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HEAT RESISTANT NICKEL ALLOYS

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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 thorium and one or more alkaline earth metals to the molten alloy prior to casting. The quantity that is added to a heat resistant alloy is such that only a small residue remains in the finished alloy as explained more fully hereinafter. It is preferred to control the residue of thorium remaining in the alloy to an amount of from about 0.01% to about 0.5% in the presence of residual amounts of an alkaline earth metal or metals, such as calcium.

In carrying the invention into practice, the molten alloy is preferably subjected to a preliminary treatment before the addition of the thorium for deoxidizing, desulphurizing or other purposes, or to improve the forgeability. This treatment may be effected with highly reactive elements, such as calcium for deoxidizing purposes and for improvement in the forgeability, and elements such as phosphorus, arsenic and/or antimony for rendering objectionable constituents innocuous. The preliminary treatment may also include the use of supplementary scavangers 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 thorium is accompanied by one or more of the alkaline earth metals in elementary, alloyed or combined form and may also be accompanied by one or more of the commercial solid elements of group V of the periodic table, particularly phosphorus, arsenic and/or antimony. If thorium alone is used, and especially when a substantial amount of impurities (in particular, oxides) is present, there is a tendency for the

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compounds formed by interaction between the thorium 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 thorium so that not only may the requisite amount of thorium be substantially reduced with a corresponding saving in cost, but the risk of any appreciable inclusions of undesired thorium compounds in the final alloy is practically eliminated and improved service life is also obtained. In the aforesaid patent it was disclosed that the molten metal was treated with an alkaline earth metal such as calcium in amounts within the range of about 0.005% to about 0.5%. It is found to be particularly advantageous to add calcium in such a quantity and in such a sequence with the thorium that there is a residue of thorium and of calcium in the finished alloy. The preferred residue of thorium in the alloy is from about 0.05% to about 0.20%.

In addition to thorium and alkaline earth metal, one or more rare earth metals, for example cerium, may be present in amounts of about 0.01% to about 0.45%. Preferably, the total of thorium and rare earth metal does not exceed 0.5%. When the expression "rare earth metal" is used herein, it is intended to include not only the elements usually called rare earth metals, but also scandium, yttrium and hafnium.

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

It has been found that when an alkaline earth metal is present, the forgeability is improved when there is a small residue of one or more of the elements of group V, particularly phosphorus, arsenic, and/or antimony in the alloy, and that in the presence of these elements larger amounts of alkaline earth metal may be incorporated in the alloy without deleterious effect upon the working properties. Thus, in the case of the well known 80% nickel–20% chromium heat resistant alloy, improved life is obtained by adding enough thorium and alkaline earth metal to leave about 0.01% to about 0.5% or more thorium and about 0.001% to about 0.05% or more alkaline earth metal. When arsenic is also present in the alloy in amounts of about 0.02% to about 0.10%, the forgeability is improved.

The amount of thorium to be added to the melt to produce the desired result or to leave the 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 thorium during melting is exceptionally small, so that the amount of residual thorium is distinctly greater than is expected, the resultant alloy may still be easily worked owing to the small extent to which the workability is effected. In cases when unusually high losses are expected or when high forgeability is not required, as much as 5% of thorium may be added to the melt to obtain higher percentages in the finished alloy. Owing to the highly reactive nature of thorium, 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. 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 thorium and alkaline 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 melta, 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 thorium is added in the presence of alkaline earth metal such as calcium, 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.

In producing the alloys contemplated by the present invention, the ingredients may be added in any suitable form. Thus, they may be added in an elementary, alloyed or combined form.

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 typical heat resistant nickel-chromium alloys for the production of electrical resistance heating elements.

Example 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 6 pounds of calcium silicide containing 25% to 35% calcium are added and the melt is held for from two to ten minutes to allow reactions to proceed. Next about 1 pound of thorium 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 thorium 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. An alloy made in this manner will contain about

	Per cent
Nickel	80
Chromium	19.83
Thorium	0.1
Calcium	0.07

Example 2

The procedure is the same as in Example 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 thorium and the metal is then cast into ingots. An alloy made in this manner will contain about

	Per cent
Nickel	80
Chromium	19.76
Thorium	0.1
Calcium	0.1
Arsenic	0.04

Example 3

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 1.

An alloy made in this manner will contain about

	Per cent
Nickel	80
Chromium	19.7
Carbon	0.075
Thorium	0.1
Calcium	0.07

Example 4

Scrap is melted as in Example 3 and is treated in the furnace with about 6 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 thorium are added in the ladle and the metal is cast into ingots. An alloy made in this manner will contain about

	Per cent
Nickel	80
Chromium	19.63
Carbon	0.075
Thorium	0.15
Calcium	0.1
Arsenic	0.045

Example 5

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 6 pounds of calcium silicide and about 1 pound of thorium are added and the molten metal is poured into the ladle. From about ½ pound to about 1 pound of calcium silicide is added in the ladle followed by from about ½ to about 2 pounds of thorium. The molten metal is allowed to stand in the ladle for from about two to about five minutes and is

then cast into ingots. An alloy made in this manner will contain about

	Per cent
Nickel	80
Chromium	19.75
Thorium	0.1
Calcium	0.15

Example 6

In the production of a thousand pound heat of a nickel-chromium alloy containing about 85% nickel and about 15% chromium, about eight hundred and fifty pounds of nickel are melted and about 0.5% manganese and about 0.2% silicon are added followed by one hundred and fifty pounds of chromium and the whole is melted. To the molten metal is added about one pound of calcium as calcium silicide containing about 25% to about 35% calcium and the melt is held for from about two to about ten minutes to allow reactions to proceed. An addition of about two pounds of thorium is then made and the melt held for about one to about two minutes for reactions to proceed. The metal is then cast into ingots. It is desirable to make the calcium and thorium additions partly in the furnace and partly in the ladle. Thus, in carrying out the above procedure about ½ pound of the calcium, as calcium silicide, is added in the furnace followed by an addition of about ½ pound of the thorium; the remainder of the additions is made in the ladle. An alloy made in accordance with the foregoing procedure will contain about

	Per cent
Nickel	84
Chromium	15.75
Thorium	0.1
Calcium	0.15

Example 7

In the production of an alloy containing about 65% nickel, about 15% chromium and about 20% iron, a molten bath of said alloy is established in the usual manner. The procedure for the calcium and thorium additions is the same as in Example 6 except that about 0.05% of arsenic is also included in the molten metal. About 0.2% calcium and about 0.2% thorium are added to the molten bath in accordance with the procedure set forth in Example 6. The final solidified alloy will contain about

	Per cent
Nickel	64.8
Chromium	15
Iron	20
Thorium	0.1
Calcium	0.07
Arsenic	0.04

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, but 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. Thus, the present invention is particularly applicable to the well known heat resistant alloys available for use at elevated temperatures in excess of about 500° C., for example for use as electric resistance elements. As those skilled in the art know such alloys contain about 10% to about 30% chromium, preferably about 12% to about 20%, and the balance metal of the iron group. Commercial alloys may also contain substantial amounts of manganese, silicon, copper, molybdenum, tungsten, aluminum, and the like in amounts up to about 10% or even more. Heat resistant alloys have been classified in three groups. For instance, Hunter and Jones in an article entitled "Some electrical properties of high-resistance alloys" in the Proceedings of the American Society for Testing Materials, vol. 24, 1924, part II, page 401, stated on page 407 as follows:

"For convenience in classification the alloys are divided into three sub-groups:

1. Nickel-chromium alloys;
2. Nickel-iron-chromium alloys;
3. Iron-chromium alloys."

It is well recognized that the nickel-chromium and nickel-chromium-iron alloys have similar properties and are therefore frequently referred to by those skilled in the art as nickel-chromium alloys. Hunter and Jones stated that binary nickel-chromium alloys containing up to 30% chromium had been made and that the commercial alloys usually contained 15% to 20% chromium. The authors also stated that a well known nickel-chromium-iron alloy contained about 60% nickel, 26% iron and 12% chromium while another common alloy contained less iron and more chromium. The iron-chromium alloys, it was stated were inferior to the nickel-chromium alloys and contained about 22% chromium. It was also pointed out that many of the alloys were worked under the Marsh patent. The Marsh United States Patent No. 811,859 of 1908 disclosed the use of nickel-chromium alloys for electric resistance elements. Marsh's alloys contained over 50% nickel or cobalt or both and less than 50% chromium but preferably contained less than 25% chromium and more than 75% nickel. As examples, the 90/10 and 85/15 nickel-chromium alloys were cited. It was later determined that the best alloy of the series was the 80/20 nickel-chromium alloy. Liddell's Handbook of Non-Ferrous Metallurgy, McGraw-Hill, 1926, vol. 2, page 1315, referred to the nickel-chromium and nickel-chromium-iron alloys and stated that the commercial alloys contain 5 to 20% chromium, 5 to 40% iron and the balance nickel. The Dempster United States Patent No. 901,428 of 1908 had disclosed the use of nickel-chromium-iron-alloys for electric resistance elements. The alloys contained more than 10% and less than 50% iron, for example, 20% iron. A typical alloy was composed of 62% nickel, 20% iron, 12.6% chromium and about 5% manganese. "The Book of Stainless Steels" edited by Thum and published by the American Society for Steel Treating, 1933, first edition, page 426, contains a section on "Electric Resistors" in which typical compositions of some commercial alloys are given. It is pointed out that the alloys may contain manganese, silicon, aluminum, molybdenum, copper, etc., in various amounts up to about 10%. The present invention is applicable to alloys of the aforementioned character. Such alloys include the group containing about 10% to about 30% chromium with about 90% to about 70% nickel constituting the balance. Small amounts of iron and the like, for example, about 0.1% or less and up to a few percent, may appear in the alloys due to commercial production methods and the amounts contained in the materials used to make the alloys. Another common group of alloys to which the present invention is applicable contain about 10% to about 30% chromium, about 5% up to about 50% iron and the balance nickel. The iron

content is preferably not greater than about 25% or 30% and the nickel content is preferably not less than about 50%. While the nickel-containing alloys are preferred for high temperature service, for example as electrical resistors, the nickel-free iron-chromium alloys also find applications. Such alloys contain about 10% to about 30% chromium and the balance iron and often contain in addition about 5% to about 10% aluminum, for example an alloy with about 20% chromium, about 5% aluminum and the balance iron. It has been mentioned that the alloys may contain carbon, magnesium, titanium, zirconium, manganese, silicon, copper, molybdenum, tungsten, aluminum, and the like in small amounts and in some instances, for example aluminum, molybdenum and the like, in amounts up to about 10% or more.

In accordance with the present invention, the well known alloys such as referred to hereinbefore contain one or more alkaline earth metals for example calcium, in a small but effective amount, say from about 0.001% up to about 0.5% and thorium in a small but effective amount, say from about 0.01% up to about 0.5%. Improved forgeability is obtained when the alloys contain, in addition to thorium and alkaline earth metal one or more of the elements phosphorus, arsenic and/or antimony within the range of about 0.02% to about 0.1%. In preparing the alloys contemplated by the present invention, it is highly desirable that alkaline earth metal or metals, say calcium or calcium silicide, be incorporated in the molten metal prior to the addition of thorium. In this manner very few deleterious impurities remain in the solidified ingot and a product is obtained after being subjected to mechanical working operations which is substantially free from deleterious surface defects such as cracks and the like.

The following examples showing approximate percentage figures are illustrative of alloys made in accordance with the present invention.

Table I

Example No.	Nickel	Chromium	Thorium	Calcium
	Per cent	*Per cent*	*Per cent*	*Per cent*
1	80	19.8	0.05	0.05
2	80	19.8	0.05	0.075
3	80	19.8	0.10	0.10
4	80	19.8	0.05	0.15
5	80	19.75	0.10	0.15
6	80	19.65	0.10	0.25
7	80	19.5	0.20	0.25
8	80	19.2	0.50	0.25
9	80	19.05	0.50	0.45

Table II

Example No.	Nickel	Chromium	Thorium	Calcium	Arsenic	Phosphorus	Antimony
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
1	80	19.7	0.05	0.15	0.05		
2	80	19.7	0.05	0.15		0.03	
3	80	19.7	0.05	0.15			0.03
4	80	19.55	0.10	0.25	0.07		

Table III

Example No.	Nickel	Chromium	Iron	Thorium	Calcium
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
1	65	14.8	20	0.10	0.10
2	68	12	19.8	0.10	0.10
3	77	20	2.8	0.10	0.10
4	82	12	6	0.10	0.075
5	36.8	18	45	0.10	0.10
6	15	19.8	65	0.10	0.10

Table IV

Example No.	Nickel	Chromium	Iron	Thorium	Calcium	Arsenic	Phosphorus	Antimony
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
1	65	14.75	20	0.10	0.10	0.05		
2	65	14.65	20	0.10	0.15	0.08		
3	65	15	19.8	0.10	0.10		0.03	
4	65	15	19.8	0.10	0.10			0.03

Heat resistant alloys made in accordance with the present invention and containing small amounts of alkaline earth metal and thorium possess improved service life over those containing alkaline earth metal alone or thorium alone or alkaline earth metal and rare earth metals such as cerium. The following schedule is illustrative of the improved life period, for example, of an alloy consisting essentially of 80% nickel and 20% chromium, under similar experimental conditions.

Additions	Life at 1200° C. (Bash & Harsch)
	Hours
With about 0.1% calcium (alone)	110
With about 0.1% thorium (alone)	100
With about 0.03% calcium and 0.07% cerium	150
With about 0.03% calcium and 0.07% thorium	350

This application is a continuation in part of our copending patent application Serial No. 77,714, filed May 4, 1936, which issued as U. S. Patent No. 2,304,353 on December 8, 1942.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such variations and modifications apparent to those skilled in the art are considered to be within the purview and scope of the appended claims.

We claim:

1. A heat resistant alloy comprising about 20% chromium, about 0.001% to about 0.5% calcium, about 0.01% to about 0.5% thorium, and the balance substantially nickel.

2. A heat resistant alloy comprising about 20% chromium, about 0.001% to about 0.5% calcium, about 0.01% to about 0.5% thorium, about 0.02% to about 0.1% of at least one of the commercial solid elements of group V of the periodic table, and the balance substantially nickel.

3. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.001% to about 0.5% calcium, about 0.01% to 0.5% thorium, and the balance substantially nickel.

4. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.001% to about 0.5% alkaline earth metal, about 0.01% to about 0.5% thorium, and the balance substantially nickel.

5. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.001% to about 0.5% alkaline earth metal, about 0.01% to about 0.5% thorium, about 0.02% to about 0.1% of at least one of the commercial solid elements of group V of the periodic table, and the balance substantially nickel.

6. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.1% to about 50% iron, about 0.001% to about 0.5% alkaline earth metal, about 0.01% to about 0.5% thorium, and the balance substantially nickel.

7. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.1% to about 50% iron, about 0.001% to about 0.5% alkaline earth metal, about 0.01% to about 0.5% thorium, about 0.02% to about 0.1% of at least one of the commercial solid elements of group V of the periodic table, and the balance substantially nickel.

8. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.001% to about 0.5% alkaline earth metal, about 0.01% to about 0.5% thorium, and the balance substantially all metal of the iron group and at least 50% of which is nickel.

9. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.1% to 50% iron, about 0.001% to about 0.5% calcium, about 0.01% to about 0.5% thorium, about 0.02% to about 0.1% arsenic and the balance substantially nickel.

10. An electric resistance element made of a heat resistant alloy comprising about 20% chromium, about 0.001% to about 0.5% calcium, about 0.01% to about 0.5% thorium, and the balance substantially nickel.

11. An electric resistance element made of a heat resistant alloy comprising about 10% to about 30% chromium, about 0.001% to about 0.5% alkaline earth metal, about 0.01% to about 0.5% thorium, and the balance substantially nickel.

12. An electric resistance element made of a heat resistant alloy comprising about 15% chromium, about 25% iron, about 0.001% to about 0.5% calcium, about 0.01% to about 0.5% thorium, and the balance substantially nickel.

13. A heat resistant alloy comprising about 10% to about 30% chromium, about 0.1% to 50% iron, about 0.001% to about 0.5% calcium, about 0.01% to about 0.5% thorium, about 0.02% to about 0.1% of at least one of the commercial solid elements of group V of the periodic table, and the balance substantially nickel.

14. An electric resistance element made of a heat resistant alloy comprising about 15% chromium, about 25% iron, about 0.001% to about 0.5% calcium, about 0.01% to about 0.5% thorium, about 0.02% to about 0.1% of at least one of the commercial solid elements of group V of the periodic table and the balance substantially nickel.

15. 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% nickel and about 20% of chromium, then treating said molten bath with such a small and controlled quantity of at least one of the alkaline earth metals as to leave a residue of about 0.001% to about 0.05% in said bath, and incorporating a small and restricted quantity of thorium 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.

16. A method of imparting increased service life to a heat resistant nickel-chromium alloy which comprises first establishing a molten bath of nickel-chromium alloy, then treating said molten bath with a small and controlled quantity of at least one of the alakaline earth metals so as to leave a residue of about 0.001% to about 0.5% in said bath, and incorporating a small and restricted quantity of thorium 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.

17. 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 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 at least one of the commercial solid elements of group V of the periodic table to the melt as to render objectionable constituents innocuous and to leave a residue of about 0.02% to about 0.1%, and incorporating in said treated melt thorium in such a controlled and restricted quantity that a small residue remains and casting the molten metal whereby a finished alloy is produced which has increased service life when subjected in use to repeated heating and cooling.

18. 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 as to leave a residue of about 0.001% to about 0.5% in the melt after the treatment, and then incorporating such a small and restricted quantity of thorium 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.

19. 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 alloy consisting of about 80% nickel and about 20% chromium, at least one of the commercial solid elements of group V of the periodic table in small and controlled amounts within a range of about 0.02% to about 0.1%, thorium 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%.

20. A heat resistant alloy comprising about 10% to 30% chromium, about 0.001% to 0.5% alkaline earth metal, about 0.01% to 0.5% thorium, about 0.02% to 0.1% of at least one of the commercial solid elements of group V of the periodic table, and the balance substantially all metal of the iron group.

21. A heat resistant alloy comprising about 10% to 30% chromium, about 0.1% to 50% iron, about 0.001% to 0.5% calcium, about 0.01% to 0.5% thorium, and the balance substantially nickel.

22. A heat resistant alloy comprising about

10% to 30% chromium, about 0.1% to 50% iron, about 0.001% to 0.5% calcium, about 0.01% to 0.5% thorium, about 0.02% to 0.1% phosphorus, and the balance substantially nickel.

23. A heat resistant alloy comprising about 10% to 30% chromium, about 0.1% to 50% iron, about 0.001% to 0.5% calcium, about 0.01% to 0.5% thorium, about 0.02% to 0.1% antimony, and the balance substantially nickel.

24. An electric resistance element made of an alloy comprising about 20% chromium, about 0.001% to 0.5% calcium, about 0.01% to 0.5% thorium, about 0.02% to about 0.1% of at least one of the commercial solid elements of group V of the periodic table, and the balance substantially nickel.

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