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METHOD OF COATING METALLIC SURFACES WITH LAYERS OF NICKEL-CHROMIUM AND ALUMINUM

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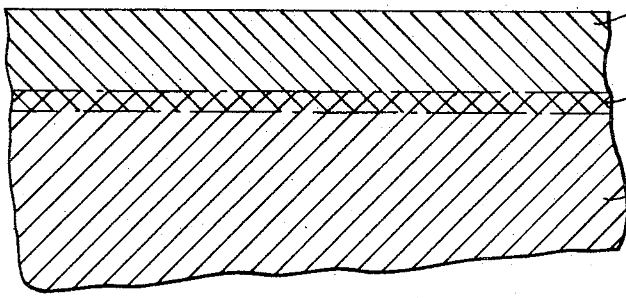

FIG. 1.

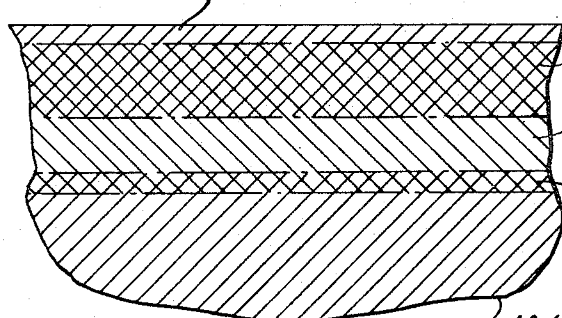

FIG. 2.

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METHOD OF COATING METALLIC SURFACES WITH LAYERS OF NICKEL-CHROMIUM AND ALUMINUM

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Original application June 26, 1959, Ser. No. 823,214, now Patent No. 3,165,823, dated Jan. 19, 1965, Divided and this application Dec. 30, 1963, Ser. No. 343,174

2 Claims. (Cl. 117—50)

This application is a division of application Ser. No. 823,214, filed June 26, 1959 and now U.S. Patent, 3,165,823 issued Jan. 19, 1965.

The present invention relates to metallic surface coatings that are resistant to corrosion and wear at elevated temperatures and to an improved process for applying and bonding said surface coatings to metallic objects.

A great number of applications exist wherein metallic articles are subjected at elevated temperatures to corrosive gases, such as air, and combustion gases resulting from the burning of a variety of fuels. Under these conditions, articles composed of metals such as iron and many ferrous base alloys, that are susceptible to such corrodents are severely attacked on their surfaces as evidenced by pitting and surface scaling and this surface deterioration materially reduces their operating efficiency and useful life. This condition is further aggravated when the objects must concurrently withstand surface to surface contact and wear, particularly when operating tolerances between said adjacent surfaces are critical. Substitution of corrosion susceptible base metals with special heat-resistant alloys to achieve a satisfactory operating life has not been entirely satisfactory because of the greater cost of such special alloys, which are generally more difficult to manufacture and to fabricate into the desired form. Quite often, the substitution of special corrosion-resistant alloys results in a sacrifice or compromise of some of the structural considerations in favor of the corrosion-resistant properties of the material. Numerous surface coatings have been applied to base metals susceptible to corrosion at elevated temperatures to obviate the necessity of substituting special heat-resistant alloys and to achieve a satisfactory operating life of the metal object. However, the processes by which surface coatings have been heretofore applied have been commercially undesirable due to their complexity, prolonged treating cycle and resultant uneconomical operation.

Accordingly, one object of this invention is to provide a metal article having an improved metallic coating tenaciously bonded thereto that is resistant to corrosion at elevated temperatures.

Another object of this invention is to provide a metal article having an improved metallic coating tenaciously bonded thereto that is extremely hard and resistant to corrosion and wear at elevated temperatures.

Still another object of this invention is to provide a simple process whereby metallic objects of various configurations, including sheets, strips, rods, bars, irregular-shaped bodies and the like can be quickly coated with corrosion and wear-resistant metals over all or a portion of the surface of said objects and tenaciously bonded thereto.

Other objects and advantages of the present invention will become apparent from the following detailed description taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a magnified longitudinal sectional view of a fragmentary portion of the base metal having on its surface a coating of nickel-chromium alloy which is tenaciously bonded thereto by means of an interdiffused chemical bond; and

FIGURE 2 is a magnified longitudinal sectional view of a fragmentary portion of the base metal having on its surface an outer coating of aluminum which has been interdiffused with the underlying coating of nickel-chromium alloy.

The surface coating treatment, as embodied in this invention, is comprised of two separable treating sequences; first, the application and bonding of a corrosion-resistant coating to the base metal and, second, the application and interdiffusion of an aluminum coating over said corrosion-resistant coating. The separability of these two treating sequences provides processing flexibility so that metal objects may be processed in only the first or in both treating sequences, depending upon the extent and nature of the surface protection required. The corrosion-resistant coating sequence is comprised principally of the following processing steps: preheating the article to be coated to an elevated temperature, metal spraying the surface or a designated portion thereof with a corrosion-resistant metal alloy, and interdiffusing the coating and the base metal at an elevated temperature. Because superior bonding of the coating if achieved when the article has a metallurgically clean surface, appropriate surface cleaning steps should precede the preheating and coating steps. In addition, the coated article may be surface finished if the texture and/or dimensional tolerances of the coated article are critical. The second coating sequence is comprised principally of preheating the coated object, applying a thin coating of aluminum over the underlying corrosion-resistant coating, and finally interdiffusing the aluminum coating with the underlying corrosion-resistant coating under controlled conditions. Application of the aluminum should be made on a metallurgically clean surface which may require a degreasing processing step prior to the preheat step. It may also be desirable, depending on the nature of the coated article, to perform a very light surface finishing operation on the overlying aluminum coating.

The object to be treated may be of any metallic composition, providing, however, that the material is sufficiently resistant to corrosion so that substantially no oxide is formed on the surface thereof during the rapid pre-heat in air prior to applying the corrosion-resistant coating. There are numerous ferrous base and nickel base stainless alloys that are resistant to oxide formation when rapidly heated in air to temperatures between about 1300 and 1800° F. and are suitable for surface treatment in accordance with this invention. Rapid heating techniques, such as induction heating, minimize surface oxidation because of the short length of time required to attain the desired temperature and consequently constitute the preferred heating method.

With reference to the first treating sequence wherein the corrosion-resistant coating is applied to the base metal, it is preferred to clean the article in a vapor degreasing operation or other suitable cleaning operation, to remove any surface film which may have been deposited thereon, such as during prior handling or in machining operations. A second surface cleaning step, comprised of sand or grit blasting the surface is also preferred, in order to remove therefrom any solid deposits and oxide scales and impart a plurality of slight depressions in the surface of the base metal to aid mechanical bonding of the initial surface coating prior to the diffusion step.

The metal article with a metallurgically clean surface is next preheated rapidly to a temperature ranging between 1300 and 1800° F., preferably 1650 to 1800° F. for most materials, which constitutes a critical step of this process. Preheating the metal article prior to coating insures intimate contact of the corrosion-resistant coating with the surface of the base metal and improves mechanical bonding therebetween by preventing rapid cooling and contraction of the coating relative to the base surface. Attempts to apply a corrosion-resistant coating of an appreciable thickness such as 0.010 inch and thicker by metal spraying a metal article which had not been preheated resulted in extremely poor adherence and even complete separation of the coating from the surface. Moreover, the use of moderate preheat temperatures of about 800° F. failed to provide sufficient adherence whereby adequate bonding might be achieved during the subsequent diffusion step. It is for this reason that preheat temperatures of at least 1300° F. are employed, and preferably 1650° F. to 1800° F. Preheat temperatures in excess of 1800° F. are undesirable because of the increasing tendency to form oxides on the surface to be coated. As heretofore mentioned, the use of rapid heating techniques such as induction heating, which constitutes a preferred heating method, generally requires only a fraction of a minute to elevate the object to be coated to the appropriate temperature. When that temperature has been attained, a metal coating of corrosion-resistant alloy is immediately applied over all or that portion of the surface of the metal object that requires protection.

In surface treating applications wherein only the first treating sequence is to be utilized, a substantially pure 80 nickel 20 chromium alloy is used, having a composition, for example, such as that specified in ASTM designation B82–57 adopted in 1946 and as revised in 1952 and in 1957, having an analysis as follows:

Element:	Weight percent
Nickel	77–79
Chromium	19–20
Iron, maximum	1
Manganese, maximum	2.5
Carbon, maximum	0.25
Silicon	0.75–1.5
Sulphur, maximum	0.03

The presence of other elements in the alloy that have a tendency to form low melting point oxides such as the element boron, for example, which reduce the overall melting temperature of the oxide on the surface of the metal object are undesirable constituents because they accelerate the normal corrosion rate.

In surface treatments which include both the treating sequences, that is, the corrosion-resistant coating followed by an aluminum coating, a nickel-chromium alloy can be utilized having a broader composition range than the alloy specified above. The initial coating should consist substantially of a nickel-chromium alloy containing between 70 and 97 percent nickel and from 3 to 30 percent chromium with other constituents such as iron, cobalt and tungsten not to exceed a combined total of 10 percent by weight. Conventional quantities of age hardening elements, such as titanium, aluminum and molybdenum are not objectionable. As aforementioned, elements such as boron forming low melting point oxides on the surface to be coated are undesirable.

In the preferred practice of this invention, the nickel-chromium alloy is applied by a metal spray technique utilizing conventional spray guns adaptable for melting and spraying nickel-chromium alloy supplied in a wire form. Generally, these spray guns utilize a combustible gas such as acetylene mixed with oxygen for converting the nickel-chromium wire into a molten state and in which state it is propelled in the form of fine droplets by an air blast toward the object to be coated. In this manner, a coating of substantially uniform thickness ranging from about 0.001 to 0.100 inch is applied to all or a designated portion of the surface of the preheated metal article. The nature of the bond between the coating and the base metal immediately after spraying is primarily a mechanical one comprised of interlocking surface irregularities and the bond is susceptible to rupture if subjected

to high stresses. For the purpose of obtaining an improved bond, the coated metal object is next treated in a diffusion step wherein the mechanical bond is converted to a chemical bond which tenaciously secures the coating to the surface of the base material. To avoid rupture of the aforementional interlocking surface irregularities, it is preferred to prevent the coated metal object from cooling rapidly to a temperature substantially below the preheat temperature prior to the diffusion step. The diffusion step is comprised of heating the coated metal object to a temperature between 1800 and 2250° F., preferably 1900 to 2100° F. for a short duration of time so that interdiffusion or alloying occurs between the coating metal and the base metal to the depth of at least one atomic layer. The rate of interdiffusion between the nickel-chromium alloy coating and base metal increases with temperature and, accordingly, the length of treatment time required to secure a satisfactory bond is inversely proportional to the temperature employed. Interdiffusion at a temperature of about 1800° F. is feasible but commercially undesirable because time periods as long as one hour are required to achieve satisfactory bonding of the coating to the base metal. On the other hand, diffusion at temperatures in excess of 2250° F. occurs rapidly, requiring a treating period of only about a minute or less, but this temperature is unsatisfactory because of the rapid growth in the grain size of the base metal and the tendency to oxidize any exposed surface of a metallic object which may have received a protective coating over only a portion of its surface. Furthermore, warping of the metal object at very high temperatures may occur and, of course, melting of the base metal is the final limiting factor. For these reasons, in the preferred practice of this invention, diffusion temperatures of 1900 to 2100° F. are employed, requiring treating periods of from about one to about five minutes for producing tenaciously bonded nickel-chromium alloy coatings.

An illustration of the relationship between a base metal **10** coated with a corrosion-resistant nickel-chromium alloy **11** and tenaciously bonded thereto is shown in FIGURE 1. The interdiffused chemical bond between the base metal **10** and corrosion-resistant coating **11** has been exaggerated for purposes of clarity and is indicated by the bond **12**. As has heretofore been mentioned, the penetration or depth of the interdiffused zone **12** to achieve adequate chemical bonding should be at least one atomic layer and, preferably, about 0.0005 inch.

Metallic articles coated with the nickel-chromium alloy and processed in accordance with the steps described above may be used in that form or, if smooth surfaces and dimensional tolerances are critical, the article may be surface finished by machining, grinding, polishing or the like.

In situations where, in addition to the nickel-chromium corrosion-resistant coating, it is desired to impart a hard, corrosion- and wear-resistant coating to the metal object the second coating treatment comprising the application of an overlying aluminum coating would sequentially follow the application and bonding of the nickel-chromium surface coating. Prior to applying the aluminum coating, it may be necessary to re-clean the surface of the coated object, particularly if an intervening machining operation has been performed on the nickel-chromium surface coating. Preheating the metal article prior to the application of the aluminum coating is not absolutely essential, nor is it as critical as in the case of the preheat step preceding the application of the nickel-chrominum alloy coating. Generally, it is preferred to preheat the object to a temperature between 300° and 1400° F. to remove all traces of moisture on the surface of the object and to facilitate intimate contact between the aluminum and the nickel-chromium intermediate coating. Although a commercially pure aluminum is preferred, such as a 2S grade, alloys of aluminum with elements such as silicon, copper and magnesium in percentages preferably not exceeding a combined total of 10 percent by weight are also satisfactory. The aluminum coating may be applied in a number of different ways, such as by dipping in a molten bath or, preferably, by the metallizing spray gun technique in a manner similar to that employed in applying the nickel-chromium alloy coating. The thickness of the aluminum spray coating may range from 0.0003 to 0.004 inch. A coating thickness of less than 0.0003 inch may not provide a sufficient quantity of aluminum to form an aluminum nickel chromium alloy layer of sufficient thickness to provide the necessary protection, while a coating thickness exceeding 0.004 inch causes excessive flow and dripping of the aluminum coating during diffusion. Adherence of the aluminum to the nickel-chromium alloy coating prior to the diffusion step is a combination of mechanical as well as chemical bonding. The rate of diffusion of aluminum into the nickel-chomium alloy coating is substantially greater that that of the nickel-chromium alloy into the base metal, so that at elevated preheat temperatures of about 1200 to 1400° F. some interdiffusion occurs during the application of the aluminum to the metal article.

After the aluminum spray coating has been applied, the coated object is heated to a temperature within the range of from 1500° to 2100° F. and maintained at that temperature for a period of from a few seconds to five minutes to achieve controlled diffusion and alloying of the aluminum into the nickel-chromium alloy coating and forming therewith an extremely hard corrosion- and wear-resistant coating. The diffusion time required is dependent on the diffusion temperature, as well as the preheat temperature of the metallic object during the spray application of the aluminum. If, for example, the aluminum is applied to the coated object, pre-heated to a temperature of about 1400° F., a substantial interdiffusion is achieved during the application of the aluminum with a lesser amount of subsequent diffusion required. In addition, during the period required to heat the aluminum coated metal article up to the diffusion treatment temperature, more interdiffusion will occur between the aluminum and nickel-chromium alloy, the extent of which is dependent on the rate of heating and time required to attain the appropriate temperature. The total on combined interdiffusion of the nickel-chromium and aluminum coatings is controlled so as to produce an alloy layer of the desired composition and hardness and which is extremely resistant to corrosion and wear. Moreover, the thickness of the interdiffused layer should be at least about 0.0003 inch thick to provide sufficient protection but, preferably, not greater than 0.004 inch thick, because of the brittle nature of the interdiffused alloy. By controlling the thickness of the interdiffused alloy layer to about 0.004 inch or less, the brittle alloy responds in a more ductile manner, thereby greatly increasing its wear and impact resistance.

The fact that partial interdiffusion of the aluminum occurs during the application of the aluminum to the nickel-chromium alloy coating forming therewith a substantially tenacious bond provides additional processing flexibility in that the diffusion step may either immediately follow the aluminizing coating or may be deferred to a later time, if desired, without risk of separation or flaking of the outer aluminum coating.

An enlarged fragmentary view of a base metal having thereon an interdiffused alloy layer of aluminum, nickel and chromium is shown in FIGURE 2. The diffused alloy layer is designated by the numeral **13** while the undiffused outer layer comprised predominantly of aluminum and oxides thereof is designated **14**. The undiffused portion of the underlying nickel-chromium alloy coating **11** is bonded to the base metal **10** by means of chemical bond **12**. It will, of course, be appreciated that the principal zones or layers on the surface of the base metal are not as definitive as shown in FIGURE 2, but rather, in actual practice, the layers gradually blend one into the other without a definite line of demarcation. Hardness determinations obtained with a Rockwell testing apparatus of the interdiffused alloy layer indicate the hardness to range from approximately 48 to 62 Rockwell C. X-ray diffraction analyses made of the composition of this unique corrosion- and wear-resistant layer produced varying diffraction patterns, indicating that the alloy lacks chemical homogeneity. These X-ray studies further indicated that the predominant phase in the hard alloy layer is based on the space lattice $Al_3(Ni,Cr)_2$. In addition, the coating contains appreciable quantities of a second phase comprised of aluminum oxide in the form Al_2O_3 in amounts up to about 10 weight percent. The aluminum oxide as well as lesser quantities of nickel and chromium oxides are formed during the spray application of the coatings and during subsequent diffusions at elevated temperatures in air.

One of the specific applications of this invention relates to the corrosion and wear protection of engine valves, particularly the exhaust valves of an internal combustion engine. It is well known that commercial gasolines inherently contain constituents such as sulfur which, on combustion, produce corrosive elements such as sulfur dioxide which have a deleterious effect on the metal objects they contact. In addition, most gasolines also contain small quantities of special additives, such as tetraethyl lead, as an anti-knock agent, halogenated hydrocarbons as scavengers for the lead oxide formed from tetraethyl lead during combustion, and phosphorus-containing compounds to inhibit pre-ignition and spark plug fouling. These additives, although effective to achieve their intended purpose, are highly corrosive and attack the surface of engine valves exposed to the high temperature exhaust gases with a resultant pitting and flaking of the valve, materially shortening its effective operating life.

By applying a corrosion- and wear-resistant surface coating on the heads and/or faces of the valves in accordance with the preferred practice of this invention, engine valves can be produced which are highly resistant to corrosion and wear under these severe operating conditions. Most engine valves are of a ferrous or nickel base stainless alloy having the requisite oxidation resistance suitable for applying the nickel-chromium alloy coating in accordance with the processing sequence heretofore described. Valves in engines which are subjected to only moderate operating severity, such as in most passenger automobiles, normally do not require additional corrosion protection beyond that afforded by the valve material. However, in modern high-compression ratio passenger car engines, iron oxide formation on the head face of the valve promotes pre-ignition, a very damaging form of combustion. Accordingly, a coating of nickel-chromium alloy over the head portion of the valve exposed to the high temperature exhaust gases is sufficient to prevent formation of the iron oxide scale. Valves in heavy-duty engine operation, as encountered in airplanes and in trucks, for example, generally require corrosion and wear protection of the seat face of the valve and head corrosion protection to assure a long and efficient operating life. The seat face of the valve is, of course, that portion of the valve which is in contact with the valve seat, forming therewith a pressure-tight seal. When applying a corrosion- and wear-resistant seat facing to a valve, it is preferred to machine the face of the valve after applying the nickel-chromium alloy coating and prior to applying the aluminum coating to assure satisfactory dimensional control. Surface finishing the face of the valve after the application and controlled diffusion of the thin aluminum coating is generally not necessary. A light surface finshing operation to remove high spots is permissible but a deep surface finishing operation is undesirable, due to the possibility of removing all or a portion of the hard nickel chromium aluminum alloy layer.

Engine dynamometer studies under accelerated test conditions designed to evaluate the relative operating life of exhaust valves of the same base material indicated that valves having a protective coating on their heads comprised of 80 nickel, 20 chromium alloy to inhibit head corrosion and applied in accordance with the preferred practice of this invention had effective operating lives about four times greater than the same valves in an uncoated condition. Similar accelerated engine tests designed to evaluate the relative effectiveness of a corrosion- and wear-resistant coating comprised of interdiffused aluminum and nickel-chromium alloy applied to the seat face of a valve indicated that the coated valve had an operating life prior to failure approximately five times greater than the same valve in an uncoated condition.

A typical processing sequence for applying a corrosion- and wear-resistant coating to the base of a valve is comprised of taking the valve that has been machined roughly to size and cleaning the surface to be coated by degreasing and grit blasting. The cleaned valve is next inserted so that its head is surrounded by an induction coil providing localized heating, whereby the surface to be coated is raised to a temperature of approximately 1700° F. within about fifteen seconds and a nickel-chromium alloy sprayed on the face of said valve immediately after its withdrawal from the coil. Immediately after application of the nickel-chromium spray coating, the head of the valve is reinserted in the induction coil and heated to a diffusion temperature of approximately 2100° F. for a period of about one minute, and then permitted to cool gradually in air prior to machining. After the coated valve has been machined and degreased, the head is reinserted in an induction coil, whereby it is preheated to approximately 500° F. in a matter of seconds, and then withdrawn from the coil to permit an aluminum spray coating to be applied over the nickel-chromium alloy coating. The coated valve is once again reinserted into the induction coil and heated to a temperature of about 2000° F. for a period of approximately four minutes to provide controlled interdiffusion of the aluminum and nickel-chromium alloy coating forming thereby the corrosion and wear resistant layer having a hardness in the range of about 48 to 58 Rockwell C. The valve is then permitted to cool gradually in air to room temperature, at which time it is ready for use.

Variations to this processing sequence include the application of the nickel-chromium corrosion-resistant alloy to the head as well as to the seat face of the valve in cases where head corrosion protection is also desired. Moreover, instead of applying a spray coating of aluminum to only the seat face of the valve, it may be desired to also apply a protective coating of aluminum on the head portion of the valve, which may be either uncoated or coated with the nickel-chromium alloy and in which case it is preferred to dip the entire head of the valve in a bath of molten aluminum. The individual treating steps are, of course, adaptable to integration by automation whereby the metallic article or valve to be coated can be automatically processed starting with the uncoated object through to the finished product.

While it will be apparent that the preferred embodiment herein illustrated is well calculated to fulfill the objects above stated, it will be appreciated that the invention is susceptible to modification, variation and change without departing from he proper scope or fair meaning of the subjoined claims.

What is claimed is:

1. A process for applying a coating on at least a portion of a metallic surface, said metallic surface being sufficiently resistant to corrosion that substantially no oxide will form thereon during the period required to rapidly heat said surface in air to a temperature in the range of about 1300 to about 1800° F., comprising the steps of preheating said surface in air to a temperature in the range of about 1300 to about 1800° F., metal spraying at least a portion of the metallurgically clean preheated surface with an alloy containing at least 90 weight percent of the elements nickel and chromium, said nickel content ranging from about 97 to about 70 weight percent, said chromium content ranging from abou 3 to about 30 weight percent, heating said coated surface to a temperature in the range of about 1800 to about 2250° F. for a period of time sufficient to interdiffuse and alloy said coating with said metallic surface thereby tenaciously bonding said coating to said surface, applying a coating comprised predominantly of aluminum over said bonded nickel chromium alloy coating, heating said coated surface to a temperature in the range of about 1500 to about 2100° F. for a period of from a few seconds to about five minutes and forming thereby a hard, interdiffused alloy layer comprised predominantly of aluminum, nickel and chromium.

2. A process for applying a coating on at least a portion of a metallic surface, said metallic surface being sufficiently resistant to corrosion that substantially no oxide will form thereon during the period required to rapidly heat said surface in air to a temperature in the range of about 1300 to about 1800° F., comprising the steps of preheating said surface in air to a temperature in the range of about 1300 to about 1800° F., metal spraying at least a portion of the metallurgically clean preheated surface with an alloy containing at least 90 weight percent of the elements nickel and chormium, said nickel content ranging from about 97 to about 70 weight percent, said chromium content ranging from about 3 to about 30 weight percent, heating said coated surface to a temperature in the range of about 1800 to about 2250° F. for a period of from about one to about five minutes so as to interdiffuse and alloy said coating with said metallic surface thereby tenaciously bonding said coating to said surface, heating said coated surface to a temperature in the range of about 300 to about 1400° F., superimposing a coating containing at least about 90 weight percent aluminum over said preheated underlying nickel chromium alloy coating, heating said coated surface to a temperature in the range of about 1500 to about 2100° F. for a period sufficient to interdiffuse and alloy said outer aluminum coating with said underlying nickel chromium alloy coating forming thereby an alloy layer of the type $Al_3(Ni,Cr)_2$ and to a thickness between about 0.0003 to about 0.004 inch.

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