



(51) International Patent Classification:

B32B 15/01 (2006.01) *C22C 21/00* (2006.01)
B23K 35/28 (2006.01) *C22C 21/02* (2006.01)
B23K 35/02 (2006.01)

(21) International Application Number:

PCT/EP2017/051278

(22) International Filing Date:

23 January 2017 (23.01.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16154886.2 9 February 2016 (09.02.2016) EP

(71) Applicant: **ALERIS ROLLED PRODUCTS GERMANY GMBH** [DE/DE]; Carl-Spaeter-Straße 10, 56070 Koblenz (DE).

(72) Inventors: **JACOBY, Bernd**; Schornstraße 13, 65553 Limburg (DE). **KIRKHAM, Steven**; Pfarrer-Hans Straße 48, 56235 Ransbach-Baumbach (DE). **SCHLEGEL, Arne**; Am Friedrich 15, 52074 Aachen (DE).

(74) Agent: **SCHINKEL, Reta**; Müller Schupfner & Partner, Bavariaring 11, 80336 München (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ALUMINIUM MULTI-LAYERED BRAZING SHEET PRODUCT AND FLUXLESS BRAZING METHOD

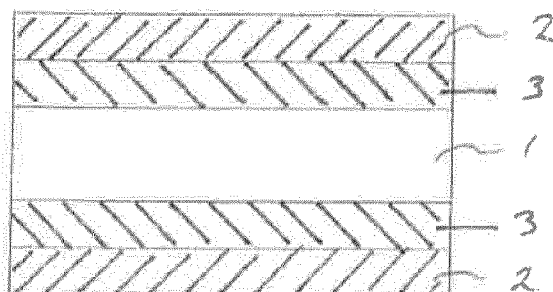


Fig. 2

(57) Abstract: The invention relates to a multi-layered brazing sheet product having an aluminium core alloy layer provided on one or both sides with a brazing clad layer material, and an inter-layer material positioned between the aluminium core alloy layer and at least one of said brazing clad layer materials, wherein the brazing layer material(s) is made from an 4xxx-series aluminium alloy having 5% to 15% Si and up to 3% Mg, and wherein the inter-layer material is made from a 1xxx-series aluminium alloy having a purposive addition of Mg of 0.10% to 2.0%. The invention relates also to the use of the brazing sheet product in a fluxless controlled atmosphere brazing process.



WO 2017/137236 A1

ALUMINIUM MULTI-LAYERED BRAZING SHEET PRODUCT AND FLUXLESS BRAZING METHOD

FIELD OF THE INVENTION

The invention relates to a multi-layered brazing sheet product made of an aluminium core alloy layer provided one or both sides with a brazing clad layer material, and an inter-layer positioned between the aluminium core alloy layer and at least one of said brazing clad layer materials. The present invention relates also to a method of fluxless brazing in a controlled atmosphere brazing process using such a multi-layered brazing sheet product. In addition, the invention relates to the use of the brazing sheet product in a fluxless controlled atmosphere brazing process. The invention further relates to a brazed heat exchanger comprising various components wherein at least one component being made from the multi-layered brazing sheet product according to this invention.

BACKGROUND OF THE INVENTION

Substrates of aluminium or aluminium alloy in the form of a sheet or an extrusion are used to make shaped or formed products. In some of these processes parts of (shaped) aluminium comprising substrates are interconnected. One end of a substrate may be connected with the other end or one substrate may be assembled with one or more other substrates. This is commonly done by brazing, a technique well known to the person skilled in the art. In a brazing process, a brazing filler metal or brazing alloy is applied to at least one portion of the substrate to be brazed. After the substrate parts are assembled or combined, then they are heated until the brazing metal or brazing alloy melts to join the individual parts to one an-

other. The melting point of the brazing material is lower than the melting point of the aluminium substrate or aluminium core sheet.

Brazing sheet products find wide applications in heat exchangers and other similar equipment. Conventional brazing sheet products have a core of rolled sheet, typically, but not exclusively an aluminium alloy of the 3xxx-series, having on at least one surface of the core sheet an aluminium clad layer (also known as an aluminium cladding layer or brazing clad layer material). The aluminium brazing clad material is made of a 4xxx-series alloy comprising silicon in an amount in the range of 2% to 20% by weight, and preferably in the range of about 5% to 15% by weight. The aluminium brazing clad layer may be coupled or bonded to the core alloy in various ways known in the art, for example by means of roll bonding, cladding spray-forming or semi-continuous or continuous casting processes, for example as disclosed in patent document WO-2004/112992 (Alcan). These aluminium brazing clad layers have a liquidus temperature typically in the range of about 540°C to 615°C.

There are various brazing processes in use for the industrial scale manufacturing of heat exchangers.

There is vacuum brazing which is carried out at relatively low atmosphere pressure in the order of about 1×10^{-4} mbar or less and is a discontinuous process and puts high demands on material cleanliness. To obtain optimum conditions for joining to take place, Al-Si brazing alloys commonly used for vacuum brazing contain purposive additions of Mg of 1% or more. The Mg destroys the hard oxide film of the filler alloy when it evaporates from the brazing sheet during brazing, and further the evaporated Mg plays the role as getter that removes oxygen and moisture remaining in the vacuum brazing furnace. There is always more magnesium present in the furnace than necessary. The excess magnesium condenses on the cold spots in the vacuum brazing furnace and has to be removed frequently. The capital investment for suitable equipment is relatively high.

NOCOLOK (registered trademark) flux brazing has been used as the principal brazing process to braze automotive heat exchangers by many heat exchanger manufacturers. Major problems that have arisen from the NOCOLOK process have been brazing flux costs, flux handling and the damage brazing flux causes to the furnaces. Also, in complex shaped assemblies the application of the brazing flux prior to brazing at the interior of the assemblies is often considered very difficult and problematic. Consequently, most of the heat exchanger manufacturers have been trying to reduce brazing flux consumption.

Another brazing process is controlled atmosphere brazing ("CAB") without using a brazing flux.

Patent document EP-1430988-A (Furukawa) discloses for such a CAB process without using a brazing flux that the brazing sheet is provided with a core alloy containing Mg in a range of 0.05% to 1.0%. Interposed between the core alloy and the filler alloy there is present a diffusion prevention layer such as an Mg-free AA3003-series aluminium alloy.

Patent document EP-1306207-B1 (Sky Aluminium) discloses another fluxless brazing process in an inert gas atmosphere. It also discloses a brazing sheet product comprising of an aluminium core alloy on one or both sides clad with an Al-Si alloy filler alloy with 0.1-5% of Mg and 0.01-0.5% of Bi as an intermediate layer, and a thin covering material clad onto the Al-Si alloy brazing alloy. It is suggested that during a brazing operation the filler material in the intermediate layer is molten as the temperature is elevated during brazing, but oxidation of the surface of the filler material does not occur because the surface is covered with the thin covering material which remains solid. When the temperature is further elevated, the portions with lower melting points, such as a segregation portion of the thin covering material close to the molten filler material, are locally molten, and then the filler material seeps and spreads over the surface of the thin covering material due to volumetric

expansion. The surface of the filler material then becomes an emerging face without an oxidation film, and new intensive oxidation does not proceed due to the inert gas atmosphere.

Patent document EP-2660043-A1 (Hydro Aluminium) discloses aluminium brazing sheet product wherein the Al-Si filler layer has been etched to facilitate fluxless brazing. The etching of the Al-Si filler layer includes an alkaline or acidic etchant.

Patent document US-2007/0099023-A1 (Alcan) discloses an aluminium core alloy clad on at least one side with an Al-Si filler layer and wherein the core comprises 0.01-0.5% of Bi and/or 0.05-0.5% of Y to facilitate fluxless brazing under a controlled atmosphere.

Patent document US-2007/0204935-A1 (Alcan) discloses a method of fluxless brazing whereby the sheets prior to brazing are etched in an acid solution and which can be preceded by alkaline etching. The sheet material comprises for an example a brazing sheet product made from an AA3916 core alloy clad on both sides with a filler material layer an AA4045 alloy.

Patent document EP-2883650-A1 (Hydro Aluminium) discloses a pre-treatment of aluminium brazing sheet for fluxless brazing, wherein the surface of the aluminium filler layer has been pickled with an acidic aqueous pickling solution comprising at least a mineral acid and at least one complexing agent or complexing mineral acid, and wherein the material removal during the pickling is between 0.05-6 g/m², and most preferably between 0.2-0.4 g/m². Preferred Al-Si filler materials are selected from the group of AA4343, AA4045 and AA4047.

There is a demand for an improved brazing sheet product suitable for use in fluxless brazing in a controlled atmosphere.

DESCRIPTION OF THE INVENTION

As will be appreciated herein below, except as otherwise indicated, aluminium alloy designations and temper designations refer to the Aluminium Association designations in Aluminium Standards and Data and the Registration Records, as published by the Aluminium Association in 2015 and well known to the person skilled in the art.

For any description of alloy compositions or preferred alloy compositions, all references to percentages are by weight percent unless otherwise indicated. The term “up to” and “up to about”, as employed herein, explicitly includes, but is not limited to, the possibility of zero weight-percent of the particular alloying component to which it refers. For example, up to 0.3% Ti may include an alloy having no Ti.

And for the purpose of this invention, and as used hereinafter, the term “controlled atmosphere brazing” or “CAB” refers to a brazing process which utilizes an inert atmosphere, for example, nitrogen or argon in the brazing of the various alloy articles, and is distinct from vacuum brazing in particular in that with CAB the brazing atmosphere in the furnace during the brazing operation is at about atmospheric pressure, although a slight under-pressure (for example working at a pressure of 0.1 bar or more) or a slight over-pressure can be used to facilitate the control of the inert atmosphere and to prevent an influx of oxygen containing gas into the brazing furnace. “Core” means an aluminium alloy which is the structural support for the aluminium alloy that is used as the filler. “Filler” means an aluminium-silicon alloy which is used to braze the core or other aluminium articles. “Fillet” means a concave junction between two surfaces.

It is an object of the present invention to provide brazing sheet product that can be used in a method of fluxless brazing in a controlled atmosphere.

This and other objects and further advantages are met or exceeded by the present invention providing a multi-layered brazing sheet product having an aluminium core alloy layer comprising on one or both sides or faces a brazing clad layer

material, and an inter-layer material or layer positioned between the aluminium core alloy layer and at least one of said brazing clad layer materials, wherein the brazing clad layer material(s) is made from an 4xxx-series aluminium alloy having 5% to 15% Si and up to 3% Mg, and preferably up to 0.9% Mg, and wherein the inter-layer material is made from a 1xxx-series aluminium alloy having a purposive addition of Mg of 0.10% to 2.0%.

In accordance with the invention it has been found that the purposive addition of Mg to the inter-layer material facilitates a good fillet formation when used in a fluxless controlled brazing operation. Part of the Mg diffuses from the inter-layer material into the filler metal during the temperature rise in the heat-up cycle in a regular brazing operation and during the brazing operation itself and breaks the oxide film on the surface of the brazing clad layer material.

In order to further facilitate a good fillet formation when used in a fluxless controlled brazing operation the outer-surface of the brazing clad layer material can be pre-treated by means of etching with an alkaline or acidic etchant making the material less sensitive against trace oxygen in the inert gas atmosphere. The etching is reducing the amount of oxides at the outer-surface of the brazing filler material and which may otherwise hinder a good fillet formation during brazing.

However, in accordance with the invention it has been found that it can only be put into reliable practice and providing for a good fillet formation when the inert gas atmosphere is dry, and furthermore provided the oxygen content in the inert atmosphere is low and there is a presence of Mg of at least 0.10% in the inter-layer. Based on a series of experiments it has been found that if there less than 0.05% Mg or no Mg is present, for example when using a filler material based on AA4343, AA4045 or AA4047 in combination with a Mg-free 1xxx-series inter-layer material, then a good fillet formation can only be obtained when the oxygen content in the dry inert gas atmosphere is less than 4 ppm and preferably even lower. In some cases no good fillet formation occurred at oxygen levels as low as 2 ppm. However, when

a purposive addition of Mg is present then a good fillet formation can be obtained while having a substantial amount of oxygen in the dry inert gas atmosphere. If the oxygen content exceeds 35 ppm no good fillet formation occurs, and preferably the oxygen content is less than 25 ppm, and more preferably less than 20 ppm. As it is very difficult to arrive at and to maintain a very low oxygen content of less than 5 ppm in industrial scale controlled atmosphere brazing furnaces, the present findings allow for fluxless CAB brazing at achievable oxygen levels in the inert gas atmosphere. This provides a significant cost benefit.

The inter-layer or inter-liner is made from an aluminium alloy of the 1xxx-series alloys together with a purposive addition of Mg of 0.10% to 2.0%. A preferred upper-limit for the Mg addition is 1.5%. A higher Mg-content may tolerate a higher oxygen content in the inert atmosphere; however, a too high Mg content is detrimental for the brazing operation itself and for that reason it should not exceed 2.0%, and a preferred upper-limit for the Mg content is 1.5%, and more preferably 1.0%, and more preferably 0.70%. The Mg content in the inter-liner layer is at least 0.10%, and preferably at least 0.15%, and a more preferred lower limit is 0.20%.

Although the brazing layer material facing the inter-liner may comprise some Mg, on a preferred basis the Mg-content is low and it is preferred that the Mg-content in the inter-layer is higher than the Mg-content in the brazing layer material, if present, to facilitate a rapid diffusion thereof during the brazing cycle.

Preferred alloys are those having a composition besides the purposive Mg addition within the ranges of AA1050, AA1060, AA1100, AA1300, AA1350, AA1350A, AA1370 and AA1235.

In a preferred embodiment the interlayer has a thickness of 60µm or less, for example of about 40µm or about 50µm, and is to control the diffusion of alloying elements, e.g. Si, from the core layer to the brazing layer, and as such limits intergranular corrosion propagation through the core layer in the post-braze condition,

and thereby significantly improves the post-braze corrosion performance of the brazing sheet product when applied in a heat exchanger, in particular a charge air cooler. The defined 1xxx-series interlayer also provides galvanic protection to the aluminium core alloy in combination with facilitating a good fillet formation when used in a fluxless controlled brazing operation.

In an embodiment of the invention, the brazing clad layer material or Al-Si brazing filler alloy has the following composition, consisting of, in wt.%:

Si	5% to 15%, preferably 8% to 14%,
Mg	up to 3%, preferably up to 0.90%, and more preferably up to 0.5%, and most preferably up to 0.15%,
Fe	up to 0.8%
Cu	up to 0.3%, preferably up to 0.1%,
Mn	up to 0.8%, preferably up to 0.2%,
Zn	up to 0.25%
Ti	up to 0.3%,

unavoidable impurities each <0.05%, total <0.2%, and balance aluminium.

Optionally the brazing clad layer material may further comprise a purposive addition of one or more wetting elements selected from the group consisting of: Bi 0.03% to 0.5%, Pb 0.03% to 0.5%, Sb 0.03% to 0.5%, Li 0.03% to 0.5%, Se 0.03% to 0.5%, Y 0.03% to 0.5%, Th 0.03% to 0.5%, and the sum of these elements being 0.5% or less.

The core alloy of the multi-layered aluminium brazing sheet is made of an aluminium alloy from the 3xxx, 5xxx, 6xxx or 7xxx-series alloys, in particular from an AA3003, AA3103, AA3005, AA3105, AA6060, AA6063 or AA6951-type alloy, or modifications thereof.

In a preferred embodiment of the multi-layered brazing sheet material the core alloy is made from a 3xxx-series alloy having a composition consisting of:

Mn	0.8% to 1.5%, preferably 0.8% to 1.40%,
----	---

Si	0.25% to 0.75%
Cu	0.5% to 1.1%
Fe	up to 0.45%
Mg	up to 0.35%
Cr	up to 0.25%
Zr	up to 0.25%
Ti	up to 0.20%
Zn	up to 0.15%,

unavoidable impurities each <0.05%, total <0.2%, and balance aluminium.

The multi-layered brazing sheet material according to the invention has a typical thickness at final gauge in the range of about 0.1 mm to 3 mm, and preferably of 0.1 mm to 1.2 mm, for example 0.2 mm or 0.5 mm or 0.8 mm. Each brazing clad layer has typically a thickness of 5% to 15% of the total thickness, for example of about 10%.

Depending on the application of the multi-layered brazing sheet product the core alloy layer can be provided on one side of its surface with a brazing clad layer material and an inter-layer interposed there between or it can be provided on both sides with a brazing clad layer material and on each side an inter-layer interposed there between. Alternatively the core layer can be provided on one side of its surface with a brazing clad layer material and an inter-layer material interposed there between whereas on the other surface of the core layer there is provided a corrosion protective water-side liner material or a brazing clad layer material devoid of an inter-layer material between the core layer and the brazing clad layer material.

The invention shall also be described with reference to the appended Fig. 1 to Fig. 3 showing a schematic representation of the multi-layered brazing sheet product according to this invention.

Fig. 1 shows a schematic representation of an embodiment of the multi-layered brazing sheet product formed by an aluminium alloy core layer (1) on one

surface clad with an Al-Si brazing clad layer material (2) and interposed between the core layer (1) and brazing clad layer material (2) there is an inter-layer material (3) made from an 1xxx-series alloy having a purposive addition of Mg.

Fig. 2 shows another embodiment of the multi-layered brazing sheet product in which starting from the embodiment of Fig. 1 the other surface of the core layer is also provided with an Al-Si brazing clad layer material (2) and interposed between the core layer (1) and brazing clad layer material (2) there is also an inter-layer material (3) made from a 1xxx-series alloy having a purposive addition of Mg.

Fig. 3 shows another embodiment of the multi-layered brazing sheet product in which starting from the embodiment of Fig. 1 the other surface of the core layer (1) is provided with a waterside liner material (4).

In an embodiment the waterside liner material is made from an 3xxx-series aluminium alloy, and more preferably it is made of an aluminium alloy consisting of:

Mn	0.5% to 1.8%, preferably 0.6% to 1.3%, more preferably 0.75% to 1.0%,
Zn	1% to 3.5%, preferably 1.5% to 3%,
Mg	< 0.3%, preferably < 0.10%,
Si	< 1.2%, preferably < 0.5%,
Fe	< 0.8%, preferably < 0.5%,
Cu	< 0.8%, preferably < 0.1%,
Ti	< 0.25%, preferably 0.01% to 0.12%,
	unavoidable impurities each <0.05%, total <0.2%, remainder aluminium.

At too high Zn-levels, in particular with thin gauge materials, too much Zn may diffuse into the core alloy during the heat-up and the brazing cycle. Furthermore, a too high Zn content may lead to evaporation of Zn from the liner during the heat-up and the brazing cycle.

The waterside liner has typically a thickness of 3% to 20% of the total thickness of the 4-layered brazing sheet structure, for example of about 15%. In an embodiment the waterside liner has a gauge in the range of 25 μ m to 70 μ m, for example of about 30 μ m or about 40 μ m, to provide the required corrosion resistance.

In another aspect of the invention it relates to a brazing method using the multi-layered brazing sheet product and its preferred embodiments, the method relates to manufacturing an assembly of joined components, in particular a heat exchanger, joined by brazing in a controlled atmosphere brazing process, comprising the steps of:

(a) providing of the components to be brazed together of which at least one is made from a multi-layered brazing sheet product having an aluminium core alloy layer provided one or both sides with a brazing clad layer material, and an inter-layer positioned between the aluminium core alloy layer and at least one of said brazing clad layer materials, wherein the brazing layer material(s) is made from an 4xxx-series aluminium alloy having 5% to 15% Si and up to 3% Mg, preferably up to 0.90% Mg, and more preferably up to 0.5%, and wherein the inter-layer is made from an 1xxx-series aluminium alloy having a purposive addition of Mg of about 0.10% to 2.0%, and wherein preferably the outer-surface of the brazing clad layer material(s) has been pre-treated by means of etching with an alkaline or acidic etchant,

(b) assembling the components into an assembly;

(c) brazing the assembly without applying brazing flux onto the assembly components, and brazing the whole assembly in a dry inert gas atmosphere at a brazing temperature, preferably at a temperature in a range of about 540°C to 615°C, for example at about 590°C or at about 600°C, for a period long enough for melting and spreading of the brazing clad layer materials, for example a dwell time of about 1 to 10 minutes, preferably of about 1 to 6 minutes, typically at around 2 or 4 minutes, to form a fillet between the multi-layered brazing sheet product and at

least one other component; and wherein the oxygen content of the dry inert gas atmosphere is controlled to be less than 35 ppm, preferably less than 25 ppm;

(d) cooling of the brazed assembly, typically to below about 100°C, e.g. to ambient temperature.

The brazing inert gas atmosphere should be dry, meaning that the dew point is less than -40°C, and more preferably of -45°C or even lower.

In another aspect of the invention it relates to the use or method of use of a multi-layered brazing sheet product having an aluminium core alloy layer provided one or both sides with a brazing clad layer material, and an inter-layer positioned between the aluminium core alloy layer and at least one of said brazing clad layer materials, wherein the brazing layer material(s) is made from an 4xxx-series aluminium alloy having 5% to 15% Si and up to 3% Mg, preferably up to 0.9% Mg, and more preferably up to 0.5%, and wherein the inter-layer is made from a 1xxx-series aluminium alloy having a purposive addition of Mg of 0.10% to 2.0%, and preferably the outer-surface of the brazing clad layer material(s) having been pre-treated by means of etching with an alkaline or acidic etchant, and applied or used in a fluxless controlled atmosphere brazing process performed in a dry inert gas atmosphere at a brazing temperature for a period long enough for melting and spreading of the brazing clad layer material to form a fillet between the multi-layered brazing sheet product and another component, and wherein the oxygen content of the dry inert gas atmosphere is controlled to be less than 35 ppm, preferably less than 25 ppm, more preferably less than 20 ppm. Preferably, the oxygen content of the dry inert gas atmosphere is controlled to be at least 5 ppm.

Preferred embodiments of the multi-layered brazing sheet product and of the brazing process conditions have been set out herein when describing the product and method according to this invention.

The multi-layered brazing sheet product and the brazing method according to this invention have proven to be of particular use in the production of heat exchang-

er devices having very high requirements on inner cleanliness, in particular oil coolers and charge-air-coolers. These heat exchangers are not suitable for production by vacuum brazing either due to their large size or for economic reasons.

The invention is not limited to the embodiments described before, which may be varied widely within the scope of the invention as defined by the appending claims.

CLAIMS

1. A multi-layered brazing sheet product having an aluminium core alloy layer provided on one or both sides with a brazing clad layer material, and an inter-layer material positioned between the aluminium core alloy layer and at least one of said brazing clad layer materials, wherein the brazing layer material(s) is made from an 4xxx-series aluminium alloy having 5% to 15% Si and up to 3% Mg, and preferably up to 0.9% Mg, and wherein the inter-layer material is made from a 1xxx-series aluminium alloy having a purposive addition of Mg of 0.10% to 2.0%.
2. A multi-layered brazing sheet product according to claim 1, wherein the brazing clad layer material has a composition, consisting of:

Si	5% to 15%
Mg	up to 0.9%, and preferably up 0.5%,
Fe	up to 0.8%
Cu	up to 0.3%
Mn	up to 0.8%
Zn	up to 0.25%
Ti	up to 0.3%,

balance aluminium and unavoidable impurities each <0.05%, total <0.2%.
3. A multi-layered brazing sheet product according to claim 2, wherein the brazing clad layer material has a composition, consisting of:

Si	5% to 15%
Mg	up to 0.9%, and preferably up 0.5%,
Fe	up to 0.8%
Cu	up to 0.3%
Mn	up to 0.8%
Zn	up to 0.25%
Ti	up to 0.3%,

and optionally one or more wetting elements selected from the group consisting of: Bi 0.03% to 0.5%, Pb 0.03% to 0.5%, Sb 0.03% to 0.5%, Li 0.03% to 0.5%, Se 0.03% to 0.5%, Y 0.03% to 0.5%, Th 0.03% to 0.5%, and the sum of these elements being 0.5% or less,
balance aluminium and unavoidable impurities each <0.05%, total <0.2%.

4. A multi-layered brazing sheet product according to any one of claims 1 to 3, wherein the inter-layer is made from a 1xxx-series aluminium alloy having a purposive addition of Mg of 0.10% to 1.5 %, preferably 0.10% to 1.0%, and more preferably 0.10% to 0.7%.
5. A multi-layered brazing sheet product according to any one of claim 1 to 4, wherein the aluminium core alloy layer is provided on both sides with a brazing clad layer material, and an inter-layer positioned between the aluminium core alloy layer and each of said brazing clad layer materials.
6. A multi-layered brazing sheet product according to any one of claims 1 to 4, wherein the aluminium core alloy layer is provided on one side with a brazing clad layer material and an inter-layer positioned between the aluminium core alloy layer and the brazing clad layer material, and is provided with a corrosion protective layer on the other side.
7. A multi-layered brazing sheet product according to claim 6, wherein the aluminium core alloy layer is provided on one side with a brazing clad layer material and an inter-layer positioned between the aluminium core alloy layer and the brazing clad layer material, and is provided with a corrosion protective layer on the other side made from an 3xxx-series aluminium alloy.
8. A multi-layered brazing sheet product according to claim 6 or 7, wherein the aluminium core alloy layer there is provided on one side with a brazing clad layer material and an inter-layer positioned between the aluminium core alloy layer and the brazing clad layer material, and is provided with a corrosion pro-

protective layer on the other side made from an 3xxx-series aluminium alloy consisting of:

Mn	0.5% to 1.8%, preferably 0.6% to 1.3%,
Zn	1% to 3.5%,
Mg	< 0.3%,
Si	< 1.2%,
Fe	< 0.8%,
Cu	< 0.8%, preferably < 0.1%,
Ti	< 0.25%,

unavoidable impurities each <0.05%, total <0.2%, remainder aluminium.

9. A multi-layered brazing sheet product according to any one of claims 1 to 8, wherein the Mg-content in the inter-layer material is higher than the Mg-content in the brazing clad layer material.
10. A multi-layered brazing sheet product according to any one of claims 1 to 9, wherein the brazing clad layer material has been pre-treated by means of etching with an alkaline or acidic etchant.
11. A multi-layered brazing sheet product according to any one of claims 1 to 10, wherein the core alloy is made from an 3xxx-series alloy having a composition consisting of:

Mn	0.8% to 1.5%
Si	0.25% to 0.75%
Cu	0.5% to 1.1%
Fe	up to 0.45%
Mg	up to 0.35%
Cr	up to 0.25%
Zr	up to 0.25%
Ti	up to 0.20%
Zn	up to 0.15%,

unavoidable impurities each <0.05%, total <0.2%, and balance aluminium.

12. Method of manufacturing an assembly of joined components, in particular a heat exchanger, joined by brazing in a controlled atmosphere brazing process, the method comprising the steps of:
 - (a) providing of the components to be brazed together of which at least one is made from a multi-layered brazing sheet product having an aluminium core alloy layer provided on one or both sides with a brazing clad layer material, and an inter-layer positioned between the aluminium core alloy layer and at least one of said brazing clad layer materials, wherein the brazing layer material(s) is made from an 4xxx-series aluminium alloy having 5% to 15% Si and up to 3% Mg, and wherein the inter-layer is made from an 1xxx-series aluminium alloy having a purposive addition of Mg of 0.10 to 2.0% according to any one of claims 1 to 11;
 - (b) assembling of the components into an assembly;
 - (c) brazing the assembly without applying brazing flux onto the assembly components, and brazing the whole assembly in a dry inert gas atmosphere at a brazing temperature, and wherein the oxygen content of the dry inert gas atmosphere is less than 35 ppm;
 - (d) cooling of the brazed assembly.
13. Method according to claim 12, wherein the brazing clad layer material has been pre-treated by means of etching with an alkaline or acidic etchant.
14. Method according to claim 12 or 13, wherein the dwell time at brazing temperature in in a range of 1 to 10 minutes, preferably 1 to 6 minutes.
15. Method according to any one of claims 12 to 14, wherein the oxygen content of the dry inert gas atmosphere is less than 25 ppm, and preferably less than 20 ppm.

16. Method according to any one of claims 12 to 15, wherein the oxygen content of the dry inert gas atmosphere is controlled to be at least 5 ppm.
17. Method according to any one of claims 12 to 16, wherein the assembly of joined components form a charge-air-cooler or oil cooler.
18. Use of a multi-layered brazing sheet product according to any one of claims 1 to 11, and preferably having been pre-treated by means of etching with an alkaline or acidic etchant, and applied in a fluxless controlled atmosphere brazing process performed in a dry inert gas atmosphere at a brazing temperature for a period long enough for melting and spreading of the brazing clad layer material to form a fillet between multi-layered brazing sheet product and another component, and wherein the oxygen content of the dry inert gas atmosphere is less than 35 ppm, and preferably less than 25 ppm.
19. Use according to claim 18, wherein the multi-layered brazing sheet product and the other component form part of oil cooler or a charge-air-cooler.

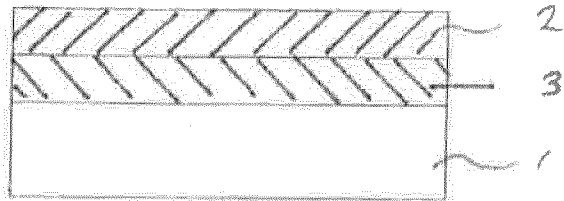


Fig. 1

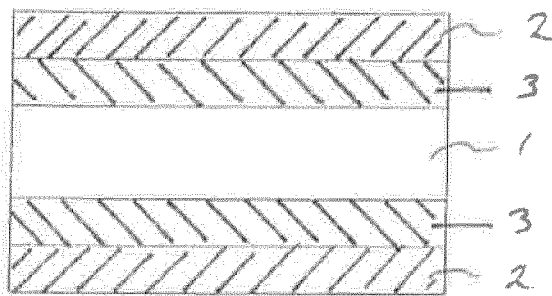


Fig. 2

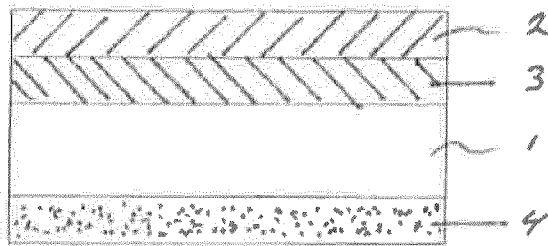


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/051278

A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B15/01 B23K35/28 B23K35/02 C22C21/00 C22C21/02
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
B32B B23K C22C
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2007/042206 A1 (CORUS ALUMINIUM WALZPROD GMBH [DE]; VIEREGGE KLAUS [DE]; DESIKAN SAMPA) 19 April 2007 (2007-04-19) page 2, line 6 - page 3, line 31; claims 1-19 -----	1-19
Y	US 2015/053751 A1 (ECKHARD KATHRIN [DE] ET AL) 26 February 2015 (2015-02-26) paragraphs [0007], [0013] - [0014]; claims 1-17 -----	1-19
A	EP 2 259 002 A1 (KOBE STEEL LTD [JP]) 8 December 2010 (2010-12-08) paragraphs [0049] - [0051]; figure 1 -----	1-19
A	US 2008/274367 A1 (KILMER RAYMOND J [US] ET AL) 6 November 2008 (2008-11-06) table 2 -----	1-19
	-/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
---	---

Date of the actual completion of the international search 13 February 2017	Date of mailing of the international search report 22/02/2017
---	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Chebeleu, Alice
--	---

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/051278

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 20 2013 101870 U1 (ALERIS ROLLED PROD GERMANY GMBH [DE]) 28 June 2013 (2013-06-28) claims 1-13 -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2017/051278

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007042206	A1	19-04-2007	CA 2624160 A1 19-04-2007
			CN 101287573 A 15-10-2008
			EP 1934013 A1 25-06-2008
			FR 2892038 A1 20-04-2007
			HU E028510 T2 28-12-2016
			KR 20080056203 A 20-06-2008
			US 2007122648 A1 31-05-2007
			WO 2007042206 A1 19-04-2007

US 2015053751	A1	26-02-2015	EP 2660043 A1 06-11-2013
			EP 2844466 A1 11-03-2015
			ES 2595044 T3 27-12-2016
			JP 5976200 B2 23-08-2016
			JP 2015526290 A 10-09-2015
			JP 2016221578 A 28-12-2016
			KR 20140146672 A 26-12-2014
			US 2015053751 A1 26-02-2015
			WO 2013164466 A1 07-11-2013

EP 2259002	A1	08-12-2010	AU 2009229974 A1 01-10-2009
			CA 2717372 A1 01-10-2009
			CA 2856597 A1 01-10-2009
			CN 101952681 A 19-01-2011
			EP 2259002 A1 08-12-2010
			JP 5222197 B2 26-06-2013
			JP 2009255171 A 05-11-2009
			KR 20100132510 A 17-12-2010
			RU 2010144072 A 10-05-2012
			US 2011011573 A1 20-01-2011
WO 2009119653 A1 01-10-2009			

US 2008274367	A1	06-11-2008	US 2008274367 A1 06-11-2008
			WO 2009142651 A2 26-11-2009

DE 202013101870	U1	28-06-2013	NONE
