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(54) Title: BRAZING FLUX COMPOSITION COMPRISING A LUBRICANT

(57) Abstract: The invention relates to a composition comprising a flux or flux-producing compound, a resin, and a wax. The invention further relates to the use of such composition in the brazing of an aluminium comprising substrate. When a composition according to the present invention is used, it is not necessary to use an additional lubricant during deforming.

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BRAZING FLUX COMPOSITION COMPRISING A LUBRICANT

This invention relates to compositions comprising a flux, which compositions are sometimes referred to as 'flux compositions'. The invention further relates to the
5 application of such compositions to aluminium comprising substrates, and the use of such compositions in the brazing of aluminium comprising substrates.

Aluminium comprising substrates, for example aluminium or aluminium alloy comprising sheets, are used to make shaped, or formed, products. In some of
10 these processes parts of (shaped) aluminium comprising substrates are interconnected. One end of a substrate may be interconnected with the other end, or one substrate may be assembled with one or more other substrates. This is commonly done by brazing. In a brazing process, a brazing filler metal or brazing alloy, or a composition producing a brazing alloy upon heating, is
15 applied to at least one portion of the substrate to be brazed. After the substrate parts are assembled, they are heated until the brazing metal or brazing alloy melts. The melting point of the brazing material is lower than the melting point of the aluminium comprising substrate(s).

20 In a brazing process it is necessary to at least provide the surface of one portion of the substrate to be brazed with a flux composition. A flux composition comprises a flux, or fluxing agent, for example an oxyfluoroaluminium, a hydroxyfluoroaluminium, a potassium fluoroaluminate, a fluoroborate, or a fluorozincate. The flux promotes the brazing connection between the aluminium
25 comprising parts. The flux may facilitate the melting of the brazing material, e.g. by removing oxides from the surfaces to be joined, or by preventing the formation of oxides on the surface.

It is known, e.g. this is described in WO 00/64626 and WO 03/037559, to apply a
30 flux composition as a coating to an aluminium or aluminium comprising substrate before such substrate is shaped or formed into a shaped product, and

brazed at a later stage. This is advantageous since the flux composition can be applied as a coating to a sheet-type substrate

In WO 03/037559-A1 and WO 00/64626 flux compositions are described
5 comprising a synthetic resin which mainly comprises a methacrylate homopolymer, a methacrylate copolymer or a olefin-acrylate copolymer. The flux compositions are applied to a sheet like aluminium or aluminium containing substrates, these substrates are shaped, and after the shaping the brazing takes place. However, to facilitate this shaping process it is generally required
10 to use a lubricant, e.g. a lubricating oil. This lubricant has to be removed before or after the brazing process.

In US 6,497,770 flux compositions are described that contains a binder of an alkyd resin, a mixture of an acrylic resin and a butyl rubber (or a petroleum
15 resin), and/or a polyethylene resin. It is stated that a product coated with a flux composition comprising a butyl rubber can be more easily subjected to plastic working after coating.

EP 1233345-A2 describes a process in which a surface of an aluminium
20 member is coated with a resin; the aluminium member is subsequently deformed, and then joined with another resin-coated aluminium member. The resin is fused to join the aluminium members. In a preferred process, a resin having lubricating properties is used so that the deformation step of the aluminium substrate can be performed without using an additional lubricant.
25 However, only few lubricating resins are mentioned (polyester resin, nylon resin, and vinylidene fluoride resin) and normally the bond formed between the aluminium members using a process as described in EP 1233345-A2 will be less strong than the bond formed in a metal brazing process.

30 The present invention relates to flux compositions that can be applied to sheet material for brazing, that can be shaped into various forms without the need to

use an additional lubricant. The composition according to the present invention comprises a resin, a wax, and a flux and/or flux-producing compound.

Within the framework of the present invention, a wax is a naturally occurring or synthetic material that is solid at 20 °C. The melting point a wax normally is at
5 least 40 °C, and at the melting temperature the material does not decompose. Waxes that are suitable for use in a composition according to the present invention may have a consistency at 20 °C ranging from soft and plastic to brittle and hard.

10 An advantage of a composition according to the present invention is that the flux composition of the present invention is self lubricating, in other words, the frictional properties are improved. Hence, an aluminium comprising substrate which is coated with a flux composition according to the present invention can be deformed without using an additional lubricant. The composition also works
15 as an anti-blocking agent during the deformation. For example, the wax in the composition reduces or eliminates the problem of sticking of the flux composition to the deformation equipment. Further, the use of a flux composition according to the present invention reduces the wear on the deformation equipment. Additionally, a substrate coated with a flux composition
20 according to the present invention does not need to be cleaned and dried after deforming.

Another advantage is the improved scratch and abrasion resistance of the substrate because the composition forms a protective layer, especially during
25 deforming. An applied layer of the composition of the present invention has, optionally after drying, an improved resistance to damage compared to conventional flux compositions.

The composition according to the present invention is very suitable to be used
30 in a controlled application process. It is relatively easy to obtain a uniform application of the composition of the invention. A uniformly applied flux

composition is advantageous as it results in an improved flux distribution. An improved flux distribution is advantageous as it results in an improved joint quality, a reduced rejection rate, and reduced waste when the substrate is brazed.

5

The flux or flux-producing compound in a composition according to the present invention may be chloride comprising, and preferably comprises fluoride. Preferably the flux or flux-producing compound is solid at room temperature, more preferably it is added to the composition as a powder. The composition
10 may comprise a mixture of one or more flux compounds and/or one or more flux-producing compounds.

As examples of fluoride comprising flux compounds the following compounds can be mentioned. Potassium fluoride (KF), aluminium fluoride (AlF_3), caesium
15 fluoride (CsF), rubidium fluoride (RbF), lithium fluoride (LiF), sodium fluoride (NaF), and calcium fluoride (CaF_2). Potassium fluoroaluminates such as potassium tetrafluoroaluminate (KAlF_4), potassium pentafluoroaluminate (K_2AlF_5 , $\text{K}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$), and potassium hexafluoroaluminate (K_3AlF_6). Examples of such fluxes have been described in GB 1438955-A, US 4428920, US
20 3951328, US 5318764, and US 4579605. Oxyfluoroaluminum such as $\text{Al}_2\text{F}_4\text{O}$ and AlFO . Hydroxyfluoroaluminium such as $\text{AlF}_2(\text{OH})$, $\text{AlF}_2(\text{OH}) \cdot \text{H}_2\text{O}$, and $\text{AlF}(\text{OH})_2$. Fluoroborates such as potassium tetrafluoroborate (KBF_4) and sodium tetrafluoroborate (NaBF_4). Examples of such fluxes have been described in GB 899171-A, GB 1007039-A, and US 4235649. Fluorozincates
25 such as potassium trifluorozincate (KZnF_3), potassium tetrafluorozincate (K_2ZnF_4), caesium trifluorozincate (CsZnF_3), and caesium tetrafluorozincate (Cs_2ZnF_4). Examples of such fluxes have been described in DE 19913111-A and WO 9948641-A. Alkali metal fluorosilicates such as caesium hexafluorosilicate (Cs_2SiF_6), potassium hexafluorosilicate (K_2SiF_6), lithium
30 hexafluorosilicate (Li_2SiF_6), rubidium hexafluorosilicate (Rb_2SiF_6), sodium hexafluorosilicate (Na_2SiF_6), and ammonium hexafluorosilicate ($(\text{NH}_4)_2\text{SiF}_6$).

Examples of such fluxes have been described in US 5785770, DE 19636897-A, US 5985233, US 6019856-A, US 5980650, and WO 9810887-A. Alkali bimetal fluorosilicates such as potassium caesium hexafluorosilicate (KCsSiF_6), lithium caesium hexafluorosilicate (LiCsSiF_6), rubidium caesium hexafluorosilicate (RbCsSiF_6), rubidium potassium hexafluorosilicate (RbKSiF_6) and ammonium caesium hexafluorosilicate ($\text{NH}_4\text{CsSiF}_6$). Alkali metal bifluorosilicates (also referred to as alkali metal hydrofluorosilicates) such as caesium hydrofluorosilicate (CsHSiF_6), potassium hydrofluorosilicate (KHSiF_6), lithium hydrofluorosilicate (LiHSiF_6), and ammonium hydrofluorosilicate (NH_4HSiF_6). Caesiumfluoroaluminate complexes such as caesium fluoride (CsF), caesium hexafluoroaluminate (Cs_3AlF_6), caesium tetrafluoroaluminate (CsAlF_4 , $\text{CsAlF}_4 \cdot \text{H}_2\text{O}$), and caesium pentafluoroaluminate (CsAlF_5 , $\text{CsAlF}_5 \cdot \text{H}_2\text{O}$). Examples of such fluxes have been described in US 4670067, US 5171377, US 5806752, US 5771962, and US 4655385. So-called super-fluid fluxes can be used as well.

As examples of flux-producing compounds the following compounds and mixtures can be mentioned so-called reactive fluxes as described in WO 0138040-A. The composition may comprise fluxes based upon K_2SiF_6 or KZnF_3 . This type of reactive fluxes can produce potassium fluoroaluminate, which acts as a flux material.

The composition of the present invention comprises at least one flux or flux-producing compound. It may comprise mixtures of the above-mentioned examples of flux and flux-producing compounds. In one embodiment potassium fluoroaluminate(s) or compound(s) producing potassium fluoroaluminates, or mixtures thereof, are used. As examples of commercially available potassium fluoroaluminate comprising flux materials can be mentioned: Nocolok[®] and Nocolok Sil[®] (ex Solvay Chemicals).

The composition according to the present invention comprises a resin. In one embodiment, this resin is a synthetic resin. In a further embodiment, the (synthetic) resin comprises as its main constituent, an acrylic acid ester, preferably a methacrylic acid ester. In a further embodiment the resin mainly
5 comprises a methacrylate homopolymer or a methacrylate copolymer. It is also possible to use mixtures of such resins.

As examples of monomers that can be used to prepare such resin(s) can be mentioned: methyl methacrylate, ethyl methacrylate, propyl methacrylate, 2-methylpropyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, isodecyl methacrylate, lauryl
10 methacrylate, tridecyl methacrylate, stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, diethylaminoethyl methacrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, glycidyl methacrylate, metatetrahydrofurfuryl methacrylate.

15 In a further embodiment the resin used in the present invention evaporates and/or decomposes during the brazing process, and can thus attain an excellent outward appearance of a brazed portion after brazing, without causing brazing insufficiency such as residual carbon.

In a further embodiment the resin is a synthetic resin comprising 90-100 wt% of
20 an acrylic acid ester, for example the resin comprises 90-100 wt% polymethyl methacrylate.

Preferably the resin has a composition which volatilizes in the range of 175-400°C, and preferably below 350°C.

25 In one embodiment the wax in a composition according to the present invention is a wax that evaporates or decomposes during the brazing process, preferably preferably during heat-up in a brazing process, which takes place at a temperature above 450°C, and more typically takes place in the range of 500 to 640°C, more typically in the range of 560 to 620°C, when aluminium substrate is
30 involved.

The composition according to the present invention comprises at least one wax. A single wax may be used, but it is also possible to use two or more waxes, for example a blend of two or more waxes. The wax may be modified or unmodified. Naturally occurring waxes, such as vegetable waxes or animal
5 waxes, may be used. Additionally, or alternatively, synthetic waxes may be used.

In another embodiment the wax is a hydrocarbon wax, i.e. a wax consisting of carbon and hydrogen atoms and no or substantially no other atoms; the hydrocarbon wax preferably consists of more than 90%, even more preferably
10 of more than 95% of carbon and hydrogen atoms.

In a further embodiment the wax is a polyolefin wax, i.e. a saturated hydrocarbon wax.

In a further embodiment mixtures of hydrocarbon waxes, (a) hydrocarbon wax(es) and (a) polyolefin wax(es) or mixtures of polyolefin waxes are used.
15 and mixtures of hydrocarbon wax(es) and/or polyolefin wax(es) are preferred.

The brazing composition according to the present invention may further comprise a brazing material formed by a brazing metal or brazing alloy, or a composition producing a brazing alloy upon heating. In another embodiment,
20 the brazing material forms an eutectic alloy or near-eutectic with aluminium upon brazing. For example, the brazing composition may comprise Si, for example Si-particles in powder form, Zn, Cu, or Ge. Other examples are alloys of metals (e.g. Si, Zn, Cu, Sn, Ge) with aluminium or with zinc. Zinc alloys being another frequently used filler metal for brazing. As examples of commercially
25 available alloys of Si with aluminium can be mentioned AA4047 and AA 4045 (ex Solvay Chemicals).

In one embodiment the brazing alloy is an Al-Si alloy having additions of Cu and/or Zn to substantially lower the melting point of the alloy, thereby allowing a brazing operation to be carried out at lower temperatures such as 520°C, 540°C
30 or 560°C.

In another embodiments the brazing alloy is an Al-Si-Zn hypereutectic alloy, preferably composed of a powder or mixture of powders, each powder or mixture of powders consisting essentially of one or more of Al, Si or Zn, and wherein in the Al-Si-Zn hypereutectic alloy has a composition such that Si is in a
5 range of 14 to 45 wt.% and the Zn is in a range of 5 to 30 wt.%.

In another embodiment a low-melting brazing alloy is used for brazing at a temperature in the range of 520 to 580°C. The brazing alloy comprises 0.001 to 3.0 wt.% of rare-earth element, 20 to 50 wt.% of Zn, 10 wt.% or less of Si, optionally 0.005 to 3.0 wt.% of Ti, and the balance Al and impurities. Ti as
10 optionally present has an effect for preventing a solidification cracking of the brazed connection. All rare-earth elements or a mixture thereof may be employed. Among these elements, misch metal, La, Ce or Sm, which can be obtained at lower cost, are preferably used.

15 The composition may comprise one or more solvents. In one embodiment the composition comprises an organic solvent.

In a further embodiment a solvent having hydrophilic properties is used. In a further embodiment a solvent or mixture of solvents is used that has good polymer solvation and/or application properties. Examples of preferred solvents
20 are 2-propanol, 1-propanol, ethylene glycol mono-ethyl ether, di-ethylene glycol mono-ethyl ether, tri-ethylene glycol mono-ethyl ether, ethylene glycol mono-butyl ether, propylene glycol mono-ethyl ether, propylene glycol mono ethyl ether, propylene glycol ether, propylene glycol ester, butan-1-ol, 1-methoxy-2-propanol, 4-hydroxy-4-methyl-pentan-2-one, and 1-methoxy-2-propylacetate, or
25 mixtures thereof.

Additives may be added to the composition according to the present invention. For example, an anti-oxidant, an anti-corrosive agent, an anti-foaming agent, a thickener, a plasticizer, a tackifier, a coupling agent, and the like may be added.

Additionally, mineral oils, paraffin oils, silicone fluids and/or polysiloxane compounds may be added, as these may influence the lubricating / slip properties of the composition.

- 5 The weight ratio of the flux and/or flux-producing compound(s) to the resin(s) normally is in the range of 1:2 to 6:1, preferably in the range of 1:2 to 3:1, and highly preferably in the range of 3:2 to 5:2, the weight ratio being calculated on the weight of these components in the uncured coating composition.

The ratio of the weight of the wax(es) to the combined weight of the flux and/or
10 flux-producing compound(s) and of the resin(s) normally is in the range of 1:99 to 30:70, preferably in the range of 1:99 to 15:85, and highly preferably in the range of 2:98 to 10:90, the weight ratio being calculated on the weight of these components in the uncured coating composition.

In case one or more dispersion agents are present, the ratio of the weight of the
15 dispersion agent(s) to the combined weight of the flux and/or flux-producing compound(s) and of the resin(s) and of the wax(es) normally is in the range of 0.2:99.8 to 10:90, preferably in the range of 0.3:99.7 to 4:96, and highly preferably in the range of 0.4:99.6 to 3:97.

- 20 In one embodiment, a composition is prepared that evaporates and/or decomposes during the brazing process in which process the brazing temperature is within the range of 500 to 700 °C. In a further embodiment the brazing temperature is within the range of 580 to 640 °C. In a further embodiment the brazing is performed in an inert atmosphere, e.g. an inert
25 nitrogen atmosphere. Brazing may be performed in batch type furnaces or, more commonly, in continuous tunnel furnaces.

The composition according to the present invention can be applied to an aluminium comprising substrate. The composition may be applied by means of
30 a roller coating, a spray method, immersion method, roll-transfer printing, or the like. In the case of an (organic) solvent containing composition, the solvent

preferably is removed partially or completely from the composition after it has been applied to the substrate. For instance, the coating may be allowed to dry naturally or may be forced to dry. In a preferred embodiment, the applied composition is heated; more preferably, the applied composition is heated until
5 the composition is dry, i.e. until the composition comprises less than 5 weight% of solvent, calculated on the total weight of the dried composition.

To improve the adhesion between the composition and the aluminium comprising substrate, the substrate may be cleaned or surface treated before the composition is applied. In one embodiment, the surface is degreased before
10 the composition is applied. In a further embodiment, the surface of the substrate is etched using, e.g. an acid or any other etching medium, before the composition is applied.

The present invention further relates to a method in which a composition
15 according to the present invention is used in the brazing of aluminium comprising substrates. A composition according to the present invention is applied to (parts of) aluminium comprising substrate(s); optionally one or more substrates are shaped; and brazing is performed. During the optional shaping / forming of substrates covered with a composition according to the present
20 invention, it is not necessary to use an additional lubricant as the composition according to the present invention shows lubricating properties.

Examples

The invention will be elucidated with reference to the following examples. These are intended to illustrate the invention but are not to be construed as limiting in any manner the scope thereof.

5

Coating compositions were prepared comprising aluminium potassium fluoride, a methyl methacrylate copolymer, optionally a synthetic hydrocarbon wax, fumed silica, and a mixture of 4-hydroxy-4-methyl-pentan-2-one and 1-methoxy-2-propyl acetate to adjust the viscosity.

10

These compositions were applied to a pre-treated aluminium alloy brazing sheet using a 3 Roll Coater (Reverse Application configuration) at 4 to 8 g/m², sufficient to obtain a dry film thickness of 5 to 10 µm.

The sheets were dried in a convection oven at a temperature in the range of

15 200 to 230°C.

After drying, some properties of the sheets were assessed.

The results of the assessment can be found in table 1 below.

20

Table 1

	Example 1	Example 2*
Composition (in parts by weight)		
Aluminium Potassium Fluoride	25	25
Methyl Methacrylate Copolymer	14	14
Synthetic Wax	2	0
Fumed Silica	0.25	0.25
Mixture of 4-hydroxy-4-methyl-pentan-2-one and 1-methoxy-2-propyl acetate	50	50

Physical properties

Surface appearance

Matt, smooth
finishMatt, smooth
finishCross Hatch Adhesion + Adhesive Tape
(Cellotape)No adhesion
lossNo adhesion
LossReverse Impact + Adhesive Tape
(Cellotape) : 20, 40, 60 inch lbsNo adhesion
loss on
indentationNo adhesion
loss on
indentationT-bend flexibility + Adhesive Tape
(Cellotape)1T – Slight
discoloration
on the tape1T – Slight
discoloration
on the tape

Coefficient of Friction

Av <0.2

Av = 0.4

Brazing Joints (up to 620°C)

Good fillet
formationGood fillet
formation

*) Comparative Example

CLAIMS

1. A composition comprising a resin, a wax, and a flux and/or flux-producing compound.
- 5 2. A composition according to claim 1, characterised in that the flux and/or flux-producing compound comprises fluoride.
3. A composition according to claim 1 or 2, characterised in that the resin
10 comprises an acrylic acid ester.
4. A composition according to any one of claims 1 to 3, characterised in that the composition comprises a hydrocarbon wax, a polyolefin wax and/or a mixture thereof.
- 15 5. A composition according to any one of claims 1 to 4, characterised in that the weight ratio of the flux and/or flux-producing compound to the resin is in the range of 1:2 to 6:1.
- 20 6. A composition according to any one of claims 1 to 5, characterised in that the composition further comprises a dispersion agent.
7. A composition according to any one of claims 1 to 5, characterized in that the composition further comprises a brazing material.
- 25 8. Use of a composition according to any one of claims 1 to 7 in the brazing of aluminium comprising substrates.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/050158

A. CLASSIFICATION OF SUBJECT MATTER

INV. B23K35/28 B23K35/36

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)

B23K

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 practical, search terms used)

EPO-Internal, PAJ, 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	US 2003/203137 A1 (TESHIMA SHOEI ET AL) 30 October 2003 (2003-10-30) pages 2-5, paragraph 24; claims 1-11	1-8
Y	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 04, 31 March 1998 (1998-03-31) & JP 09 314380 A (SUMITOMO LIGHT METAL IND LTD), 9 December 1997 (1997-12-09) abstract	1-8
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A	WO 94/29072 A (LEXOR TECHNOLOGIES LIMITED; PRIGMORE, ROBERT, MARSHALL) 22 December 1994 (1994-12-22)	

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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.

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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