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3,141,744

## WEAR-RESISTANT NICKEL-ALUMINUM COATINGS

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No Drawing. Division of application Ser. No. 829,156, July 23, 1959, now Patent No. 3,046,205, dated July 24, 1962. Continuation of application Ser. No. 665,616, June 13, 1957. This application June 19, 1961, Ser. No. 118,197

5 Claims. (Cl. 29—194)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This application is a continuation of abandoned application Serial No. 665,616, filed June 13, 1957, for Nickel-Aluminum Alloy Coatings and is a division of application Serial No. 829,156, filed July 23, 1959, now Patent No. 3,046,205, granted July 24, 1962, for Nickel-Aluminum Alloy Coatings.

The present invention relates generally to hard coatings for wear and oxidation resistance. Such coatings can be produced on metallic surfaces for increasing wear resistance of sliding or reciprocating parts of machines and the like, such as bearing surfaces, pistons, piston rings, cylinder walls and gun mechanisms. More particularly, the invention pertains to composite articles of manufacture comprising a base metal with a coating of nickel-aluminum alloys and methods of applying these coatings so that a layer of unalloyed nickel remains between the nickel-aluminum layer and the base metal.

In the coating art, it has been the general practice to employ metals which have characteristically high wear, oxidation and temperature resistance for the surface layers. For example, coatings of chromium and chromium alloys on metal surfaces have been used where surfaces are subjected to sliding friction. Chromium plated piston rings are a typical product of this approach.

However, these surface layers of pure metals or alloys thereof with other metals to form intermediate solid solutions exhibit typical metallic characteristics. Although these characteristics vary in degree from metal to metal they all have properties of hardness, ductility and toughness in a certain order of magnitude since the valence binding in these metals is the metallic bond characteristic of all metals and solid solution alloys. To obtain a surface layer of a new order of magnitude simple metals or intermediate solid solution alloys will not suffice.

It is, therefore, an object of the present invention to provide base metals such as steel, nickel or copper with coatings of nickel-aluminum which exhibit wear, oxidation and temperature resistance far beyond that which could be obtained with coatings of either nickel, aluminum, or nickel-aluminum intermediate solid solution alloys. This objective is effected by producing a coating with proper stoichiometric proportions such that the nickel and aluminum form intermetallic compounds which possess physical properties highly suitable for wear, oxidation and temperature resistance. In the nickel and aluminum system these intermetallic compounds consist of nickel aluminides such as  $\text{Ni}_3\text{Al}$  which compounds exhibit an intermediate type of binding between covalent and metallic.

It is a still further object of the present invention to provide a nickel-aluminum coating which is free of unalloyed aluminum. The presence of such aluminum will

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considerably detract from the desired wear resistance characteristics since, as is well known, aluminum is extremely ductile and would tend to gum the sliding surfaces.

Another objective of the present invention is to produce an article with a layer of unalloyed nickel between the base metal and the surface layer of nickel aluminide in order to afford a better bond between the base metal and the nickel aluminide coating thus assuring a firm, tenacious coating.

Still another object is to produce an article with a carefully controlled and readily reproducible deposit of aluminum on a nickel surface thereby permitting diffusion of the aluminum into the nickel to the point where no free aluminum remains but free nickel does remain between the thus formed nickel aluminide and the base metal.

Yet another object of the present invention is to provide a coating of nickel aluminide of a carefully controlled thickness such that the inherent brittle characteristics which intermetallic compounds exhibit in massive form will not have occasion to manifest themselves.

It is still another object to provide a coating of wear-resistant nickel aluminide which will retain its room-temperature hardness after heating to  $1000^\circ\text{C}$ . and cooling and will be more oxidation and temperature resistant than either nickel, aluminum, or intermediate solid solutions thereof.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description.

Nickel-aluminum intermetallic compounds possess many desirable properties over the separate forming metals, among the chief of which are a substantial increase in melting point, stability at high temperatures, good modulus-of-rupture strength, excellent oxidation resistance and hardness. With these desirable properties, however, nickel aluminide, in massive form, is difficult to fabricate and too brittle for practical applications. To overcome these difficulties for coating use, the nickel aluminide is formed directly on the base metal surface after the necessary shaping operations have been completed. This is accomplished by electrodeposition process steps and several modes of accomplishing this result will now be described.

In the first method, nickel is deposited on the base metal in the conventional way, as by electro-deposition from baths containing nickel sulfate or nickel chloride. If the nickel when deposited is severely soiled, degreasing of the article with subsequent pumice scrubbing thereof is required prior to aluminum plating. Unless the nickel is markedly soiled no precleaning is necessary. Aluminum is then deposited on the nickel plate by electrodeposition from a fused salt bath consisting of an aluminum halide and an alkali halide, as, for example, aluminum chloride and sodium chloride in the ratio of upwards of 1.5 moles of aluminum chloride to 1 mole of sodium chloride. Satisfactory performance results from operation at 1 to 4 amperes/sq. dm. and at a temperature in the range of  $160^\circ\text{--}200^\circ\text{C}$ . Once prepared the bath must be kept molten, for if allowed to solidify it is very difficult to remelt without breaking the vessel containing the bath. The time of treatment varies depending on the thickness of plating desired but it most commonly varies between 5 minutes and 1 hour. Very good, coherent aluminum deposits up to 0.8 mil thick can be produced by this method using aluminum (2S) anodes. When thicker deposits are desired smooth deposits of aluminum up to 0.002 inch thick can be obtained by using tungsten anodes.

After the aluminum has been deposited on the nickel coat the article is dried and placed in a furnace preferably

of the electric type such as a high frequency induction or resistance furnace. Heating may be conducted in air or in an inert atmosphere, such as in helium or nitrogen, at a temperature in the range from 550° to 750° C. for periods up to about 20 hours. At this temperature all the aluminum alloys with the nickel to form a nickel aluminum alloy layer over the unalloyed portion of the nickel layer. This arrangement is accomplished by limiting the deposit of aluminum to that of a layer having a thickness less than the thickness of the nickel layer. Actually, the optimum deposit thicknesses are an aluminum deposit approximately one-fourth the thickness of the nickel layer whereby all the aluminum is alloyed with the nickel forming a layer of nickel aluminides exceeding in thickness the prior aluminum deposit but still leaving a portion (about one-half) of the original nickel layer in unalloyed condition.

Actually, it has been found that the oxidizing effect of heating in air is beneficial in that there is a marked increase in resistance to salt spray corrosion. In case the alloy is formed by heating in an inert atmosphere the oxidation will in any event occur during normal subsequent high temperature applications.

The first method, as above described, in particularly useful where the thickness of the aluminum deposit is less than 0.001 inch or where the object being coated might be damaged by heating to too high a temperature. However, as stated above thicker deposits can be obtained by the use of tungsten anodes.

In the second method aluminum is electrically deposited on the nickel coat from a fused salt bath operated at a temperature of about 660° to 1000° C., i.e., above the melting point of aluminum, the alloy being formed simultaneously with the plating operation due to the heat of the bath. A suitable bath is cryolite at a temperature of 1000° C. or cryolite dissolved in alkali halides such as sodium chloride and potassium chloride at a temperature ranging from 660° to 900° C. Using cryolite with the bath temperature at about 1000° C., and a current flow of 50 amperes per square decimeter surface, a flow of 2 to 3 minutes will produce a coat of about 0.0005 inch thickness. A coat thickness of 0.001 to 0.002 inch is produced by a current of 20 to 25 amperes per square decimeter flowing from 15 to 30 minutes. For deposits over 0.002 inch 15 to 20 amperes per square decimeter flowing for about 1 hour are required.

In the operation of the potassium chloride, sodium chloride, cryolite bath although the bath may be operated in the temperature range stated (660°-900° C.), at the higher temperature the graphite anodes oxidize rather rapidly if an inert atmosphere is not used while at the lower temperature the aluminum diffuses slowly into the nickel. A series of runs has shown that a temperature range of about 700° to 800° C. gives a satisfactory compromise of these factors. When the bath is used in this temperature range, aluminum deposits 0.25 mil thick are produced in 5 minutes at a current density of 7 amperes/sq. dm. To produce thicker deposits of aluminum at a rate not in excess of the rate of diffusion of the aluminum into the nickel the following schedule should be employed in using this bath in the optimum temperature range.

| Current density, amp./dm. <sup>2</sup> | Maximum time permissible without producing free aluminum on the surface, minutes | Approximate thickness of aluminum deposit, mils |
|----------------------------------------|----------------------------------------------------------------------------------|-------------------------------------------------|
| 10                                     | 1                                                                                | 0.1                                             |
| 8                                      | 3                                                                                | 0.2                                             |
| 7                                      | 5                                                                                | 0.25                                            |
| 6                                      | 10                                                                               | 0.35                                            |
| 4                                      | 20                                                                               | 0.50                                            |
| 2                                      | 150                                                                              | 1.8                                             |

Since the bath used to electrodeposit the aluminum is operated at temperatures higher than the tempering tem-

perature of steel, when the base material is steel or a steel alloy, heat treatment becomes necessary to restore the temper of this base material after the nickel aluminide layer has been formed.

Samples to be plated were placed in the bath and allowed to hang there for 10 to 20 seconds to reach bath temperature before the current was turned on. Optimum concentrations for the chloride-cryolite bath are: Sodium chloride 440 gms., potassium chloride 560 gms. and cryolite 150 gms. Optimum operating conditions exist at a current density of 2 to 10 amps/sq. dm. and in the temperature range of 700°-800° C.

In order to avoid producing excess unalloyed aluminum on the surface it is often advantageous to employ varying current densities. Thus, in case of a chloride-cryolite bath operated at 700° C. deposits of 1 mil thick can be prepared by plating at 7 amp/sq. dm. for 5 minutes and then reducing the current density to 3-4 amp/sq. dm. and plating for 30 to 40 minutes. Deposits of 1.8 mils can be produced in two hours by the following schedule: 7 amp/sq. dm., 5 minutes; 4 amp/sq. dm., 20 minutes; 2 amp/sq. dm., 95 minutes. These plating rates can be increased if the bath temperature is raised above 700° C.

An excessive rate of deposition of aluminum is to be avoided since at bath temperature this aluminum is molten and nickel dissolves in molten aluminum. The problem created is that of depletion of nickel from the nickel layer since the nickel goes into solution in the molten aluminum and the aluminum collects into beads which subsequently flow into the bath carrying the dissolved nickel along. This results in a reduction in the amount of nickel available for alloying.

This is in fact one of the basic disadvantages of the hot-dip process known in the prior art. As an indication, some 4" x 6" samples were plated with about 0.001 inch of nickel and accurately weighed. These samples were then sent to a commercial firm for the deposition thereon of aluminum by the hot-dip process. All samples actually lost weight as a result of the dipping process as indicated by the following:

| Wt. of base (gms.) | Wt. of nickel coated base (gms.) | Wt. of sample after hot-dip (gms.) | Wt. of Al deposit (gms.) | Wt. of sample stripped of unalloyed Al deposit (gms.) |
|--------------------|----------------------------------|------------------------------------|--------------------------|-------------------------------------------------------|
| 126.000            | 132.682                          | 128.845                            | 3.95                     | 124.895                                               |
| 120.929            | 128.002                          | 125.372                            | 3.42                     | 121.952                                               |

The nickel aluminide, as produced by the described methods, has a hardness varying from 700 to 1050 Vickers at room temperature depending on the percentage of aluminum in the given nickel aluminide. This fact makes this compound particularly useful for wear resistance in pistons, piston rings, cylinder walls, gun mechanism, sliding parts of machines and the like. In addition, the room temperature hardness of the compound is not affected by heating to 1000° C. whereas, in the case of chromium the hardness is destroyed.

Further, the nickel aluminide is markedly oxidation resistant even at 1100° C. there being only slight surface oxidation. This oxidation resistance is apparent when comparison is made with nickel in which, over a 400 hour period, there is a gain in weight at 1100° C. of 0.05 gram per cm.<sup>2</sup> as compared with an 0.01 gram gain for nickel aluminide at the same temperature and for the same time period. Since nickel and chromium have approximately the same oxidation properties, it is apparent that the oxidation resistance of nickel aluminide exceeds that of chromium, also. Since the described methods all involve electro-deposition, the coating thickness may be readily controlled, values ranging from 0.0002 to over 0.002 inch being readily obtainable.

In addition to the beneficial results already set forth

the results of salt spray corrosion tests (set forth below) on a series of steel alloy panels coated with nickel aluminum alloy clearly indicate the excellent protection afforded in this respect by the present invention. Further, these tests indicate the superior nature of coatings in which a layer of nickel remains between the base and the nickel aluminide layer.

| Thickness of Ni in inches | Thickness of Al in inches | Percentage of surface covered with rust after a minimum of 75 hours of salt spray |
|---------------------------|---------------------------|-----------------------------------------------------------------------------------|
| 0.001                     | 0.0003                    | 1-2                                                                               |
| 0.0002                    | 0.001                     | over 50                                                                           |
| 0.0005                    | 0.0003                    | 3-5                                                                               |
| 0.002                     | 0.0003                    | less than 1                                                                       |
| 0.0005                    | None                      | 80                                                                                |
| 0.0004                    | 0.00026                   | 5                                                                                 |
| 1 0.0004                  | 0.00026                   | None                                                                              |

<sup>1</sup> Oxidized.

While any of the structural metals may be used as the base material, in common use for this purpose are steel, nickel or copper.

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 within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A composite metal article containing a hard coating which increases wear resistance of sliding or reciprocating parts comprising in combination a base metal, a layer consisting of unalloyed nickel bonded to and covering said base metal and a surface layer consisting of nickel aluminide bonded to and covering said nickel layer, said surface layer being free of contamination from the base metal and free of unalloyed aluminum.
2. The composite metal article of claim 1 wherein the base material is a metal having a melting point higher than aluminum.
3. The composite metal article of claim 2 wherein the layer of unalloyed nickel is approximately of the same thickness as the surface layer of nickel aluminide.
4. The composite metal article of claim 3 in which the nickel aluminide coating has a room temperature hardness between 700 and 1050 Vickers and retains this room temperature hardness after heating to 1000° C. and cooling.
5. The composite metal article of claim 1 wherein the aluminum content is about one-fourth the nickel content.

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