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(54) MATERIAL FOR JOINING AND PRODUCT PRODUCED THEREWITH

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(57) ABSTRACT

An iron based brazing material for joining of objects by brazing represents an alloy, which apart from iron contains maximum 40% Cr, maximum 16% Mn, maximum 40% Ni and maximum 7% Mo, all stated in weight percent and 6-40% Si, which Si-addition lowers the liquidus temperature, that is the temperature at which the brazing material is completely melted. A brazed product is manufactured by brazing of iron based objects with an iron based brazing material which is alloyed with a liquidus lowering element as Si, possibly also with B or P.

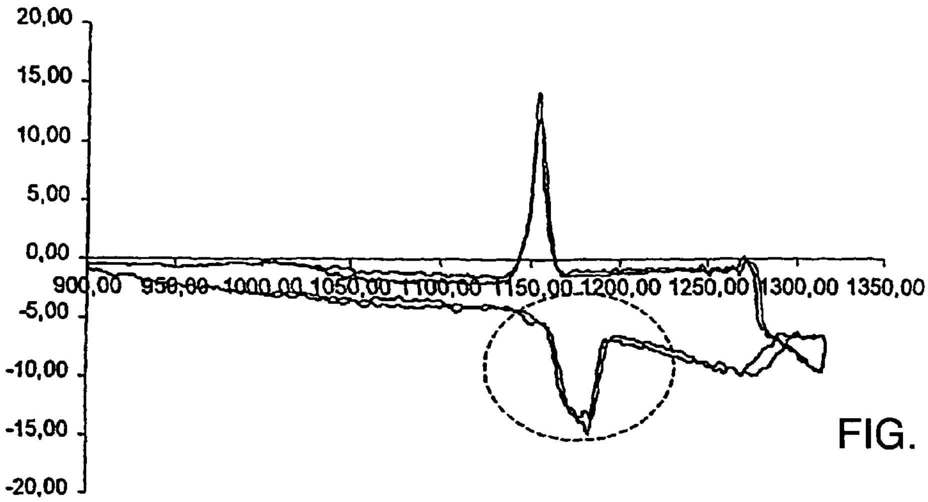

FIG. 1

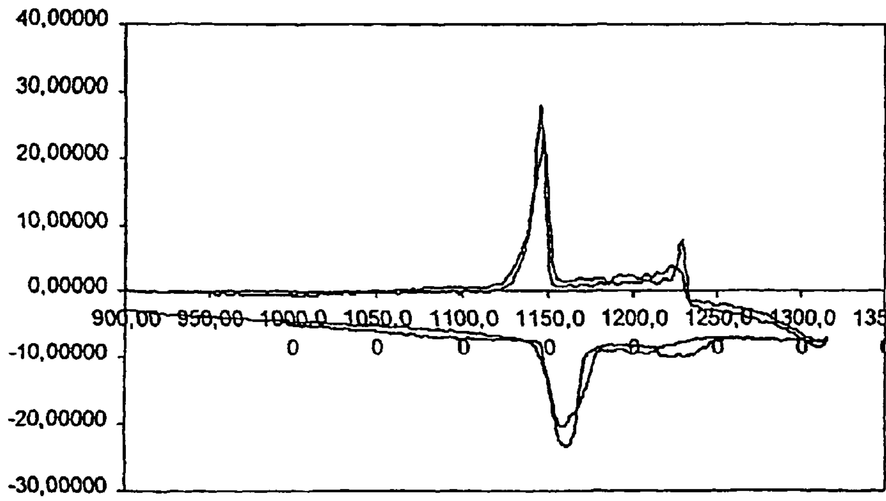

FIG. 2

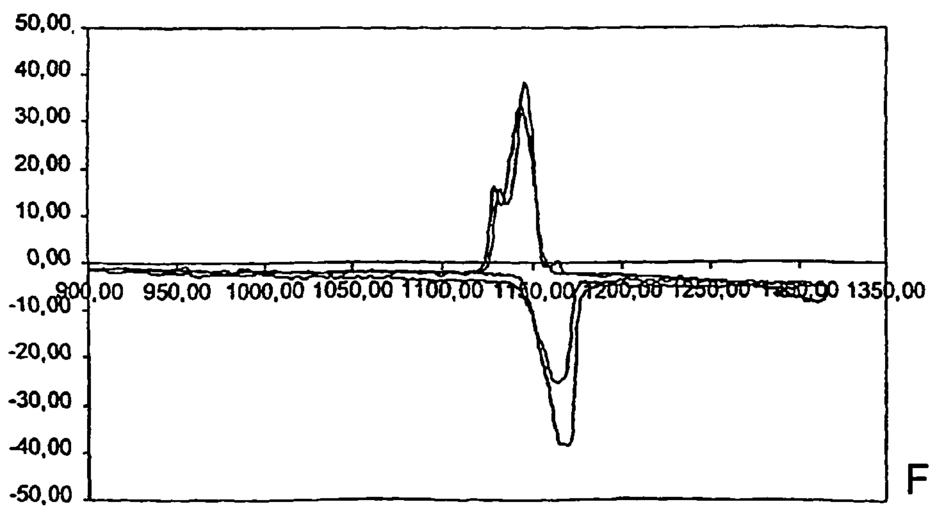

FIG. 3

MATERIAL FOR JOINING AND PRODUCT PRODUCED THEREWITH

[0001] The present invention relates to an iron based brazing material for joining objects by brazing. The invention also comprises a brazed product produced by brazing together objects of an iron based material with an iron based brazing material according to the invention.

[0002] Different steels or iron based materials are usually joined by brazing with Ni- or Cu-brazing materials. In some applications the brazing material may consists of Ag or Co.

[0003] Brazing is a process for tightening/joining, at which the temperature is below the original solidus temperature of the base material (the elements that should be joined/tightened).

[0004] Brazing materials refer to materials for joining or tightening, which completely or partly melts during the brazing process.

[0005] U.S. Pat. No. 4,135,656 describes a Ni-based alloy which contains, counted as percentage by weight, 19-23% Mn, 5-8% Si, 4-6% Cu, 0.6-1.8% B and Ni apart from smaller amounts of other elements. U.S. Pat. No. 4,314,661 describes another kind of Ni-based alloy which contains, given as a percentage of atoms, 0-4% Fe, 0-21% Cr, 0-19% B, 0-12% Si, 0-22% P and the rest is Ni.

[0006] U.S. Pat. No. 4,516,716 describes a method of brazing with iron-based alloys including approximately 2 to approximately 6% by weight of boron and from approximately 5 to approximately 12% of silicon.

[0007] When brazing with Cu one generally uses pure or almost pure Cu. The pure copper brazing material has a well defined melting point, while nickel brazing materials, depending on the fact that they consists of alloys often have a melting interval instead.

[0008] When joining plates of stainless steel in plate heat exchangers brazing materials of copper is often used. Copper is however not suitable for all kinds of applications. The use of brazing material of copper for food applications is not allowed for example, but it is used for district heating and tap water installations.

[0009] Heat exchangers joined together with brazing material of nickel are used in many connections and are also allowed for a limited number of food applications.

[0010] If brazing materials containing nickel alloys are used for joining objects of iron or non Ni-based materials, the composition of the brazed joint differs significantly from the composition of the materials, which are joined together. This can result in undesired differences in chemical and mechanical properties.

[0011] The present invention offers possibility to join objects by means Of brazing by using a brazing material with mainly the same composition as the base material used for producing the product, at which the brazing material contains additive elements which lower its liquidus temperature. Consequently, the present invention offers a possibility to produce an apparatus as a plate heat exchanger, which is compatible with food application requirements by using a brazing material according to the invention. The invention is mainly characterized in that the brazing material consists of an alloy which contains at least 50% Fe and includes 0-30% Cr, preferably 9-30% Cr, maximum 5% Mn, 0-25% Ni, maximum 7% Mo, 0-1% N and 6-20% Si, all stated as weight percent, where addition of Si lowers the liquidus temperature, that is the temperature at which the brazing material is completely melted.

[0012] Apart from Si, the brazing material may also contains B, which acts as a melting point decreasing element supplementing Si, at which the amount of B is below 2%, preferably below 1.5%. The addition of B also increases the wettability of the brazing material.

[0013] In a preferred embodiment the iron based brazing material contains 7-16% Si, preferably 812%. The active, dissolved amount of Si should lie within the said interval in order to obtain the desired lowering of the melting point. The analysed amount of Si might however be considerably higher, since Si may occur in the state of silicon carbides or silicon borides, be bonded to oxygen or have been chemically bonded in some other way.

[0014] The iron based brazing material may contain micro alloying elements as V, Ti, W, Al, Nb, Ta and others. Variations in composition may also be a consequence of small inevitable amounts of contaminating elements as C, O and S.

[0015] Instead of adding B to the brazing material it is possible to add P as a melting point decreasing element within the scope of the invention. The amount of P is in such a case maximum 15%.

[0016] The iron based brazing material is with advantage produced by gas- or water atomisation.

[0017] If the alloy contains boron it is also possible to produce the brazing material by melt spinning.

[0018] The invention also comprises a brazed product produced by brazing together iron based objects, by which the product is characterized by the joining of the objects with a iron based brazing material which is an alloy with the composition mentioned above.

[0019] The brazed product is with advantage a plate heat exchanger intended for at least two heat exchanging media, which comprises at least one plate package manufactured by brazing together a number of thin walled heat exchanger plates of an iron based material by means of an iron based brazing material. The heat exchanger plates define between themselves plate inter spaces intended for the heat exchanging media. The brazing joints have a metallurgical composition close to the composition of the iron based plate material with locally higher amounts of Si in and around the brazing joints in comparison with the iron based plate material.

[0020] When the expression thin walled is used in connection with plate heat exchangers it is used for plates with a thickness below 1 mm. Such thin plates are necessary in order to obtain an efficient heat transfer.

[0021] The brazed product may with advantage be brazed with an iron based brazing material containing B or P.

[0022] For thin walled products as plate heat exchangers it is important to have the right relation between the amount of boron in the brazing material and the weight of the plates to be brazed. In such a case the percentage of boron will be maximum 1.5% in order to avoid excessive formation of chromium borides as will be described below.

[0023] For brazing of iron based materials one has as traditionally used Cu- or Ni-brazing materials as mentioned earlier. Surprisingly it has now been found that one may start with a base material with the same composition as the material in the objects one desires to join together. By alloying such a material with silicon one may obtain well functioning brazing materials. By studying binary phase diagrams for pure iron and Si, B and P one may find that a Fe—Si alloy has a melting point minimum of 1212° C. at around 19% Si. For a Fe—B alloy there is a melting point minimum at about 1174° C. for about 4% B. In the Fe—P system there is a melting minimum at about 1048° C. at about 10% P.

[0024] In most cases pure iron materials are not used but instead alloys are used, which apart from Fe also contains relatively large amounts of Cr and Ni. In many alloys there are also Mo, Mn, Cu and N. To try to theoretically establish the effect of addition of different amounts of silicon to such alloys is almost impossible, since the number of dimensions will be as large as the number of elements in the alloy.

[0025] In order to obtain a brazing joint the liquidus temperature of the brazing material ought to be below 1220° C.

[0026] Surprisingly enough it has been found that an addition of a relatively minor amount of silicon may give such a lowering of the liquidus temperature that a suitable brazing material may be obtained.

[0027] In the U.S. Pat. No. 4,516,718 there is described a brazing material that contains silicon and boron. In this patent the amount of boron is said to be about 2 to about 6% in order to obtain the desired lowering of the liquidus temperature.

[0028] According to the present invention it is stated that the percentage of boron should be below 2%. The reason for this is that the boron is contrast to the silicon diffuses very rapidly into and in the iron based material being brazed. This affects the performance of the brazed product. The best braze joints are obtained if the gap between the elements to be joined is as small as possible. The applied braze filler creates a distance between the elements to be joined due to the thickness of the braze filler in the gap. When brazing, the braze filler melts and will be pressed aside allowing the gap to decrease. In many cases, when brazing objects, as for example plate heat exchangers, the perimeter of the objects will be heated more rapidly than the interior of the object. Consequently also the brazing material starts to melt at the perimeter. Boron starts to diffuse and with that the brazing material starts to solidify, due to the change in the composition, at the perimeter before the brazing material in the interior has melted. According to the proposed invention silicon is the element used for decreasing the melting point and boron only to a smaller extent as a melting point decreasing element. Since silicon diffuses slower than boron the diffusion time increases so that the braze filler in the interior parts can melt before the outer parts solidify. The function of boron is mainly to increase the wettability of the brazing material.

[0029] An additional reason for avoiding a high content of boron is when the brazing alloys containing chromium. Many stainless steel contain around 17% Cr. The chromium content governs to a great extent the corrosion properties of the stainless steel. If there is chromium in the object to be brazed and boron in the brazing material there is a risk for formation of chromium borides. Each boron atom binds 3.8 chromium atoms if the formula for the boride is Cr 23B6. Also the fact that the relationship in the molecule weight between Cr and B is 52.0/10.8=4.8 shows that even small percentages, e.g. 2-3% B may decrease the chromium content to such an extent that it will have severe effects on the corrosion resistance. The corrosion resistance of the steel will decrease with each boride that is formed. The chromium borides will be harder than the base material and have also a needle formed shape. Their shape may give rise to stress concentration and consequently crack formation.

[0030] The present invention is of great value for brazing different kinds of objects of steel. As an example the stainless steel, alloy 316, may be mentioned. The chemical composition of this alloy is max. 2.0% Mn, 16.5-18% Cr, 10.0-13.0% Ni, 2.0-2.5% Mo, the balance being Fe. According to the invention, a brazing material is prepared with the same composition as the alloy but with a suitable amount of Si replacing the same amount of Fe by weight. After the brazing process the brazed product will have mainly the same composition in the brazed objects as in the brazing joints

[0031] In the table below there are shown different examples of compositions of brazing materials which have been produced by melting in a small vacuum furnace. The ingot was thereafter allowed to solidify in the mould.

TABLE 1

Analysis of some experiment melts

Melt	Fe	% Si	% Mn	% P	% B	% Cr	% Mo	% Ni
1	Bal	6	1	0	0	17	2.5	12
2	Bal	8	1	0	0	17	2.5	12
3	Bal	10	1	0	0	17	2.5	12
4	Bal	12	1	0	0	17	2.5	12
5	Bal	15	1	0	0	17	2.5	12
6	Bal	6	1	0	1.5	17	2.5	12
7	Bal	6	1	3	0	17	2.5	12
8	Bal	10	1.5			17	2.5	20

[0032] The expression Bal (balance) means that the remaining material in the melt consists of Fe.

[0033] The actual composition of the melts after the cast was measured and may be seen in table 2.

TABLE 2

Measured percentage in the ingot.

?	Fe	% Si	?	% P	% B	% Cr	% Mo	?	?
1	Bal	5.86	?			17.1	2.45	11.9	
2	Bal	8.20	1.29			17.2	2.51	11.9	
3	?	10.0	1.25			17.1	2.46	12.0	?
4	?	12.1	1.20			16.8	2.47	11.9	?
5	Bal	14.7	1.81			16.6	2.54	11.9	(38:42)
6	Bal	5.93	1.46		1.20	16.7	2.42	11.9	

TABLE 2-continued

Measured percentage in the ingot.									
⑦	Fe	% Si	⑦	% P	% B	% Cr	% Mo	⑦	⑦
7	Bal	6.37	1.60	3.09		17.2	2.51	11.6	
8	Bal	10.0	1.47			16.4	2.54	20.5	(27:30)

• Two measurements
⑦ indicates text missing or illegible when filed

[0034] A powder was produced from these experimental melts and test brazing was carried through in a vacuum furnace. The maximum temperature in the furnace was about 1190° C. The specimens were examined visually for a determination, if the alloy had melted or not, that it had reached and passed the solidus temperature or had melted completely, that it had reached the liquidus temperature.

TABLE 3

Visual determination of the solidus- and liquidus properties after test brazing at 1190° C. in a vacuum furnace.		
Melt	>Solidus	>Liquidus
1	Yes	No
2	Yes	Close
3	Yes	Yes or close
4	Yes	Yes
5	Yes	Yes
6	Yes	No
7	Yes	No
8	Yes	Close

[0035] As may be seen in the table melts 2-5 and 8 indicate, that the material may be suitable for brazing material at a brazing temperature below 1200° C.

[0036] The attached drawings show how the melts 2,3 and **5** have been examined for measurement of the melting interval in a DTA-equipment (Differential Thermal Analysis). The measurement is performed by heating the material in two stages from room temperature to a temperature of 900° C. and thereafter to a maximal temperature of 1300° C. The material is thereafter cooled to a temperature of 900° C. The heating and the cooling are repeated twice. The peaks, which overlap each other and point downward in the diagram, show the amount of heat needed to achieve melting. The extension of the peak constitutes a measure of the melting interval of the studied alloy.

[0037] **FIG. 1** shows the DTA curve for melt no. **2**, **FIG. 2** shows the same curve for melt no. **3** and **FIG. 3** for melt no. **5**.

[0038] As may be seen in the drawings the melting interval for an alloy with about 9% Si is 1154-1197° C. (**FIG. 1**), for an alloy with 10% Si 1145-1182° C. (**FIG. 2**) and for an alloy with 15% Si 1142-1177° C. (**FIG. 3**).

[0039] The accuracy of the melting interval, or deviations from the value that has been measured does not only depend on differences in the mean composition. Apart from the microstructure of the material, the content of contaminants is also important. Usually contaminating elements are C, O, S and N. At higher O-percentage Si is chemically bonded during the production process, which means that the effective, dissolved percentage of Si is reduced. This means that the liquidus temperature and the solidus temperature increase.

[0040] The percentage of carbon influences the melting temperature in such a way that a higher C-content usually yields a lower melting interval (lower solidus- and liquidus temperatures), but the corrosion properties for example are influenced in a negative way when brazing an iron based materials as for example alloy 316. Variations of the solidus- and liquidus temperatures with ±10° C. are not unusual.

[0041] The accuracy of the value is also depending on which measuring instrument and on which method that is used for the analysis. An uncertainty with ±20° C. for the liquidus- and solidus temperatures is normal for alloys where an analysis with the DTA-method is common.

[0042] The brazing material according to the invention is suitably made in the form of a powder. The powder may be manufactured by producing an ingot, which is thereafter is crushed and milled. The brittle nature of the material is utilised by this manufacturing method. The disadvantages with ingot casting is that a certain risk for segregation may give rise to a non homogenous material with a melting interval which is difficult to define or is broad. For smaller ingots and/or a rapid cooling the risk for segregations is reduced. In ingot casting it is important to minimise the contact with air by using vacuum casting or casting with a shielding gas. As a consequence of the mechanical treatment the energy content of the brazing material increases and with that its reactivity.

[0043] Further manufacturing methods to produce a powder with a homogenous composition consist of water or gas atomising. The properties of the powder vary with the manufacturing method. The crushed and milled particles are angular and pointed, the water atomised are nodular and the gas atomised are almost spherical. This difference in particle shape gives the brazing material somewhat varying properties when used for brazing. By choosing different atomising methods and crushing/milling extent combined with screening the distribution of the particles size may be controlled. In water atomising the oxygen content generally will be higher since water atomising takes place at a higher oxygen potential than gas atomising. A higher oxygen content may gives rise to formation of Si-oxides in the material which may have a negative influence on the mechanical properties of the brazing joint. The effective Si-percentage in the brazing material will consequently be lower, which means that the melting interval will be displaced.

TABLE 4

Other developed compositions											
Composition	% Fe	% Si	% Mn	% P	% B	% N	% Cr	% Mo	% Ni	>Solidus	>Liquidus
9	bal	12.2	1.5				18	0.3	8	Yes	Yes
10	bal	18.1	1.2				0	0	0	Yes	Yes
11	bal	8	1.5		0.5		17	2.2	11	Yes	Yes
12	bal	5	1.5	5			17	2.2	11	Yes	Yes
13	bal	7.8	0.45			0.2	20	6.1	18	Yes	Yes
14	bal	13	0.7				13	0	0	Yes	Yes

The alloys with composition 9-12 were brazed at a temperature of 1900° C. and the alloys with composition 13-14 were brazed at 1215° C.

[0044] The brazing material according to the invention may be applied on the places where one desires a brazing joint by means of different methods. A powder of the brazing material manufactured by any of the described methods may be suspended in some binder in order to be applied in some suitable manner.

1. Iron based brazing material for joining objects by brazing characterized in that the brazing material consists of an alloy which contains at least 50% Fe and includes 0-30% Cr, preferably 9-30% Cr, maximum 5% Mn, 0-25% Ni and maximum 7% Mo, 0-1% N and 6-20% Si, all stated in weight percent, which Si-addition lowers the liquidus temperature, that is the temperature when the brazing material is completely melted.

2. Iron based brazing material according to claim 1, characterized in that the brazing material apart from Si also contains B as a melting point lowering supplement to Si, at which the amount of B is below 2%, preferably below 1.5%, which addition also increases the wettability of the brazing material.

3. Iron based brazing material according to claim 1, characterized in that the amount of Si is 7-16%, preferably 8-12%.

4. Iron based brazing material according to claim 1, characterized In that the brazing material apart from Si also contains P as a melting point lowering supplement to Si, at which the amount of P is maximum 15%.

5. Iron based brazing material according to any of the preceding claims, characterized in that the brazing material is produced by gas- or water atomising or melt-spinning.

6. Brazed product manufactured by brazing the objects with an iron based brazing material according to claim 1, characterized in that the material in the objects to be brazed is iron based.

7. Brazed product according to claim 6, characterized in that the product is a plate heat exchanger intended for at least two heat exchanging media, which comprises at least one plate package manufactured by brazing together a number of thin walled heat exchanger plates of an iron based material brazed by means of a iron based brazing material, at which the heat exchanger plates between themselves define plate inter spaces intended for the heat exchanging media, at which the brazing joints have a metallurgical composition close to the composition of the iron based plate material with locally higher amounts of Si in and around the brazing joints in comparison with the iron based plate material.

8. Brazed product according to claim 7, characterized in that the iron based heat exchanger plates are brazed together with an iron based alloy containing B or P apart from Si.

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