

[54] **CHROMIUM-BASE ALLOY FOR MAKING A CHILL-MOLD AND A PROCESS OF MAKING SAME**

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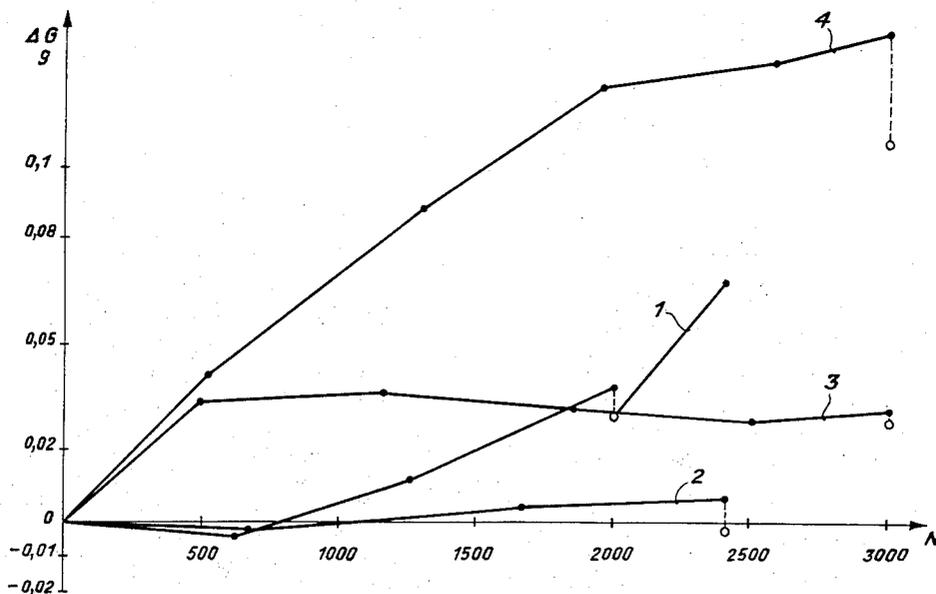
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[57] **ABSTRACT**

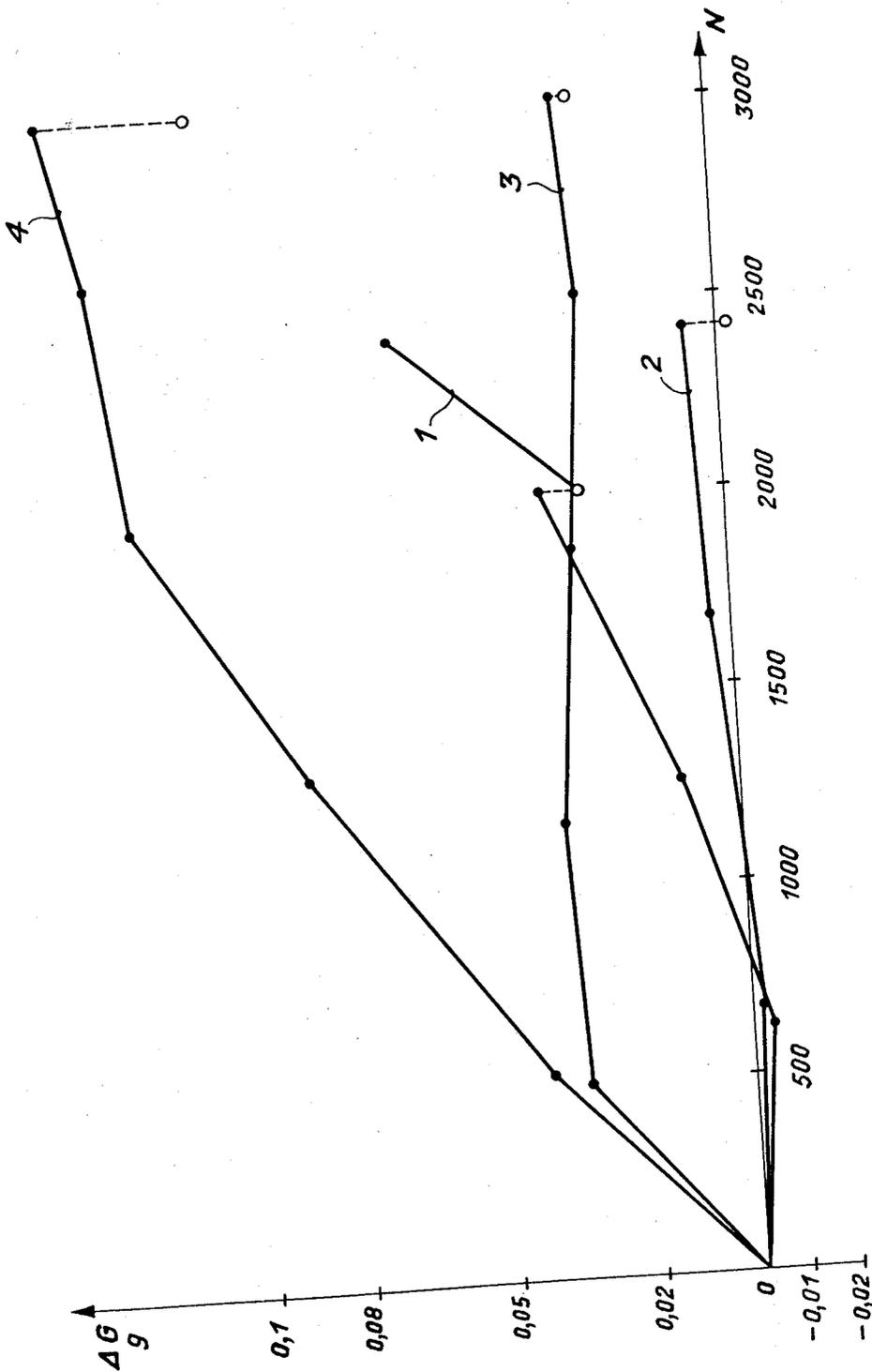
The chromium-based alloy is used for making a chill mold for high temperatures, i.e. up to 1550°C, melts. The alloy contains 15 to 35 percent cobalt and/or iron, 0 to 0.2 percent nitrogen, stoichiometric quantities relative to the nitrogen of a nitride-former selected from titanium, hafnium and zirconium, and the remainder chromium up to 64 percent. The alloy has good heat conductivity, a small heat-expansion coefficient, good resistance to corrosion and a sufficient heat resistance.

3 Claims, 1 Drawing Figure



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CHROMIUM-BASE ALLOY FOR MAKING A CHILL-MOLD AND A PROCESS OF MAKING SAME

This invention relates to a chromium-base alloy for use in the making of a chill-mold, particularly for melts of high temperatures, and a process for making the alloy.

Chromium-based alloys have been known for use as the material for cast turbine blades of gas turbines as well as for forged pieces. Usually, in order to improve the characteristics of these alloys, for example, to increase strength and/or to increase hot-strength, as well as to improve their castability by lowering the viscosity of their melts, the alloys contain up to 45 percent by weight of cobalt and/or iron and/or nickel as well as 0.01 to 0.5 percent by weight of nitrogen and stoichiometric amounts of titanium, zirconium and/or hafnium as nitride-formers.

Further, up to the present time, chill-molds for melts having temperatures of up to about 800°C have been made of steels, this is, of iron-base alloys. However, for higher melt temperatures, these steel chill-molds have not been suitable. Thus, the chill molds for the higher temperature melts to be cast have been made of molybdenum-base alloys. However, the molybdenum-base alloys have a drawback in that their ability to withstand oxidation is considerably decreased about 500°C. Moreover, molybdenum-base alloys are less desirable as chill mold material because of their high cost.

Accordingly, it is an object of the invention to increase considerably the ability of chill molds to withstand high temperatures of molten metal.

It is another object of the invention to increase substantially the number of pieces a chill mold can cast.

It is another object of the invention to replace the very expensive molybdenum-base alloys as chill mold material for casting temperatures of up to 1550°C.

Briefly, the invention provides an alloy which contains, in weight percentages, a total of 15 to 35 percent of cobalt and/or iron, 0 to 0.2 percent of nitrogen, stoichiometric quantities to the nitrogen of nitride-formers selected from the group consisting of titanium, hafnium, and/or zirconium, and the remainder being chromium, with the proportion of chromium amounting to at least 64 percent. This chromium-base alloy is used as a material for chill molds for molten metals having temperatures of up to 1550°C.

The following characteristics are particularly important with the aforesaid alloy in its use. The alloy has good heat-conductivity and a small heat-expansion coefficient which results in good ability to withstand temperature shocks. The alloy also has a heat-resistance which suffices for the requirements made while, above all, the alloy has a good resistance to corrosion which gives it superiority in comparison with the aforesaid molybdenum-base alloys.

Because the chill molds of the invention practically never become cooled below 500°C during their use, they practically never display low-temperature brittleness and relatively high transition temperature in going from the tough to the brittle state. When there are lengthy pauses in their use, damage to the chill mold during passage through the transition temperature can be avoided by suitably selected slow cooling or heating-up speeds.

By means of additional alloying elements, it is possible to substantially improve the alloy characteristics of the alloy for use as a chill mold material. For example, ductility can be improved by the addition of yttrium or rare earth metals in an amount to constitute up to 1.5 percent of the weight of the alloy. Other additives, such as molybdenum, niobium, aluminum (in association with cobalt and nitrogen), and tantalum can be added in varying quantities to improve the ability to withstand heat. Tantalum, moreover, in combination with nitrogen, improves the ductility of the alloy.

The ability of the alloy to withstand corrosion has the result that the introduction of the melts requires only a little or even no covering with coatings. Further, a dense automatically building-up and automatically self-repairing protective layer on the mold surface can be obtained by including a total of 3 to 7 percent of tantalum and niobium (with less than 4 percent of tantalum being present and with at least 1 percent of niobium) and 0.1 to 4 percent of aluminum. It has been found to be advantageous to subject this alloy, after solidification, to a heat treatment of the following kind: 2 hours of glowing in a protective gas atmosphere at 1300° to 1600°; cooling by compressed air to room temperature; 1 hour of glowing in air at 700°C; and cooling in air to room temperature.

One process for the treatment of a chromium-base alloy for use as a chill mold is characterized in that the alloy is melted in a vacuum of approximately 10^{-3} to 10^{-4} torr and then cast into a block. The block is then machined out mechanically into the form of the desired chill-mold.

The purity of the block which is cast from the melt can be increased, in a simple way. That is, prior to being machined, the block is once more remelted in a vacuum, or else is solution heat treated at around 1600°C in an argon atmosphere and then quenched in oil.

If it is advantageous to use a grain-refining medium on the molten alloy, it is possible to obtain a finer grain by chemical techniques through an addition of a maximum of 0.1 percent by weight of boron and/or up to 1 percent by weight of silicon. Physical techniques, such as, among others, a vibratory treatment, e.g. by ultrasonic or mechanical means, can also be used. Further possibilities include means to obtain a rapid solidification of the cast chill mold material.

The invention is explained in more detail in the following by the aid of Examples.

EXAMPLE 1

A vacuum induction furnace, lined with magnesium oxide (MgO) and in which a vacuum of approximately 10^{-3} to 10^{-4} torr is maintained, is charged with the individual components of the chromium-base alloy in the following sequence:

11	kg cobalt
2.5	kg molybdenum
32.5	kg chromium containing about 0.6% by weight nitrogen
0.4	kg yttrium
0.4	kg hafnium
10.	kg aluminum
2.0	kg tantalum
49.8	kilograms (kg) total

From the melt produced in the furnace there is then cast, at a casting temperature of about 1750°C, one or

more blocks of a suitable size, and preferably, large blocks. These blocks are then solution heat treated for about 4 hours at about 1600°C in a protective atmosphere of argon gas, for the chief purpose of obtaining a dissolution of chromium nitrides. The blocks are then quenched in oil from their glowing temperature and then processed by mechanical means into the desired chill molds.

Instead of this heat treatment, it is also possible, particularly in cases where only one block is cast from a 50 kilogram (kg) melt to subject this block, for purification, to a remelting process. This remelting is, for example, done in such a way that the block serves as a self-consuming electrode of an electric-arc furnace. In addition, the dripping material from the electrode drips into a water-cooled copper chill-mold and a second block is produced in this copper chill-mold which is then machined into the desired chill molds by mechanical means.

EXAMPLE 2

The same furnace with the same lining as above is, before being heated up, charged with:

12.5	kg iron
33.5	kg chromium containing 0.2% of its weight of nitrogen (N)
0.8	kg hafnium
1.0	kg tantalum
0.03	kg zirconium
0.005	kg boron (not added under certain conditions since normally contained as an impurity)
1.5	kg niobium

After the heating and melting of these constituents, there is added to the liquid melt:

0.25	kg aluminum
0.25	kg silicon
0.1	kg cerium
0.05	kg titanium

It is, of course, possible to select some other suitable sequence and/or to use one or more components in common in the form of one or more pre-alloys.

The final melt results in an alloy whose analysis should yield the following figures, although under certain circumstances the quantities of easily-volatilized components, chiefly Al and Ce, have to be increased.

In weight percentages: 25% Fe, 0.2% Cer, 1.8% HfN, 0.5% Al, 2% Ta, 0.5% Si, 0.1% Ti, 0.06% Zr, 0.01% B, 3% Nb, remainder Cr.

A chill mold is then directly produced from the melt produced in the furnace at a temperature of about 1750°C by the shaped-casting process and as a precision casting wherein the mold for casting the chill-mold, regardless of the wall thickness and the chromium content of the chill mold to be cast, is preheated for example to 300°C to 700°C. Thick walls and relatively small contents of chromium require lower pre-heating temperatures and vice versa.

In order to carry out a rapid solidification of the cast chill mold material to obtain a fine grain, the mold for casting the chill mold may be made in such a way that the side with the negative of the chill mold hollow space consists of a ceramic mold-mass, which usually is of relatively poor heat conductivity while the other

delimitations of the mold for casting the chill mold consist of metal and/or graphite, which because of their good heat-conductivity promote rapid solidification of the cast material of the chill mold.

The casting for the chill mold obtained from the chromium-base alloy is then solution heat treated at about 1500°C in an argon atmosphere for about 2 hours, for the chief purpose of obtaining dissolution of chromium nitrides. The casting is then cooled down from its temperature of the solution heat treatment by compressed air to room temperature and is once more held for about 1 hour at 700°C in air, whereby a protective layer becomes formed on the chill mold surface and is cooled in air to room temperature. The chill mold produced by the shaped-casting process is now ready to be put into use.

The superiority of the chromium-base alloys according to the invention as a material for chill molds is shown by so-called drop-impact test. Here in a test set-up, the materials that are to be compared with one another, and consisting of specimen plates of about 10 millimeters (mm) × 100 millimeters (mm) × 4 millimeters (mm) dimensions, are subjected to drops falling down from a melting steel electrode, which always have a temperature of about 1580°C, are of the same size, and drop the same distance. These drops are counted automatically to find how many are needed to produce cracks in the specimen. By means of this experimental set-up, there can be determined the ability of the chill mold material to withstand the so-called "tendency to burn-cracking" (under the chemical, physical and mechanical stressing of a chill mold) in conditions approximating the operational conditions for a chill mold.

Here, with temperatures of 340°C for the specimens, the results were:

For steel (commercial molybdenum-vanadium (Mo-V) alloy hot-worked)	10,000 drops
For molybdenum-base alloy	15,000 drops
Chromium-base alloy per the invention	12,000 drops

Tests at higher temperatures of 580°C (the upper limit possible with the testing set-up) were broken off for the chromium-base alloy after 38,600 drops without cracks appearing in the specimens. For the other two materials, at the aforesaid higher temperature, the testing could not be completed, because the investigated steel lacked the necessary ability to withstand heat, while the molybdenum alloys were useless because of the high vapor-pressure of the molybdenum oxide.

In investigations as to whether the new material for chill molds becomes coated with a dense tightly-adhering protective layer, the following tests were made with cast specimens of 65 × 25 × 8 millimeters (mm) dimensions:

The specimens were subjected to thermoshock treatment, in which they were alternately heated to 1200°C and then quenched to 600°C. During a test, about 3000 such shock-treatments were given to each specimen. In each case, after some 500 such treatments, the weight-change ΔG of the specimen was determined. The annexed Figure diagrammatically shows the results. This diagram shows by its abscissae, the number (N) of temperature changes on a time base while the ordinates are plotted to show the weight change ΔG in grams (g).

The plotted curves thus give the weight increment of various chromium-base alloys as a function of time. The investigated alloys had the following compositions,

the analysis figure being given in weight-percentages of the melt.

No. 1: 25% Fe, 0.2% Ce, 1.8% HfN, 0.5% Al, 4% Ta, 0.5% Si, 0.1% Ti, 0.06% Zr, 0.01% B, remainder chromium.

No. 2: As No. 1, but with only 15 percent Fe instead of 25 percent.

No. 3: As No. 1, but the melt contained only 2 percent Ta instead of 4 percent, but to make up for this contained also 3 percent Nb.

No. 4: As No. 1, with an addition of 3 percent Nb.

Whereas curve 1 definitely shows progressive oxidation of the specimen with time, and this tendency also exists with alloy 2, the progress of the curve of alloy 3, after a relatively steep initial rise, rapidly assumes a saturation value for the weight increment. This indicates that a tightly-adhering dense protective layer which is substantially an oxide layer becomes very rapidly formed on alloy 3, and inhibits a further increase of weight and, thus, a further absorption of oxygen.

It is true that alloy 4 appears to strive toward a saturation value for its increase of weight, this tendency is, however, far less apparent than that with alloy 3. In the case of alloy 4, therefore, saturation evidently occurs only after a substantially longer alternating-temperatures treatment, and, if it occurs at all, only after a substantially greater absorption of oxygen.

The small circles in the Figure show the measurements for weighings made after thorough brushing-off of the specimens. Here too, the tightly-clinging protective layer of alloy 3 shows up very clearly, since in this case the loss of weight through mechanical stressing of

the surface is very small in comparison with the results for the other alloys.

This invention thus provides a chromium-base alloy which is useful as a material in forming a chill mold for molten metals having temperatures of up to 1550°C, e.g. for molten cobalt-base or nickel-base alloys, for cast irons and high-alloy austenitic steels. The alloy is useful for a pressure-casting chill mold as well as for simple chill mold casting.

10 What is claimed is:

1. A chromium-base alloy chill mold for high temperature molten metal consisting essentially of by weight a total of 15 to 35 percent cobalt and/or iron of up to 0.2 percent nitrogen, stoichiometric amounts relative to said nitrogen of a nitride former selected from the group consisting of titanium, hafnium and zirconium, a total of from 3 to 7 percent tantalum and niobium, said tantalum being present in an amount of less than 4 percent and said niobium being present in an amount of at least 1 percent, 0.1 to 4 percent aluminum for forming a dense self-forming and self-healing tightly-clinging protective layer with said tantalum on the surface of the alloy, and the remainder being essentially chromium, said chromium amounting to at least 64 percent.

2. A chromium-base alloy as set forth in claim 1 further comprising up to 1.5 percent yttrium and/or rare earth metals.

3. A chromium-base alloy as set forth in claim 1 further comprising by weight 5 to 10 percent molybdenum.

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