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HEAT RESISTANT ALLOY

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The present invention relates to heat resistant alloys and, particularly to heat resistant alloys used for the manufacture of articles which are subjected in use to repeated heating and cooling, such as electrical resistance elements.

It is an object of the invention to improve heat resistant alloys that the effective life of articles made therefrom will be increased.

It is another object of the present invention to provide an improved heat resistant alloy with an increased life which can be made on an industrial scale with conventional equipment.

The invention also contemplates the provision of a method for imparting to heat resistant alloys increased service life.

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

According to the present invention increased life is imparted to a heat resistant alloy by adding to the molten alloy prior to casting one or more of the rare earth metals. When the expression "rare earth metals" is used herein, it is intended to include not only the elements usually called rare earth metals, but also scandium, yttrium, hafnium, and thorium. The quantity that is added to a heat resistant alloy is such that at the most only a small residue remains in the finished alloy. It is preferred to control the residue to an amount of from about 0.01 to about 0.5% in all of the rare earth metal or metals.

In carrying the invention into practice, the molten alloy is preferably subjected to a preliminary treatment before the addition of the rare earth metal or metals for deoxidising, desulphurising or other purposes, or to improve the forgeability. This treatment may be effected with highly reactive elements, such as calcium for deoxidising purposes and for improvement in the forgeability, and elements such as phosphorus or arsenic for rendering objectionable constituents innocuous. The preliminary treatment may also include the use of supplementary scavengers such as manganese, magnesium and silicon. Further the alloy itself may contain, in addition to the necessary elements that compose it and render it heat resistant, such elements as cobalt, molybdenum, titanium, tungsten, aluminum and zirconium. The actual addition of the rare earth metal or metals, however, is either made alone or is accompanied only by one or more of the alkaline earth metals in elementary, alloyed or combined form and the elements of group V of the periodic table. If a rare earth metal such as cerium alone is used, and especially when a substantial amount of impurities (in particular, oxides) is present, there is a tendency for the compounds formed by interaction between the rare earth metal and the impurities to remain in the melt, resulting in the production of an unclean alloy. On the other hand, by preliminary treatment with an alkaline earth metal such as calcium or an alloy thereof, for instance, calcium silicide, as described in U. S. patent specification No. 1,824,966 the major portion of the impurities may be eliminated prior to the introduction of the rare earth metal so that not only may the requisite amount of rare earth metal be substantially reduced with a corresponding saving in cost, but the risk of any appreciable inclusions of undesired rare earth compounds in the final alloy is practically eliminated. In the aforesaid patent it was disclosed that the metal was treated with an alkaline earth metal such as calcium in amounts within the range of 0.005% to 0.5%. It is found to be particularly advantageous to add calcium in such a quantity and in such a sequence with the rare earth metal that there is a residue of the rare earth metal and only a trace of calcium in the finished alloy. The rare earth metal is preferably added in the form of commercial "cerium" which contains in addition to cerium, other rare earth metals, such as lanthanium, praseodymium, neodymium, samarium and europium; the preferred residue of this is from 0.15 to 0.20%.

A particular advantage of the use of rare earth metals is that when an amount is present or has been added which will give a definite improvement in life the workability of the alloy is not substantially impaired.

It has been found that, particularly when an alkaline earth metal is present, the forgeability is improved when there is a small residue of one of the elements of group V, particularly arsenic, in the alloy. Thus in the case of the well known 80% nickel-20% chromium heat resistant alloy, improved life is obtained by adding enough rare earth, alkaline earth and arsenic to leave between 0.01 and 0.5% rare earth, between 0.001 and 0.05% alkaline earth and between 0.02 and 0.10% arsenic in the alloy.

The amount of rare earth metal to be added to the melt to produce the desired result or to leave any desired quantity in the finished alloy depends upon the melting conditions, i. e., the type of furnace, the composition and pressure of the surrounding atmosphere, the condition of the lining, the speed of melting, the nature of the

raw materials, the casting conditions, and other similar factors, and even if the loss of the rare earth metal during melting is exceptionally small, so that the amount of residual rare earth metal is distinctly greater than is expected, the resultant alloy may still be easily worked owing to the small extent to which the workability is affected. In cases when unusually high losses are expected or when high forgeability is not required, as much as 5% of the rare earth metal or metals may be added to the melt. Owing to the highly reactive nature of the rare earth metals, precautions should be taken to ensure that the addition penetrates into and is distributed in the molten metal; for example the addition may be plunged to the bottom of the molten metal.

It has been found that the molten alloy may contain substantial amounts of carbon without harm, particularly when cerium is used and is preceded by calcium. This fact is of great importance, because it allows scrap metal that is contaminated with oil or other carbonaceous material to be used in the production of the molten alloy. Thus the finished alloy may contain as much as 0.25% carbon. However the preferred alloys in their finished state contain no carbon or an amount thereof not exceeding 0.15%. When oily or carbonaceous scrap is used the carbon content may, if desired, be adjusted by any suitable treatment.

The way in which the rare earth metals act is not at present fully understood. It is possible that their deoxidising, desulphurising or similar actions play an important part during the melting operation, or that they may react with materials present at the time of melting and thus introduce beneficial amounts of elements that otherwise would not be present in the molten metal, or again that when present in the solid alloy they affect the way in which the alloy oxidises or affect the properties of the surface film formed by such oxidation. Whatever the mechanism, reactions take place when the rare earth metal is added, and it is found to be important to hold the molten alloy for sufficient time to allow these reactions to proceed to an adequate extent before the alloy is cast.

For the purpose of giving those skilled in the art, a better understanding of the invention, the following illustrative examples will be given in connection with the manufacture of 80/20 nickel-chromium alloys for the production of electrical resistance elements.

Example No. 1

About eight hundred pounds of nickel are melted and 0.5% manganese and 0.2% silicon are added followed by about two hundred pounds of chromium and the whole is melted. Then about 4 pounds of calcium silicide containing 25% calcium, i. e., one pound of calcium or 0.1%, are added and the melt is held for from two to ten minutes to allow reactions to proceed. Next about 1 pound of commercial cerium metal is added and the melt is held for about two minutes for reactions to proceed, and is adjusted to the casting temperature. The liquid metal is then poured into a ladle, a further about 1 to about 1½ pounds of cerium metal are added, the metal is allowed to stand in the ladle for from about two to about five minutes and the metal is then cast into ingots.

Example No. 2

The procedure is the same as in Example No. 1 until the nickel and chromium are completely melted and then about 3 pounds of commercial cerium metal are added and the metal is cast into ingots.

Example No. 3

The procedure is the same as in Example No. 1 until the nickel and chromium are completely melted, and then about 4 pounds of commercial cerium metal are added, the molten metal is allowed to stand for from about ten to about twenty minutes and then the metal is cast into ingots.

Example No. 4

The procedure is the same as in Example No. 1 until the metal is in the ladle. Then about ½ pound of calcium silicide is added followed by about 0.05% of arsenic and about 1 pound of commercial cerium metal and the metal is then cast into ingots.

Example No. 5

About one thousand pounds of 80/20 nickel-chromium scrap metal are melted, the scrap being selected so that allowing for the carbonaceous residue derived from oil or other material in or on the scrap, the liquid metal will contain 0.075% carbon. The remaining treatment is the same as that in Example No. 2.

Example No. 6

The scrap is melted as in Example No. 5 and the remaining treatment is the same as that in Example No. 1.

Example No. 7

Scrap is melted as in Example No. 6 and is treated in the furnace with about 4 pounds of calcium silicide. When sufficient time has been allowed for reactions to take place about 0.05% metallic arsenic is added and the metal is poured into the ladle. About ½ pound of calcium silicide and about 2½ pounds of commercial cerium metal are added in the ladle and the metal is cast into ingots.

Example No. 8

A thousand pound melt of commercially pure nickel-chromium or consisting partly of commercially pure nickel and chromium, and partly of scrap is prepared. About 4 pounds of calcium silicide, i. e., one pound of calcium or 0.01%, and about 1 pound of commercial cerium metal are added and the molten metal is poured into the ladle. From about ½ pound to about 1 pound of calcium silicide, i. e., about ⅛ pound to about ¼ pound calcium or about 0.0125% to about 0.025%, is added in the ladle followed by from about ½ to about 2 pounds of commercial cerium metal. In other words, a total of about one and one-eighth to about one and one-quarter pounds of calcium or 0.1125% to 0.125% calcium are incorporated in the molten metal. The molten metal is allowed to stand in the ladle for from about two to about five minutes and is then cast into ingots.

Although the invention has been described in connection with certain alloys that are commonly used for the manufacture of heating elements in tape or wire form, all heat resisting alloys of the nickel-chromium or nickel-chromium-iron types as well as nickel-free heat resisting alloys such as chromium-iron alloys may be treated as described hereinbefore. The

metals may be added in any form desired. Thus the metals may be added in an elementary, alloyed or combined form.

We claim:

1. The method of imparting increased service life to a heat-resistant alloy which comprises first establishing a melt of a heat-resistant alloy consisting principally of nickel and chromium, then treating said melt with at least one alkaline earth metal in such controlled and restricted quantity that only a small residue remains in the melt after the treatment and incorporating in said treated melt at least one of the rare earth metals in such a controlled and restricted quantity that only a small residue remains whereby a treated alloy is produced which has increased service life when subjected in use to repeated heating and cooling.

2. The method of imparting increased service life to a heat-resistant alloy which comprises first establishing a melt of a heat-resistant alloy consisting principally of nickel and chromium and treating said melt with at least one alkaline earth metal in such controlled and restricted quantity that only a small residue remains in the melt after the treatment, adding to said melt a member of the group consisting of phosphorus and arsenic in such a small and controlled quantity as to render objectionable constituents innocuous, and incorporating in said treated melt at least one of the rare earth metals in such a controlled and restricted quantity that only a small residue remains whereby a treated alloy is produced which has increased service life when subjected in use to repeated heating and cooling.

3. The method of imparting increased service life to a heat-resistant nickel-chromium alloy which comprises first establishing a melt of a heat-resistant nickel-chromium alloy consisting principally of nickel and chromium, then treating said melt with at least one alkaline earth metal in such controlled and restricted quantity that only a small residue remains in the melt after the treatment, and incorporating in said treated melt at least one of the rare earth metals in such a controlled and restricted quantity that only a small residue remains whereby a finished nickel alloy containing about 0.001% to about 0.05% alkaline earth metal and about 0.01% to about 0.5% rare earth metal is produced which has increased service life when subjected in use to repeated heating and cooling.

4. The method of imparting increased service life to a heat-resistant alloy which comprises first establishing a melt of a heat-resistant alloy consisting principally of nickel and chromium, then treating said melt with at least one alkaline earth metal in such controlled and restricted quantity that only a small residue remains in the melt after the treatment, adding to said melt a member of the group consisting of phosphorus and arsenic antimony in such a small and controlled quantity as to render objectionable constituents innocuous, and incorporating in said treated melt at least one of the rare earth metals in such a controlled and restricted quantity that only a small residue remains whereby a finished nickel alloy containing about 0.001% to about 0.05% of alkaline earth metal, about 0.02% to about 0.10% of the group consisting of phosphorus and arsenic, and about 0.01% to about 0.5% rare earth metal is produced which has increased service life when subjected in use to repeated heating and cooling.

5. The method of imparting increased service life to a heat-resistant nickel-chromium alloy which comprises first establishing a melt of a heat-resistant nickel-chromium alloy consisting principally of nickel and chromium, then treating said melt with calcium in such controlled and restricted quantity that only a small residue of about 0.001% to about 0.05% remains in the melt after the treatment, and incorporating in said treated melt cerium in such a controlled and restricted quantity that only a small residue remains whereby a finished alloy is produced which has increased service life when subjected in use to repeated heating and cooling.

6. The method of imparting increased service life to a heat-resistant nickel-chromium alloy which comprises first establishing a melt of a heat-resistant nickel-chromium alloy consisting principally of nickel and chromium, then treating said melt with calcium in such controlled and restricted quantity that only a small residue of about 0.001% to about 0.05% remains in the melt after the treatment, adding a small and controlled amount of arsenic to the melt as to render objectionable constituents innocuous and to leave a residue of about 0.02% to about 0.10%, and incorporating in said treated melt cerium in such a controlled and restricted quantity that only a small residue remains whereby a finished alloy is produced which has increased service life when subjected in use to repeated heating and cooling.

7. A method of imparting increased service life to a heat-resistant nickel-chromium alloy which comprises first preparing a molten bath of nickel-chromium alloy consisting of about 80% of nickel and about 20% of chromium, then treating said molten bath with a small and controlled quantity of calcium as to leave a residue of about 0.001% to about 0.05% in said bath, and incorporating a small and restricted quantity of cerium in said treated bath as to leave a residue of about 0.01% to about 0.5% therein, whereby a finished alloy is produced which has increased service life when subjected in use to repeated heating and cooling.

8. A method of imparting increased service life to a heat-resistant nickel-chromium alloy of nickel and about 20% of chromium, then treating said molten bath with a small and con- which comprises first preparing a molten bath of nickel-chromium alloy consisting of about 80% trolled quantity of calcium as to leave a residue of about 0.001% to about 0.05% in said bath, adding a small and controlled quantity of arsenic to said bath to render objectionable constituents innocuous and to leave a residue of about 0.02% to about 0.10% in said bath, and incorporating a small and restricted quantity of cerium in said treated bath as to leave a residue of about 0.01% to about 0.5% therein, whereby a finished alloy is produced which has increased service life when subjected in use to repeated heating and cooling.

9. As a new article of manufacture, a heat-resistant structure possessing increased service life when subject in use to repeated heating and cooling and constituted of a heat-resistant nickel base alloy comprising rare earth metal in a small and controlled amount within a range of about 0.01% to about 0.5%, at least one member of the group consisting of phosphorus and arsenic in small and controlled amounts within a range of about 0.02% to about 0.10%, alkaline earth metal in a small and controlled quantity and within a range of about 0.001% to about 0.05%, a minor but effective amount of chromium and the balance substantially all nickel.

10. As a new article of manufacture, a heat-

resistant structure subject in use to repeated heating and cooling and constituted of a heat-resistant nickel-chromium alloy consisting of about 80% nickel and about 20% of chromium, at least one member of the group consisting of phosphorus and arsenic in small controlled amounts within a range of about 0.02% to about 0.10%, at least one rare earth metal in a small and controlled amount within a range of about 0.01% to about 0.5%, and at least one alkaline earth metal in a small and controlled quantity and within a range of about 0.001% to about 0.05%.

11. As a new article of manufacture, a heat resistant structure possessing increased service life when subject in use to repeated heating and cooling and constituted of a heat-resistant alloy containing about 20% chromium, at least one rare earth metal in a small and controlled amount within a range of about 0.01% to about 0.5%, at least one alkaline earth metal in a small and controlled quantity and within a range of about 0.001% to about 0.05%, at least one member of the group consisting of phosphorus and arsenic to improve forgeability within the range of about 0.02% to about 0.1%, nickel constituting substantially all of the remainder.

12. As a new article of manufacture, an electric resistance element subject in use to repeated heating and cooling and constituted of a heat-resistant nickel-chromium alloy consisting of about 80% nickel and about 20% chromium, cerium in a small and controlled amount within a range of about 0.01% to about 0.5%, arsenic in a small and controlled amount within a range of about 0.02% to about 0.1%, and calcium in a small and controlled quantity within a range of about 0.001% to about 0.05%.

13. As a new article of manufacture, a heat-resistant structure possessing increased service life when subjected to repeated heating and cooling and constituted of a heat-resistant alloy of chromium and at least one metal from the group consisting of nickel and iron, and containing in addition substantailly only the following materials: at least one member of the group consisting of phosphorus and arsenic in a small and controlled amount within a range of about 0.02% to about 0.1%, at least one rare earth metal in a small and controlled quantity within a range of about 0.01% to about 0.5% and at least one alkaline earth metal in a small and controlled quantity within a range of about 0.001% to about 0.05%.

14. A method of imparting increased service life to a heat resistant chromium alloy which comprises first establishing a melt of the chromium alloy, then treating said molten bath with at least one alkaline earth metal in such controlled and restricted amounts that only a small residue of about 0.001% to about 0.05% remains in the melt after the treatment, and then incorporating such a small and restricted quantity of at least one rare earth metal in said treated bath as to leave a residue of about 0.01% to about 0.5% therein, whereby a finished alloy is produced which has increased service life when subject in use to repeated heating and cooling.

15. A heat resistant alloy comprising about 20% chromium, about 0.01% to about 0.5% rare earth metal, about 0.001% to about 0.05% alkaline earth metal, about 0.02% to about 0.1% of at least one member of the group consisting of phosphorus and arsenic, and the balance substantially all nickel.

16. A heat resistant nickel-base alloy consisting essentially of nickel and chromium with about 0.01% to about 0.5% of at least one rare earth metal, about 0.001% to about 0.05% of at least one alkaline earth metal and about 0.02% to about 0.1% of at least one member of the group consisting of phosphorus and arsenic, said alloy being characterized by improved forgeability.

17. A heat resistant nickel-base alloy comprising about 10% to 30% chromium, about 0.01% to about 0.5% rare earth metal, about 0.001% to about 0.5% alkaline earth metal, about 0.02% to about 0.1% of at least one member of the group consisting of phosphorus and arsenic, said alloy being characterized by improved forgeability over a similar alloy free from phosphorus or arsenic.

18. A heat resistant nickel-base alloy comprising about 10% to 30% chromium, about 0.01% to about 0.5% rare earth metal, about 0.001% to about 0.5% alkaline earth metal, about 0.02% to about 0.1% of at least one member of the group consisting of phosphorus and arsenic, and the balance substantially all nickel.

19. A heat resistant nickel-base alloy comprising about 10% to 30% chromium, about 0.01% to about 0.5% rare earth metal, about 0.001% to about 0.5% alkaline earth metal, about 0.02% to about 0.1% of at least one member of the group consisting of phosphorus and arsenic, at least a small but effective amount of iron, and the balance substantially all nickel.

20. A heat resistant alloy comprising about 20% chromium, about 0.01% to about 0.5% rare earth metal, about 0.001% to about 0.5% alkaline earth metal, about 0.02% to about 0.1% of at least one member of the group consisting of phosphorus and arsenic, and the balance substantially all nickel.

21. A heat resistant nickel-base alloy containing an effective amount of chromium, about 0.01% to about 0.5% of rare earth metal, about 0.001% to about 0.5% of alkaline earth metal, about 0.02% to about 0.1% of at least one member of the group consisting of phosphorus and arsenic and the balance substantially all nickel.

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