



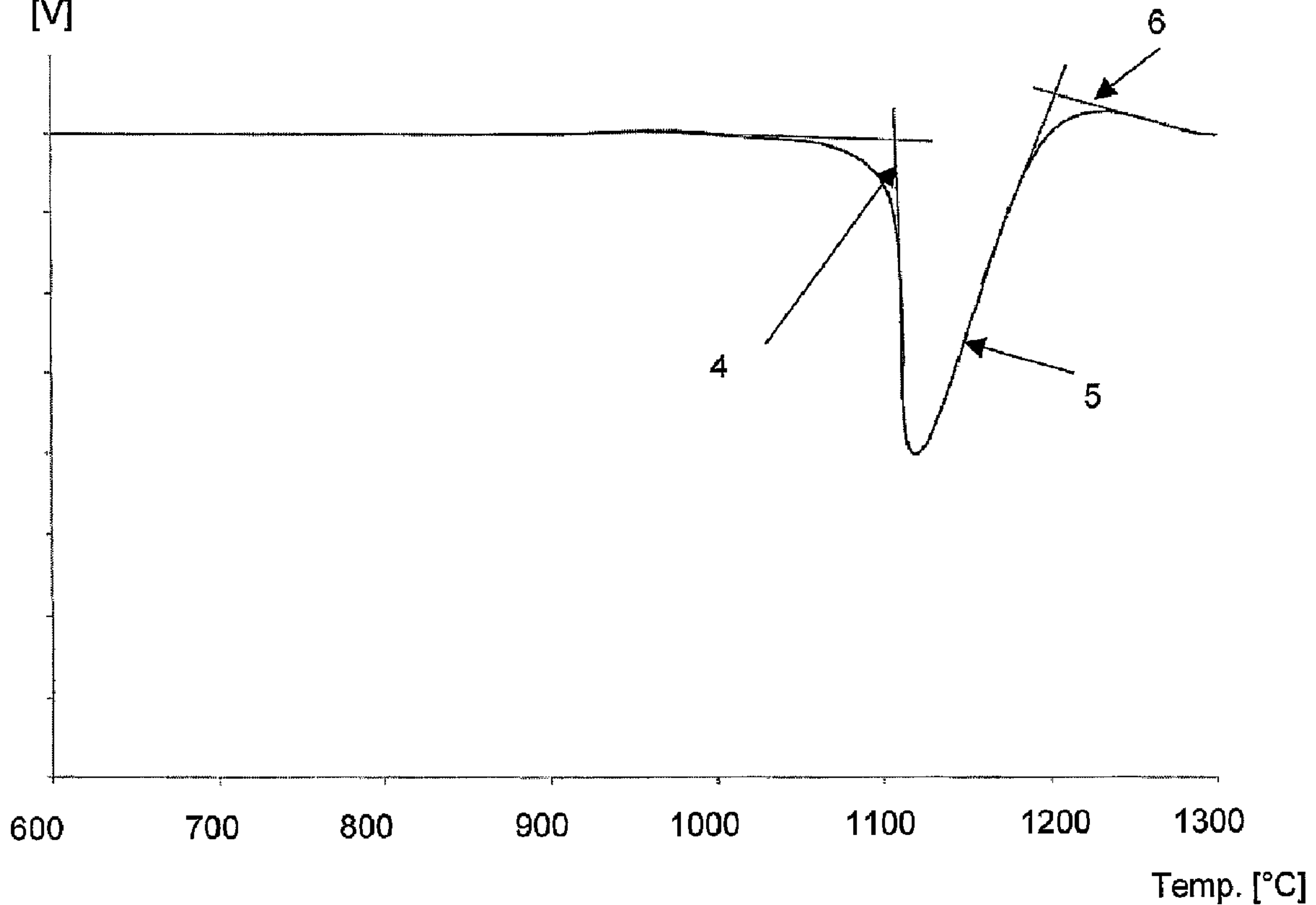
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(54) Title: BRAZING MATERIAL

Voltage

[V]



(57) Abrégé/Abstract:

The present invention relates to a brazing material comprising an alloy containing essentially of: 15 to 30 wt% chromium (Cr); 0.1 to 5.0 wt% manganese (Mn); 9 to 20 wt% nickel (Ni); 0 to 4.0 wt% molybdenum (Mo); 0 to 1.0 wt% nitrogen (N); 1.0 to 7.0 wt%



(57) Abrégé(suite)/Abstract(continued):

silicone (Si); 0 to 0.2 wt% boron (B); 1.0 to 7.0 wt% phosphorus (P); optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta); the alloy being balanced with Fe, and small inevitable amounts of contaminating elements; and wherein Si and P are in amounts effective to lower melting temperature. The present invention relates further to a method of brazing, a product brazed with the brazing material.

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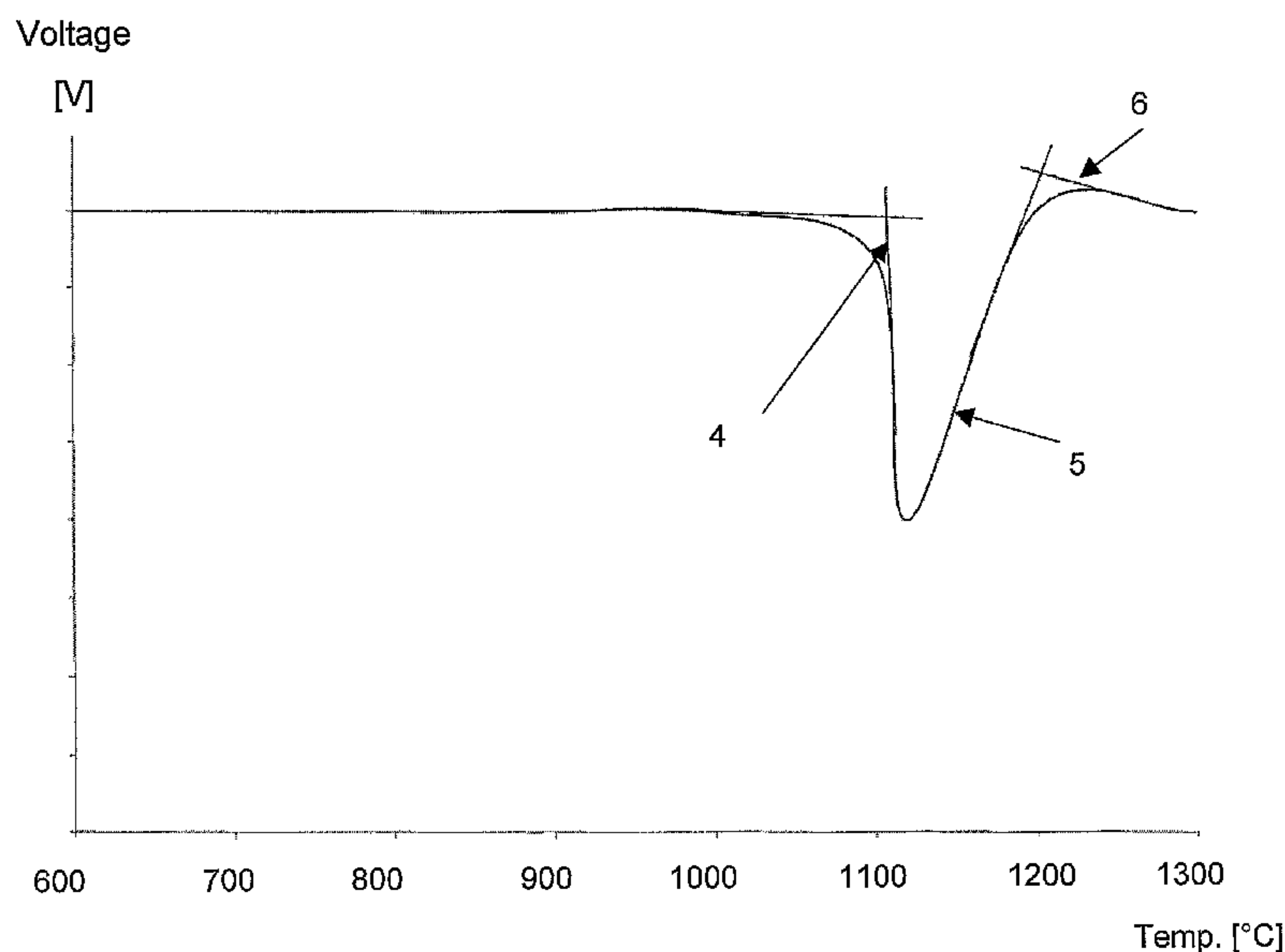
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(54) Title: BRAZING MATERIAL



(57) Abstract: The present invention relates to a brazing material comprising an alloy containing essentially of: 15 to 30 wt% chromium (Cr); 0.1 to 5.0 wt% manganese (Mn); 9 to 20 wt% nickel (Ni); 0 to 4.0 wt% molybdenum (Mo); 0 to 1.0 wt% nitrogen (N); 1.0 to 7.0 wt% silicone (Si); 0 to 0.2 wt% boron (B); 1.0 to 7.0 wt% phosphorus (P); optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta); the alloy being balanced with Fe, and small inevitable amounts of contaminating elements; and wherein Si and P are in amounts effective to lower melting temperature. The present invention relates further to a method of brazing, a product brazed with the brazing material.

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Brazing Material

The present invention relates to a brazing material, a method of brazing, a product brazed with the brazing material.

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The Invention

Objects of different steel materials or iron-based alloy materials are usually assembled by brazing or soldering with Nickel-based or Copper-based brazing materials. Hereinafter the term brazing is used, but it should be understood that the term also comprises soldering. Brazing is a
10 process for joining parts of metals, but brazing can also be used for sealing objects or coating objects. The brazing temperature is below the original solidus temperature of the base material. During brazing of materials the brazing material is completely or partly melted during the heat treatment.

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Traditional brazing of iron-based materials is performed by Nickel-based or Copper-based brazing materials, and these brazing materials can cause corrosion, for example due to differences in electrode potential. The corrosion problem will be enhanced when the brazed object is
20 exposed to a chemically aggressive environment. The use of Nickel-based or Copper-based brazing material can also be limited in a number of food applications due to jurisdictions.

One problem is the melting temperature range of the coating or brazing
25 materials. When selecting a brazing material or a coating material, considerations are based on the solidus or liquidus temperatures of the alloy and the base material. Lately iron-based brazing materials have been developed for brazing objects of traditional stainless steel. These iron-based brazing materials are functioning quite well, but when the
30 temperature range for brazing is broad, then there are risks for defects to

occur in the obtained products. A clean element has a sharp melting point, but an alloy contains many different elements in each defined alloy and has therefore often a broad melting interval.

- 5 According to the invention one consequently tries to attain that the brazing joint shall contain only a small part of brittle phases. One knows that the amount of brittle phase affects the fatigue strength negatively. The amount of brittle phase depends among all on the joint clearance, the thickness of the plate, the amount of brazing material, how the brazing
10 material is applied and by the time- temperature relation during the brazing.

When developing brazing materials there are a lot of properties of importance. One of those is the brazing temperature. A high brazing
15 temperature is quite often associated with high mechanical strength or other properties that are of importance for the braze joint, but it also has some disadvantages. A high temperature may decrease the properties of the base material, by e.g. grain growth, formation of phases in the material, a large impact from the braze filler into the base material by
20 diffusion of elements from the filler to the base material and other changes of the properties of the base material. A high temperature may also increase the risk of erosion of the base material. Costs are also associated with high temperature since there is a need for more energy input and more expensive furnaces. The high temperatures also wear the
25 furnace more, which increases the cost. A normal way when developing a Fe-based brazing material is using Si and or B as melting point depressants. Boron has a quite large impact of the melting point but has a lot of disadvantages, such as it easily forms chromium borides. Therefore it is of great importance not to use too much boron. The
30 formation of chromium borides decreases the amount of Chromium in the

base material, which then e.g. decreases the corrosion resistance and other properties of the base material. Therefore, when chromium is one of the elements of the alloy then no or very small amounts of boron are generally the best choice. Silicon is also used to decrease the melting point, however silicon itself, as a melting point depressant, does not have as great impact in comparison to e.g. B. So if silicon alone is used as a melting point decreased, a quite large amount has to be used. Silicon may also form silicides, why large amounts may cause problems. One element, which can be used as melting point depressant, is phosphorous.

Phosphorus could be a good selection if only the brazing temperature was of importance, since it has a great impact on the melting point. However, braze joints with large amounts of P are normally very fragile and have therefore has quite low strength. Phosphor can also form phosphides, such as iron-phosphides, that are fragile and decreases the strength of the braze filler and the base material. Surprisingly, when alloying with a new type of mixture comprising Si and P a new type of iron based braze filler was found, which has a low melting interval without or very low negative effects from the Si and P additives. The alloy also had another surprising positive property, a narrow melting interval, which is very positive when brazing. The reason why is that it is desirable that all elements in the braze filler should melt at approximately the same time. Another positive property is that the filler of the present invention is wetting the surface very well and has great flow ability.

Accordingly, the present invention relates to an iron based brazing material comprising an alloy essentially containing 15 to 30 percent by weight, herein after wt%, chromium (Cr), 0 to 5.0 wt% manganese (Mn), 9 to 30 wt% nickel (Ni), 0 to 4.0 wt% molybdenum (Mo), 0 to 1.0 wt% nitrogen (N), 1.0 to 7.0 wt% silicone (Si), 0 to 0.2 wt% boron (B), 1.0 to 7.0 wt% phosphorus (P), optionally 0.0 to 2.5 wt% of each of one or more

of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminium (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta); the alloy being balanced with Fe, and small inevitable amounts of contaminating elements; and wherein Si and P are in
5 amounts effective to lower melting temperature.

According to one alternative aspect of the invention may any one of the elements selected from the group consisting of carbon (C), vanadium (V), titanium (Ti), tungsten (W), aluminium (Al), niobium (Nb), hafnium (Hf),
10 and tantalum (Ta) be in an amount within the range from about 0 to 1.5 wt%.

According to one alternative aspect of the invention are the contaminating elements any one of carbon (C), oxygen (O), and sulphur (S). According to another alternative may manganese be present in the alloy and the
15 amount is within the range of 0.1 to 5.0 wt% manganese. According to another alternative may manganese be present in the alloy and the amount is within the range of 0.1 to 4.5. According to a further alternative may the alloy contain chromium within the range from about 18 to about
20 26 wt% or nickel within the range of from about 9.0 to about 20 wt% or molybdenum within the range from about 0.5 to about 3.5 wt%, or combinations thereof. According to a further alternative may the alloy contain nickel within the range from about 9.0 to about 18.0 wt%. According to a further alternative may the alloy contain silicone within the
25 range from about 2.0 to about 6.0 wt% or boron within the range from about 0 to about 0.1 wt% or phosphorus within the range from about 2.0 to about 6.0 wt%, or combinations thereof.

According to a further alternative may the alloy contain silicone within the range from about 2.5 to about 6.0 wt% and phosphorus within the range from about 3.5 to about 6.0 wt%.

- 5 According to a further alternative may the brazing material comprise an alloy containing essentially of: 16 to 18 wt% chromium (Cr); 1.5 to 2.0 wt% manganese (Mn); 11 to 17 wt% nickel (Ni); 1.5 to 2.5 wt% molybdenum (Mo); 0 to 1.0 wt% nitrogen (N); 3.0 to 5.0 wt% silicone (Si); 0 to 0.2 wt% boron (B); 4.0 to 5.5 wt% phosphorus (P); optionally 0.0 to 2.5
10 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminium (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta); the alloy being balanced with Fe, and small inevitable amounts of contaminating elements; and wherein Si and P are in amounts effective to lower melting temperature.

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The alloy may be manufactured by gas-atomising or water-atomising or melt-spinning.

- As mentioned above brazing temperature is preferably below the original
20 solidus temperature of the material of the parts to be brazed. The brazing cycle involves both melting and solidifying of the brazing material. The melting temperature and solidifying temperature may be the same for very specific materials, but the usual situation is that materials are melting within temperature range of melting, and solidifying within another
25 temperature range of solidifying. The temperature range between the solidus state and the liquidus state is herein defined as the temperature difference between the solidus state and the liquidus state, and is measured in a number of °C. The brazing material of the invention has thus a temperature range between the solidus state and the liquidus
30 state, which according to one alternative aspect of the invention may be

within a temperature range of 200°C. According to another alternative may the alloy have solidus temperature and a liquidus temperature within a temperature range of 150°C. According to another alternative may the alloy have solidus temperature and a liquidus temperature within a temperature range of 100°C. According to another alternative aspect of the invention may the alloy have solidus temperature and a liquidus temperature within a range of 75°C. According to another alternative aspect of the invention may the alloy have solidus temperature and a liquidus temperature within a range of 50°C.

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According to a further alternative aspect of the present invention may the iron-based brazing material be manufactured as a paste. The iron-based brazing paste of the invention may comprise the iron-based brazing material and an aqueous binder system or an organic binder system. The binder system may comprise a solvent, which could be hydrophilic or hydrophobic i.e. water-based or oil-based. The oil-based binder could be polymers such as poly (met) acrylate among others, Could be biopolymers such as cellulose derivatives, starches, waxes, etc. According to another alternative may the iron-based brazing paste of the invention comprise the iron-based brazing material and an aqueous binder system or an organic binder system based on a solvent such as water, oils, or combinations thereof. The alloy comprised in the paste may be in form of powder, granules etc.

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The present invention relates also to a method of brazing articles of stainless steel, comprising the following steps: step (i) applying the brazing material of the invention on to parts of stainless steel; step (ii) optionally assembling the parts; step (iii) heating the parts from step (i) or step (ii) in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or combinations thereof, to a temperature of up to at least 250°C

for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 10 minutes, heating the parts up to a temperature less than about 1200°C for at least 5 minutes and then cooling the parts; and optionally step (iv) repeating one or more of step (i), step (ii) and step (iii). Different brazed products need different brazing procedures; some products could be brazed by just going through step (i), step (ii) and step (iii), but other products are more complicated and one or more of step (i), step (ii) and step (iii) need to be repeated is indicated in step (iv).

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According to an alternative of the invention may the method also comprise that the parts in step (iii) are heated in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 30 minutes, then heating the parts up to a temperature over about 1100°C for less than 720 minutes, and then cooling the parts.

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According to one alternative of the invention may the heating the parts up to a temperature over about 1100°C be for less than 360 minutes before the cooling the parts. According to another alternative of the invention may the heating the parts up to a temperature over about 1100°C be for less than 180 minutes before the cooling the parts.

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According to an alternative of the invention may the method also comprise that the parts in step (iii) are brazed at a temperature within the range of from about 1040°C to about 1190°C for less than 30 minutes.

According to another alternative of the invention may the method also comprise that the parts in step (iii) are brazed at temperature within the range of from about 1040°C to about 1190°C for less than 20 minutes.

- 5 According to yet another alternative of the invention may the method also comprise that the parts in step (iii) are brazed at temperature within the range of from about 1040°C to about 1190°C for at least 1 minute.

- 10 According to yet another alternative of the invention may the method also comprise that the parts in step (iii) are brazed at temperature within the range of from about 1100°C to about 1180°C for at least 1 minute.

- 15 According to a further alternative of the invention may the method also comprise that the parts in step (iii) are preheated up to a temperature below 1050°C before heating up to a temperature of above 1100°C for at least 5 minutes. And then heat treating the parts at a temperature above 950°C for at least accumulated 20 min, this can be made in the braze cycle, but also after the braze in e.g. at a second heating source.

- 20 According to another alternative may the brazing material be sprayed as a powder on the surfaces, which shall be joined, by for instance by a paint spray gun, rolling, brushing, thermal spraying, e.g. high velocity oxygen fuel (HVOF) etc or may the surface, joint etc. be coated by melts.

- 25 The iron based brazing filler material may be applied to planar surfaces or to large surfaces by the aid of capillary force breakers. The capillary force breakers can be in form of grooves, traces, paths, passages, v or u shaped tracks or pathways etc. or in form of nets etc. The iron-based brazing filler material may be applied into the capillary force breakers, i.e.
30 into the grooves, traces, paths, passages, v or u shaped tracks,

pathways, nets etc., or may the brazing filler material be applied close to the capillary force breakers. During heating the applied iron-based brazing filler material will flow to the area where the capillary force may be broken and braze together the surfaces, which are adjacent to each other. Thus, the brazed area provides brazed, sealed or tight cervices, joints etc. between planar surface where it is hard otherwise to braze uniformly. The capillary force breakers enable also brazing of surfaces having large crevices, parts having odd shape, etc.

10 When the brazing material is applied between two parts close to a capillary force breaker the flowing viscous brazing material will stop the flowing motion and set at the rim of the capillary force breaker. A reactor channel may be functioning as a capillary force breaker. A plate having a reactor channel is applied with brazing material and a barrier plate or the
15 like is placed in contact with the reactor channel plate. The flowing brazing material will stop and set at boarder of the reactor channel, which will seal the reactor plate against the barrier plate without filling the reactor channel with set brazing material.

20 How far the brazing material can flow between two bordering surfaces depends partly on the brazing materials setting time and the distance between the surfaces, and the amount of brazing material. Since the brazing material "sticks" to each surface, which is to be brazed, the intermediate space between the surfaces becomes smaller. As the
25 intermediate space becomes smaller while at the same time the brazing material sets, it also becomes more difficult for the brazing material to flow in between. The desired amount of brazing material is supplied to the contact points, which are to be brazed together in any of the described or other ways. The brazing material may cover an area that is somewhat
30 larger than the contact joint point. The contact joint points may have a

diameter of at least 0.5 mm. Since the brazing process is a metallic process and the respective surfaces for brazing take the form of metallic material, then iron-based brazing material during the brazing process diffuses with bordering surfaces, which are to be brazed together. The joint or seam between the two joined surfaces will more or less "disappear" during the brazing process according to one aspect of the invention. The brazed seam together with the surfaces of the metallic parts will become a unity with only small changes in material composition of the alloys.

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During brazing will the brazing material migrate by capillary forces to areas to be joined by brazing. The brazing material according to the invention has good wetting ability and good flow ability, which will result that residual alloys around the brazing areas will be small. According to one alternative will the residual alloys after brazing have a thickness less than 0.1 mm on the applied surfaces.

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The present invention relates also to an article of stainless steel obtained by the present method. The present invention relates further to a brazed article of stainless steel, which comprises at least one base material of stainless steel and brazed brazing material of the invention.

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According to one alternative aspect may the articles or the parts be selected from reactors, separators, columns, heat exchangers, or equipments for chemical plants or food plants, or for car-industries. According to another alternative aspect may the objects be heat exchangers, plate reactors, or combinations thereof. According to another alternative aspect of the invention may the brazed article be a paring disc, which is used in a separator. According to one alternative aspect may the

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articles, be brazed heat exchanger plates, brazed reactor plates, or combinations thereof.

When the parts are heat exchanger plates, the plates can be endplates, adaptor plates, sealing plates, frame plates etc., and constitute a heat exchanger system. Each of the heat exchanger plates comprise at least one port recess, which port recesses together form part of a port channel when the plates are placed on one another. The plates are stacked together in a plate stack or a plate pack in the heat exchanger. The plate package comprises between the plates a number of channels, which accommodate a number of media. The media in adjacent channels are subject to temperature transfer through the heat transfer plate in a conventional manner. The plates may comprise an edge, which may partly extend down and over the edge portion of an adjacent heat transfer plate in the plate stack. The edges of the plates seal against the adjacent heat transfer plate in such a way that a channel may be formed between the plates. This channel either allows flow of a medium or is closed so that no flow takes place and the channel is therefore empty. To stiffen the plate package and the port regions, an adaptor plate or an endplate may be fitted to the package. The surfaces of the endplate or the adaptor plate are with may be planar so that contact surfaces between the surfaces may be maximised. As previously mentioned, the respective port recesses on the plates coincide, thereby forming a channel. On the inside of this port channel there is therefore a joint between the two plates. To prevent leakage at this joint brazing material may be applied round the port region between the plates. The brazing material may be placed in or close by a capillary force breaker, which may extend wholly or partly round the port region between the plates. In the plate package brazing material may be applied on different pre-designed or predetermined parts of the plates. During the brazing process, the brazing material will

become viscous and will flow from the applied parts out between the plates due to the action of capillary force. The advantage of applying brazing material on to predetermined places makes it possible to control volume and amount of the brazing material, and to control which parts of the surfaces to be brazed and which are not. When brazing a heat exchanger at least three heat exchanger plates are needed, but it is usual that several plates are brazed together. According to one alternative aspect of the invention are a plate pack of several plates brazed together at the same time in the same oven.

10

The brazing method of the invention may either comprise brazing the article assembled with all its parts at the same time or may the article be brazed in a stepwise fashion where parts are first assembled and brazed together, and then assembled with further parts and brazed together, and so on using the same type of brazing material in each brazing cycle.

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Further developments are specified in independent claims and the dependent claims.

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The invention is explained in more detail in by means the following Examples. The purpose of the Examples is to test the brazing material of the invention, and is not intended to limit the scope of invention.

25

Example 1

Test samples 1 to 4 were made for checking the solidus and liquidus temperatures of the brazing material of the invention. The compositions of the test samples are summarised in Table 1.

30

Table 1

Sample No.	Fe [wt%]	Cr [wt%]	Mn [wt%]	Ni [wt%]	Mo [wt%]	Si [wt%]	P [wt%]	C [wt%]	B [wt%]
1	bal.	16.48	1.63	16.65	2.02	4.57	4.9	0.016	0.01
2	bal.	17.37	1.9	11.99	2.13	4.91	5.19	0.014	0.01
3	bal.	17.42	1.67	13.33	1.99	3.69	5.0	0.013	0.01
4	bal.	16.63	1.82	15.99	1.89	3.3	4.69	0.018	0.01

The liquidus and solidus temperature of the samples was tested by means of differential thermal analysis (DTA). The atmosphere used when analysing was Argon. The test was performed with a heating and cooling rate of 10°C/min. The liquidus temperature is the temperature above which a substance is completely liquid. The solidus temperature is the temperature below which a substance is completely solid. The values for the solidus and liquidus temperature were established by estimations where the melting process started and stopped.

The estimations were performed by approximation of the melting curve, which was measured and registered as a DTA-curve, see Figure 1. The melting process can be seen in the DTA-curve by the change in the gradient of the heating curve. When the process is finalised, the gradient becomes constant again. To establish the start and stop of the melting process an approximation was made by drawing tangents (1) on the voltage drop peak (2). Tangents (3) on the base line is drawn and where the tangents (1) and (3) are crossing each other there are the approximated end values of the melting range.

The solidus temperatures and the liquidus temperatures of each sample are calculated as described above and are summarised in Table 2.

Table 2

Sample No.	Solidus temp. [°C]	Liquidus temp. [°C]	Difference [°C]
1	1058	1097	39
2	1068	1099	31
3	1055	1100	45
4	1060	1092	32

The tests show that the difference between solidus temperature and liquidus temperatures are surprisingly narrow.

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Example 2

Test samples 5 to 8 were made for checking tensile strength of joints having brazed zones of the brazing material of the invention. The compositions of the test samples of unbrazed brazing material are summarised in Table 3.

10

Table 3

Sample No.	Fe [wt%]	Cr [wt%]	Mn [wt%]	Ni [wt%]	Mo [wt%]	Si [wt%]	P [wt%]	C [wt%]
5	bal.	17.0	1,78	12,1	2,13	1,01	10,1	0,067
6	bal.	17.0	1,53	12,1	2,35	0,44	10,8	0,045
7	bal.	17,4	1,79	12.0	2,32	4,44	5,78	0,12
8	bal.	17,3	1,76	12,1	2,31	5,55	5,89	0,111

The brazing materials were tested by means of making braze trials of small pressed plates. The brazed samples were then tensile tested, the results are summarised in Table 4.

15

Table 4

Sample No.	Braze cycle for at least 15 min. at [°C]	Waffle test [kN]
5	1120	2.1
6	1120	2.4
7	1190	3.0
8	1190	2,7

As can be seen from Table 4 the tensile test results on samples brazed with braze materials having small amounts of Si, i.e. less than 1.2 wt%, and large amounts of phosphorus, see samples number 5 and 6, had a much lower strength than those brazed with a brazing material having higher amounts of Si, see samples 7 and 8. Both Example 1 and Example 2 show surprisingly, that when decreasing the amount of P and increasing the amount of Si result in increase of the tensile strength as well as lower the melting temperature, and small temperature melting intervals was found.

Example 3

Test samples of braze filler materials were compared in this Example for the purpose of checking performances on brazed prototypes. Test prototypes were brazed with different test sample of the braze fillers. The prototypes used in these tests were brazed plate heat exchangers. All prototypes were manufactured with the identical parts, such as identical plates, connections, reinforcements etc. Everything was done with the purpose to make the prototypes as identical as possible. The only difference between the prototypes were the braze filler and the braze cycles. The differences in braze cycle were of course necessary, since

different braze fillers have different braze cycles. Three different braze fillers were used filler A was a pure copper (Cu) braze filler, fillers B and C (according to the invention) are listed in Table 5 below. The inevitable amounts of contaminating elements are not listed in the Table.

5

Table 5

Filler	Fe [wt%]	Cr [wt%]	Mn [wt%]	Ni [wt%]	Mo [wt%]	Si [wt%]	P [wt%]	B [wt%]
B	Bal.	17,1	1,3	14,5	1,8	9,5	-	0,9
C	Bal.	17,3	1,9	11,9	2,1	4,9	5,1	-

The brazed heat exchangers prototypes were then evaluated by testing their burst pressure, pressure fatigue, and temperature fatigue. The burst
10 pressure test was carried out by increasing the pressure until failure, the pressure fatigue test was carried out by alternating the pressure with a set pressure variation until failure, and the temperature fatigue test was carried out by alternating the temperature with a set temperature variation and temperature heating/cooling rate until failure. The results of the tests
15 are summarised in Table 6.

20

25

Table 6

Test	Filler A	Filler B	Filler C
Burst pressure [bar]	197	111	91
Burst pressure [bar]	183	106	92
Burst pressure [bar]	189	103	97
Pressure fatigue [1000 cycles]	88	91	154
Pressure fatigue [1000 cycles]	67	101	207
Pressure fatigue [1000 cycles]	119	119	-
Temperature fatigue [cycles]	913	991	1704
Temperature fatigue [cycles]	1037	985	1442
Temperature fatigue [cycles]	1011	988	1573

The results of the burst pressure tests indicate that filler C has the lowest mechanical properties. The tests showed that the temperature fatigue performances were highest for filler C, and also that the pressure fatigue performances were highest. The results were very surprising since it was not expected that both the temperature- and the pressure fatigue performances could be highest for the new filler, since filler C had the lowest burst pressure of the three.

10

One of the reasons for the exceptional good fatigue results is the combination of the braze fillers properties. For example the new braze filler of the invention has excellent wetting and flow properties, which properties result in smooth braze joints that distribute the load evenly in

the brazed joint and decrease the risk for initiation of fatigue cracks. The good wetting and flow properties of the filler also result in large brazed joints that will decrease the total stress by increasing the loaded area.

- 5 The good flow and wetting properties of the filler were also confirmed by metallographic analysis. Some of the prototypes were cross-sectioned, grind and polished after brazing, with the purpose to study the microstructure etc. It was then observed that the flow and wetting properties were very good, seen that very little residuals of the braze filler
10 was left on the surfaces around the braze joint. Almost all filler had flown to the braze joint by capillary forces. The study confirmed that almost no residuals of the braze filler were left on the base material surface, but almost all were found in the braze joint. Of course there is braze filler on the base material surface close to the braze joint since the braze joint will
15 adapt its shape according to the wetting angle between the braze filler and the base material, consequently this filler is defined to the braze joint also.

The residuals of braze filler on the surface was measured. Measurements
20 of residuals of braze fillers were performed on areas where more than a 0.2 mm thick layer of braze filler had been applied prior to brazing. The cross-sections were studied after brazing with the braze filler. The test result showed that the thickness of the residuals were 0.01, 0.03, <0.01, 0.02, <0.01, 0.02, <0.01 mm. These measurements showed the thickness
25 of the residuals are much less than the expected based on other tested iron based braze fillers, which iron based braze filler could have a residual thickness about 0.15 mm. Other areas that differ from these measurements are where the fillers did not have any capillary contact during brazing or due to that the capillaries already were filled with braze
30 filler.

CLAIMS:

1. An iron based brazing material comprising an iron-based alloy consisting of:
 - (i) 16 to 18 wt% chromium (Cr);
 - 5 (ii) 1.5 to 2.0 wt% manganese (Mn);
 - (iii) 11 to 17 wt% nickel (Ni);
 - (iv) 1.5 to 2.5 wt% molybdenum (Mo);
 - (v) 0 to 1.0 wt% nitrogen (N);
 - (vi) 3.0 to 5.0 wt% silicone (Si);
 - 10 (vii) 0 to 0.2 wt% boron (B);
 - (viii) 4.0 to 5.5 wt% phosphorus (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta); the alloy being balanced with Fe and inevitable

15 amounts of contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulphur (S); wherein Si and P are in amounts effective to lower melting temperature, and wherein the alloy is having solidus temperature and a liquidus temperature within a range of 75°C.
- 20 2. The brazing material according to any one of the preceding claims, wherein the alloy is produced by gas-atomising or water-atomising or melt-spinning.
3. The brazing material according to any one of the preceding claims, wherein the alloy is having solidus temperature and a liquidus temperature within a range of
- 25 50°C.
4. The brazing material according to any one of the preceding claims, wherein the brazing material also comprises an aqueous binder system or an organic binder system, or combinations thereof.

30

5. The brazing material according to claim 4, wherein the binder system is any one of poly (met) acrylate, cellulose derivatives, starches, waxes, or combinations thereof.

5 6. The brazing material according to any one of the preceding claims, wherein the brazing material is a paste and the iron-based alloy is provided as powder or granules produced by gas-atomising or water-atomising.

10 7. The brazing material according to claim 6, wherein the paste also comprises an aqueous binder system or an organic binder system, or combinations thereof.

8. The brazing material according to claim 7, wherein the binder system is any one of poly (met) acrylate, cellulose derivatives, starches, waxes, or combinations thereof.

15

9. A method of brazing articles of stainless steel, comprising the following steps: step (i) applying the brazing material according to any one of claims 1 to 8 on to parts of stainless steel; step (ii) optionally assembling the parts; step (iii) heating the parts from step (i) or step (ii) in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 10 minutes, then heating the parts up to a temperature less than about 1200°C for at least 5 minutes; and optionally step (iv) repeating one or more of step (i), step (ii) and step (iii).

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10. The method of brazing according to claim 9, wherein the parts in step (iii) are heated in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 30

minutes, then heating the parts up to a temperature over about 1100°C for less than 720 minutes and then cooling the parts.

11. The method according to claim 9 or 10, wherein residual alloy after brazing
5 being less than 50% of applied alloy in step (i).

12. A brazed article obtained by the method according to claim 9, 10 or 11.

13. The brazed article according to claim 12, wherein the alloy after brazing are
10 located in one or more braze joints, and less than 0.1 mm of the braze filler being left as residuals on the surfaces.

14. The brazed article according to claim 12 or 13, wherein the article is a plate heat exchanger.

15

15. An iron based brazing material for brazing stainless steel comprising an iron-based alloy consisting essentially of:

15 to 30 wt% chromium (Cr);

0.1 to 5.0 wt% manganese (Mn);

20 9 to 30 wt% nickel (Ni);

0.5 to 3.5 wt% molybdenum (Mo);

0 to 1.0 wt% nitrogen (N);

1.0 to 7.0 wt% silicon (Si);

0 to 0.2 wt% boron (B);

25 3.5 to 5.5 wt% phosphorous (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta);

the alloy being balanced with Fe, and small inevitable amounts of contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulfur (S);

wherein Si and P are in amounts effective to lower melting temperature; and

5

wherein the brazing alloy has a difference between solidus temperature and liquidus temperature of 75°C, and the brazing alloy has flow and wetting properties for migration of the brazing alloy by capillary forces to contact points to be brazed.

10 16. The brazing material according to claim 15, wherein at least one of chromium is within the range from about 18 to about 26 wt% and nickel is within the range of from about 9.0 to about 20 wt%.

15 17. The brazing material according to claim 15, wherein at least one of silicon is within the range from about 2.0 to about 6.0 wt%, and boron is within the range from about 0 to about 0.1 wt % and phosphorous within the range from about 4.0 to about 5.5 wt%.

20 18. The brazing material according to claim 15, wherein silicon is within the range from about 2.5 to about 6.0 wt%.

19. An iron based brazing material for brazing stainless steel comprising an iron-based alloy consisting essentially of:

25 16 to 18 wt% chromium (Cr);
1.5 to 2.0 wt% manganese (Mn);
11 to 17 wt% nickel (Ni);
1.5 to 2.5 wt% molybdenum (Mo);
0 to 1.0 wt% nitrogen (N);
3.0 to 5.0 wt% silicon (Si);
30 0 to 0.2 wt% boron (B);

4.0 to 5.5 wt% phosphorous (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta);

5 the alloy being balanced with Fe, and small inevitable amounts of contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulfur (S);

wherein Si and P are in amounts effective to lower melting temperature; and

10 wherein the brazing alloy has a difference between solidus temperature and liquidus temperature of 75°C, the brazing alloy has flow and wetting properties for migration of the brazing alloy by capillary forces to contact points to be brazed.

20. The brazing material according to claim 15, wherein the alloy is produced by at least one of gas-atomising, water-atomising, or melt-spinning.

15

21. The brazing material according to claim 15, wherein the alloy is having a solidus temperature and a liquidus temperature within a range of 50°C.

22. A method of brazing articles of stainless steel, comprising the following steps:

20 (i) providing a brazing material comprising an iron-based alloy consisting essentially of:

15 to 30 wt% chromium (Cr);

1.5 to 2.0 wt% manganese (Mn);

9 to 30 wt% nickel (Ni);

25 0.5 to 3.5 wt% molybdenum (Mo);

0 to 1.0 wt% nitrogen (N);

1.0 to 7.0 wt% silicon (Si);

0 to 0.2 wt% boron (B);

3.5 to 5.5 wt% phosphorous (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta);

the alloy being balanced with Fe, and small inevitable amounts of
5 contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulfur (S);

wherein Si and P are in amounts effective to lower melting temperature; and

wherein the brazing alloy has a difference between solidus temperature and liquidus temperature of 75°C, the brazing alloy has flow and wetting properties for
10 migration of the brazing alloy by capillary forces to contact points to be brazed;

(ii) applying the brazing material on to parts of stainless steel and assembling the applied parts;

and

(iii) heating the parts from step (ii) in a non-oxidizing atmosphere, in a reducing
15 atmosphere, in vacuum, or combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 10 minutes, then heating the parts up to a temperature less than about 1200°C for at least 5 minutes migrating the brazing alloy by capillary forces to contact points to be brazed;

20 wherein the parts are assembled after the applying of the brazing material and before the heating step (iii).

23. The method of brazing according to claim 22, wherein the parts in step (iii) are heated in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or
25 combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 30 minutes, then heating the parts up to a temperature over about 1100°C for less than 720 minutes and then cooling the parts.

24. The method according to claim 22, wherein residual alloy after brazing being less than 50% of applied alloy in step 1.

25. A brazed article obtained by the method according to claim 22.

5

26. The brazed article according to claim 25, wherein the alloy after brazing are located in one or more braze joints, and less than 0.1 mm of the braze filler being left as residuals on the surfaces.

10 27. The brazed article according to claim 25, wherein the article is a plate heat exchanger.

28. A paste for brazing stainless steel comprising an iron-based alloy consisting essentially of:

15 15 to 30 wt% chromium (Cr);

0.1 to 5.0 wt% manganese (Mn);

9 to 30 wt% nickel (Ni);

0.5 to 3.5 wt% molybdenum (Mo);

0 to 1.0 wt% nitrogen (N);

20 1.0 to 7.0 wt% silicon (Si);

0 to 0.2 wt% boron (B);

3.5 to 5.5 wt% phosphorous (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium

25 (Nb), hafnium (Hf) and tantalum (Ta);

the alloy being balanced with Fe, and small inevitable amounts of contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulfur (S);

wherein Si and P are in amounts effective to lower melting temperature;

wherein the brazing alloy has a difference between solidus temperature and liquidus temperature of 75°C, the brazing alloy has flow and wetting properties for migration of the brazing alloy by capillary forces to contact points to be brazed; and

an aqueous binder system or an organic binder system, water-based, oil-based or combinations thereof, wherein the oil-based binder is at least one of polymers, poly (met) acrylate, biopolymers, cellulose derivatives, starches, and waxes.

29. The brazing material according to claim 19, wherein the alloy has a solidus temperature and a liquidus temperature within a range of 50°C.

30. The method of brazing articles of stainless steel according to claim 22, wherein the alloy has a solidus temperature and a liquidus temperature within a range of 50°C.

31. The paste according to claim 28, wherein the alloy has a solidus temperature and a liquidus temperature within a range of 50°C.

32. The method of brazing articles of stainless steel according to claim 22, wherein the assembled parts brazed in step (iii) are assembled with further parts, said further parts are applied with the brazing material of step (i); and brazing together said further parts with the brazed assembled parts from first brazing step (iii) in a second brazing step (iii).

33. A method of brazing articles of stainless steel, comprising the following steps:
(i) providing a brazing material comprising an iron-based alloy consisting essentially of:

- 15 to 30 wt% chromium (Cr);
- 0.1 to 5.0 wt% manganese (Mn);
- 9 to 30 wt% nickel (Ni);

0.5 to 3.5 wt% molybdenum (Mo);

0 to 1.0 wt% nitrogen (N);

1.0 to 7.0 wt% silicon (Si);

0 to 0.2 wt% boron (B);

5 3.5 to 5.5 wt% phosphorous (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta);

10 the alloy being balanced with Fe, and small inevitable amounts of contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulfur (S);

wherein Si and P are in amounts effective to lower melting temperature; and

15 wherein the brazing alloy has a difference between solidus temperature and liquidus temperature of 75°C, and the brazing alloy has flow and wetting properties for migration of the brazing alloy by capillary forces to contact points to be brazed;

(ii) applying the brazing material on to parts of stainless steel and assembling the applied parts;

and

20 (iii) heating the parts from step (ii) in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 30 minutes, then heating the parts up to a brazing temperature over 1100°C for less than 720 minutes migrating the brazing alloy by capillary forces to contact points to be brazed; and then cooling the brazed article.

25

34. A method of brazing articles of stainless steel, comprising the following steps:

(i) providing a brazing material comprising an iron-based alloy consisting essentially of:

16 to 18 wt% chromium (Cr);

30 1.5 to 2.0 wt% manganese (Mn);

11 to 17 wt% nickel (Ni);
 1.5 to 2.5 wt% molybdenum (Mo);
 0 to 1.0 wt% nitrogen (N);
 3.0 to 5.0 wt% silicon (Si);
 0 to 0.2 wt% boron (B);
 4.0 to 5.5 wt% phosphorous (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta);

the alloy being balanced with Fe, and small inevitable amounts of contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulfur (S);

wherein Si and P are in amounts effective to lower melting temperature; and

wherein the brazing alloy has a difference between solidus temperature and liquidus temperature of 75°C, the brazing alloy has flow and wetting properties for migration of the brazing alloy by capillary forces to contact points to be brazed;

(ii) applying the brazing material on to parts of stainless steel and assembling the applied parts;

and

(iii) heating the parts from step (ii) in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than 1080°C for at least 10 minutes, then heating the parts up to a temperature less than about 1200°C for at least 5 minutes migrating the brazing alloy by capillary forces to contact points to be brazed;

wherein the parts are assembled after the applying of the brazing material and before the heating step (iii).

35. A method of brazing articles of stainless steel, comprising the following steps:

(i) providing a paste brazing material for brazing stainless steel comprising an iron-based alloy consisting essentially of:

15 to 30 wt% chromium (Cr);

0.1 to 5.0 wt% manganese (Mn);

5 9 to 30 wt% nickel (Ni);

0.5 to 3.5 wt% molybdenum (Mo);

0 to 1.0 wt% nitrogen (N);

1.0 to 7.0 wt% silicon (Si);

0 to 0.2 wt% boron (B);

10 3.5 to 5.5 wt% phosphorous (P);

optionally 0.0 to 2.5 wt% of each of one or more of elements selected from the group consisting of vanadium (V), titanium (Ti), tungsten (W), aluminum (Al), niobium (Nb), hafnium (Hf) and tantalum (Ta);

the alloy being balanced with Fe, and small inevitable amounts of
15 contaminating elements, wherein the contaminating elements are any one of carbon (C), oxygen (O), and sulfur (S);

wherein Si and P are in amounts effective to lower melting temperature;

wherein the brazing alloy has a difference between solidus temperature and liquidus temperature of 75°C, the brazing alloy has flow and wetting properties for
20 migration of the brazing alloy by capillary forces to contact points to be brazed; and an aqueous binder system or an organic binder system, water-based, oil-based or combinations thereof, wherein the oil-based binder is at least one of polymers, poly (met) acrylate, biopolymers, cellulose derivatives, starches, and waxes;

(ii) applying the brazing material on to parts of stainless steel and assembling
25 the applied parts;

and

(iii) heating the parts from step (ii) in a non-oxidizing atmosphere, in a reducing atmosphere, in vacuum, or combinations thereof, up to a temperature of at least 250°C for at least 10 minutes, then heating the parts up to a temperature of less than
30 1080°C for at least 10 minutes, then heating the parts up to a temperature less than

about 1200°C for at least 5 minutes migrating the brazing alloy by capillary forces to contact points to be brazed;

wherein the parts are assembled after the applying of the brazing material and before the heating step (iii).

5

36. The method of brazing articles of stainless steel according to claim 22, wherein the brazing material is applied as a filler material with use of a capillary force breaker.

10 37. The method of brazing articles of stainless steel according to claim 36, wherein the capillary force breaker is selected from at least one of: a path, a passage, a net, a “v” shaped track, and a “u” shaped track.

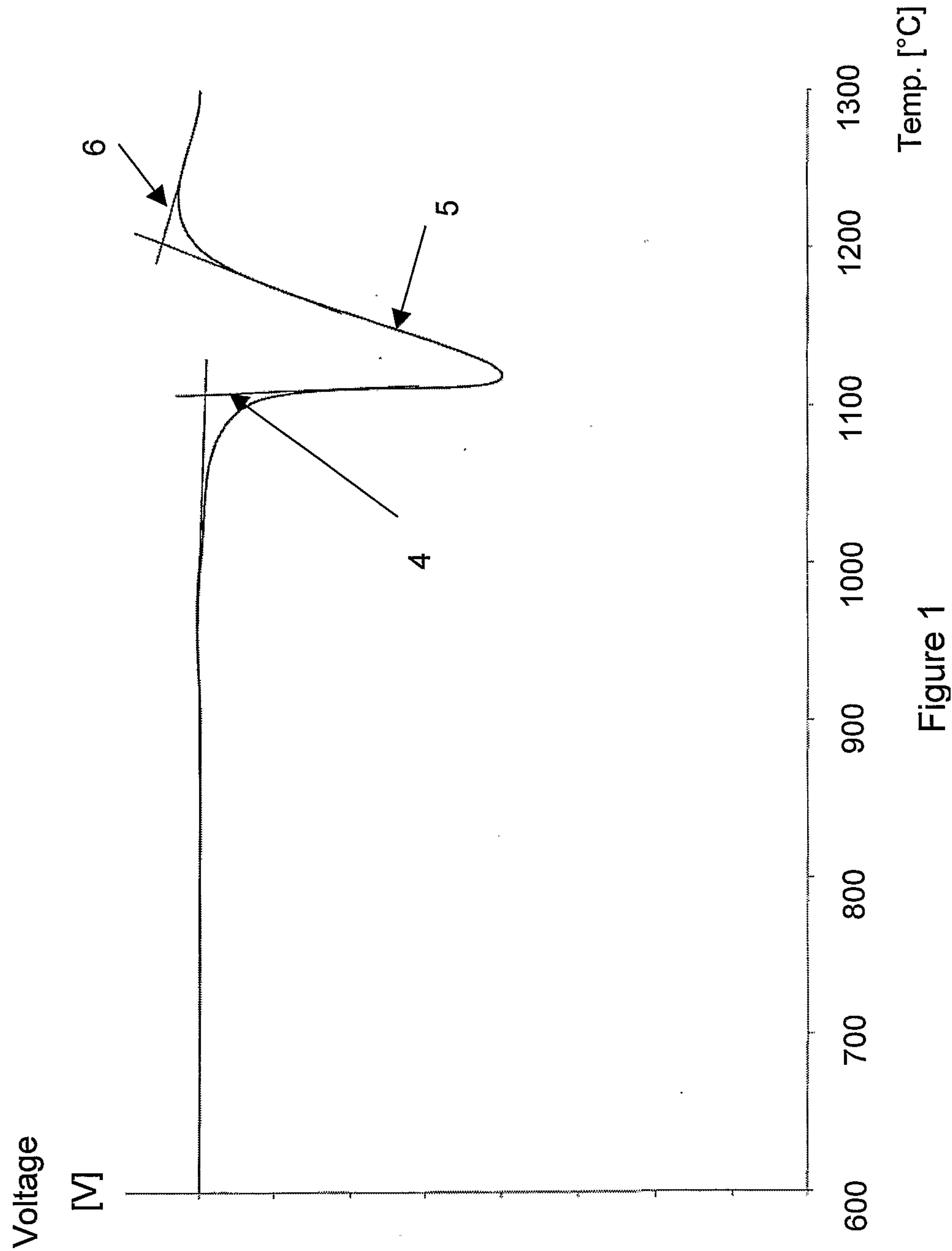
15 38. The method of brazing articles of stainless steel according to claim 34, wherein the brazing material is applied as a filler material with use of a capillary force breaker.

20 39. The method of brazing articles of stainless steel according to claim 38, wherein the capillary force breaker is selected from at least one of: a path, a passage, a net, a “v” shaped track, and a “u” shaped track.

40. The method of brazing articles of stainless steel according to claim 35, wherein the brazing material is applied as a filler material with use of a capillary force breaker.

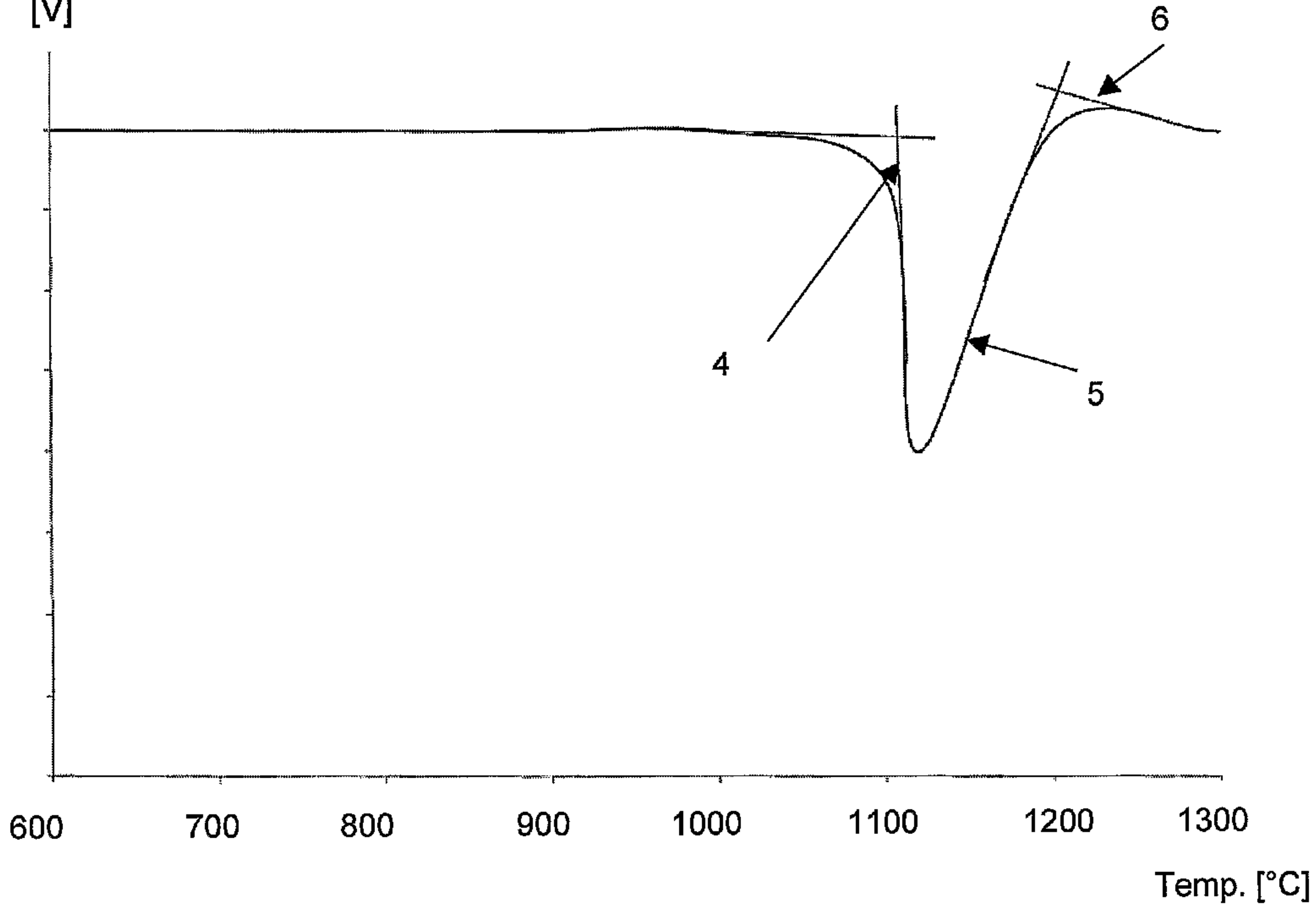
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41. The method of brazing articles of stainless steel according to claim 40, wherein the capillary force breaker is selected from at least one of: a path, a passage, a net, a “v” shaped track, and a “u” shaped track.



Voltage

[V]



Temp. [°C]