June 18, 1935. M. A. HUNTER 2,005,423

ALLOY

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Fig. 1.

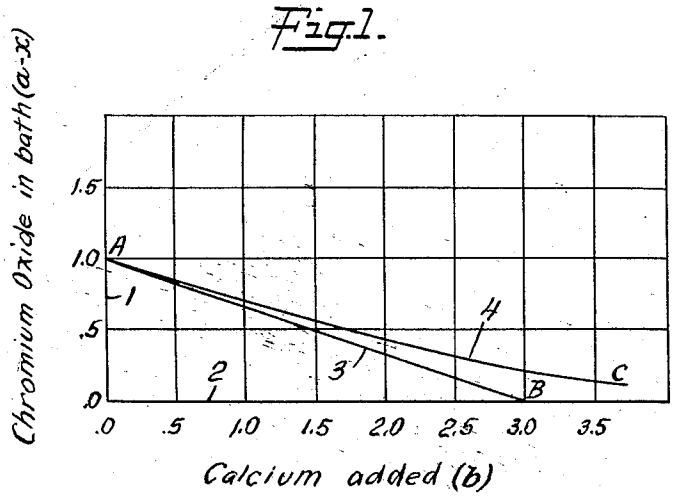
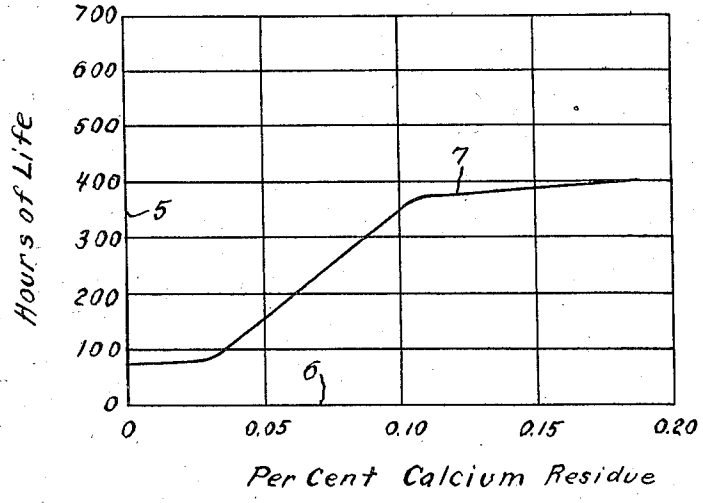


Fig. 2.



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ALLOY

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3 Claims. (Cl. 75—1)

This invention relates to nickel alloys and more particularly to nickel-chromium alloys and nickel-chromium-iron alloys used in electrical work.

Such alloys are employed for the manufacture of wire used as resistors. I have found that the life of such wire, when submitted to high temperatures, is dependent, to a large extent, on the crystal structure of the wire. I have found that the hours of life of nickel-chromium and nickel-chromium-iron alloys may be materially increased when certain deoxidizers are added to the melt in amounts of an entirely different character than the amounts heretofore employed. While such deoxidizers have been added to alloys of this character in the past, the results obtained are not comparable with the results which I have obtained. This is probably due to the fact that metallurgists have ordinarily considered these additions solely from the standpoint of increased malleability of the material and have added such other metals in proportions calculated to produce increased malleability. Thus, in the prior patent to Pilling No. 1,824,966 granted September 29, 1931, the addition of calcium and other metals of the alkaline earth-metal group to a nickel alloy is disclosed but the invention is directed solely to improving the ductility, malleability and working properties of such alloys.

In preparing such alloys, there are always certain impurities present in the metals from which the alloy is formed. They also acquire various impurities during the melting process, particularly oxides of one or more of the metals used in the preparation of the alloy. They possibly also acquire other impurities during the reduction of the metal to the finished form of wire or strip. In the preparation of alloys containing chromium, oxides are introduced into the alloy with the chromium or ferro-chromium used in the preparation of the alloys. I have found that the presence of oxides or sulphides contributes more to the breakdown of the wire than the presence of any other impurities. This is probably due to the fact that these oxides and sulphides collect along the grain boundaries of the crystals formed by the freezing of the molten metal. When such wire is heated for prolonged periods, these segregations or collections of impurities between the grains of the crystals are the points of attack. I have found that this condition can be overcome and the life of the wire materially increased by adding a deoxidizer to the bath in quantities exceeding the stoichiometric proportions necessary to reduce the oxides present whereby a residual quantity of deoxidizer will be present in the final product. In carrying out my invention, I employ known deoxidizers, such as metals of the alkali group, metals of the alkaline earth-metal group or aluminum, silicon or magnesium, but I employ these metals in definite proportions for the purpose of achieving the desired result. The deoxidizer must be added in an amount that will not only be sufficient to reduce substantially all the oxides present in the melt, but that will provide an excess of the deoxidizer which will remain in the alloy. It is impossible to remove all of the oxides from the bath because an equilibrium mixture between the oxides and the deoxidizer is eventually obtained. However, the oxides can be reduced to a point where the amount present is soluble in the metals of the alloy in a solid state, and the formation of grain boundary segregations thus prevented. My invention contemplates the use of the deoxidizer in excess of the quantity required to prevent the formation of grain boundary segregation, whereby some of the deoxidizer remains in the metal. The amount of deoxidizing agent to be added may be determined by analyzing the constituents of the alloy and ascertaining the percentage of oxides and sulphides present. The method of oxygen removal is in all cases identical. For example, calcium will reduce a metal oxide present in the melt according to the following equation:

$$MO+Ca=CaO+M$$

The effectiveness of the deoxidizer is directly related to the heat of formation of the oxide formed. Thus, the heat liberated in the formation of calcium oxide is greater than that liberated in the formation of an equivalent quantity of oxide of silica. The addition of calcium will therefore reduce the oxygen content of the bath to a lower concentration than will the addition of silicon or less effective deoxidizer. It is impossible, however, to remove all of the oxide from the bath but the quantity can be reduced to a point where the amount present is not sufficient to collect along the grain boundaries of the crystals and thus materially reduce the life of the wire when subjected to high temperatures.

By the ordinary assumption that the amount of deoxidizer which must be added is the theoretical amount necessary to react with the oxides present, a graphic illustration, such as is shown in Fig. 1 of the drawing, would produce a straight line. Thus, in the reduction of chromium oxide the reaction proceeds according to the following equation:

$$Cr_2O_3+3Ca=2Cr+3CaO$$

Plotting the concentration of chromium oxide and calcium present wherein the chromium oxide in the bath is designated in percentage on the left hand axis, indicated at 1, and plotted against the calcium added, indicated at 2, the additions of calcium would be represented by the straight line 3. However, the oxides in the bath can never be completely eliminated and the quantity of deoxidizer to be added to substantially eliminate the oxides should be calculated in the following

manner: If a represents the original concentration in molecules of chromium oxide or other oxides, b the original concentration in molecules of calcium added to the bath, and x the reduction in concentration of chromium oxide or other oxides when equilibrium is reached, the equilibrium constant of the reaction is represented by the following equation:

$$K_e=\frac{(Cr)^2(CaO)^3}{(Cr_2O_3)(Ca)^3}$$

where K_e is the equilibrium constant at a given temperature and the bracketed symbols represent the concentration of the respective constituents. The chromium, nickel or iron in the bath may be assumed to be constant since the small amount of chromium, nickel or iron produced by reduction of the oxides will have little effect on the concentration. The equation may then be written:

$$K_e=\frac{(3x)^3}{(a-x)(b-3x)^3}$$

which may be transformed into:

$$b=3x+\frac{xK}{(a-x)^{1/3}}$$

This equation may, in turn, be transformed to:

$$\frac{db}{dx}=3+\frac{(a-2/3x)}{(a-x)^{4/3}}K$$

The foregoing equation should be used to plot the concentration of chromium oxide or other oxides and the amount of calcium or other deoxidizer to be added to the bath. The straight line **3** of Fig. 1 represents the equation:

$$\frac{db}{dx}=3$$

and does not take into consideration the second factor on the right of the preceding equation, namely:

$$\frac{(a-2/3x)}{(a-x)^{4/3}}K$$

When this factor is taken into consideration, a curved line **4** is obtained. The chromium oxide content can not be actually reduced to zero but it approaches this point with increasing contents of calcium in the bath. To reduce the oxides to the lowest possible point, it is therefore necessary that the bath contain free calcium or other deoxidizer necessary to reduce any chromium, nickel and iron oxides present in an amount in excess of the stoichiometric proportions. The greater the concentration of calcium, the lower will be the concentration of chromium oxide in the resulting alloy.

In the preparation of the alloy, the calcium or other deoxidizer is, therefore, added in quantities greater than that represented by the equation:

$$\frac{db}{dx}=3$$

The amount of deoxidizer added should be such that the residual deoxidizer left in the bath is not sufficient to impair the workability or other desirable quantities of the final product. Both chromium oxide and calcium are soluble in the metal bath, but their solubility decreases when the metal freezes. If the concentration of either exceeds the solid solubility, the excess will be precipitated out of the alloy and exist as a separate phase. This precipitation usually takes place on the grain boundaries through the formation of eutectics composed of the metal oxides with some of the metal of the bath. As this result is undesirable, the quantity of deoxidizing material added to the bath must be controlled to avoid this result.

In Fig. 2 of the drawing I have plotted the hours of life in an accelerated test generally used in determining the relative efficiency of wires adapted to be used for electrical heating against the residual calcium content. The alloy in all of the tests was an alloy composed of 80% nickel and 20% chromium. The hours of life are plotted on the left hand axis indciated at **5** against the residual calcium content indicated in percentage at **6** producing the curve **7**. The test used was the "Tentative accelerated life test for metallic materials for electrical heating" of the "American Society for Testing Materials" described in volume 29 of the "Proceedings of the Thirty-second Annual Meeting of the American Society for Testing Materials" beginning on page 613. It will be noted that additions such that less than .03% of calcium remain in the alloy have very little effect on the life of the wire and that with such additions the nickel-chromium alloy lasted less than 100 hours. Between .03 and .1 residual calcium has a marked effect on the life of the wire and the hours of life are increased from less than 100 hours to more than 350 hours. Further additions result in slightly longer life with the result that the life of the wire can be increased to about 400 hours.

I have also been able to increase the hours of life of similar alloys by additions of other deoxidizers within the limits set forth above. As stated above, various metals of the alkali group, such as sodium and lithium may be employed. In addition to calcium, other metals of the alkaline earth group, such as barium and strontium may be employed and I use other metals, such as magnesium, aluminum, silicon, manganese or beryllium. Similar tests conducted with magnesium have resulted in the production of wire with a life of 400 hours when tested in the manner described above.

The absence of oxides on the grain boundaries of the alloy can also be determined by etching. If the oxides are present and form grain boundary segregations, a difference in potential exists between the material on the grain boundary and that in the body of the crystal. This difference of electrical potential brings about a solution of the material on the boundary and the outline of the respective crystals can clearly be seen by the use of a magnifying glass by using suitable magnification. If no precipitation on the grain boundary has occurred, the material etches with great difficulty or not at all. This test is employed by placing the alloy in a solution of Marble's etch consisting of hydrochloric acid, water and copper sulphate in proper proportions. The wire is permitted to remain in the solution for determined periods of time and then examined under the magnifying glass to determine the effect of the solution on the wire. An alloy of 80% nickel and 20% chromium containing .09% residual calcium after remaining in the solution for 26 seconds, shows no segregations at the grain boundaries when examined under the microscope.

As stated above, the oxides of the metals, chromium, nickel and iron, are soluble to a limited extent in the alloys in the solid phase and the presence of minute quantities of these oxides does not affect the crystal structure because they are dissolved in the alloy and not present alone

at the grain boundaries of the crystals. Likewise, a limited amount of the deoxidizing metal, such as calcium or magnesium, does not affect the substantially uniform crystal structure because it also is dissolved in the metal of the alloy. The oxide of the deoxidizing metal, such as calcium oxide or magnesium oxide, which is formed in the reduction of the oxides of the metals of the alloy, rises to the top of the bath and is removed with the slag.

In the specification the terms "alloy of nickel and chromium", "alloy comprising nickel and chromium" and "nickel-chromium alloys" are intended to cover not only alloys, the essential constituents of which are nickel and chromium, but also alloys containing iron in substantial proportions.

I claim:

1. An electric resistance element consisting essentially of nickel substantially 80 percent, chromium substantially 20 percent and from .03 to .2 percent calcium.

2. An electric resistance element consisting essentially of nickel substantially 80 percent, chromium substantially 20 percent and substantially .09 percent calcium.

3. A wire for use in electric heating elements formed of an alloy of substantially 80 percent of nickel, substantially 20 percent of chromium and from .03 to .2 percent calcium.

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