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[54] **METHOD OF PRODUCING PLASMA SPRAYED TITANIUM CARBIDE TOOL STEEL COATINGS**

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[51] **Int. Cl.**^{2} **B05D 11/10**

[58] **Field of Search** .... 117/22, 93.1 PF, 105.2, 117/46 FS; 29/195 A

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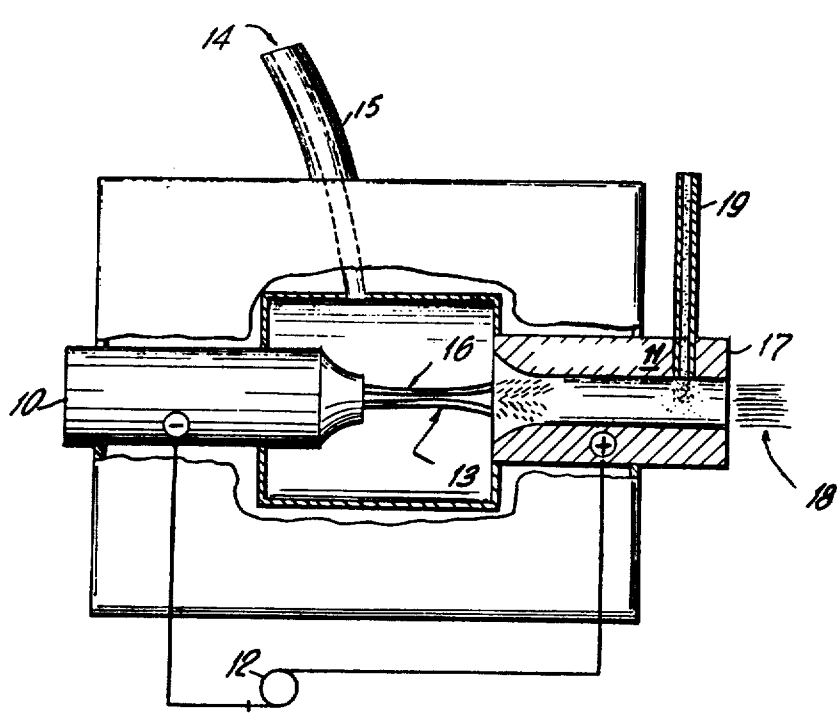
[57] **ABSTRACT**

A method is disclosed for quench-depositing by plasma spraying onto the substrate an adherent thin coating of a titanium carbide tool steel containing by weight about 10% to 80% of primary grains of TiC and the balance essentially about 90% to 20% of a steel matrix, such that the resulting coating is one characterized metallographically by the presence of martensite. The metal substrate may be aluminum. Preferably, the titanium carbide grains should be rounded to assure a low friction surface.

7 Claims, 2 Drawing Figures



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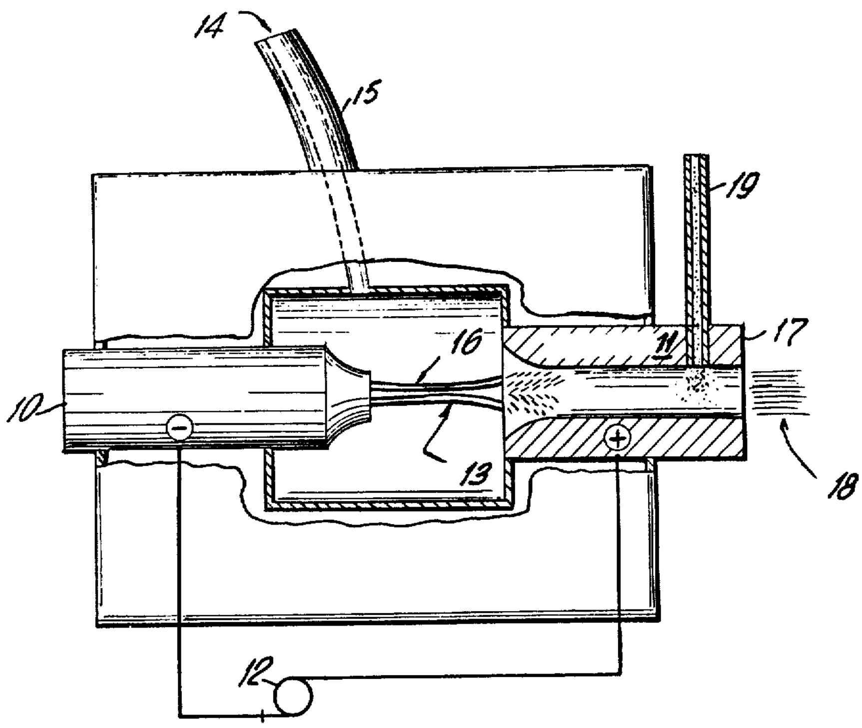

FIG.1

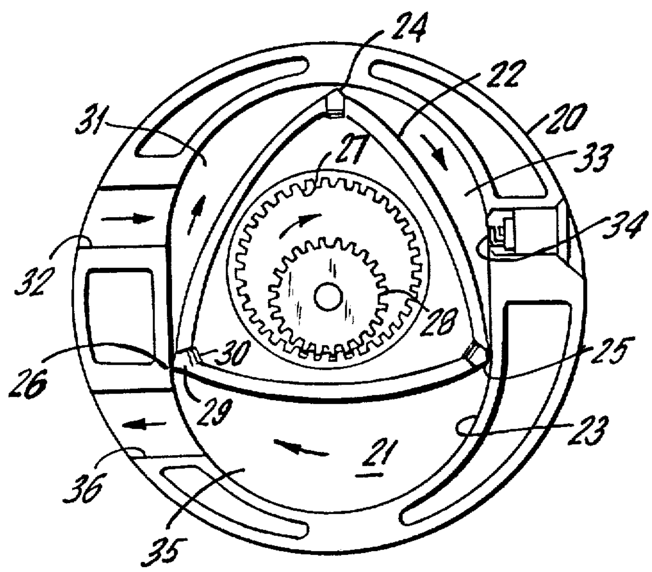

FIG.2

METHOD OF PRODUCING PLASMA SPRAYED TITANIUM CARBIDE TOOL STEEL COATINGS

This application is a division of copending U.S. application Ser. No. 199,497, filed Nov. 17, 1971, now U.S. Pat. No. 3,779,720.

This invention relates to a method for producing an adherent, hard, wear resistant coating of a heat treatable titanium carbide tool steel onto a metal substrate (e.g., steel) and, in particular, to a method for producing such coatings on relatively soft metal substrates, such as aluminum, copper, silver and the like, whereby the hard titanium carbide steel coating can be further heat treated, if desired, at temperatures below the melting point of the substrate metal. The invention also relates to composite metal structures produced by the method.

STATE OF THE ART

It is known to hard face metal substrates by using welding and brazing methods in which the metal substrate is simultaneously heated during the laying down of the hard facing material. Because of the general nature of the foregoing process, the metal substrates were limited to those having fairly high melting points, otherwise, the substrate would overheat and either melt or be adversely affected.

One attempt to enlarge the use of hard facing has been to employ flame spraying. This method comprises melting powder metal compositions in a heated zone and propelling the molten particles to the surface of a metal substrate to form a coating thereon. This method had its limitations as to the type of materials that could be sprayed. For example, if refractory carbide particles are sprayed, generally a matrix metal powder is mixed with it, e.g., nickel, cobalt, etc., and the mixture sprayed to provide the means by which to anchor the carbide particles to the receiving surface. So long as no further heat treatment is required of the coating, certain types of hard coatings could be produced, although they tended to be porous.

In recent years, a special kind of hard titanium carbide tool steel has been developed which, besides having the intrinsic hardness of the titanium carbide, also is capable of being further hardened very much as tool steel is hardened. For example, a titanium carbide tool steel containing 33% by weight of TiC (about 45% by volume) and the balance a chromium-molybdenum steel (note U.S. Pat. Nos. 2,828,202 and 3,416,976) requires a relatively high temperature for heat treatment. Thus, to obtain a martensitic matrix, the titanium carbide tool steel composition is quenched from about 1,750°F in oil. However, the foregoing heat treating temperature is higher than the melting point of certain metal substrates, such as aluminum. Moreover, the conventionally sprayed coatings tend to be quite porous.

Hard carbide coatings would be desirable on certain substrate metals, such as metals having relatively high thermal and electrical conductivity, for example, aluminum, copper, silver and the like. It would be desirable to provide such coatings having minimum porosity and exceptionally good wear resistance. Such coatings would be useful in providing long life electric contact metal having a hard, wear resistant contact face and a substrate of good thermal and electrical conductivity. Such coatings would also be useful in producing alumi-

num elements, e.g., a housing for the recently developed rotary combustion engine, having a hard surface coating to provide resistance to wear relative to the rotary piston in contact therewith.

OBJECTS OF THE INVENTION

It is thus the object of the invention to provide a method of producing a hard, dense wear resistant coating of a titanium carbide tool steel on a metal substrate.

Another object is to provide a method for producing a composite article of manufacture comprising a metal substrate having an adherent dense coating of a titanium carbide tool steel comprised metallographically of primary grains of titanium carbide dispersed substantially uniformly through a steel matrix characterized by an austenitic decomposition product comprising martensite. Other hard phases may be present, such as bainite, and the term "martensite" employed herein is meant to cover martensite with or without retained austenite and mixtures of martensite with bainite, with or without retained austenite.

An additional object is to provide a method for producing a titanium carbide tool steel coating characterized metallographically by rounded primary grains of titanium carbide, for example, on metal substrates of melting point above 1,100°F.

A still further object of the invention is to provide a method for forming a titanium carbide tool steel hardfacing coating on a metal substrate of aluminous metal in which the coating is comprised metallographically by primary grains of titanium carbide dispersed substantially uniformly through a steel matrix characterized by an austenitic decomposition product containing martensite.

These and other objects will more clearly appear when taken into consideration with the following disclosure and the accompanying drawing, wherein:

FIG. 1 depicts schematically a device for the plasma flame spraying of metal powder; and

FIG. 2 shows schematically a rotary combustion engine utilizing a heat treatable, titanium carbide steel as a hard-facing material on the inner end walls thereof.

STATEMENT OF THE INVENTION

Stating it broadly, the method aspect of the invention for producing a wear resistant coating of a heat treatable titanium carbide tool steel on a metal substrate resides in selecting a powder composition consisting essentially of about 10 to 80% by weight of primary grains of titanium carbide and the balance essentially 90 to 20% by weight of steel-forming ingredients and quench-depositing said composition from the molten state onto a metal substrate by means of a plasma flame which heats the steel ingredients to substantially above the melting point, whereby a dense, adherent coating of the composition is produced on the metal substrate, the coating being thin relative to the metal substrate and preferably ranging up to about 0.025 inch in thickness.

By employing the plasma flame for depositing the coating, rather high temperatures are obtained which melt the steel matrix of the composition at temperatures substantially above the melting point, such that thin coatings deposited on the metal substrate are drastically quenched by virtue of the cooling effect of the substrate to produce a microstructure comprising grains of titanium carbide dispersed through a matrix formed of an austenitic decomposition product containing martensite. The metal substrate should preferably have a melting point above 1100°F.

As stated hereinabove, very high temperatures are obtainable with the plasma flame. However, for most spray applications, a plasma temperature of about 12,000° to 20,000°F appears to be optimum. One of the advantages of the plasma flame is that it can be used with a controlled atmosphere. This is important to avoid decarburization of the steel matrix where carbon is essential to the heat treatment response to the titanium carbide tool steel. Thus, an inert gas or a chemically inactive gas can be employed for the flame medium.

The plasma flame is produced by striking an arc between a cathode and an anode and passing a plasma gas through the arc. By confining the arc in a chamber under pressure, the arc temperature can be increased. By constructing the anode as a hollow nozzle and introducing the plasma gas into the arc chamber and forcing it through the nozzle, the gas dissociates and ionizes in the arc stream and emerges from the nozzle as a plasma flame. A typical plasma gas is one comprised of 90% nitrogen and 10% hydrogen. Argon or other gases can be used in place of nitrogen.

A schematic representation of a plasma flame device is given in the accompanying drawing which shows cathode **10** and anode **11** electrically connected via power source **12** to produce an arc stream **13.** Plasma gas **14,** e.g., 90% nitrogen and 10% hydrogen, is fed through pipe **15** which is converted to plasma **16** which exits through nozzle **17** at a very high temperature as free plasma. Spray powder is fed through pipe **19** into the nozzle where it is heated by the plasma flame and exits with the free plasma towards the workpiece or substrate to be coated. Plasma guns for metal powder spraying are readily available and therefore need not be discussed any further than the schematic described above.

One of the advantages of plasma spraying is that relatively thin coatings can be sprayed which are dense and substantially free of large pores. By spraying thicknesses ranging up to about 0.025 inch, highly rapid quenching of the deposit is obtained generally comprised of martensite. Where the metal substrate is a metal of substantially high thermal conductivity, e.g., aluminum, copper, silver and the like, very hard coatings are obtained which can be further heat treated, e.g., tempered or aged, at temperatures below the melting point of the substrate. However, the coating can also be applied with advantageous results to ferrous metal substrates, e.g., steels.

DETAILS OF THE INVENTION

As illustrative of titanium carbide tool steel compositions that can be plasma sprayed onto metal substrates, the following examples are given.

EXAMPLE 1

Broadly, the titanium carbide tool steel is comprised essentially of about 10 to 80% by weight of primary grains of titanium carbide dispersed through a steel matrix making up about 90% to 20% of the balance. The steel may be low and high carbon steel, medium alloy steel or high alloy steel containing at least 50% iron which, when cooled substantially rapidly from above the melting point, provides metallographically a matrix containing an austenitic decomposition product containing martensite. In this connection, reference is made to U.S. Pat. No. 2,828,202. Examples of such matrix steels are: SAE 1010 to SAE 1080 steels, and including the following illustrative composition, to wit: 0.8% Cr, 0.2% Mo, 0.3% C and iron substantially the balance; 5% Cr, 1.4% Mo, 1.4% W, 0.45% V, 0.35% C and iron substantially the balance; 8% Mo, 4% Cr, 2% V, 0.8% C and iron substantially the balance; 18% W, 4% Cr, 1% V, 0.75% C and iron substantially the balance; 20% W, 12% Co, 4% Cr, 2% V, 0.8% C and iron substantially the balance.

A preferred composition is one containing about 1 to 6% Cr, about 0.3 to 6% Mo, about 0.3 to 0.8% C and the balance essentially iron.

EXAMPLE 2

A particular titanium carbide tool steel is one containing 10 to 80% by weight of TiC and the balance essentially a high chromium high carbon steel containing about 6 or 7 to 12% chromium, 0.6 to 1.2% carbon, 0.5 to 5% molybdenum, up to about 5% tungsten, up to about 2% vanadium, up to about 3% nickel, up to about 5% cobalt, and the balance essentially iron. A preferred composition of the foregoing high chromium, high carbon steel is one one containing about 10% chromium, 1% carbon, 3% molybdenum, 1% vanadium, and the balance essentially iron. This steel is characterized in that it forms martensite when applied from a plasma spray onto a relatively cold substrate, e.g., steel, aluminum, and the like and, by double tempering at 1,000°F for 1 hour each, the hardness is further augmented by secondary hardening, while, at the same time, the coating is substantially stress relieved of any thermal stresses due to the rapid cooling when deposited. As will be noted, the tempering temperature (1,000°F) is below the melting point of aluminum.

EXAMPLE 3

As illustrative of another titanium carbide tool steel composition that can be plasma sprayed onto a metal substrate and which can be further heat treated at a temperature below the melting point of the substrate is a heat treatable, low carbon nickel-containing titanium carbide tool steel (note U.S. Pat. No. 3,369,891). As in the foregoing examples, the titanium carbide ranges from about 10 to 80% by weight and the steel matrix from about 90% to 20% by weight. The matrix composition contains by weight about 10 to 30% nickel, 0.2 to 9% of titanium, and up to about 5% aluminum, the sum of the titanium and aluminum not exceeding about 9%, up to about 25% cobalt, up to about 10% molybdenum, and substantially the balance of the matrix at least about 50% iron; the metals making up the matrix composition being proportioned such that when the nickel content ranges from about 10 to 22% and the sum of the aluminum and titanium is less than 1.5%, the cobalt and molybdenum contents are each at least about 2%; and such that when the nickel content ranges from about 18 to 30% and the molybdenum content is less than 2%, the sum of the aluminum and titanium exceeds 1.5%.

When the foregoing titanium carbide tool steel is deposited from the plasma flame and rapidly quenched, the metallographic structure is essentially soft martensite. In this condition, the carbide steel in the form of a coating can be age-hardened by heating it to a temperature of about 500°F to 1,200°F (260°C to 650°C) for about 3 hours. A typical age-hardening temperature is 900°F (483°C). As will be noted, the age-hardening temperature is below the melting point of aluminum. Normally, the solution temperature for obtaining soft martensite in the matrix ranges from about 1,400°F to 2,150°F (760°C to 1,165°C). As will be observed, the foregoing temperature range is above the melting point of aluminum. However, a solution treatment is not necessary for the coating since the steel is solution-quenched due to the rapid cooling following plasma spraying of the composition.

A typical composition is one containing about 35% by weight of TiC and the 65% remainder a steel matrix containing 21.7% Ni, 8.49% Co, 3.42% Mo, 0.37% Ti and the balance essentially iron. The alloy upon aging at 900°F (483°C) for 3 hours exhibited a hardness of about 60 R_c.

It is preferred when working with compositions of the type illustrated in Examples 1, 2 and 3 to work with a pre-alloyed titanium carbide tool steel. This assures the presence of rounded grains of titanium carbide which not only provides resistance to wear but also imparts very low coefficient of friction. This is important in applications involving the continuous rubbing of parts, such as occurs in the rotary combustion engine where the apices of the rotary piston are in continuous contact with the inner side walls of the housing. Where the housing is made of aluminum, a face coating of a titanium carbide tool steel of the type illustrated in Example 2 provides adequate resistance to wear and in addition low coefficient of friction by virtue of the rounded grains of TiC.

In assuring the rounded grain structure of titanium carbide, the titanium carbide tool steel is prealloyed by liquid phase sintering a powder metallurgical composition of the carbide steel. The pre-alloyed carbide steel is then ground into a particle size passing through 200 mesh for use in plasma spraying.

In producing a pre-alloyed steel composition with rounded grains of TiC, the following method is employed.

A titanium carbide tool steel composition containing 33% by weight of TiC (45% by volume) and substantially the balance a steel matrix, such as a chromium-molybdenum steel composition, is produced by mixing 500 grams TiC (of about 5 to 7 microns in size) with 1000 grams of steel-forming ingredients in a mill half filled with stainless steel balls. To the powder mix is added 1 gram of paraffin wax for 100 grams of mix. The milling is conducted for about 40 hours using hexane as a vehicle. A specific steel-forming composition for the matrix is one containing 0.5% C, about 3% Cr, about 3% Mo and the remainder substantially iron. It is preferred to use carbonyl iron powder in producing the mixture. A carbidic tool steel of the foregoing type is disclosed in U.S. Pat. No. 3,416,976.

Following completion of the milling, the mix is removed and dried and compacts of the desired shape pressed at about 15 t.s.i. and the compacts then subjected to liquid phase sintering in vacuum at a temperature of about 2,640°F (1,450°C) for about one-half hour at a vacuum corresponding to 20 microns or less. After completion of the sintering, the compacts are cooled and then removed from the furnace. The primary titanium carbide grains which are angular before sintering, assume a rounded configuration as a result of liquid phase sintering. By "liquid phase sintering" is meant heating the compact to above the melting point of the steel matrix but below the melting point for titanium carbide, for example, up to about 180°F (100°C) above the melting point of the steel matrix.

Following the production of the sintered compact, the sintered compact may be converted into chips by machining and the chips milled in a ball mill to a size passing through 200 mesh (e.g., 1 to 5 microns). The powder is cleaned and dried for use for plasma flame spraying. As stated above, rounded titanium carbide grains are preferred in the ultimate coating since this configuration imparts low friction characteristics to the coating, the rounded grains being advantageous in wear application.

Wear is a combination of corrosion, erosion, abrasion, friction, sulfidation, fatigue, fretting and oxidation in which the net result is surface deterioration. An advantage of using a titanium carbide steel as a hard-facing material is that it has a low density compared to other hard-facing materials and provides good resistance to the foregoing phenomena. It has certain economic advantages since a unit weight of the foregoing hard-facing material on a volume basis covers more surface area of a metal substrate in comparison to the conventional hard-facing materials containing tungsten carbide which have a substantially higher density.

The rounded grain structure of titanium carbide, as stated hereinabove, is ideal because it imparts a low coefficient of friction to the coating and also because titanium carbide has a very high intrinsic hardness and, therefore, exhibits a very high resistance to wear. Moreover, the "as-coated" surfaces of this hard-facing material obtained after plasma spraying are quite smooth, e.g., about 100 to 150 microinches rms, otherwise referred to as "root-mean square average" (square root of mean square). This is advantageous because the coated surface can be inexpensively buffed to provide maximum resistance to wear, resistance to galling and low friction. The dense deposited coating can be finished to a smoothness of less than 5 microinches rms, using diamond lapping compounds and other specialized techniques.

In plasma spraying a metal substrate, the surface thereof is degreased, cleaned and preferably grit blasted with chilled iron grit or pure aluminum oxide grit to insure good adhesion of the hard-facing alloy to the base material. The hard-facing material in the finely powered form (−200+325 mesh) is fed into the stream of a superheated plasma gas. The particles are melted and are carried by the gas at high velocity to the surface being plated. A coating can be built up to the desired thickness by forming multiple layers. It is preferred that the coating be thin and preferably range up to about 0.025 inch and, more preferably, up to about 0.015 inch, to minimize cracking due to cooling stresses. Compared to most conventional coatings, the titanium carbide steel coating assured good mating compatability with metal substrates due to its low coefficient of thermal expansion. This property makes this material attractive for wear resistant applications in the automotive and aircraft industries.

As illustrative of a preferred embodiment of the invention, the following example is given:

EXAMPLE 4

A pre-alloyed titanium carbide tool steel produced by liquid phase sintering was employed as the plasma spray powder, the mesh size of the powder being in the range of about −170 to +325, the composition consisting essentially of about 33% by weight of TiC and 67% by weight of a steel matrix having the following composition by weight: 3% Cr, 3% Mo, 0.5% C and the balance essentially iron.

A plate of aluminum (AMS-4026) was employed as the metal substrate. The plasma gas used comprised 90% nitrogen and 10% hydrogen. The aluminum surface was degreased and grit blasted with pure aluminum oxide (−60) mesh) grit to provide a surface to promote adherence of the coating. Two coatings of 0.007 inch were produced, one by spraying in air and the other by plasma spraying in air using an argon shield to minimize formation of oxides in the coating.

The plasma spraying was conducted using a plasma spray gun referred to in the trade as "Metco plasma flame spray system" consisting of a specially constructed torch-type gun in which powdered coating material, suspended in a suitable carrier gas (N_2), was fed into a chamber in which plasma gas was "excited" to high temperatures by an electric arc.

Metallographic examination of each of the coatings showed the constituents of the coating to be uniformly distributed. The coatings were substantially free from cracks, massive porosity characteristic of conventionally flame sprayed coatings and substantially free from excessive oxides. The specimen sprayed with the argon shield showed less oxides present than the one sprayed without the shield. The coatings were essentially free from inclusions at the coating substrate metal interface. The interface itself appeared to be well pronounced with practically no porosity. The overall porosity in the coating was approximately 8 or 9% which is considered good.

Microhardness of the thin coating was determined across its thickness and found to range from about 650 to 770 VHN (200 gram load) which corresponds to a Rockwell "C" hardness of about 52 to 60. This hardness is characteristic of the presence of an austenitic decomposition product containing martensite. The foregoing steel composition in the annealed state (pearlitic microstructure or spheroidized carbon) normally has a hardness in the neighborhood of 40 R_C.

Thus, the invention enables the production on an aluminous metal substrate with a hardened titanium carbide steel coating without the necessity of quench hardening the coating from an austenitizing temperature of about 1,750°F which is above the melting point of the aluminous substrate. The quenching effect achieved during the deposition of the coating provides the desirable austenitic decomposition product.

No spalling, chipping, flaking, cracking, and the like, were observed on the coating surface and the general quality was good.

In a test to evaluate the adherence of the coating, a test panel of aluminum (AMS-4026) of about 3×1.75 and 0.05 inches in size was plasma coated with the same steel composition to a thickness of 0.005 inch. The coated panel was then subjected to a cup test in accordance with the Pratt & Whitney Aircraft Materials Control Laboratory Manual (Section E-53, 1963 Revision) using a 0.875 inch diameter ball and a die with a 1.375 inch diameter opening to form a depression in the panel of approximately 0.300 inch. The coating did not exhibit any separation from the base metal indicating that the plasma sprayed coating had good bond strength.

A quench deposited coating of the same steel composition was produced on aluminum having a thickness of about 0.015 inch. This coating had a quench-deposited hardness of over 50 R_C and up to about 60 R_C, indicating the presence of martensite in the coating. The coating was uniform, dense and crack-free. Hardened coatings of this type can be tempered at temperatures below the melting point of the metal substrate. A typical temperature for this steel may range from about 200°F to 500°F.

EXAMPLE 5

A hard-facing composition particularly resistant to softening at elevated temperatures ranging up to about 1,000°F is one comprising about 35% by weight of TiC and the balance 65% of a steel matrix comprising essentially about 10%, Cr, 3% Mo, 0.8% C and the balance essentially iron. As in Example 4, this steel composition is provided essentially in the pre-alloyed condition to assure the presence of rounded primary grains of TiC dispersed through the steel matrix.

A powder of the foregoing titanium carbide tool steel of −200+325 mesh is plasma sprayed onto a mild steel substrate of about one-fourth inch thick to produce a coating thickness of about 0.01 inch, the produced coating being quench deposited by virtue of the mass of metal substrate which rapidly cools the coating sufficiently to provide a martensitic-bearing metallographic structure. The hardness of this coating will generally be in the range of about 50 to 55 Rockwell "C." However, this steel composition can be further hardened by utilizing its secondary hardening characteristic by the formation of secondary carbides by heating the coated metal substrate and the coating to about 1,000°F and holding at the temperature for about 1½ hours. Thus, heating to 1,000°F will have a two-fold function; (1) to utilize the secondary hardening characteristics of the titanium carbide steel composition, and (2) to minimize the effect of any residual thermal stresses in the coating arising from the rapid quenching of the coating during deposition from the plasma flame.

EXAMPLE 6

In addition to the foregoing example, some heat treatment data were obtained on two plasma-coated aluminum substrate specimens.

Substrate A was coated with a pre-alloyed titanium carbide tool steel containing 35% by weight of TiC and the balance a steel matrix containing 3% Cr, 3% Mo, 0.5% C with the remainder iron.

Substrate B was coated with a pre-alloyed titanium carbide tool steel containing 35% by weight of TiC and the balance 10% Cr, 3% Mo, 0.8% C with the remainder iron.

Hardness readings were obtained for the coatings as sprayed and for the coatings double tempered at 975°/950°F. Each was tempered for 1 hour at temperature, cooled and tempered again for one hour. The results obtained are given in the following table.

Aluminum Substrate	Condition	Microhardness (Vickers)	Rockwell "C" (Converted)
A	As sprayed	859 (Av. of 7 readings)	65.9
	Double Tempered	788 (Av. of 7 readings)	63.5
B	As sprayed	620 (Av. of 5 readings)	56.5
	Double Tempered	1048 (Av. of 6 readings)	69.4

It will be noted that the hardness on Substrate A only dropped a few points after double tempering; whereas, the hardness on Substrate B increased markedly by about 13 points, apparently due to secondary hardening.

Example 7

This hard-facing titanium carbide steel composition is advantageous in that the coating deposited on a substrate, such as aluminum, can be hardened after deposition by heat treatment at a temperature below the melting point of aluminum or other substrate metal. A particular composition is one containing 30% by weight of titanium carbide and the balance of 70% essentially a steel matrix containing about 21.5% Ni, 8.5% Co, 3.4% Mo, 0.4% Ti and the balance essentially iron.

The foregoing steel in the pre-alloyed condition and as a powder of −150+325 mesh size is plasma sprayed onto aluminum as described in Example 4. By using a steel matrix very low in carbon, e.g., below 0.15%, soft martensite is obtained in the coating. After the substrate has been coated, the substrate and the coating are heated to a temperature of about 900°F as described in Example 3 to harden the steel to the desired hardness.

An advantage of the foregoing steel composition is that the coating can be buffed to the desired smoothness and then age hardened at the foregoing temperature to desired hardness.

The methods described in Examples 4 to 7 can be applied to a large variety of metal substrates. The method is particularly applicable to the coating of metal substrates of relatively high thermal and electrical conductivities, such as aluminum, copper, silver and the like. In this connection, the invention is applicable to such metal substrates as steels, iron-base alloys, nickel and nickel-base alloys, cobalt and cobalt-base alloys and, generally, to those metals having melting points above 1200°F.

The invention is particularly applicable to those metal substrates having thermal and electrical conductivities of at least 0.2 referred to high electrical and thermal conductivity copper taken as 1. Thus, the invention is applicable to the coating of the metals aluminum, copper and silver and Al-base, Cu-base and Ag-base alloys. The metals copper and silver and their alloys have particular use in electrical contacts where wear resistance of the contacting face may be important.

Certain steel substrates can be further augmented in their properties by plasma spraying thereon a titanium carbide tool steel composition of the type disclosed herein. One advantage of plasma spraying such substrates is in the building up of worn dies or dies inadvertently produced with an undersize.

A particular hard facing coating mentioned hereinbefore is one containing 10 to 80% by weight of TiC and the balance a steel matrix containing about 6 or 7% to 12% Cr (preferably 8 to 12%), about 0.6 to 1.2% C, about 0.5 to 5% Mo, up to about 5% W, up to about 2% V, up to about 3% Ni, up to about 5% Co and the remainder essentially iron.

A specific coating composition is one containing about 40 to 50 % by weight TiC, and the balance a steel matrix containing about 10% Cr, about 1% C, about 3% Mo, about 1% V and the remainder essentially iron. Examples of two steel substrates coated with the foregoing type of composition are as follows.

EXAMPLE 8

The coating is applicable to a steel substrate bearing the AISI designation S2 (silicon tool steel) having the following composition: 0.5 – 0.6% C, 0.4 – 0.6% Mn, 0.7 – 1.2% Si, 0.15 – 0.3 V, 0.4 – 0.6 Mo and the balance essentially iron. This steel exhibits good resistance to shock. This property can be further augmented by providing a hard coating on the surface thereof by plasma spraying the following composition by weight: about 40% TiC dispersed through a steel matrix containing about 10% Cr, 1% C, 3% Mo, 1% V and the remainder essentially iron. The coating is deposited (about 0.015 inch thich) by plasma spraying in accordance with the method of Example 4. After the coating has been smoothed by buffing, it is tempered at about 950°/975°F for about 1 hour, cooled and then tempered again at the same temperature for 1 hour to increase the hardness of the coating still further. Following tempering, the coated substrate is ground to finished size. Generally, the tempering temperature may range from about 900°F to 1050°F.

EXAMPLE 9

A worn die punch of a titanium carbide tool steel is built up by plasma spraying the surface thereof with a coating composition similar to Example 8 containing by weight about 50% TiC dispersed through a steel matrix containing 10% Cr, 1% C, 3% Mo and the balance essentially iron. The composition of the substrate comprises 35% TiC by weight in a steel matrix containing 3% Cr, 3% Mo, 0.5% C and the balance essentially iron. The coating is deposited to a thickness of about 0.01 inch, smoothed by buffing and then double tempered as in Example 8 at 950°/975°F. Following tempering, the coated die punch is finished ground to the desired dimension. While the substrate is hard, the coating provides additional hardness and markedly improved wear resistance in light of the higher titanium carbide content.

Thus, the invention provides as articles of manufacture composite metal structures of ferrous and nonferrous metal substrates with adherent coatings of titanium carbide steel compositions. Examples of such composite metal structures produced by plasma spraying are as follows.

Substrate Metal	Titanium Carbide Steel Coating
Alloy Steel	20% TiC and 80% steel matrix containing 3% Cr, 3% Mo, 0.5% C and the balance essentially iron
Nickel	30% TiC and 70% steel matrix containing 8% Mo, 4% Cr, 2% V, 0.85% C and the balance essentially iron
Aluminum	35% TiC and 65% steel matrix containing

-Continued

Substrate Metal	Titanium Carbide Steel Coating
	5% Cr, 1.4% Mo, 1.4% W, 0.45% V, 0.35% C and the balance essentially iron
Aluminum	40% TiC and 60% steel matrix containing 8% Cr, 3% Mo, 1% V, 0.9% C and the balance essentially iron
Copper	35% TiC and 65% steel matrix containing 20% Ni, 1.75% Ti, 0.8% Al, 0.15% C, 0.5% Mn, 0.2% Si and the balance essentially iron
Silver	60% TiC and 40% steel matrix containing 10% Cr, 2% Mo, 2% W, 1% C and the balance essentially iron

As will be apparent, the metal substrate may be selected from the group consisting of steel and non-ferrous metals. The non-ferrous metals of particular use as substrates are aluminum, copper and silver and alloys based on these metals, e.g., aluminum-base, copper-base and silver-base alloys.

As stated hereinbefore, the coating material should preferably be pre-alloyed before spraying so as to assure the presence of rounded grains of primary titanium carbide dispersed through a martensitic-containing steel matrix. The coatings in the foregoing table by virtue of plasma spraying are generally characterized by the presence of martensite in the matrix. If the matrix is too soft, then preferential wearing of the matrix will result in dislodgement of titanium carbide and the gradual fretting away of the coating material.

Present developments in the rotary combustion engine contemplate the use of an aluminum housing. The rotating piston which has a generally triangular shape is in contact with the end walls of the housing by means of the apices thereof which require the use of a seal material as a seal-off between the spaces defined between the apices. The seal must have wear resistance. However, the aluminum in the housing is generally soft compared to most materials of construction and has poor wear resistance. By plasma spraying the inner walls of the aluminum housing with a hard facing material of a titanium carbide tool steel composition having low friction properties, the life of the housing can be prolonged. An aluminum housing is desirable as it is capable of being air cooled easily in view of its high thermal conductivity. The heat treatable hard facing material should preferably be temper resistant so as to resist softening due to the generation of heat in the piston during fuel combustion.

A coating material which appears promising in that regard for the aluminum housing is one containing by weight about 10 to 80% TiC and the balance 90 to 20% of a steel matrix containing 6 or 7 to 12% Cr, 0.5 to 5% Mo, 0.6 to 1.2% C and the balance substantially iron. The matrix composition may contain up to about 5% W, up to about 3% Ni, up to about 5% Co, up to about 2% V, amounts of Mn and Si usually found in steel and the balance essentially iron. A specific composition is one containing 10% Cr, 3% Mo, 1% C and the balance essentially iron. This steel resists tempering at temperatures as high as 1,000°F and in fact increases in hardness due to a secondary hardening effect at the latter temperature.

FIG. 2 shows schematically a rotary combustion engine comprising an aluminum housing **20** having a chamber **21** in which is mounted a triangularly shaped rotary piston **22** in sealing contact with the end wall **23** of the chamber at its apices **24** to **26**. The rotary piston has an internal gear mounted thereon which is driven by gear **28** mounted on a shaft running perpendicular to the rotary piston. The hard facing material is applied to end wall **23** as shown by the heavy line to provide sufficient wear resistance to the material of the apices in rubbing contact with the end wall. The material of the apices may comprise spring mounted inserts **29** of the same titanium carbide tool steel maintained in continual sealing contact with the end wall via spring **30**.

In operation, as the piston rotates, fuel and air are received at intake zone **31** through intake **32**. The fuel-air mixture is then compressed and fired in compression zone **33** via spark plug **34** and the combusted gases at exhaust zone **35** exhausted through outlet **36**. The temperature in the chamber rises to levels which may tend to temper certain heat treatable steels. However, by employing a hard facing material described hereinabove containing about 35% by weight of TiC dispersed through a steel matrix containing about 10% Cr, 3% Mo, 1% C and the balance essentially iron, a temper resistant surface is provided capable of being heated up to about 1,000°F without substantially diminishing in hardness and, if anything, increases in hardness due to a secondary hardening effect engendered by the precipitation of secondary carbides containing chromium and/or through decomposition of retained austenite. By assuring the presence of rounded grains of titanium carbide in both the inserts of the seal and the end wall hard facing material, low friction is assured during operation of the engine.

It is to be understood that the term "steel substrate" referred to herein also includes cast steels, cast irons and the iron-base materials.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. A method of producing a hard, wear resistant coating of a heat treatable titanium carbide tool steel onto a metal substrate which comprises,

selecting a powder composition containing about 10 to 80% by weight of primary grains of titanium carbide and the balance essentially about 90 to 20% by weight of steel-forming ingredients which, when melted to form a steel and quenched from an austenitizing temperature, tends to form martensite,

and then spraying said powder composition with a plasma flame directly onto said metal substrate to quench-deposit a thin coating of said composition thereon of thickness ranging up to about 0.025 inch,

thereby producing an adherent thin coating of said titanium carbide tool steel composition on said metal substrate characterized by primary grains of titanium carbide uniformly dispersed through a matrix containing an austenitic decomposition product containing martensite, and further characterized in that said coating is capable of being heat treated at a temperature below the melting point of the metal substrate.

2. The method of claim 1, wherein the powder composition prior to spraying is a pre-alloyed composition characterized in that the titanium carbide grains in the particles thereof are rounded and dispersed through a steel matrix, such that the resulting adherent coating is characterized by the presence of said rounded grains of titanium carbide.

3. The method of claim 2, characterized in that the steel matrix is selected from the group consisting of (A) about 1 to 6% Cr, about 0.3 to 6% Mo, about 0.3 to 0.8% C and the balance essentially iron; (B) about 6% to 12% Cr, about 0.5 to 5% Mo, about 0.6 to 1.2% C, up to about 5% W, up to about 2% V, up to about 3% Ni, up to about 5% Co and the balance essentially iron; and (C) a high nickel alloy steel containing about 10 to 30% Ni, about 0.2 to 9% Ti, up to about 5% Al, the sum of the Ti and Al content not exceeding about 9%, up to about 25% Co, up to about 10% Mo, substantially the balance of the matrix being at least about 50% iron, the metals making up the matrix composition being proportioned such that when the nickel content ranges from about 10 to 22% and the sum of Al and Ti is less than about 1.5%, the molybdenum and cobalt contents

are each at least about 2%, and such that when the nickel content ranges from about 18 to 30% and the molybdenum content is less than 2%, the sum of Al and Ti exceeds 1.5%; said matrix produced from compositions (A), (B) and (C) being characterized metallographically by the presence of martensite.

4. The method of claim 3, wherein the metal substrate is characterized by a thermal and electrical conductivity relative to copper taken as 1 of at least about 0.2.

5. The method of claim 3, wherein the metal substrate is selected from the group consisting of steel and non-ferrous metals having a melting point above 1,100°F.

6. The method of claim 4, wherein said metal substrate is selected from the group consisting of aluminum, copper and silver and alloys based on said metals.

7. The method of claim 3, wherein the coating is derived from composition (B) and wherein after the coated substrate has been produced, it is tempered at a temperature of about 900°F to 1,050°F for a time at least sufficient to increase the hardness of the coating.

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