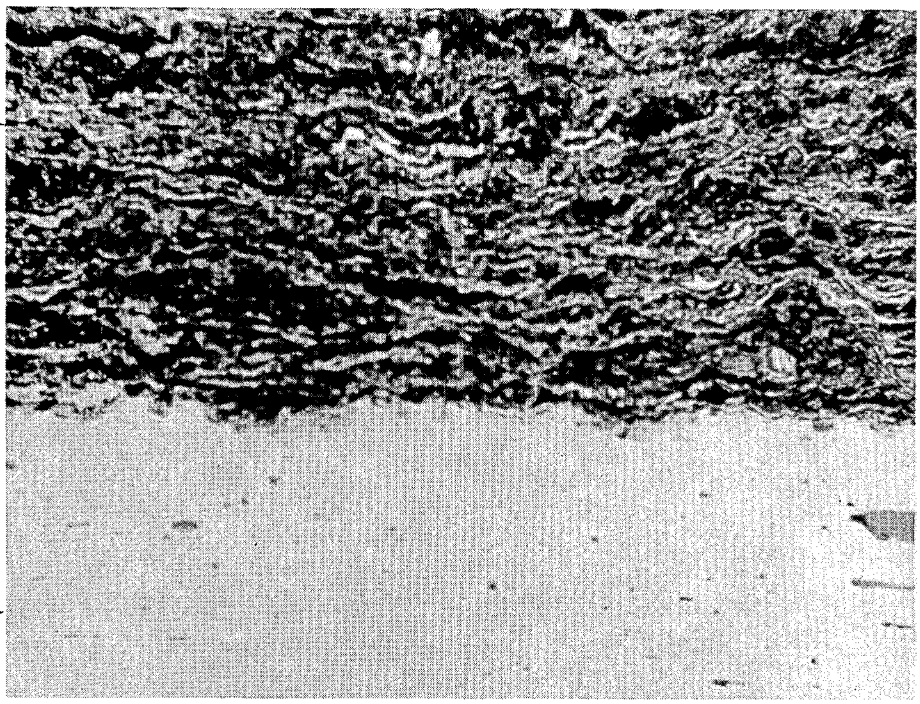
Dec. 13, 1960 R. M. POORMAN ET AL 2,964,420

REFRACTORY COATED BODY

Filed June 14, 1955

WC
Tungsten
Carbide
Alloy



S
Steel
Base

INVENTORS
RICHARD M. POORMAN
HERBERT B. SARGENT
HEADLEE LAMPREY

BY William F. Mesinger
ATTORNEY

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REFRACTORY COATED BODY

Richard M. Poorman, Speedway, and Herbert B. Sargent, Indianapolis, Ind., and Headlee Lamprey, Lakewood, Ohio, assignors to Union Carbide Corporation, a corporation of New York

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3 Claims. (Cl. 117—21)

The present invention relates to coated bodies, and, more particularly, to bodies coated by methods employing detonations.

By the term "detonation" is meant a very rapid combustion in which the flame front moves at velocities higher than the velocity of sound in the unburned gases, and therefore characterized as supersonic velocities. The rate of flame propagation is far greater in a detonation than in an explosion, which is a combustion in which the velocity of flame propagation does not exceed the velocity of sound in the unburned gases.

The flame of a detonation moves into the unburned gas with a velocity which is supersonic instead of subsonic, and it is initiated by and remains associated with a shock front. Once established in a long tube, the detonation wave travels at a constant velocity.

Detonations in gases have not been considered commercially useful. Where they have occurred they have been thought to be objectionable. The prime object of this invention is to provide bodies having adherent coatings of high melting point (refractory) abrasion-resistant (hard surface) materials by utilizing the phenomenon of a detonation. For example, the invention provides dense adherent lamellar coatings by employing detonations to impart a high velocity and a high temperature to particles, and to project the speeding particles against a surface to be coated.

The method of projecting particles to provide coatings in accordance with the present invention is described in great detail in our copending application Serial No. 275,332, filed March 7, 1952, now Patent No. 2,714,563.

In that method, a single fluid fuel charge or a rapid succession of fluid fuel charges of proper composition to be detonated is fed into a gun where it is ignited to establish a single detonation or a series of detonations following one another at short time intervals. Into this gun particles such as powder are introduced in such manner that they are accelerated by the detonations and their associated phenomena and projected from the open end of the gun onto the surface of the body desired to be coated.

The single figure of the drawing is a photomicrograph at 300 diameters' magnification showing, as one embodiment of the present invention, a steel workpiece having a coating of tungsten carbide-cobalt composition.

In accordance with the present invention a composite article is provided comprising a body, such as metal, glass, plastic, or the like having mechanically bonded thereto a thin adherent impacted lamellar coating of hard surface material. The coating comprises at least 70% of at least one material selected from the group consisting of the refractory metals, carbides, borides, nitrides, oxides and silicides having a melting point greater than approximately 2370° F. Where the refractory coating material is not alone capable of bonding to itself or to the surface of the body to be coated, the coating composition may additionally comprise up to approximately 30% of at least one member selected from the group consisting of metals and metal alloys capable of bonding the selected group material to itself and the body to be coated.

The coating of the article of the invention has greater than approximately 600 Diamond Pyramid hardness when tested with a 300 gram load, less than approximately 3% porosity, and a bulk density substantially identical with that of the solid material of the same composition.

Some of the refractory coating materials which have been successfully employed to produce articles embodying the invention are listed in the table below:

Table

Metals.—Tungsten (W) both with a cobalt binder and without a binder; tantalum (Ta) without a binder; columbium (Nb) without a binder; molybdenum (Mo) both with an 18% cobalt binder and without a binder.

Carbides.—Tungsten carbide (WC) with a 12% cobalt binder, with a 12% nickel binder, with an iron-nickel binder, with a 6% copper—2% aluminum—6% chromium binder, with a chromium-molybdenum binder, with a chromium binder, with a silver binder, or without a binder; titanium carbide (TiC) with a 20% cobalt or with a 20% nickel binder; boron carbide (B_4C) with an iron binder, a nickel and a ferrochromium binder, and without a binder; chromium carbide (Cr_3C_2) with a 25% cobalt or with a 25% nickel binder, or without a binder; tantalum carbide (TaC) with a 20% cobalt binder.

Borides.—Titanium boride (TiB_2) with an iron and a cobalt-tantalum binder; chromium boride (CrB_2) with a 20% iron binder.

Nitrides.—Titanium nitride (TiN) with a 25% copper, 25% cobalt, a 25% nickel binder, or without a binder.

Silicides.—Molybdenum disilicide ($MoSi_2$) with a 10% cobalt, a 15% chromium and a 20% silicon binder, or without a binder.

Oxides.—Aluminum oxide with a nickel binder, a chromium binder, or without a binder; titanium dioxide without a binder; chromium oxide without a binder; tantalum oxide without a binder.

Mixtures and alloys.—Tungsten carbide and titanium carbide alloy with a cobalt binder; titanium carbide and tantalum carbide alloy with a cobalt binder; 50% chromium—40% molybdenum—10% tantalum oxide; 50% chromium—40% tungsten—10% tantalum oxide; 40% chromium boride and 40% titanium boride with a 20% nickel binder; tungsten carbide—25% chromium—20% molybdenum—5% tantalum oxide; tungsten carbide and 2.4% titanium boride with 9.6% cobalt binder; 86.7% tantalum carbide—13.3% boron carbide; 80% zirconium dioxide and 20% titanium dioxide; 65% tungsten—35% molybdenum; and 50% tungsten and 25% silicon with a 25% nickel binder.

The coating material of the invention comprises at least approximately 70% by weight of the refractory material and may also comprise up to 30% by weight of a metal or alloy (binder) to bond the refractory material to itself and the body to be coated. The characteristics of the refractory metal employed as well as the characteristics of the binder (melting point, wettability, ductility, etc.) determine the percentage by weight of binder addition required in the coating for desired coating characteristics. In general, increasing the binder content will decrease the porosity of the coating.

It has been found that the provision of up to 30% by weight of bonding metal or alloy is in all cases sufficient to produce coatings that adhere tightly to the base material with less than 3% porosity.

In the case of all materials coated in accordance with the detonation coating process, the as-formed coating, regardless of composition and presence or absence of bonding agents, was found to have less than 3% porosity and the characteristic lamellar structure with firm adherence to the base material without any substantially alloying therewith.

It has been found that the base material to which the coating of the invention is to be applied may be of any material which is solid and chemically stable at application temperatures. During the application of the coating of the invention the temperature of the base material may be raised to as high as approximately 600° F. Therefore, to prevent alloying of the coating and base materials, it is imperative that the base material be a solid having a melting point higher than approximately 600° F.

It has been found that the optimum powder size is that which permits the particles to be softened enough to give good adherence but does not permit excessive vaporization of the particles. Generally, materials of lower melting point may be of larger particle size, say up to 150 microns, and those of higher melting point, such as tungsten and tungsten carbide, have been most successfully used when smaller than about 50 microns to produce dense adherent coatings. However, these size limits are not critical, for instance tungsten carbide-cobalt alloy powder as coarse as 74 microns has been successfully coated on a metal body.

In an example of the invention, a steel body was coated by feeding a finely powdered (mostly 10 to 40 microns particle size) cast tungsten carbide composition containing, apart from the tungsten, about 9% by weight cobalt and 4% by weight carbon at a rate of about 10 to 15 pounds per hour to a detonation gun about five feet in length and having a one-inch inside diameter. Acetylene and oxygen were fed, in a ratio of about 1 cubic foot of the former to 1 to 2 cubic feet of the latter, at an average rate of about 360 cubic feet per hour of the mixture. The average flow of nitrogen gas for purging was about 180 cubic feet per hour, total. The ignition frequency was about four per second. A clean steel surface was roughened by grit blasting and positioned about three inches from the open end of the gun. A dense, adherent layer of tungsten carbide composition 0.06-inch thick was deposited at a rate of about one square inch of surface area per minute. Thinner or much thicker coatings can be applied by varying the time of application.

The drawing shows, at a magnification of 300×, the appearance of a tungsten carbide-cobalt alloy coating deposited on a steel base S in the manner described above. The coating material included 9% by weight of cobalt as a bonding agent. The sample was polished and then given an anodic etch with chromic acid, followed by a potassium permanganate stain.

The detonation-deposited coatings of tungsten carbide composition as shown in the drawing are fine grained, dense, lamellar structures which are believed to be composed of mixed layers of tungsten carbide (WC), complex carbides of cobalt and tungsten, and some secondary tungsten carbide (W_2C). The particles which form the coating are elongated and flattened by impact with the surface forming thin, overlapping discs or leaves such that their diameter is many times larger than their thickness. This structure is characteristic of all refractory material coatings produced by the detonation coating process. Such a structure is in direct contrast to sintered carbide articles and the like which have a fine dense equiaxial structure, and to tungsten carbide alloy coatings sprayed on by conventional flame spray methods which have a relatively coarse, porous, weakly-bonded structure. The conventional flame spraying methods produce a coating of tungsten carbide which is formed of particles which are essentially unchanged in shape and are poorly bonded with high porosity, while the detonation gun flattens out the particles forming excellent bonding between the individual particles with less than 3% porosity.

The coating described in the example above was found to have a bulk density substantially identical with that of the solid material applied, 14.5 g./cc. Porosity was less than 1%. Adherence of the coating to the base was excellent, as shown by the fact that portions were ground down to and through the interface without peeling. The hardness of the coating for all refractory materials is greater than 600 Diamond Pyramid hardness when tested with a 300 gram load. The coating had a smooth matte surface which was brought to a high polish by standard percision grinding and polishing procedures.

The properties of the coating of the present invention adapt it particularly for application to surfaces which might be grouped generically as follows: non-skid (high friction) surfaces, as exemplified by the hammer head; irregularly shaped wear surfaces, as exemplified by the cotton picker spindle; precision wear surfaces supported by a strong tough core, as exemplified by a spindle, core rod or burnishing broaches; wear surfaces on parts having low inertia; as exemplified by thread guides and ball bearings; or abrasive surfaces on rotating parts for cutting their own clearance, as exemplified by labyrinth seals for gas turbines.

Some specific applications wherein the coatings of the present invention may be advantageously employed are as follows: core rods for pressing and coining, snap and plug gages, crusher jaws, shaft seal rings, and plates, electrical contacts, boring bars, saw teeth, knife blades, valve seats and plugs, and bearing surfaces generally.

This application is in part a continuation of our copending application Serial No. 307,742, filed September 4, 1952, now abandoned.

What is claimed is:

1. An article of manufacture comprising a workpiece having bonded to a surface thereof a thin, highly adherent coating exhibiting a Diamond Pyramid hardness of at least 600 under a 300 gram load, less than 3% porosity, and a bulk density substantially the same as that of solid material of the same composition and having a lamellar structure of interlocking and overlapping microscopic leaves mechanically bonded to each other and to said workpiece without substantial alloying at the interface thereof, said coating being formed by introducing powdered refractory material of less than 150 microns diameter and containing at least 70% of at least one refractory material having a melting point greater than approximately 2370° F. selected from the group consisting of metals, metal carbides, metal nitrides, metal borides, metal oxides and metal silicides into a high velocity, high temperature gas stream and directing such powder laden gas stream against said workpiece.

2. An article of manufacture as set forth in claim 1 wherein the refractory material is aluminum oxide.

3. An article of manufacture as set forth in claim 1 wherein the refractory material is tungsten carbide containing a cobalt binder.

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