



(86) Date de dépôt PCT/PCT Filing Date: 2000/11/15
(87) Date publication PCT/PCT Publication Date: 2001/05/25
(45) Date de délivrance/Issue Date: 2007/05/15
(85) Entrée phase nationale/National Entry: 2002/05/15
(86) N° demande PCT/PCT Application No.: EP 2000/011550
(87) N° publication PCT/PCT Publication No.: 2001/036697
(30) Priorités/Priorities: 1999/11/17 (EP99203824.0);
2000/07/31 (US60/221,959)

(51) Cl.Int./Int.Cl. *C22C 21/02* (2006.01),
C22C 21/00 (2006.01), *C22C 21/04* (2006.01),
C22C 21/10 (2006.01)

(72) Inventeurs/Inventors:
WITTEBROOD, ADRIANUS JACOBUS, NL;
BURGER, ACHIM, DE;
VIEREGGE, KLAUS, DE;
VAN DER HOEVEN, JOB ANTHONIUS, NL;
HALLER, SCOTT W., US

(73) Propriétaires/Owners:
CORUS ALUMINIUM WALZPRODUKTE GMBH, DE;
CORUS L.P., CA

(74) Agent: RIDOUT & MAYBEE LLP

(54) Titre : ALLIAGE DE BRASAGE D'ALUMINIUM
(54) Title: ALUMINIUM BRAZING ALLOY

(57) **Abrégé/Abstract:**

The invention relates to an aluminium brazing alloy, ideally suitable as fin stock material, having the composition, in weight %: Si 0.7 - 1.2, Mn 0.7 - 1.2, Mg up to 0.35, Fe up to 0.8, Zn up to 3.0, Ni up to 1.5, Cu up to 0.5, optionally one or more selected from the group comprising (Ti up to 0.20, In up to 0.20, Zr up to 0.25, V up to 0.25, Cr up to 0.25), others up to 0.05 each, up to 0.15 in total, Al balance.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 May 2001 (25.05.2001)

PCT

(10) International Publication Number
WO 01/36697 A3

(51) International Patent Classification⁷: **C22C 21/02**,
21/04

Haarlem (NL). **HALLER, Scott, W.** [US/US]; 9523
Chipping Drive, Richmond, VA 23237 (US).

(21) International Application Number: PCT/EP00/11550

(74) Agent: **HANSEN, Willem, Joseph, Maria**; Corus Technology BV, P.O. Box 10000, NL-1970 CA IJmuiden (NL).

(22) International Filing Date:

15 November 2000 (15.11.2000)

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

99203824.0 17 November 1999 (17.11.1999) EP
60/221,959 31 July 2000 (31.07.2000) US

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicants (*for all designated States except US*):
CORUS ALUMINIUM WALZPRODUKTE GMBH [DE/DE]; Carl-Spaeter-Strasse 10, 56070 Koblenz (DE).
CORUS L.P. [CA/CA]; 290, Saint-Laurent Street, Cap-de-la-Madeleine, Quebec 9BT 7WG (CA).

Published:

— with international search report

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **WITTEBROOD, Adrianus, Jacobus** [NL/NL]; Vederkruid 8, NL-1991 HB Velserbroek (NL). **BÜRGER, Achim** [DE/DE]; Jacques-Remy-Strasse 5, 56203 Hoeher-Grenzhausen (DE). **VIEREGGE, Klaus** [DE/DE]; Am Kettenhaehnchen 10a, 56237 Nauort (DE). **VAN DER HOEVEN, Job, Anthonius** [NL/NL]; Nieuwe Gracht 200, NL-2011 NM

(88) Date of publication of the international search report:
29 November 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ALUMINIUM BRAZING ALLOY

(57) Abstract: The invention relates to an aluminium brazing alloy, ideally suitable as fin stock material, having the composition, in weight %: Si 0.7 - 1.2, Mn 0.7 - 1.2, Mg up to 0.35, Fe up to 0.8, Zn up to 3.0, Ni up to 1.5, Cu up to 0.5, optionally one or more selected from the group comprising (Ti up to 0.20, In up to 0.20, Zr up to 0.25, V up to 0.25, Cr up to 0.25), others up to 0.05 each, up to 0.15 in total, Al balance.



WO 01/36697 A3

ALUMINIUM BRAZING ALLOY**FIELD OF THE INVENTION**

The invention relates to an aluminium alloy which can be used for heat
5 exchangers. Ideally the aluminium alloy according to the invention is provided as fin
stock material for heat exchanger devices. Furthermore, the invention relates a brazed
assembly comprising at least one component of the aluminium alloy according to this
invention.

DESCRIPTION OF THE RELATED ART

10 In the prior art, aluminium alloys are the alloys of choice for heat exchanger
applications. These alloys are selected for their desirable combination of strength, low
weight, good thermal and electrical conductivity, brazeability, corrosion resistance, and
formability.

An aluminium alloy heat exchangers can be fabricated by stacking aluminium
15 alloy clad sheets (brazing sheet), which have been formed to a desired configuration, so
as to form fluid passages (tubes) and securing corrugated aluminium alloy fins between
fluid passages by brazing. The bonding between the alloy clad sheets or the tube
material and fins is achieved by melting the brazing filler metal of the core plates and/or
fin material. As a brazing method, typically vacuum brazing or flux brazing is being
20 applied. In an effort to improve the corrosion resistance of the fluid passage materials,
some fin materials may be used which are electrochemically anodic (less noble) relative
to the fluid passage material by the sacrificial anode effect of these fin materials.

Some disclosures of aluminium brazing sheet alloys found in the prior art
literature will be mentioned below.

25 The publication by J. Althoff, in the technical journal Light Metal Age,
December, 1980, pp. 20-21, "Aluminium Alloy 3009: High Strength Without
Magnesium", discloses the 3009 alloy without magnesium. The 3009 alloy has the
following composition, in weight percent:

Si	1.0 - 1.8
30 Fe	max. 0.7
Cu	max. 0.10
Mn	1.2 - 1.8

Mg max. 0.01
 Cr max. 0.05
 Ni max. 0.05
 Zn max. 0.05
 5 Zr max. 0.10
 Ti max. 0.10

others each max. 0.05, total max. 0.15

balance aluminium,

and further has the proviso that Si:Fe should be 2:1 to 4:1,

10 and that Mn+Si should be in the range of 2.5 - 3.5.

The disclosed alloy may replace the known AA3003 alloy, and may be used for brazing applications.

EP-A-0637481 (Furukawa) discloses an aluminium alloy brazing sheet having a
 three-layer structure clad one side of the core material with a brazing material and clad
 15 of the other side of the core material with a sacrificial material. The defined core
 material has a very wide compositional window, in weight percent:-

Si 0.6 - 2.5

Cu 0.5 - 2.5

Mn up to 2.0

20 at least one kind selected from the group consisting of:-

Mg 0.03 - 0.5

Cr 0.03 - 0.3

Zr 0.03 - 0.3

Ti 0.03 - 0.3

25 Ni 0.03 - 1.5

balance aluminium and impurities.

This document further discloses an aluminium alloy brazing sheet having a three-layer
 structure clad on both sides of the core material with a brazing material and whereby
 the core material has a very wide compositional window, in weight percent:-

30 Si 0.03 - 2.5

Fe 0.05 - 2.0

Cu 0.05 - 2.0

Mn 0.6 - 2.0

at least one kind selected from the group consisting of:-

Zn 0.05- 5.0

5 In 0.002 - 0.3

Sn 0.002 - 0.3

balance aluminium and inevitable impurities.

There is a market demand in the automotive industry for aluminium alloys which may be used for application in heat exchangers, which alloys have improved post-
10 brazed strength in combination with a good corrosion resistance. Further, there is a demand from the side of the manufacturers of such aluminium alloys, for alloys having a tolerance for impurity elements from a recycling point of view without compromising to the required properties of such an aluminium alloy.

SUMMARY OF THE INVENTION

15 It is an object of the present invention to provide an aluminium alloys which can be used for heat exchangers having an improved post-braze 0.2% yield strength over conventional alloys for the same application. It is another object of the present invention to provide an aluminium alloy having an improved tolerance for impurity elements. It is a further object of the present invention to provide an aluminium alloy
20 which is ideally suitable for providing fin stock material for heat exchanger devices.

In one aspect the invention provides an aluminium alloy having the composition, in weight percent:

Si 0.7 - 1.2

Mn 0.7 - 1.2

25 Mg up to 0.35

Fe up to 0.8

Zn up to 3.0

Ni up to 1.5

Cu up to 0.5

30 Ti up to 0.20

In up to 0.20

Zr up to 0.25
V up to 0.25
Cr up to 0.25
others up to 0.05 each, up to 0.15 in total

5 Al balance.

This aluminium alloy has a good corrosion resistance, which includes the sacrificial anode effect where required, in combination with good mechanical properties in the post-brazing state and is capable of providing an increase in post-braze 0.2% yield strength (PS) of at least 15% over conventional finstock alloys, such as AA3003
10 in the same temper. The aluminium alloy in accordance with the invention is capable of achieving a post-braze 0.2% yield strength (PS) of at least 60 MPa, and in the best examples of at least 65 MPa and even as high as 70 MPa or more.

Although this aluminium alloy can be used for tube plate, side supports and header tanks in heat exchanger units, and may have other uses, it is primarily intended
15 as a finstock alloy for heat exchangers. The corrosion demand for finstock is such that if the heat exchanger unit is attacked by corrosion, the fin material is preferentially attacked and not the tube material. The alloy according to this invention has this sacrificial anode effect. The alloy can be stronger, so the finstock can be thinner and lighter than conventional finstock alloys, such as AA3003 alloys. The alloy of the
20 invention used as finstock material may be used in combination with a cladding of a brazing alloy, e.g. an Al-Si alloy known in the art or other similar Al-Si systems alloys, such as Al-Si-Mg alloy, Al-Si-Mg-Bi alloy, Al-Si-Bi alloy or the like.

The heat exchanger market, particularly in the automotive industry, requires that finstock alloys offer a balance of properties, i.e. strength, formability, brazeability and
25 corrosion potential. A key feature of the novel alloy of this invention is the relatively high Si content as compared to AA3003 alloys, in combination with a medium Mn content. Consequently this increases the post-braze strength, by more than 15% relative to conventional finstock alloys. The alloy exhibits amongst others excellent brazeability properties.

30 The reasons for the limitations of the alloying elements of the aluminium alloy according to the present invention are described below. All composition percentages are by weight.

Si is an important alloying element in the alloy according to this invention. The addition of Si results in an increased solution hardening of the alloy. Below 0.7% there is only little effect of the Si, and above 1.2% it may result in the formation of detrimental low-melting eutectics and also in the formation of large intermetallic particles. A more suitable range for the Si content is 0.75 to 1.0%. In many aluminium alloys a Si-level at a medium range is other regarded as detrimental. An advantage of this medium range Si-content is that the alloy has a tolerance for impurity elements, and allows this alloy to be composed from large amounts of scrap material. Preferably the sum of Si+Mn is in the range of 1.6-2.3, and more preferably in the range of 1.75-2.1, and allows for a good compromise in desired properties of the alloy such as post-braze strength and sag-resistance, while the alloy can be manufactured without great difficulties from scrap material.

Mn is also an important alloying element in the alloy according to this invention. The addition of Mn in a medium range of 0.7 to 1.2%, A more preferred lower limit for the Mn content is 0.8%. A more preferred upper limit for the Mn content is 1.1% And more preferably the Mn should be in the range of 0.8 to 1.0%. A very high Mn content might lead to the detrimental formation of large Fe-Mn intermetallics. To allow for the alloy to be composed of large amounts of scrap, which might contain relatively high Fe contents, the Mn level should not exceed 1.2%. Above 1.2% Mn the casting of an ingot becomes more difficult.

Mg increases the strength of the alloy significantly, but has a detrimental influence on controlled atmosphere brazeability because it tends to interact with the flux applied. For this reason the Mg content is restricted to a maximum of 0.35%, and a more preferred range for the Mg level is 0.2 to 0.35% as a compromise in post-braze strength and brazeability.

Fe is present in all known aluminium alloys. With a too high Fe content among other things the formability of the material decreases and also the corrosion performance is decreasing. The admissible Fe content is 0.8% maximum, and preferably 0.5% maximum. Such relatively high Fe contents may be tolerated by limiting the Mn content. A suitable Fe content is in the range of 0.20 to 0.45%, and allows for a good compromise in desired properties of the alloy such as post-braze

strength and sag-resistance, while the alloy can be manufactured without great difficulties from scrap material.

The addition of Zn leads to a more electronegative corrosion potential. To allow for the sacrificial anode effect, the fin material should be more electronegative as the tube material. Since different types of tube material can and will be used in heat exchangers, the Zn content can be used to tune the corrosion potential of the alloy of this invention to fit to the tube material. The Zn content should be at a level below 3.0% to avoid a too rapid corrosion attack of the fin material. Since Zn may be tolerated up to 3.0%, and preferably up to 2.0%, and more preferably up to 1.5%, and most preferably up to 1.0%, this achieves an advantage in the tolerance of this alloy for impurity elements, and allows this alloy to be composed from large amounts of scrap material, such as discarded heat exchangers, but not limited to this example. A suitable lower limit for the Zn-level is 0.2%.

Ni may be present in the alloy according to the invention in a range up to 1.5% in order to further increase the post-braze strength without resulting in a significant loss in thermal conductivity. A preferred range for Ni as an alloying element is 0.3 to 1.2%, and more preferably 0.5 to 0.75%. This enables the alloy of the invention to reach a better and desirable balance between post-braze strength, thermal conductivity and corrosion resistance.

Cu is preferably included as a strengthening component. Cu is believed not to reduce corrosion resistance in a way that has previously been reported. Since Cu may be tolerated up to 0.5%, this achieves an advantages in the tolerance of this alloy for impurity elements, and allows this alloy to be composed from large amounts of scrap material, such as discarded heat exchangers, but not limited to this example. A suitable maximum for the Cu content is up to 0.5%, and preferably up to 0.4%. A more preferred range for the Cu-level is 0.2 to 0.4% as a compromise in achieving post-braze strength, corrosion resistance and brazeability.

Ti may be present up to 0.20% to act as a grain refining additive during the casting of an ingot of the alloy of the invention. Additional Ti may be added, for example due to their presence in scrap material, in order to increase the strength of the alloy by solubility hardening. The total amount of Ti present in the alloy should not exceed 0.20%, but preferably is less than 0.15%.

The element Indium in a range of up to 0.20% may be added to the alloy of the invention in order to reach a more electro-negative corrosion potential. Furthermore, it has been found in accordance with the invention that in this aluminium alloy In is much more effective in reducing the corrosion potential of the alloy as compared to zinc additions. Typically 0.1% In is as effective as 2.5% Zn. When added as a deliberate alloying element a more preferred range for In is 0.01 to 0.10%.

Zr in a range of up to 0.25% may be added to the alloy of this invention in order to further improve the strength of the alloy in the post-braze condition. Further, this element may be tolerated as an impurity element without deteriorating the desired properties of the alloy. A more suitable Zr addition is in the range of 0.05 to 0.20, and more preferably in the range of 0.05 to 0.15%.

Cr in a range of up to 0.25% may be added to the alloy of this invention in order to further improve the strength of the alloy in the post-braze condition.

Other components including Sn and V may be tolerated in the alloy according to the invention in a range up to 0.25%, preferably up to 0.15%, and more preferably up to 0.05%. The total of these elements should not exceed 0.3%. Such element may be present to reduce the corrosion potential of the alloy, and V has further the potential of increasing post-braze strength.

The balance is made by aluminium and unavoidable impurities, typically each up to 0.05% maximum, and in total 0.15% maximum.

In another aspect of the invention there is provided in a brazed assembly, typically a heat exchanger, comprising the alloy of the invention as fin stock material. In such a heat exchanger having the alloy of the invention as fins, the fins may act as a sacrificial anode. The aluminium alloy according to the invention may also be clad on one or both of its surfaces. The purpose of such a cladding is essentially to provide the brazing material for the fillets, and is used for example in the case of unclad tubes like for condensers made from extruded tubes or for serpentine type evaporators. Typically each clad layer thickness is in the range of 2 to 15% of the total thickness of the clad product. The composition of the clad layer is typically in the range of 5 to 15% Si, optionally up to 2.0% Mg, optionally up to 3.0% Zn, and optionally up to 0.2% Bi.

EXAMPLES

The aluminium alloy in accordance with the invention will now be illustrated by non-limitative and comparative examples.

On a laboratory scale of testing six alloys have been cast with solidification rates
5 in the same range as obtained with industrial scale DC casting. Although manufactured here on a laboratory scale of testing, the aluminium alloy in accordance with this invention can be manufactured using various standard industrial scale DC casting and continuous aluminium casting methods, followed by hot and/or cold rolling. The chemical compositions are listed in Table 1, where Alloys 1 to 4 are alloys according to
10 the invention with Ti at grain refiner level, Alloy 5 and 6 are alloys according to the invention with a somewhat increased Mg- and Ti-level, Alloy 6 further has an increased Zn-level. In all alloys according to the invention the Ni-, In-, and V-levels are at impurity level. Alloy 7 is the example in the H14 temper known from the international patent application WO-97/18946 for comparison reasons, and further an Alloy 8 has
15 been used which is the known AA3003 alloy commercially used as finstock material. The four cast ingots were preheated and hot rolled to a thickness of 5.7 mm. The sheets were then cold rolled to 0.15 mm and annealed at 360-400°C for 2 hours before cold rolling to a final gauge of 0.10 mm. This is the H14 temper.

The cold rolled sheets had the following mechanical properties before and after
20 being subjected to a simulated brazing cycle (approx. 5 min at 590°C and air cool), see Table 2. The mechanical properties are valid for non-clad material. However, for certain applications the alloy of the invention may be provided with a thin cladding, resulting in a small decrease of the mechanical properties (both in the pre- and post-braze conditions) of a few MPa, typically about 2 to 10 MPa.

25 From these results it can be seen that the aluminium alloy of the invention has a significant improvement in mechanical properties over the conventional used AA3003 alloy in the same temper, and offer the opportunity for down gauging of units prior to the brazing cycle and having a reduced rate of corrosion attack on the fin.

Table 1. Chemical composition, in wt.%, of the aluminium alloys tested, the balance is aluminium and impurities.

Alloy	Si	Mn	Mg	Fe	Zn	Cu	Zr	Cr	Ti
1	0.9	1.1	0.1	0.3	0.4	0.3	0.08	-	0.01
2	0.9	1.05	0.1	0.3	0.4	0.3	0.09	-	0.01
3	0.9	1.1	0.1	0.3	0.4	0.3	0.08	0.09	0.01
4	0.9	0.95	0.1	0.3	0.4	0.3	0.09	0.01	0.01
5	0.97	0.9	0.3	0.3	0.2	0.25	-	-	0.15
6	0.97	1.1	0.3	0.3	1.0	0.25	-	-	0.15
7	0.9	1.3	0.1	0.4	-	0.3	-	-	-

Table 2. Mechanical properties before and after simulated brazing cycle.

Alloy	Before brazing		After brazing	
	0.2 PS [MPa]	UTS [MPa]	0.2 PS [MPa]	UTS [MPa]
1	226	232	63	138
2	225	231	62	137
3	234	240	63	139
4	225	231	60	135
5	243	252	77	153
6	236	239	81	158
7	-	-	59	155
8 (AA3003)	168	174	40	135

5

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made without departing from the spirit or scope of the invention as herein described.

- 10 -

CLAIMS:

1. Fin stock material formed by an aluminium alloy having the composition, in weight percent:

Si	0.7 – 1.2
Mn	0.7 – 1.2
Mg	0.2 – 0.35
Fe	up to 0.8
Zn	0.2 – 3.0
Ni	up to 1.5
Cu	up to 0.5
Ti	up to 0.20
In	up to 0.20
Zr	up to 0.25
V	up to 0.25
Cr	up to 0.25

Impurities up to 0.05 each, and up to 0.15 in total,

Al balance.

2. A fin stock material according to claim 1, wherein the Mn-level is in the range of 0.8 to 1.1%.

3. A fin stock material according to claim 2, wherein the Mn-level is in the range of 0.8 to 1.0%.

4. A fin stock material according to any one of claims 1 to 3, wherein the Zr-level is in the range of 0.05 to 0.15%.

5. A fin stock material according to any one of claims 1 to 4, wherein the Fe-level is in the range of 0.20 to 0.45%.

6. A fin stock material according to any one of claims 1 to 5, wherein the Cu-level is in the range of 0.20 to 0.40%.

- 11 -

7. A fin stock material according any one of claims 1 to 6, wherein the Si-level is in the range of 0.3 to 1.2%.
8. A fin stock material according to claim 7, wherein the Si-level is in the range of 0.5 to 0.75%.
9. A fin stock material according to any one of claims 1 to 8, wherein the Si-level is in the range of 0.75 to 1.0%.
10. A fin stock material according to any one of claims 1 to 9, wherein the In-level is in the range of 0.01 to 0.1%.
11. A fin stock material according to any one of claims 1 to 10, wherein the fin stock material is capable of obtaining a post-braze 0.2% yield strength of at least 60 MPa.
12. A fin stock material according to claim 11, wherein the fin stock material is capable of obtaining a post-braze 0.2% yield strength of at least 70 MPa.
13. A brazed heat exchanger having fins made of a fin stock material according to any one of claims 1 to 12.
14. A brazed heat exchanger having fins of an aluminium alloy having the composition, in weight percent,

Si	0.75 – 1.0
Mn	0.8 – 1.0
Mg	0.2 – 0.35
Fe	up to 0.5
Zn	up to 3.0
Ni	up to 1.5
Cu	up to 0.4
Ti	up to 0.20
In	up to 0.20

- 12 -

Zr up to 0.25

V up to 0.25

Cr up to 0.25

impurities up to 0.05 each, and up to 0.15 in total,

Al balance,

and wherein said fins have a post-braze 0.2% yield strength of 70 MPa or more.

15. A brazed heat exchanger according to claim 14, wherein the Fe content in said aluminium alloy is in the range of from 0.2 to 0.45 weight percent.

16. A brazed heat exchanger according to claim 14 or claim 15, wherein the Cu content of said aluminium alloy is in the range of 0.2 to 0.4 weight percent.