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(54) **Corrosion resistant aluminium alloy**

(57) An aluminium-based alloy consisting of

0,05-1,00 % by weight of iron,
0,05-0,60 % by weight of silicon,
up to 0,70 % by weight of copper,
up to 1,20 % by weight of manganese,
0,02 to 0,20 % by weight of zirconium,
up to 0,50% by weight of chromium,
up to 1,00 % by weight of zinc,
0,02 to 0,20% by weight of titanium,
0,02 to 0,20 % by weight of vanadium,
up to 2,00 % by weight of magnesium,
up to 0,10 % by weight of antimony,
up to 0,02 % by weight of incidental impurities

and the balance aluminium, said aluminium-based alloy
exhibiting high corrosion resistance and high extruda-
bility.

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Description

[0001] The present invention is directed to a corrosion resistant aluminium alloy and, in particular, to an AA3000 series type aluminium alloy including controlled amounts of one or more of titanium, vanadium and zirconium for improved extrudability and/or drawability.

[0002] In the prior art, aluminium is well recognized for its corrosion resistance. AA1000 series aluminium alloys are often selected where corrosion resistance is needed.

[0003] In applications where higher strengths may be needed, AA1000 series alloys have been replaced with more highly alloyed materials such as the AA3000 series types aluminium alloys. AA3102 and AA3003 are examples of higher strength aluminium alloys having good corrosion resistance.

[0004] Aluminium alloys of the AA3000 series type have found extensive use in the automotive industry due to their combination of high strength, light weight, corrosion resistance and extrudability. These alloys are often made into tubing for use in heat exchanger or air conditioning condenser applications.

[0005] One of the problems that AA3000 series alloys have when subjected to some corrosive environments is pitting corrosion. This type of corrosion often occurs in the types of environments found in heat exchanger or air conditioning condenser applications and can result in failure of an automotive component where the corrosion compromises the integrity of the aluminium alloy tubing.

[0006] In a search for aluminium alloys having improved corrosion resistance, more highly alloyed materials have been developed such as those disclosed in U.S. Patent nos. 4,649,087 and 4,828,794. These more highly alloyed materials while providing improved corrosion performance are not conducive to extrusion due to the need for extremely high extrusion forces.

[0007] U.S. Patent no. 5,286,316 discloses an aluminium alloy with both high extrudability and high corrosion resistance. This alloy consists essentially of about 0.1 - 0.5 % by weight of manganese, about 0.05-0.12 % by weight of silicon, about 0.10 - 0.20 % by weight of titanium, about 0.15 - 0.25 % by weight of iron, with the balance aluminium and incidental impurities. The alloy preferably is essentially copper free, with copper being limited to not more than 0.01 %.

[0008] Although the alloy disclosed in U.S. Patent no. 5,286,316 offers improved corrosion resistance over AA3102, even more corrosion resistance is desirable. In corrosion testing using salt water - acetic acid sprays as set forth in ASTM Standard G85 (hereinafter SWAAT testing), condenser tubes made of AA3102 material lasted only eight days in a SWAAT test environment before failing. In similar experiments using the alloy taught in U.S. Patent no. 5,286,316, longer durations than AA3102 were achieved. However, the improved alloy of U.S. Patent no. 5,286,316 still failed in SWAAT testing

in less than 20 days.

[0009] Accordingly, it is a first object of the present invention to provide an aluminium alloy having improved combinations of corrosion resistance and hot formability.

[0010] A still further object of the present invention is to provide an aluminium alloy which has good both hot- and cold- formability, corrosion resistance. Other objects and advantages of the present invention will become apparent as a description thereof proceeds.

[0011] In satisfaction of the foregoing objects and advantages, the present invention provides a corrosion resistant aluminium alloy consisting essentially of, in weight percent, 0.05 - 1.00 % of iron, 0.05 - 0.60 % of silicon, up to 0.70 % of copper, up to 1.20 % of manganese, 0.02 - 0.20 % of zirconium, up to 0.50 % of chromium, up to 1.00 % of zinc, 0.02 - 0.20 % of titanium, 0.02-0.20 % of vanadium, up to 2.00 % of magnesium, up to 0.10 % of antimony, up to 0.02 % of incidental impurities and the balance aluminium.

[0012] Considering in more detail the amounts of the individual components, iron preferably is between 0.05 - 0.55 %, more preferably, between 0.05 - 0.25 %. Reducing the Fe content improves the corrosion resistance. Silicon is preferably between 0.05 and 0.20 %, more preferably, not more than 0.15 %. Copper is preferably not more than 0.05 %, zirconium is preferably between 0.02 and 0.18 %, zinc is preferably between 0.10 and 0.50 %, more preferably between 0.10 and 0.25 %, titanium is preferably between 0.02 and 0.15 %, vanadium is preferably between 0.02 and 0.12 %. The preferred amount of manganese is highly dependent on the intended use of the article because manganese impacts extrudability, especially with thin sections.

[0013] With applications with these type of alloys in which the corrosion resistance and excellent extrudability is the primary concern, manganese is preferably present in amounts between 0.05 - 0.30 % by weight. Fe is preferably present in the amounts between 0.05 - 0.25 % by weight. For these applications the preferred amount of chromium is between 0.02 and 0.25%. The magnesium amount is preferably below 0.03 %. Zn is preferably present in amounts between 0.10 - 0.5 % by weight. By making an appropriate selection of the amount of these elements it is possible to have an alloy with good extrusion characteristics, very good mechanical properties and superior corrosion resistance. When the alloy is intended to be used in applications, in which after extrusion further deformation processes will be used in order to obtain a final product, such as cold deforming as e.g. drawing and/or bending, and where higher strength is required, it is preferred to have the amount of manganese between 0.50 and 0.80 % by weight. In this application chromium is preferably between 0.02 and 0.18 % by weight. When the alloy is intended to be used in applications, in which after extrusion further deformation processes will be used in order to obtain a final product, such as cold deforming as e.g.

drawing and/or binding, it is preferred to have the amount of manganese between 0,50 and 0,80 % by weight. In this application chromium is preferably between 0,02 and 0,18 % by weight and magnesium below 0,30 % by weight, for brazability reasons. The Fe content should be kept low for improved corrosion resistance. To further improve corrosion resistance 0,10 - 0,5 % Zn is added. Likewise, controlled additions of V, Zr and Ti each not more than 0,2 % by weight are made to further improve corrosion resistance.

[0014] If the alloy is to be used in high temperature applications the role of V, Ti and especially Zr becomes important. The amounts added of each of these elements will depend on the functional requirements, however, the amount of zirconium is preferably between 0,10 and 0,18 % by weight. Further it is preferred in these applications to use post treatment of the cast alloy in that it is heated to a temperature between 450 and 550°C with a heating rate of less than 150°C/hour, and maintain the alloy at that temperature between 2 and 10 hours. The final product may also for certain applications and especially after cold working, require a "back annealing" treatment consisting of heating the work piece to temperatures between 150 and 350 degrees Centigrade and keep at temperature for between 10 and 10000 min.

Improved corrosion resistance.

[0015] Zr and Ti in solid solution, are used separately to improve corrosion resistance in low alloy highly extrudable alloys for use in extruded tubes for automotive A/C systems. The useful maximum additions of Zr and Ti when added separately is about 0,2% by weight. Above this level primary compounds are formed that reduces the level of these elements in solid solution. In addition, the primary compounds from Zr and Ti (Al₃Zr, Al₃Ti) will initiate pitting corrosion as they are more noble than the Al matrix.

[0016] Both Zr and Ti will upon solidification go through a peritectic reaction. The product of this reaction is revealed as a highly concentrated region of the elements in the centre of the grain (positive partition ratio). These regions or zones will upon rolling or extrusion form a lamellae structure parallel to the surface of the work piece and slow down the corrosion in the through thickness direction.

Additions of both Zr and Ti in combination, will give larger and more concentrated zones and hence improve corrosion resistance.

V is an element with much the same behaviour and effect as Zr and Ti, but has up to now not been used much in these type of alloys. V will improve corrosion resistance in the same way as Zr and Ti. However, due to the smaller atomic radius compared to Zr and Ti the negative effect on the high temperature deformation resistance (extrudability) will be smaller.

Combination of all three elements will give the most op-

timal balance of the corrosion, strength and workability properties.

The concentration of the elements in this enriched central zone of the grain is different for the three elements and is also sensitive to casting speed.

While the total amount of the element added separately before deleterious primary particles are formed is approx. 0,2wt%, dependent on melt temperature and casting conditions, the amount of the sum of the elements added together is significantly higher. Thus, a combination of the three elements will give a higher concentration in the enriched central zone of the grains and therefore steeper concentration gradients between matrix and the lamellae and enhanced effect with respect to stopping through thickness corrosion propagation.

Improved formability.

[0017] The transition elements such as Zr, Ti, and V is known to improve formability by increasing the work hardening coefficient ("n"). (Ref. latest Reynolds patent). The "n" increases with increased amount of the transition elements almost linearly up to some 0,5%. By combining Zr, Ti and V up to 0,45% of the transition elements may be added as opposed to approx. 0,2% if only one of the elements is added.

Improved elevated temperature mechanical properties.

[0018] Zr, Ti and V, and in particular Zr are known to impede the tendency of recrystallization, provided optimum heat treatment before high temperature processing. The ability to retard recrystallization is related to the number and size of small coherent precipitates that are stable at temperature up to 300- 400 degrees Centigrade for prolonged times. The fine polygenized structure that will result from back annealing at temperatures in the 150 to 350 degrees Centigrade range will have higher mechanical strength than the corresponding recrystallized structure resulting in the absence of such transition elements.

[0019] The density of these precipitates increases with increased amount of the transition elements, therefore combining the three elements would improve the mechanical property in the temperature range from ambient temperature to approx. 400 degrees centigrade.

Claims

1. An aluminium-based alloy consisting of

0,05-1,00 % by weight of iron,
0,05-0,60 % by weight of silicon,
up to 0,70 % by weight of copper,
up to 1,20 % by weight of manganese,
0,02 to 0,20 % by weight of zirconium,
up to 0,50% by weight of chromium,

up to 1,00 % by weight of zinc,
 0,02 to 0,20% by weight of titanium,
 0,02 to 0,20 % by weight of vanadium,
 up to 2,00 % by weight of magnesium,
 up to 0,10 % by weight of antimony,
 up to 0,02 % by weight of incidental impurities

and the balance aluminium, said aluminium-based alloy exhibiting high corrosion resistance and high extrudability.

2. The alloy of claim 1, wherein said iron content ranges between 0,05 - 0,55 % by weight.
3. The alloy of claim 2, wherein said iron content ranges between 0,05 - 0,25 % by weight
4. The alloy of any one of the preceding claims, wherein said silicon content ranges between 0,05 - 0,20 % by weight.
5. The alloy of any one of the preceding claims, wherein said silicon content ranges between 0,05 - 0,15 % by weight.
6. The alloy of any one of the preceding claims wherein said copper content ranges below 0,05 % by weight.
7. The alloy of any one of the preceding claims wherein said zirconium content ranges between 0,02 and 0,18 % by weight.
8. The alloy of any one of the preceding claims wherein said zinc content ranges between 0,10 and 0,50 % by weight.
9. The alloy of any one of the claims 1 to 8 wherein said zinc content ranges between 0,10 and 0,25 % by weight.
10. The alloy of any one of the preceding claims wherein said titanium content ranges between 0,02 and 0,15 % by weight.
11. The alloy of any one of the preceding claims wherein said vanadium content ranges between 0,02 and 0,12 % by weight.
12. The alloy of any one of the preceding claims wherein said manganese content ranges between 0,05 and 0,30 % by weight.
13. The alloy of claim 12 wherein said chromium content ranges between 0,02 and 0,25 % by weight.
14. The alloy of any one of the claims 12 or 13 wherein said magnesium content ranges between 0,00 and

0,03 % by weight.

15. The alloy of any one of the claims 1 to 11 wherein said manganese content ranges between 0,50 and 0,80 % by weight.
16. The alloy of claim 15 wherein said chromium content ranges between 0,02 and 0,18 % by weight.
17. The alloy of any one of the claims 15 or 16 wherein said magnesium content ranges between 0,00 and 0,30 % by weight.
18. The alloy of any one of the claims 1-11 wherein said zirconium content ranges from 0,10 to 0,18 % by weight.
19. The alloy of claim 18 which after casting has been heated with a rate of less than 150 °C/hour heating rate to a temperature of between 450 and 550°C, and kept at said temperature from 2 to 10 hours.
20. The alloy of claim 19 that after cold forming has been annealed with controlled and slow heating rate to temperatures of between 150 and 350 degrees C and kept at temperature for between 10 and 10000 min.



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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 1808

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 431 (C-0759), 17 September 1990 (1990-09-17) & JP 02 166250 A (SUMITOMO LIGHT METAL IND LTD), 26 June 1990 (1990-06-26) * abstract; examples 19,20 *	1-20	C22C21/00 C22C21/10 F28F21/08
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 448 (C-1240), 22 August 1994 (1994-08-22) & JP 06 136476 A (MITSUBISHI ALUM CO LTD), 17 May 1994 (1994-05-17) *examples A-18, A19* * abstract *	1-20	
X	US 4 673 551 A (SUGIYAMA YOSHIHIKO ET AL) 16 June 1987 (1987-06-16) * claims 1-4; table 1 *	1-20	
X	WO 99 55925 A (HOOGO VENS ALU WALZPROD GMBH ;BUERGER ACHIM (DE); VIEREGGE KLAUS (D) 4 November 1999 (1999-11-04) *page 5, bottom*	1-20	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	US 4 574 878 A (SUGIYAMA YOSHIHIKO ET AL) 11 March 1986 (1986-03-11) * column 2, line 32-37; table 1 *	1-20	C22C F28F
A	JP 63 186847 A (SUMITOMO LIGHT METAL IND LTD;OTHERS: 01) 2 August 1988 (1988-08-02) * table 1 *	1-20	
-/--			
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 30 October 2000	Examiner Badcock, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 063 (C-406), 26 February 1987 (1987-02-26) & JP 61 221350 A (NIPPON DENSO CO LTD;OTHERS: 01), 1 October 1986 (1986-10-01) * abstract; table 1 *	1-20	
A	US 5 863 669 A (MILLER WILLIAM S) 26 January 1999 (1999-01-26) * claims 1-12 *	1-20	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 30 October 2000	Examiner Badcock, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 1808

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30-10-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 02166250 A	26-06-1990	NONE	
JP 06136476 A	17-05-1994	NONE	
US 4673551 A	16-06-1987	JP 1445193 C JP 60248859 A JP 62056941 B DE 3518407 A FR 2564962 A GB 2159175 A, B	30-06-1988 09-12-1985 27-11-1987 28-11-1985 29-11-1985 27-11-1985
WO 9955925 A	04-11-1999	EP 0955387 A AU 2934599 A	10-11-1999 16-11-1999
US 4574878 A	11-03-1986	JP 58156197 A BE 896893 A DE 3319440 A FR 2547037 A GB 2139246 A, B	17-09-1983 16-09-1983 29-11-1984 07-12-1984 07-11-1984
JP 63186847 A	02-08-1988	NONE	
JP 61221350 A	01-10-1986	NONE	
US 5863669 A	26-01-1999	CA 2165408 A EP 0718072 A JP 3012506 B JP 8232033 A KR 178444 B	20-06-1996 26-06-1996 21-02-2000 10-09-1996 18-02-1999

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