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METHOD OF MAKING A NICKEL-CHROMIUM DIFFUSION ALLOY

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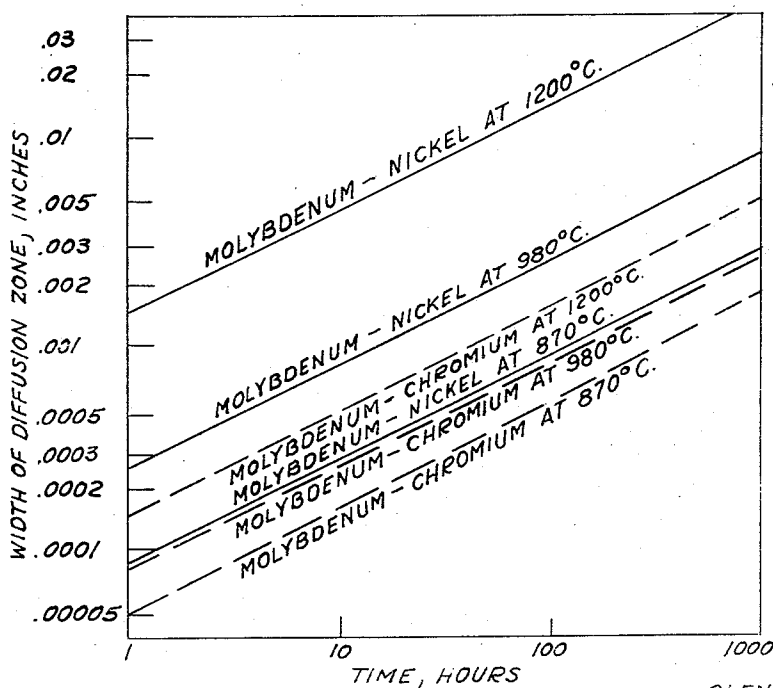
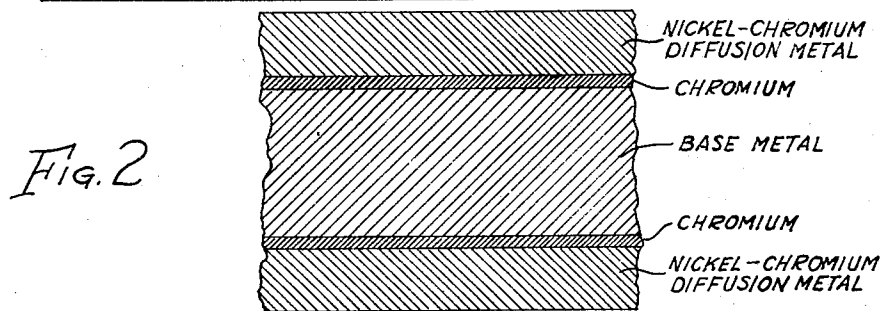
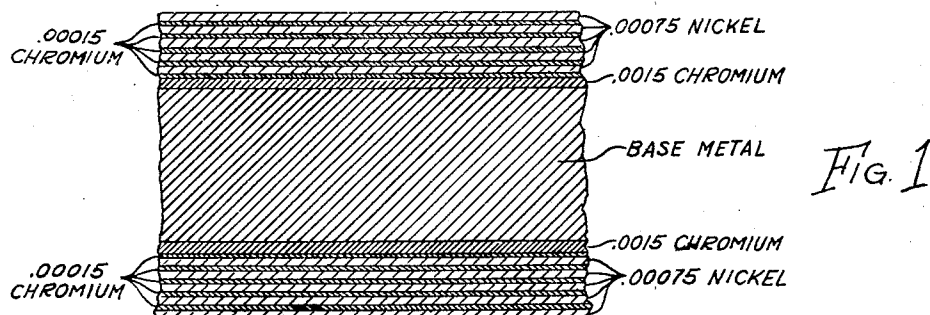


Fig. 3

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METHOD OF MAKING A NICKEL-CHROMIUM DIFFUSION ALLOY

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The present invention relates to the electrodeposition of metal coatings on base metals and more particularly to nickel and chromium electrodeposits for use at elevated temperatures.

Many base metals and alloys having high strengths at elevated temperatures do not have satisfactory oxidation resistance. For example, molybdenum oxidizes rapidly at temperatures above 650° C. The domestic abundance of molybdenum coupled with the fact that it is an extremely hard metal with a melting point that ranks fifth highest among the metallic elements has placed increased demands upon finding a suitable coating for molybdenum that will prevent rapid oxidation.

Various methods for applying protective coatings on molybdenum and other refractory metals are known, and, of these, several electroplated coatings have particular merit. A protective electroplated metal at a high temperature must not only resist oxidation from the environment in which the coating will be placed but must also prevent deterioration of the base metal caused by the environment. The oxidation resistance of most commercially usable electrodeposited metals is dependent upon the formation of an adherent and impervious oxide coating. In addition to oxidation resistance, the electroplate and its scale must withstand impact and abrasion, stress corrosion, and creep. If the electroplate diffuses rapidly with the base metal, the coating life might be shortened.

Discontinuities in the coating reduce its ability to protect the base metal. Thus the density and structure of electrodeposits are important properties. The coating must prevent the diffusion of gas that could oxidize the base metal and also prevent the diffusion of the base metal through the coating. In addition, the electrodeposit must be strong and ductile enough to resist stress introduced by impact or by force resulting from any difference in expansion between the base metal and the electrodeposit while they are being heated or cooled. Furthermore, the bond strength of the electroplate to the base metal and any alloy formed by diffusion of the base metal and the electroplate must also withstand such stresses.

Among the electrodeposits that were often considered previously for high temperature protection, nickel and chromium enjoyed prominent positions. Of these two, chromium resists oxidation in air better and is harder than nickel at high temperatures. Also chromium diffuses more slowly with other metals than nickel and, furthermore, chromium can be deposited on many refractory materials, particularly molybdenum, with a better adherence than is possible by plating nickel. However, chromium ruptures at high temperatures with relatively light loads and the oxide scale on chromium is more brittle and less adherent than the oxide scale on nickel, so chromium plate is less satisfactory than nickel for cyclic applications.

As both nickel and chromium each have some desirable

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properties required for a satisfactory electroplate coating, it is expedient to combine these two metals to take advantage of their desirable features. One known method of combining nickel and chromium is to electroplate alternate layers of these metals on a base material and then alternately heat treat and cold roll the material until the alloying metals are completely diffused into surface portions of the base metal. This method of combining nickel and chromium has two inherent disadvantages. First of all, the alternate heat treating and cold rolling makes the process expensive and time consuming. Additionally, the cold rolling step prohibits the plating of parts that are already formed or shaped, and consequently the process is limited to use on flat, unfinished materials.

Another method of combining refractory alloys and base metals provides for heating the plated metals to a temperature at or above the melting point of the eutectic of the metals in contact. This method is described in U. S. Patent No. 2,156,262 to Fink et al., and, as explained, has an advantage over the cold rolled process in that formed articles can be coated and do not lose their form even though heated at or above the melting point of the eutectic.

The present invention provides an improved process for making a diffusion alloy of nickel-chromium by electrodepositing alternate layers of nickel and chromium on a base metal and then heating from 4–24 hours at a temperature substantially below the melting point of the eutectic. Successful formation of a nickel-chromium diffusion alloy at temperatures substantially below the melting points of the eutectic is surprising as the expected result of lowering the temperature would be to extend the required heat treatment over a period of days.

It is therefore a general object of the present invention to provide a simplified method of making a nickel-chromium diffusion alloy wherein the heat treatment is carried out at temperatures substantially below the melting points of the metals and wherein no cold-rolling step is required.

Other objects and advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing wherein:

Figure 1 is a partial sectional view showing laminates of chromium and nickel deposited on a base metal;

Figure 2 is a partial sectional view showing the condition of the laminates of Figure 1 after heat treating; and

Figure 3 is a diagram comparing the growth of molybdenum-nickel and molybdenum-chromium diffusion zones with time at various temperatures.

Referring now to the drawing, there is shown in Figure 1 a cross-sectional view of deposited laminates of chromium and nickel as they would appear after plating and before heat treating. Various numbers of layers of laminates can be deposited, depending upon the final desired thickness, and the thickness of the various layers can be varied to determine the desired ratio of nickel to chromium in the alloy. By way of example, if an 80 nickel-20 chromium (by weight) diffusion alloy is desired, five (5) layers of each may be deposited, alternately, the nickel layers each being .00075 inch thick and the chromium layers each being .00025 inch thick.

As shown in Figure 3 of the drawing, nickel diffuses and alloys faster with molybdenum than does chromium. Also nickel forms hard, brittle compounds with molybdenum, whereas chromium does not. For these reasons, chromium is the better of the two electrodeposits for direct contact with molybdenum at high temperatures,

and it is desirable to plate a substantial thickness (about .0015 inch) of chromium on the molybdenum base metal before depositing the laminates thereon.

By way of example, a specimen to be plated with nickel-chromium laminates is first pretreated by degreasing in an alkali, pickled in nitric acid solution, and then etched in a chromic acid-sodium dichromate solution. A .0015 inch thick chromium plate is then deposited using the following bath formulation and operating conditions:

Formulation:

250 g./l. chromic acid

2.5 g./l. sulfuric acid

Operating conditions:

Cathode current density----- 750 amps./sq. ft.

Anodes----- Chemical lead sheet.

Bath temperature----- 185° F.

After plating with a .0015 inch layer of chromium, which requires about 60 minutes of plating time, the specimen is then etched in 37 percent hydrochloric acid, and then the following procedure is followed to deposit alternate layers of chromium and nickel:

(1) Soak for 1 minute in 180° F. distilled water made acid with sulfuric acid to pH 1.

(2) Place in a chromium plating bath, as described above, and plate with a .00025 inch of chromium.

(3) Rinse in water.

(4) Apply a nickel-strike plate in a nickel sulfate bath having the following formulation and operating conditions:

Formulation:

450 g./l. nickel sulfate

50 g./l. sulfuric acid

Operating conditions:

Cathode current density----- 100 amps./sq. ft.

Anodes----- Carbon rods.

Plating time----- 1 minute.

Bath temperature----- 105° F.

(5) Apply nickel plate .00075 inch thick from a sulfamate-nickel bath having the following formulation and operating conditions:

Formulation:

450 g./l. nickel sulfamate

30 g./l. boric acid

0.375 g./l. antipit agent (for example, SNAP, a product of Barrett Chemical Products, Shelton, Conn.)

Bath pH—4.0

Operating conditions:

Cathode current density----- 80 amps./sq. ft.

Anodes----- Cast nickel.

Plating time----- 11.2 minutes.

Bath temperature----- 145° F.

Agitate specimen.

(6) Rinse in water.

The above 6 steps are then repeated until the desired number of layers are obtained, depending upon the desired thickness of the coating. For example, by repeating steps 1-6, inclusive, until six layers each of chromium and nickel are deposited, the total thickness of the coating will be approximately .0075 inch.

Referring now to Figure 2 of the drawing, there is shown the appearance of a laminated nickel-chromium coating of .0075 inch thickness after 4 hours' heating in air at a temperature of 980° C. In actual practice, metallographic study of several heat-treated specimens established that all the nickel and chromium layers were alloyed after 4 hours' heating in air at a temperature of 980° C., as the alloy was not attacked by the oxalic

acid electrolytic etch for chromium or the 50:50 lactic-nitric acid chemical etchant for nickel. The diffusion alloy was nonmagnetic, indicating that all the nickel had absorbed at least 6 percent chromium as a nickel-chromium alloy transforms from a magnetic to a non-magnetic state at 6 percent chromium, as the chromium content increases. Metallographic evidence of the diffusion alloy shown in Figure 2 of the drawing indicated that the alloy was homogeneous and also Knoop hardness measurements across an etched section were between 170 and 185, confirming the metallographic evidence for homogeneity.

In an experiment conducted by the inventor, molybdenum rods, $\frac{5}{8}$ inch in diameter and 2 inches long, were heat treated for 2 hours at 980° C. in hydrogen, plated with .0015 inch of chromium plus alternate layers of nickel (.0075 inch) and chromium (.00025 inch), as explained above, until a total coating thickness of .0075 inch was applied. The nickel and chromium were then diffused by heating for 24 hours at 980° C. in hydrogen. The diffusion alloy was then evaluated by heating in air for 100 hours at 1796° F. which caused no blistering or pin holing in the protective coating visible at 10× magnification. The scale was uniform in appearance and was adherent.

Although electroplates of nickel plate or chromium have been made that have survived simulated service tests, the advantage of this invention is that the nickel-chromium diffusion alloy is more oxidation-resistant than either nickel or chromium and it also appeared that the coating probably would be satisfactory for a much longer period of exposure.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A process for coating molybdenum with a diffusion alloy which consists of depositing sequentially a layer of chromium about .00025 inch thick and a layer of nickel about .00075 inch thick, repeating said sequence of depositions a plurality of times, and then heating the coated molybdenum for 4 hours at a temperature above 980° C. and substantially below the melting point of the eutectic of the metals.

2. A process for coating molybdenum with a diffusion alloy which consists of the steps of first electroplating a .0015 inch thick layer of chromium on said molybdenum; next depositing sequentially a layer of chromium about .00025 inch thick, a nickel strike plate from a nickel sulfate bath, and a layer of nickel about .00075 inch thick by plating from a nickel sulfamate bath; repeating said sequence of depositions a plurality of times, and then heating said coated molybdenum about 4 hours at a temperature between 980° C. and a temperature substantially below the melting point of the eutectic of the metals.

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