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NICKEL-CHROMIUM ALLOYS CONTAINING RARE EARTH METALS AND BORON

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The present invention relates to alloys of the nickel-chromium type.

The general object of the invention is to provide alloys of the type referred to which are particularly adapted for use as electric resistance materials at elevated temperatures.

Resistance materials of the kind specified may be divided into three principal classes:

(1) Alloys with a very low content of iron, iron being present merely as an impurity, and a chromium content of about 20 percent, the remainder being substantially all nickel.

(2) Alloys with an iron content of about 20 percent and a chromium content of about 15 percent, the balance being substantially all nickel.

(3) Alloys with an iron content of about 45 percent and a chromium content of about 20 percent, the remainder being substantially all nickel.

The invention to be described hereinafter is applicable in respect of any one of these three classes of alloys.

A great number of patents of invention have already been granted on improvements in resistance materials of the nickel-chromium type. The object of these prior inventions has been, by the addition of various elements to improve the useful life of the alloy as measured according to the standard indicated by The American Society for Testing Materials (A. S. T. M.) in the publication "Accelerated Life Test for Metallic Materials," B. 76–39. The prior disclosures are based in part on an addition of zirconium and on combinations of zirconium and other elements such as calcium, aluminium, etc., and in part on an addition of rare-earth elements which may also be combined with other elements. Thus, the British patent specification No. 451,601 only discloses an addition of rare-earth metals. The British patent specification No. 488,926 discloses an addition of rare-earth metals in combination with calcium, and the U. S. patent specification No. 2,687,956 discloses additions of rare-earth metals in combination with calcium and aluminium.

It has been found in attempts made by us to improve resistance alloys of the nickel-chromium type by the addition of rare-earth metals, that such addition involves the formation of a more dense and adhesive oxide. This improvement of the oxide causes a substantially extended life as measured according to the A. S. T. M. testing standard above referred to. It has been stated, however, that, at elevated temperature, alloys of the nickel-chromium type containing additions of rare-earth elements display an increased trend towards oxidation along the grain boundaries than do alloys without any addition of this kind. This phenomenon is particularly pronounced in respect of the alloys of the class having a low iron content, but it also exists in alloys of higher percentages of iron. It should be noted, however, that this grain boundary oxidation will set in to any substantial extent only at temperatures which are higher than those usually employed in life testing according to the A. S. T. M.

standard. Thus the non-ferrous nickel-chromium alloys are tested at 1175° C., whereas according to our testing practice, the marked trend towards grain boundary oxidation has been observed only from temperatures in excess of 1200° C.

This grain boundary oxidation will decrease the utility of the material as a resistance alloy, due in part to the fact that the oxidation will change the electric resistance value of the alloy, and in part to the fact that the grain boundary oxidation causes the body of the material to grow and thus to change its dimensions. Therefore, if it were possible to reduce the tendency towards grain boundary oxidation, this would enable the quality of the material to be materially improved, particularly owing to the fact that the maximum operating temperature could be increased.

Our experiments have led to the unexpected result that an addition of boron is very favorable and causes a great reduction of the tendency towards grain boundary oxidation. Since the boron added will in part volatilize and in part react with other ingredients of the molten bath, the quantity of boron added will have to be substantially larger than that to be found afterwards in the alloy. It has been found that even if, after boron having been added, only traces of this element are to be found in the alloy produced, nevertheless it has resulted in a pronounced improvement of the resistance of the alloy to grain boundary oxidation. The content of boron present in the alloy produced must not be too high since this may reduce the useful life of the alloy. Therefore, it is considered as preferable with a final percentage of boron not exceeding about 0.02.

The quantity of rare-earth metals added to the alloy may be in the form of so-called misch metal containing approximately 50 to 55% cerium, 22 to 25% lanthanum, 15 to 17% neodymium and 8 to 10% of other rare-earth metals. It is understood, however, that other alloys of rare-earth metals, or such metals uncombined, may also be used, as well as oxides of such metals in combination with a reducing agent adapted to transform the oxides into a free metallic state.

As a further alloying element we use silicon in percentages of 0.2 to 2%.

It is practical in the production of resistance alloys of the nickel-chromium type to add metals adapted to cause deoxidation and outgassing of the alloy, such as manganese, aluminium, zirconium, magnesium and calcium, as well as carbon stabilizing metals such as vanadium, titanium, columbium and tantalum. Further there will usually be a certain amount of cobalt present in the nickel as an impurity. The expression "balance nickel" as used hereinafter is to be interpreted as including the presence of the above-mentioned metals separately or in any combination and in percentages of the order of fractions of 1%.

The following examples of compositions alloyed in accordance with the present invention may be mentioned:

(1) 15 to 30% chromium, 0.2 to 2% silicon, 0.01 to 0.5% rare-earth metals, traces to 0.02% boron, and the balance nickel.

(2) 10 to 25% chromium, 15 to 30% iron, 0.2 to 2% silicon, 0.01 to 0.5% rare-earth metals, traces to 0.02% boron, and the balance nickel.

(3) 10 to 25% chromium, 40 to 60% iron, 0.2 to 2% silicon, 0.01 to 0.5% rare-earth metals, traces to 0.02% boron, and the balance nickel.

In order further to elucidate the signification of the addition of boron, a brief report will be given of the results obtained from the tests carried out by us. The material to be tested was rolled into strips 0.3 mm. in thickness and 10 mm. in width. From these strips samples 35 mm. in length were cut and were heated in an electric

furnace to a temperature of 1210° C. The samples were operated cyclically for 2 hours at this temperature and were allowed to cool for 1½ hours. However, every third cycle was chosen to last longer, the samples being then maintained at the high temperature for 15½ hours and were allowed to cool for 1½ hours. The total period of time during which the samples were maintained at a high temperature was 425 hours. Used as a measure of the grain boundary oxidation may be the elongation exhibited by the samples after the above treatment.

The following results may be specified:

Alloy I.—19.5% chromium, 1.5% silicon, 0.07% cerium, balance nickel. Elongation after testing completed: 10.3%.

Alloy II.—19.5% chromium, 1.5% silicon, 0.07% cerium, 0.002% boron, balance nickel. Elongation after testing completed: 2%.

In the production of both alloys as just described aluminium was utilized as a deoxidizer.

What is claimed is:

1. A nickel-chromium alloy containing 10 to 30% chromium, 0 to 60% iron, 0.2 to 2% silicon and 0.01 to 0.5% rare-earth metals, and further characterized in that it contains, in its finally produced condition, traces of boron amounting to a maximum content of 0.02%, and the balance nickel.

2. A nickel-chromium alloy containing 15 to 30% chromium, 0.2 to 2% silicon and 0.01 to 0.5% rare-earth metals, and further characterized by containing, in its finally produced condition, traces of boron amounting to a maximum content of 0.02%, and the balance nickel.

3. A nickel-chromium alloy containing 10 to 25% chromium, 15 to 30% iron, 0.2 to 2% silicon and 0.01 to 0.5% rare-earth metals, and further characterized by containing, in its finally produced condition, traces of boron amounting to a maximum content of 0.02%, and the balance nickel.

4. A nickel-chromium alloy containing 10 to 25% chromium, 40 to 60% iron, 0.2 to 2% silicon and 0.01 to 0.5% rare-earth metals, and further characterized by containing, in its finally produced condition, traces of boron amounting to a maximum content of 0.02%, and the balance nickel.

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