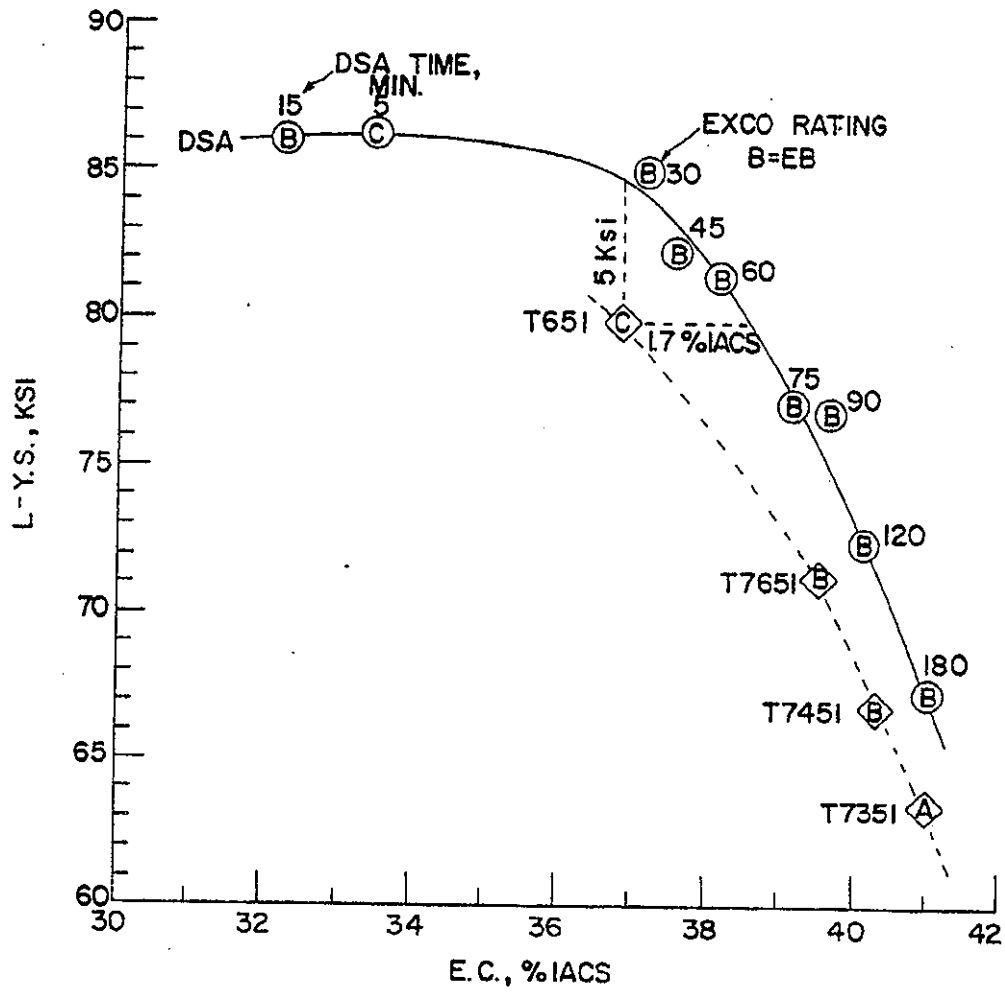


FIG. 9

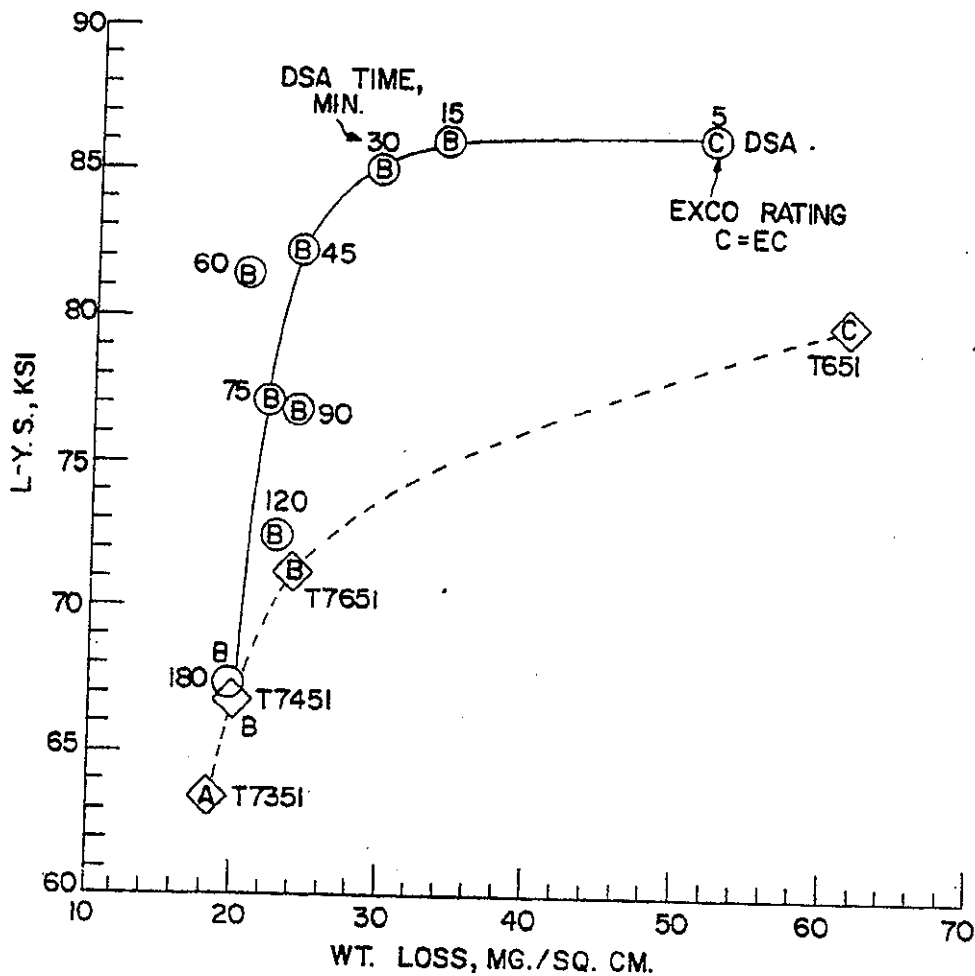


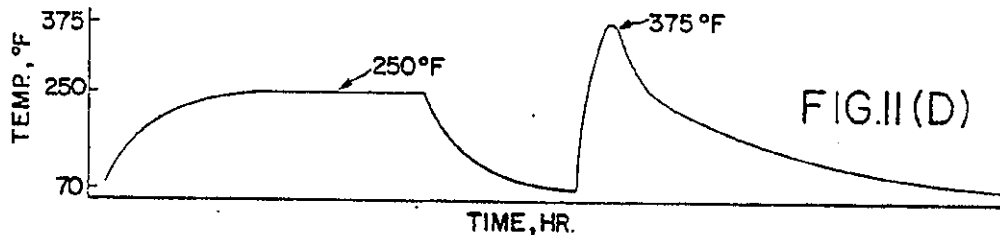
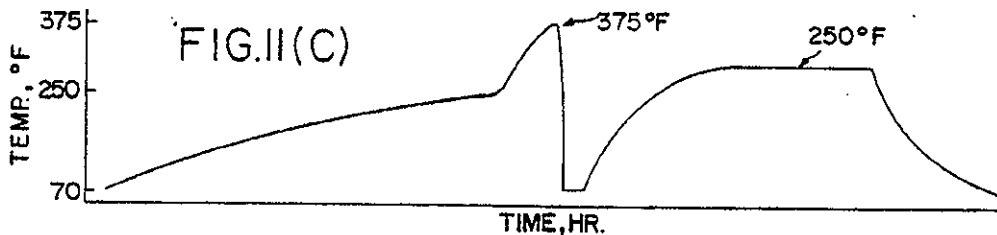
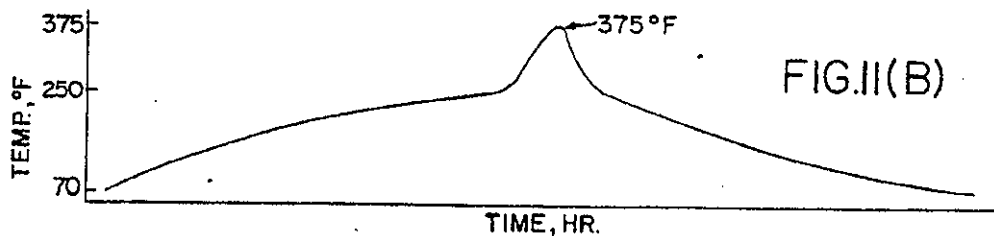
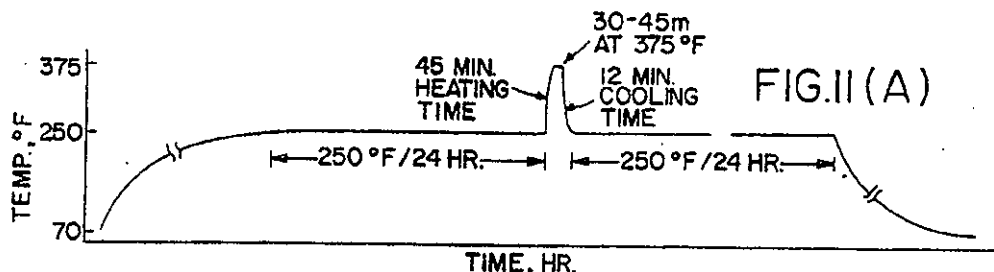
FIG.10

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HEAT TREATMENT OF PRECIPITATION HARDENING ALLOYS: CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of U.S. patent application Ser. No. 07/019,995 filed Feb. 27, 1987, now abandoned.

DESCRIPTION

1. Technical Field

This invention relates to the heat treatment of precipitation hardening alloys, particularly those of aluminum.

2. Background Art

Although high-solute alloys of the 7000 series (Al-Zn-Mg-Cu) aluminum alloys provide high strength and stiffness, they are susceptible to exfoliation and stress-corrosion cracking (SCC) when aged to the near peak strength T6-type tempers. Optimization of chemical composition and thermal treatments to improve the corrosion resistance became a major emphasis in alloy development. An important outcome was the discovery of T76 and T73 type tempers (See Sprowls, D. O. and Brown, R. H., *Metals Progr.*, Vol. 81 (1962), p. 77), which provide increased resistance to exfoliation and SCC through overaging. However, these treatments also result in a 11-17% loss in strength for 7075 and 7×50 alloys.

In 1974, Cina of Israeli Aircraft Company disclosed a three-step aging treatment, known as Retrogression and Reaging (RRA) which employed 3 steps, one at about 250° F., followed by a very brief (typically 30 second) step at a higher temperature such as around 420° F., followed by a third step at about 250° F. See: Cina, B. and Ranish, B., "New Technique for Reducing Susceptibility to Stress Corrosion of High Strength Aluminum Alloys" in *Aluminum Industrial Products*, Pittsburgh Chapter, ASM, 1974 October; Cina, B. in *Second Israel-Norwegian Technical and Scientific Symposium, Electrochemistry and Corrosion* (Norway, 1978 June); and U.S. Pat. No. 3,856,584; Dec. 24, 1974.

M. H. Brown (British Patent 1,480,351 of Jul. 20, 1977; U.S. Pat. Nos. 4,477,292 of Oct. 16, 1984 and 4,832,758 of May 23, 1989) of Alcoa Laboratories developed three-phase low-high-low, temperature agings that held an advantage over Cina's in using longer times and generally lower temperatures for a second (higher temperature) aging which was more applicable to commercial aging furnaces.

DISCLOSURE OF INVENTION

An object of the invention is to provide improved three-phase aging treatments for precipitation hardening alloys in general and particularly for alloys of the 7×××, also termed the 7000, series of alloys of aluminum, especially the aluminum alloys 7075 and 7050.

Another object is to provide a precipitation hardened alloy combining essentially T6 yield strength with essentially T7 corrosion resistance. In general, T6 refers to the condition of a precipitation hardening alloy in which it has been aged directly substantially to peak strength. T7 refers to a condition where corrosion resistance has been improved. In the past, strength had been sacrificed, in achieving a T7 condition. Other numbers may follow the "6" or "7" to indicate variations.

According to the invention, a specific aging sequence, which we refer to as DSA (Desaturation Ag-

ing), was found to develop unique material characteristics.

In a nutshell, our aging sequence comprises a three-phase aging of solution-heat-treated precipitation hardening alloy. In the first phase, we age to a point still significantly below peak strength. We believe this forms a uniform, fine distribution of islands of increased concentration of alloying elements. This is followed by a higher temperature aging phase wherein we increase the resistance to corrosion. We believe this second phase increases stability of the islands formed in the first phase, and, during it, elements are moved to the islands to decrease the electrochemical difference between grain boundaries and grain interiors (matrix). The third aging is performed at temperatures lower than the second phase to develop added strength and resistance to corrosion. We believe this strength is achieved by exploiting residual supersaturation.

The benefits of the invention may be thought of in the following way. The invention provides aging treatments for solution heat treated, precipitation hardenable alloys that permit attainment of various levels of corrosion resistance matching those of prior art tempers. For a given level of corrosion resistance, material treated according to the invention will tend to have significantly higher strength than those processed by conventional aging practices.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 presents L-YS vs. EC and EXCO ratings for aging according to the invention ("DSA"), as compared to conventional tempers, for 0.92 in. thick solution heat treated 7150 plate.

FIG. 2 is a graphical representation of four aging regimes of the invention for 0.965 in. 7150 plate.

FIG. 3 presents cooling curves from 375° F. (See FIG. 2).

FIG. 4 provides L-YS vs. EC for the invention and standard tempers, discontinuous, 3 min. to 375° F. (See FIG. 2A).

FIG. 5 presents L-YS vs. EC for the invention and standard tempers, discontinuous, 11 min. to 375° F. (See FIG. 2B).

FIG. 6 gives L-YS vs. EC for the invention and standard tempers, continuous, 45 min. to 375° F. (See FIG. 2C).

FIG. 7 is L-YS vs. EC for the invention and standard tempers, discontinuous, 38 min. to 365° F. (See FIG. 2D).

FIG. 8 is a chart of S-L (Short-transverse directional load, Longitudinal direction of crack propagation) K_{Ic} (measure of toughness) vs. L-YS for the invention and standard tempers, discontinuous, 11 min. to 375° F. (See FIG. 2B).

FIG. 9 is for the invention of 1.5 in. plate, L-YS vs. EC, including exfoliation ratings, compared to standard tempers;

FIG. 10 charts results of the invention applied to 1.5 in. plate in terms of L-YS vs. wt. loss, compared to standard tempers.

FIG. 11 is a schematic presentation of temperature-time plots.

MODES OF CARRYING OUT THE INVENTION

Examples of precipitation hardening metal alloys which may benefit from the principles of the invention are as follows:

Aluminum and magnesium alloys

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Inconel 718
 Fe-Al-Mn alloys
 Cu-Be alloys
 Certain steels, such as 0.2% C, 3.83% Mo, and 0.22% Ta, remainder essentially Fe, where secondary hardening is a precipitation hardening phenomenon
 Certain chromium steels, such as that containing 0.1% C, 12% Cr, 2% Ni, 0.02% N, remainder essentially Fe

In the case of magnesium alloys, examples of precipitation hardenable alloys are those based on the combination of magnesium with zinc.

The present invention is particularly advantageous in the case of the 7××× series of aluminum alloys.

The 7××× series of aluminum alloys has, in general, a composition as follows: 4 to 12%, typically 4 to 8%, zinc, 1.5 to 3.5% magnesium, 1 to 3.5% copper, and at least one element from the group chromium at 0.05 to 0.35%, manganese at 0.1 to 0.7%, and zirconium at 0.05 to 0.3%, the alloy further permitting the presence of titanium at 0 to 0.2%, iron at 0 to 0.5%, silicon at 0 to 0.4%, boron at 0 to 0.002%, beryllium at 0 to 0.005%, others each at 0 to 0.05%, others total at 0 to 0.15%.

The invention is especially applicable to the 7×50 subseries of the 7××× series, examples being the 7050 and 7150 alloys. The composition of 7050 is about as follows: 5.7 to 6.7 zinc, 1.9 to 2.6% magnesium, 2.0 to 2.6% copper, zirconium at 0.08 to 0.15%, the alloy further permitting the presence of titanium at 0 to 0.06%, iron at 0 to 0.15%, silicon at 0 to 0.12%, others each at 0 to 0.05%, others total at 0 to 0.15% balance essentially aluminum. Alloy 7150 is a variant of 7050 with zinc, magnesium and copper in the ranges 5.9 to 6.9% zinc, 2 to 2.7% magnesium and 1.9 to 2.5% copper. Particular examples of 7×50 compositions appear in Tables I and II herein. A general composition for 7050 and 7150 (7×50) contains about 5.7 to 6.9% Zn, 1.9 to 2.7% Mg, 1.9 to 2.6% Cu, 0.08 to 0.18% Zr, balance essentially Al and impurities. These alloys are described in U.S. Pat. No. 3,881,966, which is incorporated here by reference.

Composition ranges of aluminum alloys in general, are published in:

1. Registration Record of the Aluminum Association Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys, by the Aluminum Association, Inc., Washington, D.C., Rev. Jan./89, and

2. Aluminum standards and data 1988, from the same association.

Typical temperature and times for practicing the invention for 7××× aluminum alloys are a first step of 175° to 325° F. generally in terms of hours, but not including combinations of time and temperature achieving peak strength, followed by 360° to 395° F. in terms of minutes to hours, and then 175° to 325° F. again in terms of hours.

Products in accordance with this invention may be formed by the various techniques for producing metal products. Examples of such techniques are rolling, forging, extruding or any other metal working operations. Accordingly, the alloy products produced may include sheet, plate, extrusions, forgings or rods, bars or any other shapes.

The improved products of the invention are produced by providing an ingot or other suitable working

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stock from the alloy compositions and working said stock into the desired product, shape or configuration. Prior to working, the working stock can be homogenized by heating to a suitable high temperature, typically between about 860° and 920° F. The alloy may also be cast into final shape, although wrought or worked products are preferred. After desired working or shaping, the alloy is solution heat treated by heating to one or more elevated temperatures from about 840° or 850° F. to about 880° or 900° F., or at still higher or lower temperatures depending on alloy composition. The solution heat treatment is carried out to take into solid solution substantial portions of the alloying elements, preferably substantially all of the zinc, magnesium and copper in the case of the 7×50 aluminum alloys. It is to be recognized that physical processes are often not perfect such that every last vestige of these alloying ingredients may not be dissolved. Nonetheless, it is preferred where toughness and fatigue properties are concerned that not more than about one or two volume percent, preferably 0.5 vol. % or less, of undissolved intermetallic phases over one micron in size containing Zn, Cu and/or Mg remain in the alloy product after solutionizing.

After the aforesaid heating for solutionizing, the alloy is rapidly cooled or quenched by immersion or other suitable treatment in a quenching medium. This usually includes immersing in water, although water sprays or even air chilling may be useful in this respect. After quenching and prior to aging for precipitation hardening, the alloy may be cold worked such as by stretching to relieve internal stresses. The solution heat treated and quenched alloy, with or without cold working, is then considered to be in a precipitation-hardenable condition.

The precipitation-hardenable alloy is then aged in three steps, phases or treatments, although there may not be clear lines of demarcation between steps or phases. That is, it is known that ramping up to a particular aging temperature and ramping down therefrom are in themselves precipitation treatments which can, and often need to be, taken into account by integrating them, and their precipitation-hardening effects, in the treatment. This effect is described in U.S. Pat. No. 3,645,804, which is incorporated herein by reference. Thus while the three phases of aging according to this invention can be effected in a single furnace operation, properly programmed, they are described herein for purposes of convenience as three phases or treatments. In accordance with the invention, the first phase or treatment precipitation hardens the alloy, but not to peak strength. Then the second phase treats the alloy at an elevated temperature to increase resistance to exfoliation corrosion and stress corrosion cracking (SCC). Then the third phase further precipitation hardens the alloy to a high strength level.

In the first phase, the alloy is precipitation hardened to strengthen it to a point substantially less than peak strength (an underaged strength). This is believed to form a uniform, fine distribution of islands of increased concentration of alloying elements. This first aging can be effected in the case of 7000-series aluminum alloy by treating at one or more temperatures between something above room temperature and about 325° F. or 330° F., preferably between about 175° F. and 325° F. This treatment typically can extend a significant period of time, typically between about 2 to 30 or more hours and can occur through a temperature ramp-up to an

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elevated temperature for the second treatment phase. This precipitation hardening should strengthen the alloy product substantially over the strength achieved immediately after the quenching of the solutionizing treatment (herein referred to as the as-quenched strength or solution treated strength) by at least 30% of the difference between as-quenched strength and peak yield strength, preferably to about 40% or 50% or more, for instance 60% or 70% or more of the difference between the as-quenched strength, or solution treated strength, and peak strength (the solution-peak strength differential) for the alloy product. Putting it another way, the precipitation-hardening of the alloy entering the second phase or treatment should have carried (increased) the product's strength by at least 30% (preferably more) of the way from as-quenched or solution treated strength (low strength) toward the peak strength.

The first phase can extend until the strength reaches up to about 95% of peak strength, although preferably in the case of 7000-series aluminum alloy, the strength reaches a point substantially below peak yield strength, such point being at least 3, 4, 5, and even 6 ksi or more below peak yield strength.

The alloy in the condition reached by the first phase of the aging treatment is then subjected to the second phase or treatment, in the case of 7000-series aluminum alloy, at one or more higher temperatures of about 325° or 330° or more, for instance above about 340° F. or 350° F., preferably at one or more temperatures within the range of about 360° F. to about 500° F., preferably for more than a few minutes but preferably not more than 3 hours, higher temperatures generally favoring shorter times. In general, temperatures of 360° F. or higher are preferred. The temperatures employed in the second phase normally exceed those in the first and third phases. One preferred second phase treatment for 7×50 aluminum alloys is within 360° F. to 400° F. for about 5 minutes to 2 or 2½ or 3 hours, the time depending somewhat on temperature with higher temperature favoring shorter times. The second treatment phase increases resistance to stress corrosion cracking (SCC), exfoliation and other corrosion effects. Excessive time-temperature exposure in this phase can impede the desired strength gain from the subsequent third aging phase. The second phase serves to increase the stability of the islands of increased alloying element concentration achieved in the first phase and moves additional alloying elements to the islands to decrease the electrochemical difference between grain boundaries and grain interiors.

In some embodiments of the invention, the second treatment phase proceeds by subjecting the alloy to treatment at several different temperature levels producing a cumulative time and temperature effect corresponding to an isothermal treatment within the aforesaid temperature ranges. For instance, the effects of this treatment for a particular alloy can commence at a temperature of about 345° or 350° F. and continue as the temperatures are further increased such that "ramping up" and/or "ramping down" of temperatures between about 345°, 350° or 355° F. and higher temperatures within the aforesaid range. The effect of the different times at the different temperatures can be taken into account and integrated into determining the equivalent aging effect, using the teachings of the above cited U.S. Pat. No. 3,645,804. Such treatment may proceed, for instance, for 3 or more minutes at one or more tempera-

tures between about 360° and 490° F.; for 4 or more minutes at one or more temperatures between about 360° and 480° F.; or for 5 or more minutes at one or more temperatures between about 360° and 475° F. When referring to heating to one or more temperatures for a time of "x" minutes, such embraces heating to any number of temperatures in the designated range but for a cumulative time of "x" above the lowest temperature in the range. For instance, heating for 5 or more minutes at one or more temperatures from about 360° to 475° F. does not require holding for 5 minutes at each of several temperatures in said range, but rather, that the cumulative time at all temperatures between 360° and 475° F. is 5 minutes or more.

The second phase or treatment can be carried out by immersion in hot liquid such as molten salt, hot oil or molten metal. A furnace (hot air and/or other gases) may also be used. One advantageous practice utilizes a fluidized bed for the second treatment. Suitable media for the fluidized bed include alumina particles of about 50 or 60 mesh. The fluid bed heating media can provide fairly rapid heating (faster than a hot air furnace but slower than molten salt) and uniform heating of large or complex parts while presenting easier clean-up and environmental aspects than some other approaches. Induction heaters may also be used in the practice of the invention.

As indicated elsewhere herein, heating operations can be ramped-up fairly slowly such that much or even all of the treatments, especially the precipitation-hardening treatments of the first and/or third phases, can be accomplished by or during ramping-up to and/or -down from the elevated second phase temperature or temperatures such that there may not be discrete disruptions or interruptions between phases. However, the second phase can be considered to start when the corrosion properties start to improve. This typically involves some time at temperatures of about 340° or 350° or 360° for so, in the case of 7000-series aluminum alloy, or more, after achieving the strengthening described (precipitation-hardening) in the first phase as mentioned hereinbefore. In some embodiments, the second phase can be considered accomplished when the desired degree of corrosion resistance is achieved and the temperature is suitably lowered for third phase precipitation-hardening. However, in some cases, the corrosion resistance can improve in the third phase such that the second phase can be shortened to a level less than the desired corrosion resistance to allow for this effect.

The alloy is then precipitation hardened in the third treatment or phase, typically, in the case of 7000-series aluminum alloy, at one or more temperatures between something above room temperature and about 325° or 330° F., typically from about 175° to 325° F. In the third phase, the aging exploits residual supersaturation to develop added strength. This precipitation-hardening step may proceed at substantially the same general level of temperature or temperatures employed in the earlier (first phase) precipitation-hardening operation. The times employed are about 2 to 30 or more hours. It is quite desirable in this third phase to utilize substantial exposures, typically for several hours, at one or more temperatures substantially below the higher (or highest) temperatures used in the second phase. During this precipitation-hardening phase, the strength of the product is increased to a very high level, above that accompanying the improved corrosion resistance achieved in

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the second phase and typically to the desired final yield strength level.

As can be seen from the foregoing, either or both preprecipitation-hardening phases and/or the intermediate higher temperature treatment can be performed at one or more temperatures by ramping up and/or down within a particular temperature range. As is generally recognized in the art, integration of aging effects under ramp-up or ramp-down conditions is useful in determining the total aging effect as described in U.S. Pat. No. 3,645,804, the disclosure of which is incorporated herein by reference.

It is preferred that the second phase treatment not be carried for time-temperature combinations excessively exceeding the extent needed to develop the desired level of corrosion resistance properties. Use of excessive time-temperature exposure in the second phase can impede the ability of the third phase to achieve the desired high level of strength. Also, it may be of advantage in some cases to rapidly cool the product after a desired amount of treatment. Such cooling can be relatively drastic, such as by water quenching (immersion or sprays), or less drastic, such as by removal from the furnace and air or forced air (fans) cooled. Some advantage to rapid cooling from the second treatment, or rapid heating at the commencement of the second phase, can arise in some cases because of improvement in control of time and temperature. Thus, while ramping-up to and/or down from a temperature (more or less gradual heat-up and cool-down) can be employed, especially if ramp-up and ramp-down effects are appropriately accounted for, nonetheless, it may be advantageous in some cases to utilize rapid heat-up and/or rapid cool-down in one or more treatment phases, for instance in the second phase.

Among the advantages achieved by the present invention, is that its aging process for precipitation hardening metal alloys provides a means by which strength and resistance to intergranular corrosion (hence the resistance to exfoliation and to SCC) can be improved simultaneously. Corrosion resistance has been substantiated, EXCO, and alternate immersion testing. Treatment according to the invention appears commercially feasible and applicable particularly in the case of 7×50 aluminum alloy plate and other 7×50 products. Thus, it has been found that plate of 7050 and 7150 aluminum alloys responded favorably to three-step aging treatments of the invention consisting, for example, of an underaged first step aging (e.g. 250° F./24 hr), a high temperature (e.g. 360° F.-375° F.) second step, followed by a third step aging similar to the first step. The resulting combination of strength and corrosion resistance is significantly better than that of conventionally aged plate.

The response of product treated according to the invention is relatively insensitive to small compositional differences, the presence or absence of stretcher stress-relief, variations in second step heat-up times, and cooling rate from the second step. For instance, in the case of 7×50 plate, aging results were not affected by slight Zn, Mg and Cu composition difference in alloys 7050 and 7150, by presence or absence of stretcher stress-relief, by second step heat-up times of from 3 to 45 minutes, or by significant variations in cooling rate from the second step temperature.

Conclusions regarding the resistance to SCC of material treated according to the invention, for instance 7×50 plate, to alternate immersion SCC tests have been confirmed by results of DCB (Double Cantilever Beam)

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and breaking load tests and by the results of similar SCC tests in seacoast atmosphere.

A very important advantage of the invention resides in the provision of process technology achieving or surpassing previously attained strength levels at improved levels of corrosion resistance. For instance, the aging treatment of the present invention achieved the 7050-T651 strength level combined with a one letter grade improvement in EXCO exfoliation resistance rating and consistent improvement in resistance to SCC. Treatment of 7×50 material to achieve a level of resistance to exfoliation corrosion and SCC similar to that of the T7651 temper resulted in a strength increase of between 5.7 ksi and 10.2 ksi, average 8.5 ksi, which is a 12% improvement in strength. Similarly, as much as 10.1 ksi or 15% improvement in strength with respect to T7451 appear possible through the aging treatment of the invention.

In the case of 7×50 aluminum alloy, there is no sacrifice in the fracture toughness/yield strength relationship as compared with conventional aging.

EXAMPLES

Further illustrative of the invention are the following examples.

In General

In the examples the following applies in general.

In all aging treatments discussed below, heating rate and temperature were monitored by insertion of iron-constant thermocouples in mid-thickness of samples. All temperatures are to ±2° F.

Aging practices for standard "T" tempers of aluminum alloys can be found in:

1. MIL-H-6088E of the United States Department of Defense, and
2. Tempers for Aluminum and Aluminum Alloy Products Registered with the Aluminum Association, by the Aluminum Association, Washington, D.C., Sep. 1, 1984.

Unless indicated otherwise, tests herein were done as follows:

1. Stress Corrosion Cracking (SCC) Alternate Immersion Test:

To determine stress-corrosion resistance, short-transverse, ½ inch (3.2 mm) diameter specimens were stressed in constant strain fixtures. The fixtures are described in ASTM Standard G44-75. Both the control and test specimens were exposed by an alternate immersion test comprising ten minutes immersion in 3.5% aqueous NaCl solution and a 50-minute drying cycle. Stresses were maintained constant ksi (kilopounds per square inch) values throughout the tests.

2. EXCO Test:
ASTM Standard G34-72.
3. Toughness Test:
Standard Test Method for Plain Strain Fracture Toughness of Metallic Materials, ASTM-E399.
4. Tensile Test:
Standard Method of Tension Testing for Wrought and Cast Aluminum and Magnesium Alloy Products, ASTM-B557.

5. Electrical conductivity (EC) values were determined as % of International Annealed Copper Standard (IACS), using a Magnaflux FM100 Eddy Current Conductivity Meter.

EXAMPLE SET I

In this set of examples, 0.92 in. thick 7150 alloy (composition as set forth in Table I), in the form of solution heat treated plate, was in accordance with the invention subjected to an underaged first step of 225° F. or 250° F. for 24 hours, second step of soak at 375° F. for 30–90 minutes (rapidly brought to the prescribed soaking temperature –3 min. heating time) followed by water quenching and third step aging at 250° F. for 24 hours. All aging experiments were carried out in air furnaces. The plate was obtained by re-solution heat treating plant produced 7150-T651 plate, quenching and aging in accordance with the invention.

Electrical conductivity, longitudinal tensile properties and EXCO ratings were obtained for the samples treated according to the invention. For comparison with conventional tempers, a T6-type aging curve was generated, along with standard T76 and T74 (formerly T736) tempers. Table III and FIG. 1 present the longitudinal yield strength, electrical conductivity and exfoliation data generated in Set I. The advantage of the invention for improved combinations of strength and exfoliation performance is clear. When the plate is treated by the invention to the T6 strength level, about 2% IACS higher EC is observed relative to conventional aging.

EXAMPLE SET II

Four different lots of 0.965 in. thick 7150 plate were solution heat treated, spray quenched and stretched. Each lot was given a different regime of aging treatment in accordance with the invention, and standard tempers were generated from each lot to address the issue of lot-to-lot variability. All aging treatments involved a first and third step of 250° F. for 24 hours. The second step was varied in four ways and all treatments were carried out in air furnaces. The four regimes are depicted in FIG. 2 and detailed below. The term “discontinuous” refers to the specimens reaching room temperature between the steps; such appears in FIGS. 2A, 2B, and 2D. In the “continuous” example shown in FIG. 2C, movement is from one temperature directly to the next, without interposition of a room temperature residence.

In the regime shown in FIG. 2A, samples were first step aged at 250° F. for 24 hours and air cooled to room temperature. Using a 1000° F. heatup furnace, they were heated essentially up to the 375° F. second step in 3 minutes (as determined by a thermocouple in the center of the specimen), then transferred to a holding furnace operating at 375° F. and held for 30–120 minutes and water quenched. In addition to water quenching, the DSA-60 (For brevity, a DSA treatment of (250° F./24 hr +375° F./X min +250° F./24 hr) will be referred to as DSA-X; thus, DSA-60 represents 60 minutes at 375° F.) condition of the invention also was air cooled from 375° F. All samples were subsequently third step aged at 250° F. for 24 hours and air cooled.

In the regime as shown in FIG. 2B, all experimental conditions were exactly the same as in “A” except for the use of a different heating rate to the second step. A 500° F. heatup furnace was used which gave an 11 minute heatup time to 375° F.

In the regime of FIG. 2C, a programmable air furnace was used. Upon completion of the first step of 250° F. for 24 hours, the furnace temperature was raised to 375° F. in 45 minutes on a logarithmic time scale. After

holding at 375° F. for 30–180 minutes, samples were immediately transferred to another furnace already stabilized at 250° F. and held for 24 hours. Hence, this continuous aging regime does not involve transition to room temperature between first and second and second and third step aging treatments.

In the regime shown in FIG. 2D, samples were given the first step treatment of 250° F. for 24 hours and air cooled to room temperature. Then they were placed in a 365° F. furnace and heated to temperature in 38 minutes. Upon soaking for 30–60 minutes, they were transferred to a 250° F. furnace, held for 24 hours and then air cooled.

Tensile properties, electrical conductivity and EXCO ratings were obtained for all examples of the invention and standard tempers. Selected samples from regime “B” (discontinuous, 11 minute heating time to 375° F.) were evaluated for plane strain fracture toughness (K_{Ic}) and for resistance to SCC by alternate immersion using C-rings (0.75 in. OD and length, 0.060 in. thickness) stressed to 35 and 45 ksi with five replicates for each stress level. DSA-60 was evaluated for resistance to fatigue crack growth.

The second step heating rates (70° F.–375° F.) for regimes (A) and (B) (see FIG. 2) were substantially linear, and those for regimes (C) (250° F.–375° F.) and (D) (70° F.–375° F.) were substantially logarithmic. The second step cooling curves for cold water quenching (375° F.–80° F.), air cooling (375° F.–80° F.) and furnace cooling (375° F.–250° F.) are presented in FIGS. 3a, b and c, respectively.

The DSA practice of the invention and standard practices plus the corresponding electrical conductivity (EC), longitudinal tensile properties, EXCO ratings and weight loss for regimes (A), (B), (C) and (D) are given in Tables IV, V, VI and VII. These data are plotted (except weight loss) in FIGS. 4, 5, 6 and 7, respectively. Also given in Table V are SCC and K_{Ic} data for regime (B) (discontinuous, 11 minutes to 375° F.). The latter is plotted in FIG. 8 as a function of yield strength. Evaluation for resistance to fatigue crack growth (da/dN) showed DSA-60 to be comparable, but somewhat better, than T651.

Examination of FIG. 4 shows the DSA tempers of the invention exhibit a displaced strength/EC relationship with respect to the standard tempers aged from the same production lot. The DSA and standard tempers can be compared in two manners: (a) conductivity and EXCO rating for a particular strength level of interest, and (b) strength at the conductivity or EXCO rating of interest. For example, a horizontal line at 84 ksi first intersects the “standard tempers” at 36.7% IACS with an EXCO rating of EC. The intersection at the same strength level of 84 ksi with the “DSA tempers” occurs at 38.8% IACS, with an EXCO rating of EB. Hence, treatment according to the invention results in one grade improvement (EC to EB) in EXCO rating at T6 strength for this lot of material. Alternatively, for a vertical line at a conductivity of 39.8% IACS, the invention shows an advantage of 6 ksi strength with the same EXCO rating of EB.

As shown in FIGS. 4 to 7 and Tables IV to VII, the four different regimes all show that the strength/EC relationship for the material of the invention is displaced towards higher EC and higher strength. This is accompanied by an improvement in EXCO rating with respect to the standard tempers, FIGS. 7 through 11. A larger displacement is observed at low EC (where su-

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persaturation is still high) and the displacement diminishes at high EC (where overaging has taken place).

This displacement of strength/EC relationship along with improvement in EXCO rating is quite similar for heating times from 3 minutes to 38 minutes to the second step temperature (see FIGS. 4 to 7). Even the continuous DSA treatment had the similar displacement when compared to the standard tempers aged from the same lot.

Material treated according to the invention to the T651 strength level consistently shows an improvement in EXCO rating similar to the rating for conventional T7651 plate as shown in FIGS. 4 through 7.

Both DSA-type and standard tempers possess the same K_{IC} -yield strength relationship as shown in Table V and FIG. 8, it bearing repeating that for a given strength-toughness level the DSA material exhibits better corrosion resistance.

Conventional aging beyond peak strength typically results in overaging, characterized by EC increase and strength loss. In the invention, the third step can result in an EC increase of about 0.6-1.1% IACS, but is always accompanied by a strength increase. This suggests the precipitation of a strengthening phase(s) more than compensates for any loss in strength that could be caused by concomitant coarsening or overaging during the third step. The effect of the third step on EC and strength should be dependent on the microstructure and the residual supersaturation after the second step.

EXAMPLE SET III

Procurement of plant fabricated, heat treated and stretched 1.5 in. thick 7050-W51 plate as the starting material permitted the use of short-transverse tensile specimens in alternate immersion SCC tests to determine SCC resistance.

The type of treatment of the invention employed in these examples comprised first step underaging in an air furnace at 250° F. for 24 hours, air cooling, second step aging in an electrically heated oil bath (Dow Corning 200 fluid) at 375° F. for 15-180 minutes, air cooling and third step aging at 250° F. for 24 hours. The second step heatup time from 70°-375° F., following immersion of the 4-inch wide by 8-inch long by 1.5-inch thick sample into the oil bath was 7-minutes (temperature was considered to have been achieved when the thermocouple read to within 5° F. of 375° F., in view of the asymptotic character of the approach to temperature) in a logarithmic manner. A motorized agitator was placed at the bottom of the bath to ensure temperature uniformity. Drop in bath temperature was less than 2° F. Cooling from 375° was by air cooling which is expected to be similar to previously experienced cooling rate shown in FIG. 3b.

As before, conventional tempers were produced for comparison. Those were T651, T7651, T7451 and T7351 tempers. Longitudinal tensile properties, EXCO ratings and weight losses were obtained for all DSA and conventional tempers. In addition, the following tests were performed to evaluate the resistance to SCC of selected material conditions:

- (1) 30-day alternate immersion (ASTM G44-75) in 3.5% NaCl solution at stresses of 35 and 45 ksi using short-transverse 0.125 in. dia. tensile specimens with 5 replicates per stress level.
- (2) One-year exposure to seacoast atmosphere at Point Judith, R.I., of short-transverse tensile speci-

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mens stressed at 35 and 45 ksi, 5 replicates per stress level.

- (3) Breaking load test of samples subjected to AI stressed at 0, 25, 35, and 45 ksi exposed for 0, 2, 4 and 6 days with 5 replicates per condition.

In addition, coupons were exposed at Point Judith for one year to evaluate resistance to exfoliation.

The chemical composition of the plate material used in this set of examples was within Aluminum Association limits for 7050. See Table II.

L-YS and EC results are listed in Table VIII and plotted in FIG. 9. As in the previous set of examples, the DSA curve of the invention in FIG. 9 is shifted towards higher strength and EC with respect to the conventional aging curve. At the T651 strength level, the aging treatment of the invention results in 1.7% IACS higher EC, and, at the same EC as T651, aging according to the invention yields about a 5 ksi strength advantage. At the T7651 strength level, the EC increase through the invention is reduced to about 0.8% IACS, but, at the same EC as T7651, the 5 ksi strength advantage through the invention is maintained. Similar comparisons may be made for other tempers.

EXCO ratings and weight loss results are contained in Table VIII. EXCO ratings and DSA times are superimposed on the L-YS versus EC plot in FIG. 9 and the L-YS versus weight loss plot in FIG. 10.

Although the DSA-5 plate is equally susceptible to exfoliation corrosion as the T651 plates, the DSA-5 plate has a 6 ksi L-YS strength advantage. Both of these plates were rated EC in the EXCO test and had high weight loss (difference in weight per unit exposed area between unexposed sample and exposed condition of the same sample with corrosion products removed), as shown in FIGS. 9 and 10 and Table VIII. Material given DSA-15 and DSA-30 treatments exhibited distinctly improved exfoliation resistance relative to the T651 plate along with a 5-6 ksi strength increase; EXCO rating was improved from EC to EB and the corresponding weight loss from about 60 mg/cm² to about 30 mg/cm². It should be noted that one letter grade improvement in EXCO rating is quite significant due to the coarseness of the rating scale, as is evident from the reduction in weight loss (FIG. 10).

At an exfoliation-performance level comparable to T7651 as measured by EXCO rating and weight loss, about a 10 ksi strength advantage is possible through the DSA treatment of the invention, e.g., DSA-45 and DSA-60 (FIG. 10).

The shapes of the two curves in FIG. 10 are of interest. It appears that for both DSA and standard aging schemes, weight loss dramatically increases above a critical strength level with concomitant degradation in EXCO rating. This critical strength is of the order of 85 ksi for DSA, but only about 75 ksi or less for standard aging.

The 30-day AI SCC test results are presented in Table IX.

The results of 30-day AI SCC test in this study show that T651, DSA-5 and DSA-15 all are quite susceptible to SCC under sustained stress levels of 35 and 45 ksi. All samples of these three conditions failed within 3 days of exposure. DSA-60 (YS = 81.4 ksi) compares favorably with T651 (YS = 79.9 ksi): with 1.5 ksi strength advantage, it is more resistant to SCC. The T7651 plate (YS = 71.2 ksi) is intermediate in performance with respect to DSA-60 and DSA-90 (YS = 76.9 ksi), suggesting that aging according to the invention results in a strength

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advantage of between 5.7 ksi and 10.2 ksi at a SCC resistance level comparable to T7651. L-YS versus days to first failure of 5 replicates stressed at 45 ksi leads to a similar conclusion: With a level of resistance of SCC comparable to T7651, DSA results in 8.5 ksi strength advantage, which is a 12% improvement in strength. The AI results also indicate that the difference in performance between T7451 and DSA-90 conditions is not statistically significant: both tempers show a high level of SCC resistance. However, in comparison with T7451, DSA-90 is 10.1 ksi higher in YS, which is a 15% improvement in strength.

One year of exposure to seacoast atmosphere at Point Judith was completed and substantiated the strength improvement of DSA-90 compared with T7651 Results as of somewhat over three months are presented in Table VIII, and are in agreement with the 30-day accelerated AI SCC test results.

The breaking load results are presented in Table IX. The breaking load data support the conclusion that treatment according to the invention provides increased strength at the same or improved resistance to SCC.

In defining the present invention, it has been divided into three phases or steps for the sake of convenience. The phases may in practice merge with one another. For instance, the first and second phases, all three phases, or the second and third phases may merge to form a single phase. These ideas are illustrated in FIG. 11. Consider, for instance, FIG. 11(a), representing FIG. 2(C), one of the proven successful processing routes. All three steps were carried out continuously without cooling down to room temperature. In short, the entire procedure may be described as [L+H+L], where "L" and "H" mean "low" and "high", respectively. By smoothing the transitions between L, H and L, which is readily done in a programmable furnace, these three steps can be made to appear as a one-step process, while still containing the essence of all three stages. This situation, [LHL], is shown in FIG. 11(b). Similarly, an apparent two-step treatment by combining L and H and keeping the final step separate, the situation of [LH+L], is possible, FIG. 11(c). Of course, another two-step procedure, [L+HL], as shown in FIG. 11(d), is just as easily done.

What is claimed is:

1. An aging process for solution-heat-treated, precipitation hardening metal alloy, comprising the steps of aging the alloy to a point substantially below peak yield strength to form a uniform, fine distribution of islands of increased concentration of alloying elements, subsequently aging the alloy at a higher temperature or temperatures for increasing the stability of the islands and for moving elements to the islands to decrease the electrochemical difference between grain boundaries and grain interiors, and thereafter aging the alloy at one or more temperatures below said higher temperatures for exploiting residual supersaturation to develop added strength.

2. An aging process as claimed in claim 1, the alloy being an aluminum alloy.

3. An aging process as claimed in claim 2, the aluminum alloy being a 7000-series aluminum alloy.

4. An aging process as claimed in claim 3, the aluminum alloy being a 7×50 alloy.

5. An aging process as claimed in claim 2, said point being at least 3 ksi below peak yield strength.

6. An aging process as claimed in claim 5, said point being at least 4 ksi below peak yield strength.

7. An aging process as claimed in claim 6, said point being at least 5 ksi below peak yield strength.

8. An aging process as claimed in claim 7, said point being at least 6 ksi below peak yield strength.

9. An aging process as claimed in claim 1, both yield strength and resistance to intergranular corrosion being improved by the process.

10. An aging process as claimed in claim 1, the process providing at least, or better than, T6 yield strength combined with T7 corrosion resistance.

11. An aging process as claimed in claim 4, the aging step at a higher temperature or temperatures being carried out at or above about 330° F., the aging steps for forming the islands and exploiting residual supersaturation being carried out below about 330° F.

12. An aging process as claimed in claim 11, the aging steps for forming the islands and exploiting residual supersaturation being carried out below about 295° F.

13. An aging process for solution-heat-treated, precipitation hardening 7×××-type aluminum alloy, comprising (1) aging the alloy at one or more temperatures substantially above room temperature but below about 325° F. to substantially below peak yield strength, (2) subsequently aging the alloy at one or more temperatures of about 330° F. for higher for increasing resistance of the alloy to corrosion, and thereafter (3) aging the alloy at one or more temperatures substantially above room temperature but below about 325° F. for increasing yield strength.

14. An aging process as claimed in claim 13, the aluminum alloy consisting essentially of about 5.7 to 6.9% Zn, about 1.9 to 2.7% Mg, about 1.9 to 2.6% Cu, about 0.08 to 0.18% Zr, balance substantially aluminum and incidental elements and impurities.

15. An aging process as claimed in claim 13, wherein, in said recitation (1), said aging is to 3 ksi or more below peak yield strength.

16. An aging process as claimed in claim 13, wherein, in said recitation (1), said aging is to 4 ksi or more below peak yield strength.

17. An aging process as claimed in claim 13, wherein, in said recitation (1), said aging is to 5 ksi or more below peak yield strength.

18. An aging process as claimed in claim 13, wherein, in said recitation (1), said aging is to 6 ksi or more below peak yield strength.

19. An aging process as claimed in claim 13, both yield strength and resistance to intergranular corrosion being improved by the process.

20. An aging process as claimed in claim 13, the process providing at least, or better than, T6 yield strength combined with T7 corrosion resistance.

21. An aging process for an aluminum alloy containing about 5.7 to 6.9% Zn, about 1.9 to 2.7% Mg, about 1.9 to 2.6% Cu, and about 0.08 to 0.18% Zr, said process comprising:

(1) aging the alloy at one or more temperatures within about 175° F. to 325° F. to a yield strength below peak yield strength by 4 ksi or more;

(2) aging the alloy at one or more temperatures above about 330° F. to increase the alloy's resistance to corrosion; and

(3) aging the alloy at one or more temperatures within about 175° to 325° F. to increase the alloy's strength.

22. An aging process as claimed in claim 21 wherein said recitation (2) aging is within about 360° to 400° F. for about 5 minutes to three hours.

23. An aging process for solution-heat-treated, precipitation hardening 7×××-type aluminum alloy, comprising (1) aging the alloy at one or more temperatures substantially above room temperature but below about 325° F. to a yield strength below peak yield strength by about 3 ksi or more, (2) aging the alloy at one or more temperatures of about 330° F. or higher for at least 3 minutes but not more than 3 hours cumulative time at temperatures of 330° F. or higher, and (3) aging the alloy at one or more temperatures above room temperature but below 325° F. for about 2 hours or more.

24. An aging process for solution-heat-treated, precipitation hardening 7×××-type aluminum alloy, comprising (1) aging the alloy at one or more temperatures within about 175° F. to about 325° F. to a strength substantially below peak yield strength, (2) aging the alloy at one or more temperatures of at least about 330° F. but less than 500° F. for about 4 minutes to about 3 hours cumulative time at temperatures of 330° F. or higher, and (3) aging the alloy at one or more temperatures within about 175° F. to about 325° F. for about 2 hours or more.

25. An aging process as claimed in claim 24, the aluminum alloy consisting essentially of about 5.7 to 6.9% Zn, about 1.9 to 2.7% Mg, about 1.9 to 2.6% Cu, about 0.08 to 0.18% Zr, balance substantially aluminum and incidental elements and impurities.

26. An aging process as claimed in claim 24, wherein, in said recitation (1), said aging is to 3 ksi or more below peak yield strength.

27. A process for aging an aluminum alloy consisting essentially of about 5.7 to 6.9% Zn, about 1.9 to 2.7% Mg, about 1.9 to 2.6% Cu, about 0.08 to 0.18% Zr, balance substantially aluminum and incidental elements and impurities, comprising (1) aging the alloy at one or more temperatures within about 175° F. to about 325° F.

for about 2 hours or more to a strength at least 3 ksi below peak yield strength, (2) aging the alloy at one or more temperatures of at least about 330° F. but less than 500° F. for about 4 minutes to about 3 hours cumulative time at temperatures of 330° F. or higher, and (3) aging the alloy at one or more temperatures within about 175° F. to about 325° F. for about 2 hours or more.

- 28. A product produced by the process of claim 1.
- 29. A product produced by the process of claim 13.
- 30. A product produced by the process of claim 21.
- 31. A product produced by the process of claim 23.
- 32. A product produced by the process of claim 24.
- 33. A product produced by the process of claim 27.
- 34. A product produced by the process of claim 2.
- 35. A product produced by the process of claim 3.
- 36. A product produced by the process of claim 4.
- 37. A product produced by the process of claim 5.
- 38. A product produced by the process of claim 6.
- 39. A product produced by the process of claim 7.
- 40. A product produced by the process of claim 8.
- 41. A product produced by the process of claim 9.
- 42. A product produced by the process of claim 10.
- 43. A product produced by the process of claim 11.
- 44. A product produced by the process of claim 12.
- 45. A product produced by the process of claim 14.
- 46. A product produced by the process of claim 15.
- 47. A product produced by the process of claim 16.
- 48. A product produced by the process of claim 17.
- 49. A product produced by the process of claim 18.
- 50. A product produced by the process of claim 19.
- 51. A product produced by the process of claim 20.
- 52. A product produced by the process of claim 22.
- 53. A product produced by the process of claim 25.
- 54. A product produced by the process of claim 26.

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IN THE UNITED STATES DISTRICT COURT
FOR THE NORTHERN DISTRICT OF ILLINOIS
EASTERN DIVISION

MCCOOK METALS, L.L.C. an Illinois limited liability corporation)

Plaintiff,)

v.)

ALCOA, Inc., a Pennsylvania corporation)

Defendants.)

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U.S. DISTRICT COURT

00C 6782

No. 00 C _____

JUDGE ANDERSEN

Judge _____

Magistrate Judge _____

MAGISTRATE JUDGE LEVIN

Jury Demanded

NOTICE OF CLAIMS INVOLVING PATENTS

Pursuant to Local Rule 3.4, notice is hereby given that McCook Metals has brought a claim for declaratory judgment, declaring, *inter alia*, US Patents 4,477,292, 4,832,758, 4,863,528, and 5,108,520 invalid and/or unenforceable.

The plaintiff is McCook Metals L.L.C. with an address of 4900 First Avenue, McCook, Illinois.

The defendant patentee is Alcoa, Inc., whose headquarters is in Pittsburgh, Pennsylvania

The named inventor in U.S. Patent No. 4,477,292 is Melvin H. Brown. The named inventor in U.S. Patent No. 4,832,758 is Melvin H. Brown. The named inventors in U.S. Patent No.

4,863,528 are Melvin H. Brown, James T. Staley, John Liu and Sootae Lee. The named inventors in U.S. Patent No. 5,108,520 are John Liu and Michael M. Kersker.

Dated: October 30, 2000

MCCOOK METALS L.L.C.,
Plaintiff

By: _____

One of its attorneys.

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Firm ID# 37326

UNITED STATES DISTRICT COURT
NORTHERN DISTRICT OF ILLINOIS

Civil Cover Sheet

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This automated JS-44 conforms generally to the manual JS-44 approved by the Judicial Conference of the United States in September 1974. The data is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. The information contained herein neither replaces nor supplements the filing and service of pleadings or other papers as required by law. This form is authorized for use only in the Northern District of Illinois.

000 6782

Plaintiff(s): MCCOOK METALS, L.L.C.

Defendant(s): ALCOA, INC., a Pennsylvania corporation

County of Residence:

County of Residence: Allegheny County

Plaintiff's Atty: Jenkins & Gilchrist
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(312) 425-3900

Defendant's Atty:
JUDGE ANDERSEN

MAGISTRATE JUDGE LEVIN

cat1

II. Basis of Jurisdiction: 4. Diversity (complete item III)

III. Citizenship of Principle Parties (Diversity Cases Only)

Plaintiff:- 4 IL corp or Principal place of Bus. in IL
Defendant:- 5 Non IL corp and Principal place of Business outside IL

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IV. Origin : 1. Original Proceeding

V. Nature of Suit: 890 Other Statutory Actions

VI. Cause of Action: Suit for declaratory judgment, tortious interference, disparagement and false advertising under 15 USC § 1125(a), 15 USC §§ 101 et seq., 35 USC §§ 200 et seq.

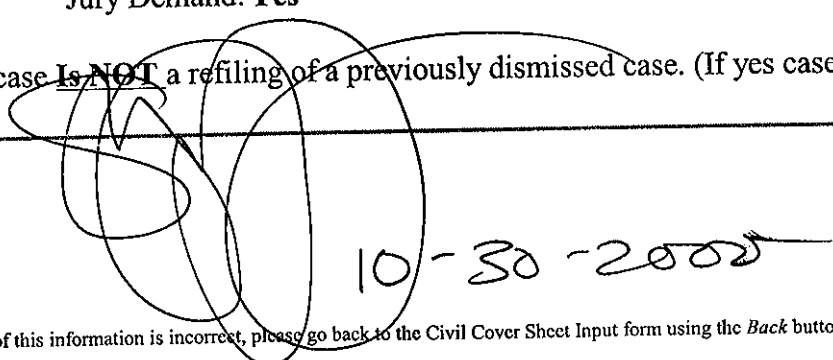
VII. Requested in Complaint

Class Action: No
Dollar Demand: In Excess of \$75,000.00
Jury Demand: Yes

VIII. This case is ~~NOT~~ a refiling of a previously dismissed case. (If yes case number __ by Judge __)

Signature:

Date:



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**UNITED STATES DISTRICT COURT
NORTHERN DISTRICT OF ILLINOIS**

In the Matter of

MCCOOK METALS, L.L.C.

Plaintiff

00C 6782
Case Number:

v.

ALCOA, INC., a Pennsylvania corporation

Defendant.

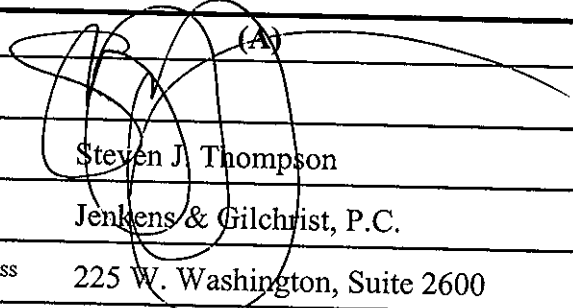
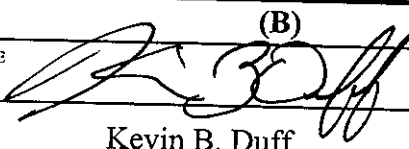
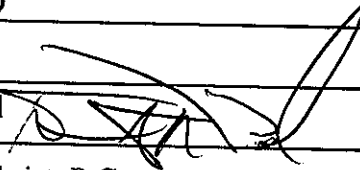
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APPEARANCES ARE HEREBY FILED BY THE UNDERSIGNED AS ATTORNEY(S) FOR:

Plaintiff, McCook Metals, L.L.C.

JUDGE ANDERSEN
DOCKETED
 OCT 31 2000

MAGISTRATE JUDGE LEVIN

(A)		(B)	
SIGNATURE 		SIGNATURE 	
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IDENTIFICATION NUMBER (SEE ITEM 4 ON REVERSE) 6196230		IDENTIFICATION NUMBER (SEE ITEM 4 ON REVERSE) 6210491	
MEMBER OF TRIAL BAR? YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>		MEMBER OF TRIAL BAR? YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>	
TRIAL ATTORNEY? YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>		TRIAL ATTORNEY? YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>	
		DESIGNATED AS LOCAL COUNSEL? YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>	
(C)		(D)	
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MEMBER OF TRIAL BAR? YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>		MEMBER OF TRIAL BAR? YES <input type="checkbox"/> NO <input type="checkbox"/>	
TRIAL ATTORNEY? YES <input type="checkbox"/> NO <input checked="" type="checkbox"/>		TRIAL ATTORNEY? YES <input type="checkbox"/> NO <input type="checkbox"/>	
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