Patented May 23, 1939 2,159,048

UNITED STATES PATENT OFFICE

2,159,048

METHOD OF IMPROVING THE WORKABILITY OF NICKEL AND NICKEL ALLOYS

Leonard Bessemer Pfeil, Edgbaston, Birmingham, England, assignor to The International Nickel Company, Inc., New York, N. Y., a corporation of Delaware

No Drawing. Application October 6, 1936, Serial No. 104,179. In Great Britain October 15, 1935

10 Claims. (Cl. 75—171)

The present invention relates to the method of improving the workability of nickel and nickel alloys and products resulting therefrom including electric resistance units.

Nickel and its alloys have, in some cases, been somewhat difficult to work and under certain circumstances an alkaline earth metal has often been added to the molten materials. In order to obtain the full benefits of the addition of the alkaline earth, it is desirable to add more of the alkaline earth metal, calcium for example, than is consumed by the desired chemical reactions. This results in a residue of calcium or other alkaline earth in the finished material (or a residue of some other element reduced from the furnace lining, slag, and so forth, by the excess calcium, etc.), but it is important to control the amount of alkaline earth metal that is left as the presence of more than a certain amount of calcium or other alkaline earth metal makes the material unworkable.

I have made the surprising discovery that the necessity for strict control of the amount of calcium or other alkaline earth metal can be avoided and yet the materials can be rendered easily workable.

It is an object of the present invention to provide a method of improving the workability of nickel and/or nickel alloys.

It is another object of the present invention to provide means for obviating the need for extreme care in regulating the initial amount of alkaline earth metal added to nickel and/or nickel alloys.

It is a further object of the present invention to compensate for the excess of alkaline earth present in a nickel and/or nickel alloy material by the addition of a regulated, critical amount of another element usually considered deleterious.

The present invention also contemplates the production of nickel alloys particularly suitable for use as electrical resistance units.

Other objects and advantages will become apparent from the following description.

In general, the present invention contemplates melting nickel and/or nickel alloying metals in the usual manner followed by the usual deoxidising, desulfurising, etc. The deoxidising, desulfurising, etc., may be carried out by the addition of calcium silicide or other alkaline earth metals or alkaline earth metal alloys, or by means of aluminum, cerium and related elements (including thorium, hafnium, scandium, yttrium, and zirconium); and manganese, molybdenum, silicon and titanium may be added with advantage. Other elements that may be added are barium, beryllium, boron, cobalt, copper, lithium, magnesium, strontium, sulfur, and tungsten. Moreover, more than one of the alkaline earth metals may be added to the melt, whether or not more than one such metal is left in the finished material, and similarly more than one of the metals usually considered deleterious may be added.

It is convenient to describe the nature of the present invention in connection with calcium and arsenic, but it is to be understood that these may be replaced respectively by other alkaline earth metals and other elements of Group V, i. e., antimony, phosphorus, bismuth, vanadium, columbium, and tantalum.

The amount of calcium and the accompanying arsenic to be added to the melt varies according to the working conditions, i. e. the type of furnace, conditions of the lining, the speed of melting, the nature of the raw materials, and other similar factors, but in order to give an indication of the relative amounts of calcium and arsenic, it may be stated that when between about 0.05 and about 0.15% calcium is present in the finished material this may advantageously be accompanied by about 0.01 to about 0.05% arsenic. In general, it is preferred so to carry on the process that small quantities of calcium and an element of Group V remain in the finished material because in this way, it can be ensured that the beneficial effects obtained by their addition to the molten material are produced to the full. The preferred ranges are as follows:

Element	Percent by weight	Element	Percent by weight
Calcium	0.01 to 0.10	Phosphorus	0.01 to 0.06
Do	0.01 to 0.15	Arsenic	0.01 to 0.2
Do	0.01 to 0.2	Antimony	0.01 to 0.25
Do	0.01 to 0.075	Vanadium	0.01 to 0.25
Do	0.01 to 0.05	Columbium or niobium	0.01 to 0.75
Do	0.01 to 0.05	Tantalum	0.01 to 0.25

In the case of bismuth, not more than 0.075%, should be added.

As is well known, the calcium may be added as a metal or as an alloy or compound, such as calcium silicide and the Group V element may be added in the elemental form or as an alloy or compound, such as, for example, nickel arsenide or calcium phosphide. The alloying process may be carried out in any suitable manner. Thus, a preliminary addition of calcium silicide may be made to the melt and any substantial excess of calcium removed by oxidation. A final calcium

silicide addition may be made just before casting. The less oxidizable of the Group V elements may be added at any stage in the melting process, or may be added in a suitable alloyed form with the cold charge, but with those elements of the Group V with a high affinity for oxygen, that is to say, vanadium, niobium or columbium and tantalum, it is preferred to add the element after the main part of the charge has been melted and subjected to a preliminary deoxidation treatment.

The additions may be made by plunging the elements or alloys to the bottom of the molten metal by any suitable means so as to improve the alloying process. The Group V elements together with part or all the calcium, or other alkaline earth metal, may, however, be added to the molten stream during the pouring of the metal.

For the purpose of giving those skilled in the art a better understanding of the present invention, the following examples are given by way of illustration.

Example No. 1

In the production of the well-known 80/20 nickel-chromium alloy according to the present invention, the following procedure may, for example, be followed:

About 800 pounds of nickel are melted and subjected to deoxidation by the addition of about 0.25 to about 0.5% manganese and about 0.25% silicon, about 200 pounds of chromium are added and when the mass is molten about 6 pounds of calcium silicide containing about 25% calcium are added. This is equivalent to adding about 0.13% calcium to the melt. When sufficient time has been allowed for the desired reactions to proceed and the temperature of the metal has been adjusted to that correct for casting, the metal is poured into a ladle, and about 0.5 of a pound of metallic arsenic is added thereto. About 1 pound of calcium silicide is introduced into the ladle, and the metal is cast. These last additions represent about 0.045% and about 0.08%, respectively, of the total mass.

Example No. 2

The procedure of Example No. 1 is followed until the chromium has been added to the melt, and then about 4 pounds of the calcium silicide and, for example, about 1 pound of commercial cerium are added. The melt is poured into the ladle while adding about 0.25 pound of metallic arsenic. About 0.50 pound of calcium silicide and about 1 pound of cerium are added while the metal is in the ladle.

Example No. 3

As illustrative of the process according to the present invention as applied to the production of nickel, the following example is given

About 1000 pounds of commercial nickel are melted together with about 0.25% manganese and about 0.1% silicon. When molten, the metal is poured into the ladle and during the pouring operation, an addition of about 0.025% arsenic is made followed by about 0.05% calcium either in the metallic form or in the form of calcium silicide.

In the application of the present invention to the preparation of iron-nickel alloys the following example is presented for illustrative purposes:—

Example No. 4

In the production of a 50–50 nickel-iron alloy, about 500 pounds of nickel and about 500 pounds of iron are melted together with about 0.25% manganese and about 0.1% silicon. When molten, the metal is poured into the ladle and during the pouring operation an addition of about 0.025% arsenic is made followed by the addition of about 0.05% calcium either in the metallic form or in the form of calcium silicide.

The present invention may be applied with particular advantage to those nickel-chromium and nickel-chromium-iron alloys from which, as a general rule, electrical resistance elements are made. From their nature, these alloys give rise to substantial difficulty during the wire producing processes on which the life of the wire may depend. Accordingly, the invention includes electrical resistance elements made from such alloys embracing small quantities of one or more alkaline earth metals and one or more of the Group V elements.

While the present invention has been described in connection with certain preferred embodiments, it is to be understood that variations and modifications may be made by those skilled in the art. Such variations and modifications are considered to be within the spirit and scope of the appended claims.

It is to be understood that the term deoxidation, as used herein, includes such preliminary treatment as deoxidizing, desulfurising, etc.

I claim:

1. The process of manufacturing nickel-chromium alloys which comprises melting a suitable amount of nickel, deoxidizing the nickel by the addition of a deoxidizer, adding a suitable amount of chromium, allowing the materials to become molten, adding a suitable amount of calcium silicide containing about 25% calcium, allowing sufficient time to elapse for the desired reactions to proceed, adjusting the temperature of the metal to that correct for casting, pouring the metal into a ladle, adding a suitable amount of arsenic to the stream of molten metal, introducing further amounts of calcium silicide into the ladle and casting the metal containing small amounts of calcium and arsenic whereby the workability of the finished material is improved.

2. The process of manufacturing nickel-chromium alloys which comprises melting about 800 pounds of nickel, deoxidizing said nickel by the addition of about 0.25 to about 0.5% manganese and about 0.25% silicon, adding 200 pounds of chromium, allowing the mass to become molten, adding about 6 pounds of calcium silicide containing about 25% calcium, allowing sufficient time to elapse for the desired reactions to proceed, adjusting the temperature of the metal to that correct for casting, pouring the metal into a ladle, adding about 0.5 pound of metallic arsenic to the stream of molten metal, introducing about 1 pound of calcium silicide into the ladle and casting the metal whereby nickel chromium alloys are obtained having improved workability and containing small amounts of calcium and arsenic.

3. The process of manufacturing nickel-chromium alloys which comprises melting a charge of nickel, deoxidizing said nickel, adding a suitable amount of chromium, allowing the mass to become molten, adding a quantity of calcium equivalent to about 0.13% of the mass, allowing sufficient time to elapse for the desired reactions to proceed, adjusting the temperature to that correct for casting, pouring the metal into a ladle, adding a quantity of arsenic equivalent to about

0.045% of the mass to the stream of molten metal, adding a quantity of calcium silicide equivalent to about 0.09% of the mass to the metal in the ladle and casting the metal whereby nickel-chromium alloys are obtained having improved workability and containing small amounts of calcium and arsenic.

4. The process of counteracting the deleterious effect of excess amount of calcium on the workability of nickel alloys containing about 80% nickel and about 20% chromium which comprises subjecting a molten mass of said nickel alloys to deoxidation treatment; subsequently treating said molten mass with about 0.01% to about 0.15% calcium and incorporating in said molten mass restricted and controlled amounts of arsenic within the range of about 0.01% to about 0.2%; and solidifying the thus-treated metal whereby sound, solid nickel alloys containing about 80% nickel and about 20% chromium are produced having improved workability and being devoid of the deleterious effect of an exces amount of calcium.

5. The process of counteracting the deleterious effect of excess amount of calcium on the workability of nickel-chromium alloys which comprises subjecting a molten mass of nickel-chromium alloy to deoxidation treatment; subsequently treating said molten mass with about 0.01% to about 0.15% of calcium and incorporating in said molten mass restricted and controlled amounts of arsenic within the range of about 0.01% to about 0.2%; and solidifying the thus-treated metal whereby sound, solid nickel-chromium alloys are produced having improved workability and being devoid of the deleterious effect of an excess amount of calcium.

6. The process of counteracting the deleterious effect of excess amount of alkaline earth metal on the properties of nickel-chromium alloys which comprises subjecting a molten mass of nickel-chromium alloy to deoxidation treatment, subsequently treating said molten mass with about 0.01% to about 0.2% of alkaline earth metal and incorporating in said molten mass at least one element from the group consisting of arsenic, antimony and phosphorus in restricted and controlled amounts within the range of about 0.01% to about 0.2%, about 0.01% to about 0.25%, and about 0.01% to about 0.06%, respectively; and solidifying the thus-treated metal whereby sound solid nickel-chromium alloys are produced having improved properties and being devoid of the deleterious effect of an excess amount of alkaline earth metal.

7. The process of counteracting the deleterious effect of excess amount of calcium on the workability of nickel and nickel alloys which comprises subjecting a molten nickel mass, to deoxidation treatment; subsequently treating said molten mass with about 0.01% to about 0.15% calcium and incorporating in said molten mass restricted and controlled amounts of arsenic within the range of about 0.01% to about 0.2%; and solidifying the thus-treated metal whereby sound, solid nickel and nickel alloys are produced having improved workability and being devoid of the deleterious effect of an excess amount of calcium.

8. The process of counteracting the deleterious effect of excess amount of alkaline earth metal on the properties of nickel and nickel alloys which comprises deoxidizing a molten nickel mass; treating said molten mass with about 0.01% to about 0.20% of alkaline earth metal and incorporating in said molten mass restricted and controlled amounts of at least one element from the group consisting of arsenic, antimony and phosphorus within the range of about 0.01% to about 0.25%; and solidifying the thus-treated metal whereby sound, solid nickel and nickel alloys are produced having improved properties and being devoid of the deleterious effect of an excess amount of alkaline earth metal.

9. The process of counteracting the deleterious effect of excess amount of alkaline earth metal on the properties of nickel and nickel alloys and of avoiding the necessity for strict control of the amount of alkaline earth metal in nickel and nickel alloys which comprises deoxidizing a molten nickel mass; subsequently treating said molten mass with about 0.01% to about 0.2% of alkaline earth metal and incorporating in said molten mass at least one element from the group consisting of arsenic, antimony and phosphorus in restricted and controlled amounts within the range of about 0.01% to about 0.2%, about 0.01% to about 0.25%, and about 0.01% to about 0.06%, respectively; and solidifying the thus-treated metal whereby sound solid nickel and nickel alloys are produced having improved properties and being devoid of the deleterious effect of an excess amount of alkaline earth metal.

10. The process of counteracting the deleterious effect of excess amount of calcium on the workability of nickel which comprises subjecting a molten mass of nickel to deoxidation treatment; subsequently treating said molten mass with about 0.01% to about 0.15% of calcium and incorporating in said molten mass arsenic in restricted and controlled amounts within the range of about 0.01% to about 0.2%; and solidifying the thus-treated metal whereby sound, solid nickel is produced having improved workability and being devoid of the deleterious effect of an excess amount of calcium.

LEONARD BESSEMER PFEIL.