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PROCESS OF PRODUCING COLORED OXIDE COATINGS ON NICKEL AND NICKEL ALLOYS

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6 Claims. (Cl. 148—13.1)

The present invention relates to a process of producing oxide coatings of various colors on nickel and nickel alloys, and more particularly to a process of producing such oxide coatings by heating the nickel or nickel alloy articles under controlled conditions of atmosphere, temperature and duration of treatment to form the desired colored oxide coating.

It is an object of the present invention to provide a process of producing oxide coatings of desired color on nickel and nickel alloys.

It is another object of the invention to provide a process of producing uniformly colored adherent oxide coatings of desired color on nickel and nickel alloys which can be carried out on an industrial scale.

It is a further object of the invention to provide a process of consistently producing uniformly colored adherent oxide coatings of desired color on nickel and nickel alloys on an industrial scale.

Other objects and advantages of the present invention will become apparent from the following detailed description of the process of the present invention.

Generally speaking, the process of the present invention comprises exposing pieces of the nickel or nickel alloy after suitable pretreatment to a heated oxidizing atmosphere effective to produce a uniform oxide coating on the surface thereof maintained within a critical temperature range and maintaining the pieces in said heated oxidizing atmosphere until the surface thereof has been at oxidizing temperature for a critical short period of time. The color of the oxide coating produced depends not only upon the temperature, atmosphere and duration of the oxidizing treatment but upon the composition and pretreatment of the metal or alloy as well. In order to obtain consistent results, it is necessary to control the temperature and duration of treatment within relatively narrow limits and to correlate these with each other and with the composition and pretreatment of the metal being treated.

The temperature used to produce the desired colored oxidized coating and the duration of the heating depend upon the thickness of the metal being treated and also upon each other. In general, if a higher temperature is used the duration of the treatment of a given piece of metal or alloy would be shortened and vice versa. Similarly, if a thicker piece is to be treated the temperature and/or duration of heating must be appropriately increased. In other words, the surface of the piece of nickel or nickel alloy exposed to the oxidizing atmosphere must be raised to and maintained at a proper oxidizing temperature for a critical short period of time sufficient to produce the desired adherent uniformly colored oxide coating, as explained more fully hereinafter.

The present invention is directed to the process of producing uniformly colored adherent oxide coatings on substantially pure nickel and high nickel alloys containing at least about 98% nickel. Although some variation in composition is possible, these high nickel alloys will usually comprise the following elements within the indicated ranges:

	Per cent
Nickel	About 98.33 to about 99.98
Manganese	Trace to about 1.00
Iron	About .01 to about .25
Copper	About .005 to about .20
Silicon	None to about .05
Sulphur	.001 to about .015
Carbon	None to about .15

Other species of the invention relating to the production of oxide coatings on other nickel alloys are described and claimed in applicants' copending application U. S. Serial No. 219,588, filed July 16, 1938, now Patent No. 2,206,392, dated July 2, 1940, of which the present application is a division.

In order to give those skilled in the art a better understanding of the present invention the following illustrative examples are given:

EXAMPLE NO. I

Green Oxidized Nickel Sheet

An ingot having approximately the following composition: 99.5% nickel, .15% manganese, .15% iron, .005% sulphur, and .07% carbon, was forged at a temperature of about 2250° F. to blooms which were rolled at a temperature of about 2200° F. to sheet bar approximately ⅜" by 11½" by 39". Hot rolled sheets were produced from the bars by roughing down and finishing on a hot sheet mill in the usual manner to sheets approximately 0.039" by 39" by 72". The hot rolled sheet thus obtained was reduced in thickness to about 0.037" by cold rolling and then annealed for about 5 minutes at about 1650° F. in a reducing atmosphere containing approximately 4% carbon monoxide. The annealed sheet was thereafter pickled in hot sulphuric acid, sodium nitrate pickling solution. The pickled sheet, which was free from scale, oxides, etc., had a bright, smooth metallic surface, was

next subjected to an oxidizing treatment. A gas-fired sheet furnace heated to a temperature of about 1800° F. was utilized for the oxidizing treatment which lasted for about 1 minute and 20 seconds. The atmosphere by Orsat analysis comprised about 2.5% oxygen and 10.5% carbon dioxide. A uniform adherent oxide coating was produced having a distinct greenish hue particularly when viewed at an oblique angle to the surface of the sheet.

In using this type of furnace, the temperature may vary from about 1700° F. to about 1850° F., depending upon the thickness of the metal object being oxidized, and upon the time at which the surface of the object is maintained at an oxidizing temperature in contact with the oxidizing atmosphere which may vary from about 1 to about 4 minutes.

EXAMPLE NO. II

Green Oxidized Nickel Strip

The metal used had substantially the same composition as that used in Example No. I. The preliminary treatment involved hot forging a 14" x 14" ingot at about 2250° F. to 8" x 8" blooms, hot rolling the blooms at about 2250° F. to billets 3" x 4½", and the billets thus produced to strip about 0.125" x 5". The strip was annealed at about 1350° F., pickled in a sulphuric acid-sodium nitrate solution and cold rolled to about 0.050" gauge; annealed again at 1350° F. and cold rolled to about 0.021" gauge. The cold rolled strip was passed through an oxidizing catenary furnace maintained at a temperature of about 2000° F. The strip was exposed for about 1 minute in the heated oxidizing atmosphere which contained about 5% oxygen and about 8% CO_2 by Orsat analysis. An adherent uniform beautiful green coating was produced. In using this type of furnace, the temperature range may extend from about 1700° F. up to about 2100° F. and the time of exposure to the hot oxidizing atmosphere may vary from about ½ minute, e. g., about 40 seconds, up to about 4 minutes.

Other examples illustrating satisfactory time of exposure and furnace conditions for producing green oxide coating on nickel strip of different thicknesses are given in Schedule I.

Schedule I

Thickness of metal	Furnace temperature	Time of exposure	Furnace atmosphere
	° F.		
.010"	2,000	1 min.	5.1% O_2:8.0% CO_2
.025"	2,100	40 sec.	4.7% O_2:10.0% CO_2

EXAMPLE NO. III

Brown Oxidized Nickel Sheet

The metal used had substantially the same composition as that used in Example No. I, and it was worked in the same manner to sheet approximately 0.039" x 39" x 72". The hot rolled sheet thus obtained was cold rolled without removal of the hot rolled surface to .037" and then oxidized by exposing it in a continuous type sheet furnace at a temperature of about 1500° F. for about three minutes. The atmosphere was composed of about 3.5% O_2 and 9.5% CO_2 by Orsat analysis. An adherent uniform brown oxidized coating was produced. A temperature up to about 1800° F. may be used in this type furnace provided the time of exposure is properly correlated therewith and with the thickness of the metal object being treated, in accordance with the present invention.

It will be seen from the foregoing specific examples that the surface of the nickel and nickel alloy articles is maintained at an oxidizing temperature in contact with the heated oxidizing atmosphere for relatively short periods of time of the order of about ½ minute to 4 minutes. The oxidizing atmosphere is heated to a temperature within the range of about 1500° F. to about 2100° F. The particular time and temperature within these ranges which will be chosen for treating any particular nickel or nickel alloy article will depend upon the type of furnace which may govern to some extent the duration of the treatment, and the thickness of the article being treated. Generally speaking, the duration of the treatment will be longer when thicker sections are being oxidized or when the temperature of the oxidizing atmosphere is lower, whereas the time of treatment may be shortened if the temperature is raised or if thinner material is being treated.

The sheet and strip, when colored as taught hereinbefore, may be fabricated into a wide variety of useful and attractive articles. The nickel and nickel alloys are inherently immune to rust and resistant to corrosion, and in the colored condition may generally be used where the plain metal has been found useful with the added advantage of color stability. The latter property is particularly advantageous in applications where the metal becomes heated in use. Common examples include deflector or reflector pans for heating elements on electric ranges, burner bowls on gas ranges, sheathing of electric heating elements, laboratory oven linings, etc. Railroad car roofs may be mentioned as an example of a field of general utility where resistance to corrosion is advantageous. The firm adherence of the colored oxide coating produced by the present invention permits the colored oxide coated sheet and strip to be formed and shaped into fabricated products without cracking or flaking the adherent colored oxide coating. The colored nickel and nickel alloys of the present invention may also be applied where the color is used for decorative purposes, e. g., camera cases, clock hands, gauge pointers, etc.

In the above examples specific conditions of rolling, annealing and pickling have been given but it will be understood that modification of these conditions within certain limits is possible, as those skilled in the art will understand. Moreover, the surfaces to be coated may be prepared for the oxidizing treatment by methods other than cold rolling and pickling. For example, surfaces that had been cleaned or freed from scale, etc., by sand blasting, by grinding, by electrolytic cleaning or by various other cleaning methods have been given satisfactory adherent colored oxide coatings by subjecting the metal or alloy to oxidizing atmospheres under conditions comparable to the specific examples given hereinbefore.

Although the specific examples have illustrated the invention as applied to the coloring of sheet and strip material, it will be readily understood by those skilled in the art that the invention may also be used for applying colored oxide coatings to nickel and nickel alloy rods, tubes, bars, and other shapes and forms. Such shapes and forms are to be understood as coming within

the scope of the foregoing description and the appended claims.

We claim:

1. In the production of useful and attractive articles of manufacture of shapes rolled from nickel and nickel alloys containing at least about 98% nickel and not substantially more than about 1% manganese, the process of forming on such rolled shapes a decorative and strongly adherent oxide coating of special selected color uniform throughout the treated surface which comprises exposing the shapes after rolling to an oxidizing atmosphere in an enclosed furnace chamber, said atmosphere being heated at controlled temperature within the range of about 1500° F. to about 2100° F. by means other than heat derived from the shapes being treated and being effective at the controlled temperature to produce an oxide coating of the special selected uniform color, and maintaining said shapes in said heated oxidizing atmosphere within said enclosed furnace chamber until the surface of the shapes has been at an oxidizing temperature in contact with said heated oxidizing atmosphere within said enclosed furnace chamber for a controlled period of time within the range of about ½ minute to about 4 minutes sufficient to form an oxide coating on said shapes having the special selected color uniformly developed over the entire treated surface, said oxide coating adhering thereto so tenaciously that the shape can be bent to the desired contour for the finished article of manufacture without cracking or loosening the uniform decorative coating from the base.

2. In the production of useful and attractive articles of manufacture from nickel and nickel alloys containing at least about 98% nickel and not substantially more than about 1% manganese, the process of forming on the surface of such alloys a decorative and strongly adherent green oxide coating uniform throughout the treated surface which comprises exposing clean pieces of the alloy to an oxidizing atmosphere in an enclosed furnace chamber, said atmosphere being heated at controlled temperature within the range of about 1700° F. to about 2100° F. by means other than heat derived from said pieces being treated and being effective at the controlled temperature to produce a green oxide coating, and maintaining said pieces in said heated oxidizing atmosphere within said enclosed furnace chamber until the surface of the pieces has been at oxidizing temperature in said enclosed furnace chamber for a controlled period of time within the range of about ½ minute to about 4 minutes sufficient to form a green oxide coating on said pieces having the green color uniformly and permanently covering substantially the entire treated surface and adhering thereto so tenaciously that the piece may be bent to the desired contour for the finished article of manufacture without cracking or loosening the uniform decorative coating from the base.

3. In the production of useful and attractive articles of manufacture from nickel and nickel alloys containing at least about 98% nickel, the process of forming on the surface of such alloys a decorative and strongly adherent green oxide coating uniform throughout the treated surface as set forth in claim 2 in which the alloy being treated is in the form of rolled pieces.

4. In the production of useful and attractive articles of manufacture from nickel and nickel alloys containing at least about 98% nickel, the process of forming on the surface of such alloys a decorative and strongly adherent green oxide coating uniform throughout the treated surface as set forth in claim 2 in which the alloy being treated is in the form of rolled sheet and strip.

5. In the production of useful and attractive articles of manufacture from metal containing at least about 98% nickel, the process of forming on the surface of pieces of the metal a decorative and strongly adherent green oxide coating of uniform color throughout the treated surface which comprises exposing clean pieces of said metal to an oxidizing atmosphere in an enclosed furnace chamber, said atmosphere being heated at controlled temperature within the range of about 1500° F. to 2100° F. by independent controllable heat other than that derived from the pieces being treated and being effective to produce a uniform green color at the controlled temperature, and continuing the supply of said independent heat to said pieces in said heated oxidizing atmosphere within said enclosed furnace chamber until the surface thereof has been at controlled oxidizing temperature for a critical period of time within the range of about ½ minute to 4 minutes sufficient to produce on the surface thereof an adherent green oxide coating uniformly and permanently covering substantially the entire treated surface and adhering thereto so tenaciously that the piece may be bent to the desired contour for the finished article of manufacture without cracking or loosening the uniform decorative coating from the base.

6. In the production of useful and attractive articles of manufacture of worked pieces of nickel and nickel alloys containing at least about 98% nickel and not substantially more than about 1% manganese, the process of forming on such worked pieces a decorative and strongly adherent brown oxide coating uniform throughout the treated surface which comprises hot rolling pieces of the metal substantially to finished gauge, cold rolling the hot rolled pieces to finished gauge without first removing the hot rolled surface, exposing the thus worked pieces to an oxidizing atmosphere in an enclosed furnace chamber, said atmosphere being heated at controlled temperature within the range of about 1500° F. to about 1800° F. by means other than heat derived from the pieces being treated and being effective at the controlled temperature to produce a brown oxide coating, and maintaining said pieces in said heated oxidizing atmosphere within the enclosed furnace chamber until the surface of said pieces has been at oxidizing temperature in said enclosed furnace chamber for a controlled period of time within the range of about ½ minute to about 4 minutes sufficient to form a brown oxide coating on said pieces having the brown color uniformly developed over the entire treated surface, said brown oxide coating adhering thereto so tenaciously that the piece may be bent to the desired contour for the finished article of manufacture without cracking or loosening the coating from the base.

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