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3,313,633

HIGH TEMPERATURE FLAME SPRAY POWDER
 Frank Nicholas Longo, Mineola, N.Y., assignor to Metco,
 Inc., Westbury, N.Y., a corporation of New Jersey
 No Drawing. Filed July 24, 1963, Ser. No. 297,198
 11 Claims. (Cl. 106—1)

This invention relates to a high temperature flame spray powder and process.

The invention more particularly relates to a flame spray powder mixture containing a self-fluxing alloy powder and a powder of a metal which melts at a high temperature, such as tungsten, rhenium, tantalum, molybdenum, columbium, or alloys thereof, and to a process for flame spraying such powder mixtures at high temperatures to produce dense, coherent coatings which show excellent wear and load-resistant characteristics.

In the flame spray art, there is a well known class of powders which are commonly referred to as spray-weldable, self-fluxing metal powders, or simply as self-fluxing alloy powders. Such powders are, for example, described in United States Patent Nos. 2,875,043 of Feb. 24, 1959, and 2,936,229 of May 10, 1960. These powders contain a base metal, such as nickel or cobalt, and a constituent to provide fluxing properties, such as boron or preferably boron and silicon. The powders are most frequently used for applying fused coatings to steel or steel-alloy bases by a process known as "spray welding." The "spray welding" process involves the steps of first spraying the powder onto the surface to be coated, using the conventional flame-spray process, and thereafter fusing the coating in place. The fusing may be done, for example, in a furnace, by means of induction heating or the like, but is often done by directly heating the coated surface with a heating torch.

The flame spraying in the sprayweld process is simply a mode of positioning the alloy powder on the surface to be coated in order to allow the fused coating to be formed by the subsequent fusing operation. The coating thus sprayed prior to the fusing operation is porous, is not firmly bonded in place, and is not useful in the same manner as subsequent fused coatings, i.e. is not a hard, dense, wear-resistant surface. The particles of a ground-finished, as-sprayed coating, will for example pull out when pressure-sensitive tape, such as Scotch tape, is applied and then stripped off.

It is an object of this invention to provide a flame spray powder mixture containing a self-fluxing alloy powder which may be sprayed, under special conditions of temperature, to produce dense, coherent coatings which are similar in certain respects to "fused" coatings formed by the sprayweld process but which do not require a subsequent fusing operation.

A further object of this invention is a process for producing dense, wear- and load-resistant coatings, utilizing a flame spray powder mixture containing a self-fluxing alloy powder.

These and still further objects will become apparent from the following description:

In accordance with the invention I have discovered that if conventional self-fluxing alloy powder is flame-sprayed in admixture with about 5 to 95% and preferably 15 to 30% by weight, or alternately 70 to 90% by weight, of a metal powder having a melting point above 3500° F.,

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and preferably from the group consisting of tungsten, rhenium, tantalum, molybdenum, columbium, and alloys thereof having a melting point above 3500° F. under flame spray conditions which will cause a melting of the high melting point metal, as for example utilizing a plasma flame, that superior, dense, strong, wear- and load-resistant coatings are formed, which for instance show superior properties as bearing and other wear- and load-resistant surfaces.

The metal powder which is admixed with the self-fluxing alloy powder preferably should have a melting point above 4000° F., as for example between 4600 and 6200° F. The percents by weight of the higher melting point powder, as given herein, refer to the percents by weight based on the mixture of this powder with the self-fluxing alloy powder.

The high melting powder component which makes up the 5 to 95% by weight of the mixture thereof with the self-fluxing alloy powder need not be a single metal powder but may be a mixture of one or more separate metal powders and/or alloys as specified, as for example a mixture of any of tungsten, rhenium, tantalum, molybdenum, columbium and/or their alloys.

The self-fluxing alloy powder used in accordance with the invention may be any known or conventional self-fluxing alloy powder, as for example any of the powders described in United States Patent Nos. 2,875,043 and 2,936,229. These powders are often referred to as self-fluxing sprayweld or spray-weldable powders but the term "self-fluxing alloy powders" will be generically used herein and in the claims to designate these materials. The self-fluxing alloy powders are preferably of the nickel or cobalt type containing boron, and most preferably boron and silicon as the self-fluxing element. The most preferable self-fluxing alloy powders are of the nickel or nickel-chromium alloy type containing boron and silicon. In addition to the base metal, i.e. the nickel and/or cobalt and the fluxing element or elements, the powder may be formed of additional alloy components, as for example up to 20% chromium, to impart corrosion and oxidation resistance, carbon in an amount of not more than a few percent, iron in an amount not exceeding about 10%, and preferably not exceeding about 5% in weight of the total alloy.

An example of a typical self-fluxing alloy powder of the boron-nickel type consists of 0.7-1% carbon, 3.5-4.5% silicon, 2.75 to 3.75% boron, 3-5% iron, up to 18% chromium, as for instance 16-18% chromium with nickel making up the balance.

An example of a typical sprayweld alloy of the cobalt base type may, for example, contain 1½ to 3% boron, 0-4.5% silicon, 0-3% carbon, 0-20% chromium, 0-30% nickel, 0-20% molybdenum, 0-20% tungsten, and the balance cobalt.

The self-fluxing alloy powder should generally have a particle size below 100 mesh U.S. Standard screen size. When intended for spraying with a plasma flame in accordance with the preferred embodiment of the invention, the particles should be of a size between -100 mesh and +8 microns and preferably between -230 mesh and +15 microns.

The high melting point metal powder used in admixture with the self-fluxing alloy powder must be a metal powder having a melting point above 3500 and preferably above

4000° F., and is preferably a powder of tungsten, rhenium, tantalum, molybdenum, columbium, or alloys based on these metals having a melting point above 3500° F. and preferably between 4000 and 6200° F., as for example:

99.42% molybdenum—.5% titanium—.08% zirconium
 90% tantalum—10% tungsten
 85% tantalum—10% hafnium—5% tungsten
 50% rhenium—50% molybdenum
 80% columbium—10% molybdenum—10% titanium
 75% tungsten—25% rhenium.

Any mixture of these metal powders or alloy powders may also be used. The most preferable metal powders are powders of tungsten, tantalum, or molybdenum, or alloys thereof having a melting point between 4600° F. and 6200° F.

The high melting point metal powder must be a metal per se and cannot be in the form of a refractory oxide, carbide, or the like. Furthermore, the high melting point metal powder must be independent of the self-fluxing alloy powder and may not be alloyed therewith or the like. The particle size of the high melting point metal powder should be similar to that of the self-fluxing alloy powder and should generally be between -100 mesh and +8 microns, and preferably between -270 mesh and +8 microns, the mesh sizes being U.S. Standard screen sizes.

The high melting point metal powder must be present in an amount of about 5 to 95% by weight and preferably 15 to 30%, or alternatively 70 to 90%, by weight based on the total weight of the mixture thereof with the self-fluxing alloy powder.

The powder mixture in accordance with the invention is preferably sprayed per se but may be sprayed in admixture or in conjunction with other spray materials, as for example, aluminum; or refractory carbides, such as carbides of tungsten, tantalum, titanium, etc., with or without a cobalt or nickel matrix; refractory oxides, such as aluminum oxide or zirconium oxide, molybdenum disilicide, etc. The powder mixture in accordance with the invention may, for example, be sprayed in amounts of 5-95%, or preferably 10-90%, by weight of the other spray material, said percentage being based on the total mixture.

The powder mixture is preferably sprayed in a powder type flame spray gun but must be sprayed under conditions of temperature which will cause melting of the high melting point metal powder component. For this purpose the temperature in the heating zone should exceed 4000° F. and should preferably exceed 7000° F.

The spraying in accordance with the invention is preferably effected with a plasma flame spray gun, as for example of the type which produces a plasma flame by constricting an electric arc in a nozzle with a plasma-forming gas, for instance nitrogen or argon alone, or in mixture with hydrogen. Guns which produce a plasma flame in this manner are, for example, described in U.S. Patent 2,960,594.

It is also possible to effect the spraying in a wire-type gun, with the powder mixture held in spray wire or rod shape by a binder, as for example a synthetic plastic, for example in the manner described in U.S. Patent 2,570,649, of Oct. 9, 1951. The term "powder" as used herein is generically intended to designate not only powder in a loose form, but powder in such bonded form. In such case the wire-type gun must utilize a flame of sufficient temperature to melt the high melting point metal, as for instance a plasma flame.

In all other respects the spraying is effected in the well-known and conventional manner for flame spraying, particularly for flame spraying with a plasma flame spray gun.

The coatings may be formed on conventional surfaces, as for example iron and steel alloyed surfaces for any purposes which require a wear- and/or load-resistant surface. Coatings of a depth of between .002 and 0.125"

and preferably between .005 and 0.030" may be formed, and are extremely useful as bearing surfaces, as for example on crankshafts subject to high loading forces. The coatings in accordance with the invention may also be used for forming polished rod liners, pump plungers, medium-to-high temperature-resistant steel roller bearings, furnace rolls, engine valve trim, glass molds, engine piston tops and annealing rolls or the like.

The surface which is sprayed in accordance with the invention should be prepared in the well known and conventional manner for flame spraying, for example with steel grit propelled with air at a pressure of 100 lbs. per square inch, or surface rolled in any other conventional manner, as for example rough-threading, coating, or the like. In addition to iron and steel, copper, brass, aluminum, titanium, molybdenum, or any other material whose surface is suitable for flame spraying by conventional methods, may be coated with the powder and by the process in accordance with the invention.

While the coatings produced in accordance with the invention may be substituted in their "as sprayed" condition for the fused coatings produced by the sprayweld process, they are not identical to these fused coatings, and in certain respects are superior thereto. The structure is different, in that individual high melting point metal particles can usually be individually identified in metallographically prepared sections. While the coatings in accordance with the invention do not require a subsequent fusing operation and are generally utilized without fusing, the same may be fused or heat-treated in many cases, forming a desirable, high-melting alloyed coating.

The following examples are given by way of illustration and not of limitation:

EXAMPLE 1

Tungsten powder of a particle size between -270 mesh and +8 microns and a self-fluxing alloy powder of a particle size between -230 mesh and +15 microns are intimately mixed, in the proportions of 75% by weight of the self-fluxing alloy powder and 25% by weight of the tungsten powder.

The self-fluxing alloy powder is a nickel boron alloy having the following analysis:

	Percent
B -----	3.5
Si -----	4
Fe -----	4
Cr -----	17
C -----	1.0
Nickel -----	Balance

The powder mixture is flame-sprayed on a mild steel plate which was degreased and then blasted with G-18 steel grit, propelled with air at a pressure of 100 p.s.i.g.

The spraying is effected at a distance of 4-6" from the plate, using the plasma flame spray gun Type 2M, as sold by Metco, Inc., of Westbury, N.Y., operated at 500 amps, 80-85 volts, to produce a plasma temperature of 10,000° F.

The spraying is effected at a rate of 6 to 7 lbs. of powder per hour, using nitrogen at a pressure of 50 p.s.i.g. and a flow rate of 100 CFH, and hydrogen at a pressure of 50 p.s.i.g. and a flow rate of 15 CFH. The spray coating produced on the base is a dense coating which is built up to a layer thickness of 0.030". The preliminary grind-finish of the sprayed coating was 7 micro inches as compared to the ordinary 30-40 micro inch finish for conventional sprayed coatings.

When Scotch tape was applied to the ground-finish surface of the coating and then stripped away, there was very little particle pull-out as compared with considerable particle pull-out which may be observed with the conventional "as sprayed" sprayweld coatings.

EXAMPLE 2

Example 1 is repeated on the bearing surfaces of a

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crank shaft for an internal combustion engine having an outer diameter of 2" for the main bearings and 1½" for the connecting rod bearings. The bearing surfaces, as formed, are excellent, wear-resistant bearing surfaces, which are able to withstand the extremely high loading forces of modern engines.

EXAMPLE 3

Example 1 is repeated using, however, a self-fluxing alloy of the following composition: Fe 2.5%, Cr 10%, C .15%, Si 2.5%, B 2.5%, Ni balance, and tungsten powder of a size between -325 mesh and +8 microns, in a mixture ratio of 75% of the self-fluxing alloy powder and 25% of the tungsten powder.

The coating produced had the appearance of wrought metal when ground-finished, and a surface finished of 5 micro inches was obtained.

EXAMPLE 4

Example 1 is repeated using the following powder mixtures of the particle size, composition and proportions indicated:

(a) 80% by weight of tungsten of a particle size between -200 mesh and +30 microns, 20% of the self-fluxing alloy of Example 3 of a particle size between -270 mesh and +8 microns

(b) 80% by weight of molybdenum of a particle size between -170 and +325 mesh and 20% of the self-fluxing alloy of Example 1

(c) 15% by weight of tungsten of a particle size between -270 mesh and +8 microns, 15% of molybdenum of a particle size between -270 mesh and +8 microns, 70% of the self-fluxing alloy powder of Example 1

(d) 25% by weight of a tungsten-rhenium alloy containing 25% rhenium of a particle size between -270 mesh and +8 microns, and 75% of the self-fluxing alloy of Example 1.

In each case an extremely high tensile-strength, dense coating is obtained, for example a coating obtained with (a) above has a tensile strength which is double that obtained when conventionally spraying tungsten per se. When this coating is post heat-treated at 1900° F. for two hours in an inert atmosphere, the resulting coating will alloy and have a melting point above 4000° F.

EXAMPLE 5

Several mixtures of the self-fluxing alloy of Example 1 with molybdenum powder of a particle size between -140 mesh and +15 microns and in the following proportions were made up:

90% self-fluxing alloy, 10% molybdenum

70% self-fluxing alloy, 30% molybdenum

50% self-fluxing alloy, 50% molybdenum.

These mixtures were each sprayed with the oxygen-acetylene powder flame spray gun sold by Metco, Inc., Westbury, N.Y., as the ThermoSpray gun. Spraying was effected on cold rolled steel which had been blasted with G-18 steel grit under a pressure of 100 p.s.i.g. of air at a distance of 6-8 inches, using acetylene at 12 p.s.i.g. pressure and 30 flow rate, oxygen of 14 p.s.i.g. pressure and 30 flow rate, with 5 lbs. of powder per hour entrained in acetylene. In each case a coating which had the characteristics of a partially fused coating was obtained. The coatings produced in this manner are excellently suitable for repairing worn rolls and bearings.

In the examples, in place of the specific, self-fluxing alloy powders described, any of the powders set forth in U.S. Patents 2,875,043 and 2,936,229 or any other conventional self-fluxing alloy powder may be used.

The percentages of the higher melting point powder as set forth in the claims are indicated as "based on the self-fluxing alloy powder" and this specifically designates that the percentages given are the percentages of the sum of the high melting powder and the self-fluxing alloy pow-

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der. Thus, for example, 5% by weight of the higher melting powder based on the self-fluxing alloy powder designates that of the combined weight of the higher melting powder and the self-fluxing powder 5% is attributable to the higher melting powder and 95% to the self-fluxing alloy powder. Similarly, 95% by weight of the higher melting powder based on the self-fluxing alloy powder designates that of the sum of the weight of the higher melting powder and self-fluxing alloy powder 95% is attributable to the higher melting powder and 5% to the self-fluxing alloy powder.

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention is therefore only intended to be limited by the appended claims or their equivalents wherein I have endeavored to claim all inherent novelty.

I claim:

1. A flame spray powder comprising a mixture of a boron containing nickel or cobalt base self-fluxing alloy powder and about 5-95% by weight, based on the total thereof with said self-fluxing alloy powder, of a powder of at least one metal selected from the group consisting of tungsten, rhenium, tantalum, molybdenum, columbium, and alloys thereof having a melting point about 3500° F. which powder is characterized by forming in its as flame-sprayed condition an adherent coating on a substrate.

2. A flame spray powder according to claim 1 in which said powder of said group member is present in amount of about 15-30%.

3. A flame spray powder according to claim 1 in which said powder of said group member is present in amount of about 70-90%.

4. A flame spray powder according to claim 1 having a particle size between -100 mesh and +8 microns.

5. A flame spray powder according to claim 1 having a particle size between -230 mesh and +8 microns.

6. A flame spray powder comprising a mixture of a boron containing nickel or cobalt base self-fluxing alloy powder and about 5-95% by weight, based on the total thereof with said self-fluxing alloy powder, of a powder of at least one refractory metal having a melting point above 3500° F. which powder is characterized by forming in its as flame-sprayed condition an adherent coating on a substrate.

7. A mixture of a self-fluxing metal powder, essentially consisting of at least one base metal selected from the group consisting of nickel and cobalt and containing boron as a self-fluxing element with about 5-95% by weight of a tungsten powder, the powder mixture having a particle size between -100 and +8 microns which powder is characterized by forming in its as flame-sprayed condition an adherent coating on a substrate.

8. A mixture of a self-fluxing metal powder, essentially consisting of at least one base metal selected from the group consisting of nickel and cobalt and containing boron as a self-fluxing element with about 5-95% by weight of a tantalum powder, the powder mixture having a particle size between -100 mesh and +8 microns which powder is characterized by forming in its as flame-sprayed condition an adherent coating on a substrate.

9. A mixture of a self-fluxing metal powder, essentially consisting of at least one base metal selected from the group consisting of nickel and cobalt and containing boron as a self-fluxing element with about 5-95% by weight of a molybdenum powder, the powder mixture having a particle size between -100 and +8 microns which powder is characterized by forming in its as flame-sprayed condition an adherent coating on a substrate.

10. A mixture of a self-fluxing metal powder, essentially consisting of at least one base metal selected from the group consisting of nickel and cobalt and containing

boron as a self-fluxing element with about 5-95% by weight of a columbium powder, the powder mixture having a particle size between -100 mesh and +8 microns which powder is characterized by forming in its as flame-sprayed condition an adherent coating on a substrate.

11. A mixture of a self-fluxing metal powder, essentially consisting of at least one base metal selected from the group consisting of nickel and cobalt and containing boron as a self-fluxing element with about 5-95% by weight of a rhenium powder, the powder mixture having a particle size between -100 mesh and +8 microns which

powder is characterized by forming it its as flame-sprayed condition an adherent coating on a substrate.

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DAVID L. RECK, *Primary Examiner.*

10 HYLAND BIZOT, *Examiner.*

R. O. DEAN, *Assistant Examiner.*