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ELECTRIC RESISTANCE ELEMENTS AND
THE LIKE

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The present invention relates to heat-resisting alloys and articles made therefrom and to a method of producing such alloys and articles, and more particularly to heat-resisting alloys and articles having an improved combination of prop-
erties.

It is well known to incorporate in heat-resisting alloys, such, for example, as those used for electrical resistance elements, small quantities of one or more elements such as the rare earth metals, particularly cerium, the alkaline earth metals, particularly calcium, thorium, etc., in addition to those of which the alloy is basically composed, for the purpose of improving the high temperature properties and in particular the service life of the alloys and articles made therefrom. As an example, the heat-resisting properties, and in particular the resistance to oxidation, of alloys consisting basically of 80% nickel and 20% chromium are materially improved by the inclusion of small quantities of calcium, cerium, calcium and cerium or calcium and thorium. Many other elements may be used and, for convenience, in view of their capacity for increasing the life of the alloy under high temperature conditions, they are referred to herein as "long-life elements."

I have found that the long-life elements, when incorporated in the alloys to improve their life, may have an adverse effect on other properties of the alloys. In an increasing number of applications of heat-resisting alloys, resistance to creep at high temperatures is an essential requirement, and long-life additions to the alloys may seriously impair this resistance. Furthermore, the addition of the long-life elements to the molten alloys may be a matter of difficulty, as many of the long-life elements are extremely reactive. Again, the presence of long-life elements in the alloys may render them difficult to fabricate, and in some cases the alloys cannot be hot worked.

I have discovered that some of the elements will produce the desired effect of an increase in the service life of the basic alloys if they are applied in the form of films to the surfaces of the alloys.

It is an object of the present invention to provide heat-resisting alloys and articles having an improved combination of properties.

It is another object of the present invention to provide heat-resisting alloys and articles made therefrom having high service life combined with improved resistance to creep.

It is a further object of the present invention to provide a novel method of improving the life

of heat-resisting alloys and articles made therefrom.

It is also an object of the present invention to provide a method of improving the life of heat-resisting alloys and articles made therefrom without seriously impairing the creep resistance of the alloy or article.

Other objects and advantages of the invention will become apparent to those skilled in the art from the following description.

The elements which I have found may be applied as films are thorium, calcium, zirconium and the rare earth elements. According to this invention the alloys or articles that are made therefrom and by their nature are necessarily subjected to high temperatures in service are provided on their surfaces with films of one or more of these long-life elements in the elementary form or in the form of oxides or hydroxides or in the form of salts that will decompose to oxides at high temperatures.

The service life of the alloys or articles provided with such surface films is not always so great as when the long-life element is included in the alloy, but compensating advantages are often obtained. For example, the addition of the elements to the molten alloys may be a matter of difficulty, as many of the long-life elements are extremely reactive. Again, the presence of long-life elements in the alloys may render them difficult to fabricate, and in some cases the alloys cannot be hot-worked. These difficulties are avoided altogether by means of the invention. In an increasing number of applications of heat-resisting alloys, resistance to creep at high temperatures is an essential requirement, and long-life additions to the alloys may seriously impair this resistance. Surface application of the long-life elements has the great advantage of allowing of the production of articles and machine parts for high temperature operations having high resistance to oxidation and without any reduction in their normal resistance to creep.

It appears that the long-life elements produce the effect indicated by their influence on the formation of scale on the surface of the alloy. Whether this is so or not, I find that what is necessary is to produce a fine dispersion of the long-life element or elements on the surface. This need not be continuous, although the particles that compose it should be uniformly distributed, and it must not be a thick coating such as would either completely exclude oxygen from the surface or would tend to flake off under rapid

changes of temperature. With such a thick coating the desired effect is not produced.

Of the long-life elements defined above, the best results are obtained with thorium and the rare earth elements. The latter may advantageously be used in the form of a so-called "mischmetall" containing cerium and other elements, for example, lanthanum.

In practice, the film may be formed in a number of different ways. In general, it is best to form it after the desired article (e. g., an electrical resistance wire, tape or ribbon, or electrical resistance heating element made therefrom) has been fabricated from the alloy. When this is done, the preferred method is to dip the article in a solution of a salt of a long-life element, or to deposit an oxide or hydroxide of the element anodically. In the former case, the finished article should first be heated to give it a light oxide scale as this causes more satisfactory wetting of the surface and also makes the coating more adherent. The oxidized article may be dipped into the solution, e. g., into a solution of any appropriate concentration, e. g. about 10%, while hot and withdrawn while still hot enough to evaporate off the solvent, or it may be dipped cold and then heated to remove the solvent and decompose the salt of the long-life element to oxide. Solutions of the nitrates of the long-life elements may be most conveniently used in most cases and slightly acid solutions containing about 10% by weight of the salt give a film of the desired thickness.

When anodic deposition is used, the article to be treated should have a clean metallic surface produced by bright annealing, pickling or sand blasting, and should be degreased before placing in the depositing bath. The bath may contain any soluble salt of the long-life elements of any concentration from about 10% to saturation, and this should be made progressively more alkaline until precipitation commences. Acid should then be added until the precipitate disappears and then a further slight excess. Again, the conditions may be varied over a wide range, but successful deposition may be obtained by using a 10% solution, making the article to be plated the anode and increasing the applied voltage from about 2 volts until deposition is indicated by the evolution of gas round the article being treated. If the voltage is increased further the deposition becomes more rapid, but the gas evolution tends to strip off the film. The gelatinous film deposited should have a thickness of a few thousandths of an inch. After coating the article is heated to dehydrate the film and to convert it to oxide.

Sometimes I may apply the film to the alloy or partly-fabricated article and thereafter fabricate, or complete the fabrication of, the article, and then I may use other methods of forming the film. For instance, the surface of the alloy or partly-fabricated article may be provided with an integral film by cementation, brought about by heating the alloy in a powdered long-life element in an inert atmosphere, or in a mixture of an oxide or other compound of the element with a reducing agent. Again, the alloy or partly-fabricated article may be passed through a bath of the molten element or this may be electrolytically deposited from a bath of a molten salt of it. Of course these methods may also be used to form films on finished articles, but for this purpose the two methods first described are preferred because of their simplicity.

The following results have been obtained in tests on an 80/20 nickel-chromium alloy having a life of 33 hours at 1200° C.

Treatment	Life at 1200° C.
	Hours
Alloy dipped in solution of "mischmetall" nitrate.....	50
Alloy coated anodically with "mischmetall" oxide.....	65
Alloy dipped in solution of thorium nitrate.....	54
Alloy coated anodically with thorium (thorium dioxide).....	65
Alloy dipped in calcium-thorium solution.....	60

The invention is particularly applicable to the well-known nickel-chromium and nickel-chromium-iron alloys containing from 10 to 30% chromium, 20 to 90% nickel and 0 to 50% iron and to articles made therefrom which are subjected in use to elevated temperatures below their melting point. It may also be applied, however, to all the alloys (including austenitic steels), and to articles made therefrom, that are commonly called heat-resisting, such as the iron-nickel-chromium, nickel-cobalt-chromium, cobalt-iron-chromium, iron-chromium, iron-chromium-aluminium, and complex alloys based on systems such as these alloys but containing in addition one or more of the elements molybdenum, tungsten, titanium, columbium, zirconium, aluminium and the like. These alloys include those containing about 10 to 35% chromium, and may optionally contain from a small amount, say about 0.01%, to about 20% of one or more metals from the group consisting of molybdenum, tungsten, titanium, columbium, zirconium, aluminium, silicon and manganese, and the balance substantially all metal of the iron group, i. e. metal of the group consisting of nickel, iron and cobalt. As will be apparent to those skilled in the art, these alloys may also contain small amounts of incidental elements and impurities, e. g. sulphur, phosphorus, etc. While the total of iron group metals will usually exceed about 50%, the invention contemplates not only those alloys in which one of the iron group metals exceeds about 50% but also those alloys in which no one particular iron group metal exceeds about 50% although the sum of all the iron group metals will exceed about 50%.

Although the present invention has been described in conjunction with preferred embodiments, it is 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 are considered to be within the purview and scope of the appended claims.

I claim:

1. A method of improving the high temperature service life of chromium-containing heat-resisting alloys substantially free from long-life elements which comprises providing such alloys with an adhering surface film of at least one member selected from the group consisting of thorium, calcium, zirconium and the rare earth elements, oxides and hydroxides thereof and salts thereof that will decompose to oxides at high temperatures.

2. An article subjected in use to elevated temperatures made of a chromium-containing heat-resisting alloy and having a surface film of at least one member selected from the group consisting of thorium, calcium, zirconium and the rare earth elements, oxides and hydroxides thereof

and salts thereof that will decompose to oxides at high temperatures.

3. Electrical resistance wires, tapes, ribbons and the like made of a chromium-containing heat-resisting alloy and having a surface film of at least one member selected from the group consisting of thorium, calcium, zirconium and the rare earth elements, oxides and hydroxides thereof and salts thereof that will decompose to oxides at high temperatures.

4. An alloy composed essentially of chromium, nickel and iron and containing from 10 to 30% chromium, 20 to 90% nickel and 0 to 50% iron, said alloy being provided on its surface with a film comprising at least one member selected from the group consisting of thorium, calcium, zirconium and the rare earth elements, oxides and hydroxides thereof and salts thereof that will decompose to oxides at high temperatures.

5. A heat-resisting chromium-containing alloy provided on its surface with a film comprising a member selected from the group consisting of "mischmetall" or compounds thereof.

6. A heat-resisting chromium-containing alloy provided on its surface with a film comprising a member selected from the group consisting of thorium and compounds thereof.

7. A method of increasing the service life of an article that is made from a heat-resisting chromium-containing alloy and that by its nature is necessarily subjected to high temperatures in service, comprising forming a film on the surface of said article by dipping said article in a solution of at least one member of the group consisting of the salts of thorium, calcium, zirconium and the rare earth metals.

8. A method of increasing the service life of an article that is made from a heat-resisting chromium-containing alloy and that by its nature is necessarily subjected to high temperatures in service, comprising forming a film on the surface of said article by anodic deposition thereon of at least one member of the group consisting of the oxides and hydroxides of thorium, calcium, zirconium and the rare earth metals.

9. A method of increasing the service life of an article that is made from a heat-resisting chromium-containing alloy and that by its nature is necessarily subjected to high temperatures in service, comprising applying to the alloy a film of at least one member selected from the group consisting of thorium, calcium, zirconium and the rare earth elements, oxides and hydroxides thereof and salts thereof that will decompose to oxides at high temperatures, and thereafter fabricating the article from said alloy.

10. A method of increasing the service life of an article that is made from a heat-resisting chromium-containing alloy and that by its nature is necessarily subjected to high temperatures in service, comprising partly fabricating the article from said alloy, applying to the partly-fabricated alloy a film of at least one member selected from the group consisting of thorium, calcium, zirconium and the rare earth elements, oxides and hydroxides thereof and salts thereof that will decompose to oxides at high temperatures, and thereafter completing the fabrication of said article.

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