COATED METAL PRODUCT AND METHOD OF PRODUCING SAME

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Fig. 1

Fig. 2

Inventor: Robert Graham
By: Oswald W. Milmore
His Attorney
The present invention relates to metal products having surface coatings which will prevent or inhibit oxidation and other decomposition, such as will occur at high temperatures, and with an improved process for coating or alloying metal surfaces with an aluminum alloy to apply such a coating. In one of its specific embodiments the invention pertains to a process for coating valves, particularly valves for internal combustion engines, to provide a surface comprising or consisting of a ternary alloy of nickel, cobalt and aluminum, which is resistant to attack by products resulting from the combustion of fuels, and especially those containing lead compounds. The invention also includes corrosion- and/or decomposition-resistant metal articles, such as the above named engine valves, which are coated with the above-mentioned alloys.

It is well known that motor fuels, particularly gasoline, which is to be used as fuel in internal combustion engines frequently contain anti-knock compounds, such as tetraethyl lead, and certain halogenated compounds. Since the tetraethyl lead is at least in part decomposed during fuel combustion, the products of such combustion contain lead compounds which attack the valves of the engine. For instance, when standard-type valves are employed in aircraft engine cylinders, the face of the exhaust valve, i.e., the portion of the valve head exposed to the combustion chamber, is attacked by the products of combustion, particularly when the gasoline employed in such aviation engines contains tetraethyl lead. The metal on this part of the valve becomes removed or eaten away, leaving a sharp edge on the hard metal used for the valve seat. This weakens the valve to such a degree as to result in valve failures. Also, the sharp edge frequently induces pre-ignition.

It is one of the objects of the present invention to provide ferrous or non-ferrous metal articles, particularly valves for internal combustion engines, which have thereon an intimately bonded coating resistant to attack by products of combustion of fuels, especially those containing lead compounds produced during the combustion of fuels, e.g. gasoline containing tetraethyl lead and the like. Another object of the invention is to provide an efficient and economical process for coating engine valves and the like with a metallic surface which is resistant to the aforementioned attack by products of combustion.

Many metallic articles other than engine valves are also used in places where they are exposed to high temperatures and to the influence of corrosive gases such as air or oxygen-containing gases, as well as the combustion products of various fuels. These articles, and particularly those of a ferrous or cuprous nature, i.e., made of or having a surface consisting of or containing iron and/or copper, when exposed to such corrosive gases at relatively high temperatures, will corrode very rapidly so that their useful life is generally relatively short. For example, ordinary carbon steel when exposed in conventional gas furnaces at temperatures of between about 800°C and about 1200°C will become badly corroded and scaled in a few hours. In order to obviate such heat corrosion, the metallic materials have heretofore been subjected to various treatments to render them substantially resistant. All such processes, however, have been either difficult or uneconomical, and usually necessitate the employment of complicated procedures wherein the metallic materials are subjected to a number of treatments or steps. It is, therefore, a still further object of the present invention to provide a simple, efficient and economical process whereby various metallic materials or articles, particularly those of a ferrous and/or cuprous nature, may be readily and effectively rendered substantially resistant to heat corrosion. Another object is to provide a simple process for coating various metallic articles, such as metal sheets, strips, wire, tubes, pipes, and the like, consisting of or containing copper, nickel, iron, steel or alloys thereof, with a metallic material which is resistant to the aforementioned heat corrosion.

The invention is illustrated in the accompanying drawing, wherein:

Figure 1 is a diagrammatic vertical sectional view taken through a heating furnace in which the valve may be immersed in a molten bath of alloy while rotating the valve; and

Figure 2 is an elevation view of a coated valve according to the invention, parts being shown in section and the coating being enlarged out of scale for clarity.

The resistance of a given metal surface to attack by lead compounds, particularly by lead oxides, depends on a number of factors. Above a certain temperature, which depends at least in part on the melting point of the particular lead compounds, the ability of a metallic surface to resist attack is a function of (1) the density of the protective oxide film which is normally present on the surface of all metals ex-
cept the so-called noble metals, and (2) the stability of such protective oxide when in contact with a specific lead compound. The various metals, metallic alloys, and intermetallic compounds, all of which form protective oxide films which are resistant to scaling when subjected to high temperatures, may or may not be resistant to lead compound attack, particularly when contact is effected at said elevated temperatures. This resistance to attack by the lead compounds is dependent on the tendency of the oxide film to react with the lead compounds, e.g., lead oxide. If the conditions are such that there occurs a reaction between the oxide film and the aforementioned lead compounds, the majority of heat-resisting steels and the other heat-resisting alloys (although they are resistant to ordinary corrosion by air and/or oxygen-containing gases at ordinary temperatures) will nevertheless be rapidly attacked by the various lead compounds such as lead oxide or mixtures containing lead oxide or other oxidized or oxygenated compounds such as those present in the products of combustion of motor fuels containing tetraethyl lead.

According to one feature of the present invention ferrous or non-ferrous metal articles, such as valves for steam or power engines, are provided at least on that part of the surface exposed to the hot combustion products of the engine fuel with a coating consisting of or comprising a ternary alloy containing nickel, cobalt, and aluminum. In particular, it was found that valves provided with such a coating are especially adapted to resist prolonged attack by the combustion products of fuel containing lead compounds.

According to a further feature of this invention valves or other metal articles are provided at least on that part of the surface exposed to the hot combustion products of the engine fuel with a coating as aforesaid by immersing the valve or other article, or the part thereof to be coated, in a molten bath of a ternary alloy of nickel, cobalt, and aluminum, and thereafter subjecting the article to a heat diffusion treatment. Preferably the metal surface to be coated is degreased and etched by treatment with a suitable acid, e.g., sulfuric acid. It is usually advantageous immediately thereafter to provide the surface to be treated with a thin skin or coat of a low melting metal, such as cadmium, with a view to protecting the surface against appreciable oxidation prior to the application of the ternary alloy. Such a protective coating can be applied with the aid of a usual plating bath. The coating is preferably made as thin as possible compatible with a sound envelope.

The metal article which has been protected by a thin coat of a protective metal such as cadmium loses all or substantially all of this protective metal coat on immersion in the molten bath of the ternary alloy under the temperature conditions prevailing in the bath, and in this way presents a metallurgically clean surface on which a uniform coating of the ternary alloy can be deposited and bonded.

Preferably in the application of the ternary alloy the article is moved rapidly through the bath and an electric current is passed through the bath and article while the latter is moved. This treatment is especially applicable to valves, which are rotated at a fairly high and uniform speed in the molten alloy. The thickness of the alloy coating on the valve surface can be controlled by adjusting the speed of rotation of the valve. It appears that above a certain speed the coating tends to become rather thin irrespective of the time of immersion, while, on the other hand, there is a minimum speed of rotation which is believed to be the range of the oxide coating for a minute below which the coating obtained is somewhat thick and uneven. The use of an electric current is efficacious whether the metal article is made anodic or cathodic and also when either direct or alternating current is employed, although it is preferable to use direct current. The mechanism involved in securing advantage with the aid of a small electric current passing through the valve or other article has not yet been elucidated, but it may be that this use of a small current assists in the formation of a satisfactory uniform coating properly bonded to the base metal by inhibiting any tendency towards oxidation of the metal surface under treatment.

Referring to Figure 1, coating may be applied in a furnace containing a block 8 of refractory material which supports a mandrel 11 in the form of a valve body which contains a molten bath 8 of the alloy. The furnace has a top opening 9 covered by a plate 10 which has a smaller opening 11 large enough to permit a suitable chuck 12 or other securing device and the valve 13 held thereby to be passed through it in the form of the lower part of the valve into the molten bath. The chuck is on a rotatable shaft 14 which is mounted on any suitable device (not shown) permitting it to be raised or lowered and rotated about its axis. For passing the electric current between the valve and the molten bath there is further provided a suitable source of electromotive force 15 which is connected by suitable electric conductors to an electrode 16 immersed in the bath and by brushes to a contact ring 17 on the shaft 14, it being understood that the ring is in electrical contact with the valve through the chuck 12.

After this coating of the surface with the alloy as aforesaid the article is subjected to a heat diffusion treatment which may be effected by heating the valve to a high temperature, for example, 1100°C. In a furnace or in a bath of salt, sodium cyanide, or a mixture of sodium cyanide and sodium carbonate. It is also possible to pass an electric current through the coated article and the bath during the heat diffusion treatment, whereby it is possible to use lower temperatures, for example, down to 600°C. The finished valve is shown in Figure 2 wherein the coating is drawn thicker for clarity and no effort is made to indicate the interdiffusion.

If desired, after the application of a thin skin of cadmium or other low melting metal and prior to the application of the ternary alloy, the article may be immersed in a bath of molten aluminum so as to provide it with a thin aluminum coat on which the ternary alloy is thereafter deposited. In providing the article or part thereof to be coated with such a deposit of aluminum the technique described above in connection with the application of the ternary alloy is likewise of advantage, namely, the article is moved, preferably in the case of a valve or other round object, at a uniform speed and a small electric current is passed through it during the movement.

While the preferred technique of application is as set out in the foregoing paragraphs, the application of these coatings may be the subject of some variations, many of which would suggest themselves to persons skilled in the art. Thus, for example, a valve not containing nickel may be given a coating of this metal, as, for example,
by electroplating, prior to the application of the ternary alloy, and the nickel coating may be protected by a skin of a low melting metal such as cadmium to prevent alloying and oxidation. Such a nickel coating may, for example, be between about 0.001 and 0.005 inch in thickness, and the ternary alloy may be coated thereon either directly or after applying a thin coating of aluminum.

Furthermore, in cases where the metal article is to be coated immediately after cleaning and etching with acid the initial application of a protective coat of a low melting metal such as cadmium may be found to be superfluous.

In the application of these ternary alloy coatings to various articles, such as internal combustion engine valves or parts thereof it will be readily apparent to those familiar with the metallurgical considerations involved that the proportions of these three metals in the coatings need to be chosen with due regard to the obvious desirability of securing subdued, uniform coatings. As already stated, coatings of nickel, cobalt, and aluminum alloy are preferred and the alloy employed for the production of such coating preferably contains:

- Aluminum, from 33 to 96%
- Nickel, from 2 to 65%
- Cobalt, from 2 to 65%

The change in the properties of these ternary alloys with varying proportions of nickel and cobalt are only gradual changes and while I prefer in most cases to use more than 2% of these metals it is not feasible to furnish specific lower limits at which the properties change abruptly. In general, I prefer to use between 50 and 70% aluminum, and between 5 and 45% nickel, and between 5 and 35% cobalt for the treatment of valves for internal combustion engines. It was found that an alloy containing 61% aluminum, 26% nickel and 13% cobalt is particularly efficacious. A ternary alloy of this approximate composition has a rigidity, that is, a resistance to distortion at high temperature such as 850° to 950° C., comparable with that of the binary alloy containing 60% aluminum and 40% nickel, and a melting point comparable with that of the binary alloy containing 70% aluminum and 30% nickel. The melting point of the latter binary alloy is lower than that of the binary alloy containing 60% aluminum and 40% nickel. This lower melting point facilitates the application of a coating to the metal article and in this respect the binary alloy containing 70% aluminum and 30% nickel is preferable to the binary alloy containing only 60% aluminum, but, on the other hand, the binary alloy with the higher aluminum content distorts more readily when subjected to a temperature of 850° C. for a few hours. It thus follows that the aforesaid ternary alloy possesses both the rigidity properties of the binary alloy containing 60% aluminum and 40% nickel and the property of easy application exhibited by the binary alloy containing 70% aluminum and 30% nickel. A satisfactory combination of these two properties cannot be found in any binary aluminum-nickel alloy.

While the desired coatings consist essentially of ternary alloys containing nickel, cobalt and aluminum, minor quantities of additional metals may also be present; thus, minor quantities of iron, chromium, titanium or manganese may also be present.

It should be understood that, while the composition of the alloy applied to the surface of the valve or other article determines the nature of the coating on the valve, the composition of the finished coating is not necessarily identical with that of the alloy used for application. The subsequent heat treatment gives rise to variations in the composition of the alloy on the metal article and there may also be diffusion of the base metal into the alloy.

It should also be understood that the surface of the coating resulting from the heat diffusion treatment is not generally of a texture which renders the valve best adapted for the duty it is designed to perform, and that surface finishing, as by grinding and polishing, is usually necessary.

Valves and other articles fabricated from ferrous and non-ferrous metals may be treated by the aforesaid technique, for example, valves made of austenite steel, stainless steels, or silicon-chromium heat resisting steels. Stellite valves may also be treated by the technique of this invention.

By way of illustration, the following example is furnished describing the application of a corrosion resistant coating to an internal combustion engine exhaust valve fabricated from an austenite steel.

The valve is cathodically degreased in a caustic soda-sodium carbonate bath for 30 to 15 minutes, using a current density of approximately 50 amp. per sq. ft., and then placed in an etching bath of sulfuric acid for a short time. On removal from this etching bath it is washed and immediately immersed in a standard cadmium plating bath in order to provide a thin cadmium coat of the order of thickness 0.0005 to 0.001 inch.

After washing and drying the cadmium coated valve it is immersed in a molten aluminum bath maintained at about 800° C., care being taken to ensure that all trapped air bubbles are released from the article as quickly as possible. A small electric current (for example, one having a current density of 1 to 2 amperes per sq. in. and a voltage of 4 volts) is passed from the valve to the bath for about 15 to 60 seconds, the valve being rotated during this period in an electrically driven chuck at a uniform speed, which is dependent upon the size of the valve head. For an engine valve having a head of approximately 1½ in. diameter, a speed of the order of 300 revolutions per minute is found to give a satisfactory coating. Valves with smaller heads could be subjected to a somewhat higher rate of rotation, e.g., 750 to 1500 revolutions per minute, while valves with larger heads can be rotated somewhat more slowly. Following this treatment the valve is steadily withdrawn from the bath, rotation being continued until the aluminum coating is solidified.

The aluminum coated valve is thereby immersed in a molten bath of nickel, cobalt and aluminum which metals are present in the approximate ratio 26:13:61, the bath temperature being in the region 1050° to 1100° C. In this bath the valve is subjected for about 60 seconds to the application of an electric current while being rotated at a uniform speed in a manner similar to that described above when applying the aluminum coat.

After the coated valve is removed from the bath of molten alloy it is cooled and again heated for about an hour in a furnace at 1,000° C. and thence carefully ground on a felt buff with fine emery, followed by a polishing treatment equivalent to that used for electro-plated articles.

If desired, the initial application of an aluminum coat prior to the application of the ternary
alloy may be omitted without substantial disadvantage.

The finished valve resulting from this treatment is found to exhibit excellent resistance to corrosion attack by the hot combustion products of leaded fuel formed during engine operation and to withstand serious attack even after severe engine operating conditions. This resistance to corrosion attack appears to be greater than any obtainable in the case of valves provided with binary nickel-aluminum coatings.

I claim as my invention:

1. A coated metal article having a body of a base metal and on at least a portion thereof a protective coating containing from 33% to 96% aluminum, from 2% to 65% nickel, and from 2% to 65% cobalt, said coating being resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead.

2. A coated metal article having a body of a base metal and on at least a portion thereof a protective coating which is the interdiffusion product with said base metal of a thin external layer consisting essentially of aluminum, nickel and cobalt, said coating containing from 33% to 56% of aluminum, from 2% to 65% of nickel, and from 2% to 65% of cobalt, and being resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead.

3. A coated engine valve comprising a body made of a base metal and having a protective coating on at least that part thereof which is exposed to attack by the products of combustion of engine fuel, said coating being the interdiffusion product with said base metal of a thin external layer containing from 50% to 70% of aluminum, from 5% to 45% of nickel, and from 5% to 45% of cobalt, said coating being resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead.

4. The valve according to claim 3 wherein the layer contains aluminum, nickel and cobalt in the approximate ratio 61:28:13.

5. A process for rendering metal articles resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead which comprises the steps of immersing said article in a bath of a molten alloy containing from 33% to 65% aluminum, from 2% to 65% nickel, and from 2% to 65% cobalt to deposit a thin coating of said material on at least that part of the article which is exposed to attack from said products of combustion.

6. The process according to claim 5 wherein the molten alloy contains from 50% to 70% aluminum, from 5% to 45% nickel, and from 5% to 35% cobalt.

7. A process for rendering metal valves for internal combustion engines resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead which comprises the steps of immersing said article in a bath of a molten alloy containing from 33% to 65% aluminum, from 2% to 65% nickel, and from 2% to 65% cobalt to deposit thereon a thin coating thereof at least on that part of the valve which is exposed to said products of combustion, withdrawing said valve from the molten bath, and subjecting the coated valve to a diffusion treatment at an elevated temperature above about 600° C.

8. The process according to claim 7 wherein at least the part of the valve to be coated is treated to form a dull mattly clean surface and said clean surface is coated with a thin skin of a low melting metal before immersion in said bath.

9. The process according to claim 8 wherein the valve is immersed in a bath of molten aluminum to deposit a thin coating of aluminum thereon prior to immersion in the said bath of molten alloy.

10. The process according to claim 8 wherein the valve is rotated at a uniform speed and an electric current is simultaneously passed through the bath and valve while immersed in said bath.

11. The process according to claim 8 wherein the valve is immersed in a bath of molten aluminum to deposit a thin coating of aluminum thereon prior to immersion in the said bath of molten alloy.

12. The process according to claim 8 wherein the molten alloy contains from 50% to 70% aluminum, from 5% to 45% nickel and from 5% to 35% cobalt.

13. A process for the manufacture of valves for internal combustion engines comprising the steps of cleaning at least the portion of a ferrous valve which is exposed to attack by the combustion products of engine fuel to provide a metallurgically clean surface, protecting said clean surface by applying a thin skin of a low melting metal, immersing the coated valve in a bath of molten alloy containing from 33% to 96% aluminum, from 2% to 65% nickel and from 2% to 65% cobalt, to deposit at least on said portion thereof a coating of said alloy, withdrawing the valve from said bath, and subjecting the coated valve to a diffusion treatment at a temperature above about 600° C.

14. The process according to claim 13 wherein the alloy contains from 50% to 70% aluminum, from 5% to 45% nickel and from 5% to 35% cobalt.

15. The process according to claim 13 wherein the alloy contains aluminum, nickel and cobalt in the approximate ratio 61:28:13.

16. A process for rendering a metal article resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead which comprises applying thereto a coating containing from 33% to 96% aluminum, from 2% to 65% nickel, and from 2% to 65% cobalt.

17. A process for rendering metal valves for internal combustion engines and made essentially of steel resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead, which comprises applying at least to the part thereof exposed to the products of combustion a coating containing from 33% to 96% aluminum, from 2% to 65% nickel, and from 2% to 65% cobalt.

18. A coated engine valve comprising a body made essentially of steel and having a protective coating at least on that part which is exposed to attack by the products of combustion of engine fuel, said coating being applied by immersing the valve in a molten alloy containing from 50 to 70% aluminum, from 5 to 45% nickel, and from 5 to 35% cobalt to deposit a thin coating thereon, and subsequently interdiffusing the said alloy with the steel, said coating being resistant to attack by lead compounds present in products of combustion of motor fuels containing tetrythyl lead.

19. The valve according to claim 18 wherein
the alloy contains aluminum, nickel and cobalt in the approximate ratio 61:26:13.

20. A coated metal article having a body of a base metal and on at least a portion thereof a protective coating containing from 5% to 45% nickel, from 5% to 35% cobalt, and the balance being substantially aluminum, the aluminum constituting at least 33% of the coating, said coating being resistant to attack by lead compounds present in products of combustion of motor fuels containing tetraethyl lead.

21. A coated engine valve comprising a body made essentially of steel and having a protective coating at least on that part which is exposed to attack by the products of combustion of engine fuel, said coating containing from 5% to 45% nickel, from 5% to 35% cobalt and the balance being substantially aluminum, the aluminum content of the coating being at least 50%, said coating being resistant to attack by lead compounds present in products of combustion of motor fuels containing tetraethyl lead.

22. A coated engine valve comprising a body made essentially of steel and having a protective coating at least on that part which is exposed to attack by the products of combustion of engine fuel, said coating containing from 50% to 70% aluminum, from 5% to 45% nickel, and from 5% to 35% cobalt, said coating being resistant to attack by lead compounds present in products of combustion of motor fuels containing tetraethyl lead.

References Cited in the file of this patent

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
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<tbody>
<tr>
<td>1,126,484</td>
<td>Kirby</td>
<td>Jan. 26, 1915</td>
</tr>
<tr>
<td>1,731,202</td>
<td>Phillips</td>
<td>Oct. 8, 1929</td>
</tr>
<tr>
<td>1,932,849</td>
<td>Dean et al.</td>
<td>Oct. 31, 1933</td>
</tr>
<tr>
<td>2,128,692</td>
<td>Whitfield</td>
<td>Nov. 8, 1938</td>
</tr>
<tr>
<td>2,273,250</td>
<td>Charlton</td>
<td>Feb. 17, 1942</td>
</tr>
</tbody>
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ROBERT GRAHAM.