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(54) **Member for use in contact with molten nonferrous metals**

(57) The member for use in contact with molten nonferrous metals comprises a substrate made of an Fe-base alloy and a dense surface layer composed of an oxide or oxynitride. The oxide or oxynitride surface layer is formed by preheating the substrate in a non-oxidizing atmosphere such as a nitrogen gas, and then heat-treating it in an oxidizing or oxynitriding atmosphere containing steam such as a mixture of the air and an overheated steam, or in an atmosphere generating oxygen and steam such as a mixed gas comprising a hydrogen gas and a carbon dioxide gas, at a temperature of 650°C and 1100°C.

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Description**BACKGROUND OF THE INVENTION**

5 The present invention relates to a member for use in contact with molten nonferrous metals, particularly to a member which is highly resistant to dissolution loss by molten nonferrous metals such as aluminum, zinc, copper, brass, etc.

OBJECT AND SUMMARY OF THE INVENTION

10 Members adapted to be brought into contact with molten nonferrous metals, for instance thermocouple protection tubes immersed in molten nonferrous metals, dies into which molten nonferrous metals are injected, etc., have conventionally been made of ceramics or nitrided steel in general. Particularly, most immersion members are made of ceramics, and most contact members are made of nitrided steel. However, the ceramics are disadvantageous in their high cost and vulnerability to cracking and breakage, and the nitrided steel is disadvantageous in its small resistance to dissolution loss by molten nonferrous metals.

15 Accordingly, an object of the present invention is to provide a member for use in contact with molten nonferrous metals, which has a substrate made of iron or its alloy and is highly resistant to dissolution loss by molten nonferrous metals such as aluminum, zinc, copper, brass, etc.

As a result of research, the inventors have achieved the present invention based on the following findings.

20 (1) By forming an oxide or oxynitride layer on a surface of a substrate of an Fe-base alloy member by a heat treatment in an oxidizing or oxynitriding atmosphere containing steam or in an atmosphere generating oxygen and steam, the member is made highly resistant to dissolution loss by molten nonferrous metals such as aluminum, zinc, copper, brass, etc.

25 (2) A dense oxide or oxynitride layer can be formed on the Fe-base alloy substrate, when the substrate is preheated in a non-oxidizing atmosphere and then heat-treated in an oxidizing or oxynitriding atmosphere containing steam or in an atmosphere generating oxygen and steam.

(3) A preferred example of the atmosphere generating oxygen and steam is a mixture of a hydrogen gas and a carbon dioxide gas.

30 (4) Particularly preferable among the Fe-base alloys are Fe-Cr alloys which contains 40 weight % or less of Cr.

(5) The member made of an Fe-base alloy can be provided with an extremely high resistance to dissolution loss by molten aluminum when formed with such an oxide or oxynitride layer.

35 (6) By subjecting a member made of an Fe-(Al, Si) alloy to an oxidation or oxynitriding treatment, the member is provided with an extremely high resistance to dissolution loss by molten nonferrous metals such as aluminum, zinc, copper, brass, etc.

(7) The member is preferably made of an Fe-(Al, Si)-Cr alloy which contains 40 weight % or less of Cr.

40 Thus, the member for use in contact with molten nonferrous metals according to the present invention comprises a substrate made of an Fe-base alloy and a dense surface layer composed of an oxide or oxynitride formed in the presence of steam. Preferably, the dense surface layer is formed by preheating the member substrate in a non-oxidizing atmosphere and then heat-treating it in an oxidizing or oxynitriding atmosphere containing steam or in an atmosphere generating oxygen and steam.

BRIEF DESCRIPTION OF THE DRAWINGS

45 Fig. 1 is a graph showing the relations between the Cr content (weight %) and crack resistance and peel resistance (expressed by the number of repetition) in the members for use in contact with molten nonferrous metals according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**[1] Types of melt-contacting members**

55 The members for use in contact with molten nonferrous metals according to the present invention include members such as thermocouple protection tubes, heater tubes and slag filters which are directly immersed in molten nonferrous metals, and members such as die-casting cylinders, plunger heads, die-casting molds, melt supply tubes, inner walls of melt pumps and melt kilns which are brought into contact with molten nonferrous metals, etc. The members for use in contact with molten nonferrous metals are sometimes simply called "melt-contacting members" herein.

[2] Structure of melt-contacting member

The melt-contacting member of the present invention comprises a substrate made of an Fe-base alloy and a surface layer composed of an oxide or oxynitride formed in the presence of steam.

(a) Substrate

The substrate of the melt-contacting member of the present invention may generally be made of Fe-base alloys ranging from usual carbon steel to cast iron to alloyed steel and to alloyed cast iron.

The alloying elements for the Fe-base alloys are preferably Cr, Si and Al, which are effective for enhancing denseness, adhesion, crack resistance, etc. of the oxide or oxynitride surface layers formed on the member substrates.

The Cr content is preferably 40 weight % or less based on the total weight (100 weight %) of the member substrate. Even if the Cr content exceeds 40 weight %, the further growth of an oxide or oxynitride layer is not expected, only deteriorating the denseness, adhesion, crack resistance, etc. of the resultant layer and making the melt-contacting member expensive. For better effects, the Cr content is preferably 5 weight % or more.

When Si and/or Al is added to the member substrate, remarkable effects of improving denseness, adhesion, crack resistance, etc. of the oxide or oxynitride surface layers formed on the member substrates can be achieved as long as the amount of Si and/or Al added is 4 weight % or less. When both Si and Al are added together, their total amount is 4 weight % or less. The lower limit of the amount of Si and/or Al added is preferably 1 weight %.

With respect to other elements than Cr, Si and Al, they may be added in proper amounts for the purpose of improving denseness, adhesion, crack resistance, etc. of the oxide or oxynitride surface layers formed on the member substrates. Typical examples of such other elements are rare earth elements such as yttrium, etc., and their amounts may be 0.1-2 weight %. The rare earth elements such as yttrium, cerium, dysprosium, lanthanum, etc., are effective for improving the adhesion of the oxide or oxynitride surface layer to the melt-contacting member substrate.

The substrate structure of the melt-contacting member may be austenite, ferrite, martensite or mixtures thereof, depending on the uses of the melt-contacting members. The substrate structure can metallurgically be controlled by adjusting heat treatment conditions or by adding alloying elements.

When the substrates of the melt-contacting members are made of the above Fe-base alloys, the members with oxide or oxynitride layers formed in the presence of steam exhibit excellent resistance to dissolution loss by molten non-ferrous metals.

(b) Surface layer

The oxide or oxynitride layer is obtained by an oxidation or oxynitriding treatment in an oxidizing or oxynitriding atmosphere containing steam or in an atmosphere generating oxygen and steam. The detailed descriptions of such atmospheres will be given in [3] (2) below.

The composition of the oxide or oxynitride layer directly formed on the melt-contacting member appears to be an MO-type oxide such as FeO or an M(ON)-type oxynitride such as Fe(ON). Further formed thereon may be an M_3O_4 -type oxide such as Fe_3O_4 or an M_2O_3 -type oxide such as Fe_2O_3 . The MO-type oxide or M(ON)-type oxynitride layer has a high resistance to peeling from the melt-contacting member as well as an excellent crack resistance.

The thickness of the oxide or oxynitride layer is preferably 10-500 μm . When the oxide or oxynitride layer is thicker than 500 μm , it easily peels off from the melt-contacting member substrate. On the other hand, when the oxide or oxynitride layer is thinner than 10 μm , it fails to have a sufficient resistance to dissolution loss by molten nonferrous metals. The more preferable thickness of the oxide or oxynitride layer is 20-100 μm .

[3] Production of melt-contacting member

(1) First heating step

The important feature of the present invention is that in the temperature elevation process to a temperature T_1 which is preferably between [an oxidizing or oxynitriding temperature $T_2 - 100^\circ\text{C}$] and [an oxidizing or oxynitriding temperature $T_2 + 0^\circ\text{C}$], the member substrate is placed in a non-oxidizing atmosphere in a furnace to prevent premature oxidation or oxynitriding. If the temperature T_1 is lower than an oxidizing or oxynitriding temperature T_2 by more than 100°C , a dense oxide or oxynitride layer cannot be obtained. On the other hand, if the temperature T_1 is higher than an oxidizing or oxynitriding temperature T_2 , the oxide or oxynitride layer is likely to peel off from the melt-contacting member substrate. The more preferred temperature T_1 is between [an oxidizing or oxynitriding temperature $T_2 - 50^\circ\text{C}$] and [an oxidizing or oxynitriding temperature $T_2 + 0^\circ\text{C}$]. Specifically, the temperature T_1 is $650-1100^\circ\text{C}$.

The non-oxidizing atmosphere means an atmosphere which does not contain oxygen and steam. It naturally does not contain a nitriding gas such as ammonia. The preferred non-oxidizing atmosphere is an inert gas such as a nitrogen

gas, an argon gas, etc.

The heating of the Fe-base alloy substrate to the temperature T_1 in the non-oxidizing atmosphere makes it possible to form a dense oxide or oxynitride layer on the Fe-base alloy substrate in the subsequent oxidizing or oxynitriding step.

5 (2) Second heating step

An oxidizing or oxynitriding gas containing steam or an atmosphere generating oxygen and steam is supplied to a furnace in which the Fe-base alloy substrate is preheated. The addition of steam to these atmospheres turns them to slightly oxidizing, suitable for forming an oxide or oxynitride layer on the melt-contacting member substrate.

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(a) Oxidizing or oxynitriding gas containing steam

The oxidizing gas may be the air, and the oxynitriding gas may be the air to which a nitriding gas such as ammonia is added. Typical examples of the steam-containing oxidizing gas are (i) a mixture of the air and an overheated steam,

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(ii) an exhausted gas generated by burning oil or natural gas, etc.

In the case of the steam-containing oxidizing gas, the percentage of steam may be 12-35 volume %, and the percentage of oxygen may be 88-65 volume %. If the percentage of steam is less than 12 volume % or more than 35 volume %, a sufficiently dense oxide layer cannot be formed on the Fe-base alloy substrate. Preferably, the percentage of steam is 15-30 volume %, and the percentage of oxygen is 85-70 volume %.

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In the case of the steam-containing oxynitriding gas, the percentage of steam may be 14-35 volume %, the percentage of oxygen may be 57-81 volume %, and the percentage of the nitriding gas may be 5-8 volume %. If the percentage of steam is less than 14 volume % or more than 35 volume %, a sufficiently dense oxide layer cannot be formed on the Fe-base alloy substrate. Preferably, the percentage of steam is 18-25 volume %, the percentage of oxygen is 67-77 volume %, and the percentage of the nitriding gas is 5-8 volume %.

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(b) Atmosphere generating oxygen and steam

The atmosphere generating oxygen and steam is an atmosphere capable of generating oxygen and steam at the oxidizing or oxynitriding temperature T_2 , for instance, a mixture of hydrogen gas and a carbon dioxide gas, etc.

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In the case of the mixture of a hydrogen gas and a carbon dioxide gas, the percentage of the hydrogen gas may be 20-55 volume %, and the percentage of the carbon dioxide gas may be 80-45 volume %. If the percentage of a hydrogen gas is less than 20 volume % or more than 55 volume %, a sufficiently dense oxide layer cannot be formed on the Fe-base alloy substrate. Preferably, the percentage of a hydrogen gas is 30-45 volume %, and the percentage of a carbon dioxide gas is 70-55 volume %. Of course, the mixture of a hydrogen gas and a carbon dioxide gas may further

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(c) Oxidizing or oxynitriding temperature

The oxidizing or oxynitriding temperature T_2 is preferably between 400°C and 1250°C. If the oxidizing or oxynitriding temperature T_2 is lower than 400°C, a dense oxide or oxynitride layer cannot be formed on the Fe-base alloy substrate. On the other hand, if the oxidizing or oxynitriding temperature T_2 is higher than 1250°C, the oxide or oxynitride layer is likely to peel off from the melt-contacting member substrate. The more preferred oxidizing or oxynitriding temperature T_2 is between 700°C and 1200°C.

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45 (d) Oxidizing or oxynitriding time

The oxidizing or oxynitriding time may vary depending on the oxidizing or oxynitriding temperature T_2 , but it may generally be 15-45 minutes. If the oxidizing or oxynitriding time is shorter than 15 minutes, a sufficient surface layer cannot be formed. On the other hand, even if the oxidizing or oxynitriding time is longer than 45 minutes, further improvements cannot be obtained.

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The heat-treated member may be left to cool in the air, or forced to cool by air blow, water spray, etc. Since the oxide or oxynitride layer thus formed is extremely dense and has strong adhesion to the member substrate, it has an excellent resistance to dissolution loss by molten nonferrous metals such as aluminum, zinc, copper, brass, etc.

The present invention will be explained in further detail by way of the following Examples without intention of

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Example 1

With respect to various types of Fe-base alloys shown in Table 1 below, experiments were carried out to measure

a dissolution loss by molten aluminum.

Table 1

| No. | Composition of Sample (weight %) |
|-----|--|
| 1 | SS41 (Soft Steel) |
| 2 | SUS304 (Austenite Stainless Steel) |
| 3 | SUS310S (Austenite Stainless Steel) |
| 4 | SUS410 (Martensite Stainless Steel) |
| 5 | SUH1 (Heat-Resistant, Si-Cr Stainless Steel) |
| 6 | Fe-25%Cr-2%Al Steel (Heat-Resistant, High-Cr, Al, Steel) |
| 7 | Fe-3%C-25%Cr Cast Iron |

(1) Shape of each sample

Each sample was in the shape of a round rod of 200 mm in length and 20 mm in diameter.

(2) Oxidation treatment

Each sample was placed in a furnace at room temperature, which was evacuated and filled with a dry nitrogen gas at atmospheric pressure. Each sample was heated to about 850°C (Sample Nos. 1-3, 6 and 7) and about 950°C (Sample Nos. 4 and 5) in the dry nitrogen gas. After reaching the above temperature, a mixture of the air and an overheated steam (volume ratio: 20/1) at 850°C was introduced into the furnace while heating each sample, to carry out an oxidation treatment at 900°C (Sample Nos. 1-3, 6 and 7) and at 1000°C (Sample Nos. 4 and 5) for 1 hour. After the completion of the heat treatment, each sample was cooled in the furnace. Incidentally, Sample Nos. 4 and 5 were annealed at 750°C.

(3) Measuring dissolution loss by molten aluminum

Each sample was immersed in molten aluminum kept at 750°C for 10 hours to measure its loss by dissolution into the molten aluminum.

Comparison with respect to the dissolution loss was conducted between the samples subjected to the oxidation treatment of the present invention and those subjected to no oxidation treatment. The results are shown in Table 2 below, in which the numerical values (mm) show decreases in the diameter of the round rod.

Table 2

| Dissolution loss by Molten Aluminum | | |
|-------------------------------------|----------------------------------|--------------------|
| No. | Oxidation Treatment | |
| | Present Invention ⁽¹⁾ | Non ⁽²⁾ |
| 1 | 0.1 mm | 1-2 mm |
| 2 | Trace | 1-6 mm |
| 3 | Trace | 1-7 mm |
| 4 | Trace | 2-4 mm |
| 5 | No | 2-8 mm |
| 6 | No | 5-7 mm |
| 7 | No | 1-3 mm |

Note

(1) Oxidation treatment according to the present invention.

(2) No oxidation treatment.

It is clear from the above results that the oxide layer of the present invention is remarkably effective for improving a resistance to dissolution loss by molten aluminum.

Example 2

With respect to various types of Fe-base alloys shown in Table 3 below, experiments were carried out to measure a dissolution loss by molten aluminum.

Table 3

| No. | Composition of Sample (weight %) |
|-----|---------------------------------------|
| 1-7 | Same as in Table 1 |
| 8 | SUS430 (Ferrite Stainless Steel) |
| 9 | Ordinary Cast Iron (FC15) |
| 10 | Spheroidal Graphite Cast Iron (FCD40) |

(1) Shape of each sample

Each sample was in the shape of a round rod of 200 mm in length and 20 mm in diameter.

(2) Oxidation treatment

Each sample was placed in a furnace at room temperature, which was evacuated and filled with a dry nitrogen gas at atmospheric pressure. Each sample was heated to about 850°C in the dry nitrogen gas. After reaching the above temperature, a mixture of hydrogen and carbon dioxide (volume ratio: 2/3) at 850°C was introduced into the furnace while heating each sample, to carry out an oxidation treatment at 900°C for 1 hour. An excess hydrogen gas was burned outside the furnace. After the completion of the heat treatment, each sample was cooled in the furnace.

(3) Measuring dissolution loss by molten aluminum

Each sample was immersed in molten aluminum kept at 750°C for 10 hours to measure its loss by dissolution into the molten aluminum.

Comparison with respect to the dissolution loss was conducted between the samples subjected to the oxidation treatment of the present invention and those subjected to no oxidation treatment. The results are shown in Table 4 below, in which the numerical values (mm) are the same as in Table 2.

Table 4

| Dissolution loss by Molten Aluminum | | |
|-------------------------------------|----------------------------------|--------------------|
| No. | Oxidation Treatment | |
| | Present Invention ⁽¹⁾ | Non ⁽²⁾ |
| 1 | No | 1-2 mm |
| 2 | No | 1-6 mm |
| 3 | No | 1-7 mm |
| 4 | No | 2-4 mm |
| 5 | No | 2-8 mm |
| 6 | No | 5-7 mm |
| 7 | No | 1-3 mm |
| 8 | No | 2-4 mm |
| 9 | No | 0.3-0.6 mm |
| 10 | No | 0.4-0.7 mm |

Note

(1)-(2) Same as in Table 2.

It is clear from the above results that the oxide layer of the present invention is remarkably effective for improving a resistance to dissolution loss by molten aluminum.

Example 3

Samples having various Cr contents were measured with respect to crack resistance and peel resistance of their surface oxide layers. Each sample was made of an Fe-Cr-base alloy having a Cr content of 0 weight %, 5 weight %, 10 weight %, 20 weight %, 30 weight %, 40 weight % and 50 weight %, respectively. The total amount of other elements was less than 1 weight %. 0.1 weight % of Y was added to the first group of samples, and no Y was added to the second group of samples.

Each sample was repeatedly subjected to treatment cycles each consisting of immersion in molten aluminum at 750°C for 2 hours and a forced cooling to room temperature by air blow. The crack resistance and peel resistance were evaluated by counting the number of the above cycles until cracking or peeling of the surface layer took place. The cracks were tested by a permeation liquid usually called "color check." The results are shown in Fig. 1.

It is clear from Fig. 1 that the addition of 5 weight % or more of Cr is effective for improving the crack resistance and peel resistance of the surface oxide layers formed on the melt-contacting members. It has also been found that the addition of Y further improves the crack resistance and peel resistance of the surface oxide layers.

Example 4

With respect to the same Fe-base alloys as in Example 2, experiments were conducted to measure a resistance to dissolution loss by molten zinc.

(1) Shape of each sample

Each sample was in the shape of a round rod of 200 mm in length and 20 mm in diameter.

(2) Oxidation treatment

Each sample was placed in a furnace at room temperature, which was evacuated and filled with a dry nitrogen gas at atmospheric pressure. Each sample was heated to 950°C (Sample Nos. 1-3, 6-10) and 1000°C (Sample Nos. 4 and 5) in the dry nitrogen gas. After reaching the above temperature, a mixture of the air, an overheated steam and an

ammonia gas (volume ratio: 11/3/1) at 950°C was introduced into the furnace while heating each sample, to carry out an oxidation treatment at 1000°C (Sample Nos. 1-3, 6-10) and 1050°C (Sample Nos. 4 and 5) for 1 hour. After the completion of the heat treatment, each sample was cooled in the furnace. Incidentally, Sample Nos. 4 and 5 were annealed at 650°C.

(3) Measuring dissolution loss by molten zinc

Each sample was immersed in molten zinc kept at 650°C for 20 hours to measure its loss by dissolution into the molten zinc.

Comparison with respect to the dissolution loss was conducted between the samples subjected to the oxynitriding treatment of the present invention and those subjected to no oxynitriding treatment. The results are shown in Table 5 below, in which the numerical values (mm) are the same as in Table 2.

Table 5

| Dissolution loss by Molten Zinc | | |
|---------------------------------|----------------------------------|--------------------|
| No. | Oxidation Treatment | |
| | Present Invention ⁽¹⁾ | Non ⁽²⁾ |
| 1 | Trace | 2-3 mm |
| 2 | No | 2-4 mm |
| 3 | No | 1-5 mm |
| 4 | No | 1-3 mm |
| 5 | No | 2-3 mm |
| 6 | No | 1-2 mm |
| 7 | No | 1-1.5 mm |
| 8 | No | 1-2 mm |
| 9 | No | 0.2-0.4 mm |
| 10 | No | 0.3-0.6 mm |

Note

(1)-(2) Same as in Table 2.

It is clear from the above results that the oxynitride layer of the present invention are remarkably effective for improving a resistance to dissolution loss by molten zinc.

Example 5

An Fe-base alloy sample having the same composition and size as those of Sample No. 4 in Example 2 was subjected to the same oxidation treatment as in Example 2, and immersed in molten brass kept at 1100°C for 2 hours to measure its loss by dissolution into molten brass. Comparison was made with a sample having the same substrate composition without oxidation treatment. The results are shown in Table 6 below.

Table 6

| Sample | Dissolution loss by Molten Brass |
|------------------|---------------------------------------|
| With Oxide Layer | No |
| No Oxide Layer | Disappeared by Dissolution into Brass |

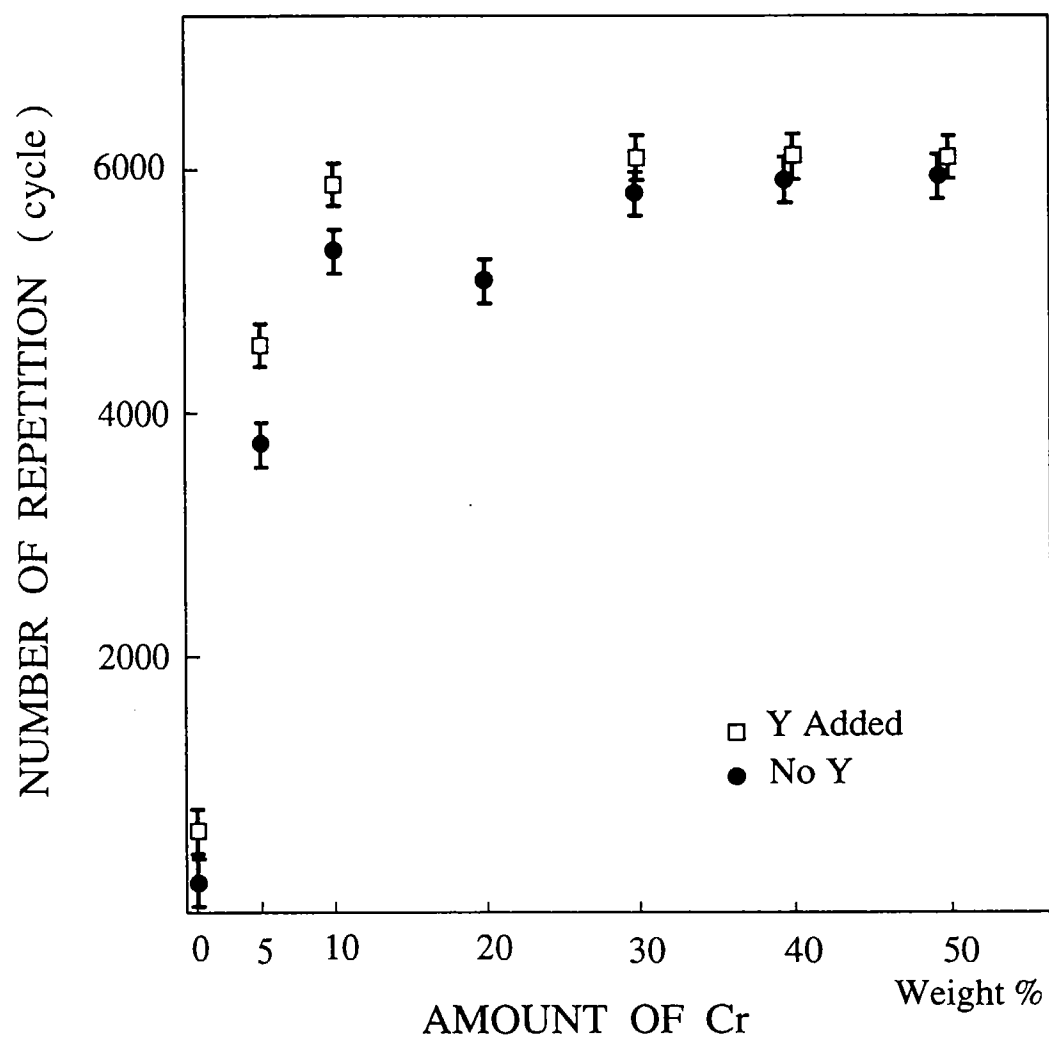
As described in detail above, the melt-contacting member of the present invention has an excellent resistance to

dissolution loss by nonferrous molten metals such as aluminum, zinc, copper, brass, etc. The melt-contacting members of the present invention, such as thermocouple protection tubes, heater tubes, die-casting cylinders, plunger heads, die-casting molds, melt supply tubes, inner walls of melt pumps and melt kilns, etc., are useful in the field of casting of molten nonferrous metals.

Claims

1. A member for use in contact with molten non-ferrous metals, comprising a substrate made of an Fe-base alloy and a dense surface layer composed of an oxide or oxynitride formed in the presence of steam.
2. The member of claim 1, wherein said substrate is made of an Fe-Cr alloy containing 40 weight % or less of Cr, or of an Fe-(Al, Si) alloy containing 4 weight % or less of Al and/or Si, or of an Fe-(Al, Si)-Cr alloy containing 4 weight % or less of Al and/or Si and 40 weight % or less of Cr.
3. The member of claim 1 or 2, wherein said Fe-base alloy further contains 0.1-2 weight % of yttrium.
4. The member of any one of claims 1 to 3, wherein said non-ferrous metal is aluminium, zinc, copper or alloys thereof.
5. A method of producing the member of any preceding claim, wherein said substrate is preheated in a non-oxidising atmosphere and then heat-treated in an oxidising or oxynitriding atmosphere containing steam or in an atmosphere generating oxygen and steam.
6. The method of claim 5, wherein said non-oxidising atmosphere is nitrogen gas.
7. The method of claim 5 or 6, wherein the preheating temperature is between the oxidising or oxynitriding temperature and a value of 100°C below the same.
8. The method of claim 7, wherein said preheating temperature is between 650 and 1100 °C.
9. The method of claim 7 or 8, wherein said oxidising or oxynitriding temperature is between 700 and 1200 °C.
10. The method of any one of claims 5 to 9, wherein said steam containing oxidising atmosphere is a mixture of air and overheated steam, or a mixture of air, overheated steam and a nitriding gas.
11. The method of any one of claims 5 to 9, wherein said oxygen and steam generating atmosphere is a mixed gas comprising hydrogen and carbon dioxide.

FIG. 1





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EUROPEAN SEARCH REPORT

Application Number
EP 97 10 8034

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
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| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 8 September 1997 | Examiner Elsen, D |
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