

[54] **CERAMIC CLAD FLAME SPRAY POWDER**

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[22] Filed: **July 1, 1969**

[21] Appl. No.: **838,319**

[52] U.S. Cl. **117/100 M**, 29/191.2, 106/1,
117/105.2, 117/130 R, 117/160 R

[51] Int. Cl. **B44d 1/094**, B44d 1/02

[58] Field of Search 29/191.2; 117/100 M, 105.2,
117/160 R, 169; 106/1

[56] **References Cited**

UNITED STATES PATENTS

3,293,029	12/1966	Broderick et al.	29/191.2
3,310,400	3/1967	Alexander et al.	117/100 X
3,348,967	10/1967	Hucke 29/191.2	X
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[57] **ABSTRACT**

A flame spray powder comprises finely-divided core particles of a metal or a metal alloy coated with discrete particles of a ceramic or cermet that remains in solid phase at least 100°F above the fusing or melting temperature of the metal. The average particle size of the ceramic is less than 25 percent of the average particle size of the metal and the amount used is insufficient to totally cover the surface of the metal particles so that on the average in the range of 5 to 75 percent of the surface area of the metal particles is exposed to ambient conditions.

When used in flame spraying, this new ceramic clad metal powder in one embodiment forms a flame spray coating where the ceramic is in the continuous phase and the coating is relatively soft and abrasible, and in another embodiment the metal of the coating is in the continuous phase and the coating is relatively hard and erosion resistant.

10 Claims, No Drawings

CERAMIC CLAD FLAME SPRAY POWDER

PRIOR ART

U.S. Pat. No. 3,084,064 issued to Cowden et al., Apr. 2, 1963, discloses that in the manufacture of turbines it is desirable to reduce the clearance between the turbine blade and turbine housing by flame spraying an abradable metal composition onto the housing and then to allow the blades to seat themselves within the housing by abrading the coating. This invention is particularly concerned with a flame spray powder for producing abradable coatings.

U.S. Pat. No. 3,322,515 issued to Dittrich et al., May 30, 1967 and assigned to the assignee of the present invention, discloses that rather than using the wire rod flame spray method and separately introducing a second material in powder form as disclosed in U.S. Pat. No. 3,084,064 powders formed of two or more materials can be used and in one embodiment proposes that aggregates be formed by cladding a core powder with a second powder. The aggregate powders basically comprise two metal components one of which will exothermically react with the other when subjected to the flame spray.

BACKGROUND OF THIS INVENTION

Flame spraying involves the heat softening of a heat fusible material such as a metal or ceramic and the propelling of the softened material in particulate form against the surface to be coated to which the heat fusible material bonds. A flame spray gun is usually used for the purpose and with one type, heat fusible material is supplied in powder form to the gun. Such powders are of quite small particle size, e.g., below 100 mesh U.S. standard screen size to about one micron.

A flame spray gun normally utilizes a combustion or plasma flame to effect melting of a powder but other heating means such as electric arcs, resistant heaters or induction heaters can also be used, alone or in combination. In a powder-type combustion flame spray gun, the carrier gas for the powder can be one of the combustion gases or it can be compressed air. In a plasma flame spray gun the primary plasma gas is generally nitrogen or argon. Hydrogen or helium is usually added to the primary gas. The carrier gas is generally the same as the primary plasma gas although other gases such as hydrocarbons are used in special cases.

The nature of the coating obtained by flame spraying a metal powder can be quite specifically controlled by proper selection of the composition of the powder, control of the physical nature of the powder and the use of select flame spraying conditions. It is well known and common practice to flame spray a simple mixture of a ceramic powder and a metal powder. Hard coatings that are useful may be produced with mixtures. Many ceramic powders such as boron nitride or silicon carbide do not have normal melting points and cannot be satisfactorily sprayed in mixtures. Others such as tungsten carbide or zirconium diboride tend to oxidize and decompose when heated to melting point in the flame. When softer coatings are desired the ceramic is usually not melted to any extent during the spraying and accidental entrapment of the unmelted ceramic powder particles is relied on. If greater heat is used to melt the ceramic, if the ceramic has a melting point, this may be too much heat for the metal and may cause oxidation of the metal and produce too hard a coating. In the case of the metal-clad ceramic particles, as is taught in the U.S. Pat. No. 3,254,970, in practice the powder usually comprises a major portion of ceramic because it is difficult to obtain very thick cladding layers of the metal onto the ceramic and the sprayed coating produced therefrom often does not have suitable properties for the application, for example the proper degree of abradability.

THIS INVENTION

In the present invention it has been found that by partially cladding metal particles with a finer ceramic or cermet powder, abradable coatings can be produced from the clad

metal powder by flame spraying that have properties not previously obtainable. The reason for this is not known with any certainty. It is speculated that by leaving a certain portion of the metal core particles exposed, the melting of the core particles, i.e., their ability to pick up heat from the flame, is greatly facilitated, which in the end results in a more adherent uniform coating.

If the metal core particles were completely surrounded by the ceramic, as has been the case in the past for some compositions, the ceramic which has a low thermal conductivity may effectively insulate the metal core particles from the flame. In one case, wherein a nickel alloy was clad with boron nitride with 100% coverage, coatings produced by flame spraying with this powder were totally unsatisfactory.

DESCRIPTION AND EXAMPLES

There is no standard method for determining the percent of coverage of one powder clad with another more finely divided powder. For this reason an empirical test was devised wherein the clad powder is observed under polarized light microscopically and a microscopic grid is used to estimate the percent of the areas of the metal core particles that is covered with the ceramic powder. This might be termed the polarized light-microscopic grid method, or the PLMG method for short.

More particularly, the PLMG method is carried out by placing about one-half gram of powder on a 1-inch by 3-inch glass slide. The powder is evenly distributed and then a mirror is gently placed on top of the powder to make a cover glass. It is fastened with tape with the reflector side of the mirror facing the powder. This slide is then placed in a metallurgical microscope. Light is passed through the glass slide across the powder and reflected back off the mirror. When viewed under normal reflected light, a dull outline of the powder is visible. When polarized light is used the mirror appears grey, the exposed metal shows dark and the ceramic is very bright. Examination of the specimen in a plain polarized light requires a polarizing prism and analyzer. When the polarizer and analyzer are rotated 90° out of phase, or other angle as determined by trial, the ceramic appears bright and the mirror and exposed metal are darkened. If the ceramic is not sensitive to polarized light, experimentation with incident light may be required to contrast the ceramic with the metal.

The core and coating particles will usually appear to have a generally globular to spherical shape. By measuring the relative percentage of dark areas to bright areas on the particles the amount of exposed metal can be determined. To do this, a square grid is superimposed on the image magnified 150 times. This may be done by using an appropriate eye piece reticle or by placing a grid on a photograph, with the grid 1 inch by 1 inch comprising 100 squares each 0.1 inch square. The grid must be positioned so that the particles are within the outer lines of the grid. By counting the number of squares which are not covered by the particles, the area of the particle is estimated. With the grid in the same position, the metal surface area is also estimated by counting the squares filled by dark areas. Dividing the estimated dark area by the particle area gives the percent of the exposed metal surface. This procedure is usually carried out on 25 to 30 particles selected at random.

The ceramic powder should remain in solid phase, that is, it should not melt, soften, vaporize or decompose significantly at a temperature at least 100° F above the melting or fusing temperature of the core metal.

It often is desirable to additionally include particles of a third material which, together with the ceramic particles, are coated on to the metal core particles. The third material will usually be less than 25 percent of the size of the core particles. It may be either a metal or ceramic in an amount in the range of 0.5 to 15% of the volume of the amount of metal core. As an example, when the core is nickel, cobalt or iron, or an alloy thereof, it is preferable to mix fine aluminum powder with the ceramic powder before bonding the mix to the core particles.

The aluminum addition results in improved deposit efficiency and coating quality. The reason for this is not clear by it is speculated that it involves the exothermic reaction disclosed in U.S. Pat. No. 3,322,515.

The ceramic cladding powder is preferably bonded to the metal core particles with a resinous binder although other types of bonding methods can be used. The metal core particles will usually have a size in the range of minus 100 mesh (U.S. standard screen size) to 3 microns, preferably of -140 to +325 mesh. The ceramic coating particles will usually have the size of less than 25% of the size of the core particles. The amount of the ceramic powder will usually be in the range of 1 to 30 volume percent of the volume of the core particles so that incomplete cladding of the core particles is assured.

The cladding is accomplished by mixing the core particles, the ceramic cladding particle and the resinous binder, carried in a suitable solvent, together followed by removing of the solvent and the breaking up of any agglomerates that may have been formed. Upon drying the binder is present in an amount between 0.05 and 5 volume percent of the volume of the core particles. Any one of many types of binders can be used such as starches, sugars, celluloses, polyamides, rubbers, urethanes, phenols, polyesters, epoxies, acetates and the like. The water soluble polyvinyl alcohols, the inorganic and organic silicates and organic resins such as the phenolics and vinyls are perhaps preferred. The incomplete ceramic cladding can be achieved without a binder by other known methods such as vapor deposition.

The term "ceramic" is used broadly, such as is described by W. D. Kingery, *Introduction to Ceramics*, John Wiley & Sons, Inc., New York (1960). Ceramics are usually compounds although carbon, especially the higher temperature form of graphite, is now considered a ceramic. Usually ceramics are resistant to high temperatures. Preferably the ceramics used have a melting point, if any, or are stable, at least 100° F. above the melting point of the metal of the core particles. Typical ceramics are carbides such as tungsten carbide, chromium carbide and titanium carbide; simple oxides such as aluminum oxide, zirconium oxide, titanium oxide and chromium oxide; complex oxides such as magnesium zirconate, borosilicate glasses, diatomaceous earth and talcum powder; nitrides such as boron nitride, borides such as zirconium diboride, halides such as calcium fluoride, silicides such as chromium silicides, etc.

The core metal or alloy can include such metals as tungsten, titanium, tantalum, columbium, zirconium, nickel, cobalt, iron, aluminum, copper, tin, and alloys thereof. Typical core metals are: essentially pure molybdenum; titanium with six parts aluminum and four parts vanadium; nickel with 16 parts chromium and eight parts iron; monel (67 percent nickel — 33 percent chromium); a cobalt alloy having 25.5 parts chromium, 10.5 parts nickel, 7.5 parts tungsten, 0.5 parts carbon with the balance cobalt; Type 316 or Type 431 stainless steel; aluminum with 12 parts silicon, and aluminum-bronze such as one with 9.5 parts aluminum, 1 part iron and the balance copper; and a Babbit of 7.5 parts antimony, 3.5 parts copper, 0.25 parts lead with the balance being tin.

EXAMPLES

Example I

Eighty-nine parts of a nickel-chromium alloy powder of -140 to +325 mesh was coated with 4 parts by weight of a 3 to 4 micron aluminum powder and 7 parts of a -325 mesh boron nitride powder (HTP grade-Carborundum Co., Latrobe, Pa.) using 5 parts of a phenolic varnish (Metcoseal AP — Metco, Inc., Westbury, N.Y.) as a binder. The aluminum and boron nitride powders were first preblended, and the varnish was mixed with the alloy powder. The materials were then blended together using additional solvent as necessary. The solvent was removed by stirring, agglomerates were broken up and the clad powder was screened to -100 to +325 mesh. The yield was 94 percent based on original ingredients.

When examined by the PLMG method, the metal cores were 75 percent covered by the boron nitride and aluminum. When flame sprayed at a flame temperature of about 5,500° F. (Thermospray 5 P gun, Metco, Inc., acetylene gas and oxygen) onto a mild steel surface, a soft and easily abraddable coating resulted. The coating hardness was measured on a superficial Rockwell Hardness Tester using a 15 kg load and a 1/8-inch-diameter ball. The hardness read as R 15W = -100 + 55 = -45. The spray distance in this case was 8 inches. An increase in the spray distance will increase the hardness.

A microscopic examination of the coating showed there was a continuous interconnected boron nitride phase. The composition of the coating was 49 volume percent boron nitride, 49 volume percent nickel-chromium alloy and 2 volume percent free aluminum. The balance of aluminum presumably combined exothermically with the nickel.

Aircraft turbine engine tests of this coating gave excellent results.

Example II

The nature of the coating, i.e., its abrasability, erosion resistance and hardness, will vary with the spray parameters. The same clad powder as in Example I was sprayed with the same gun with the essential conditions changed being air and spray distance to give additional coating specimens: B, C and D. The coating of Example I is designated as specimen A. The conditions and results are given in Table I.

TABLE I

	A	B	C	D
Conditions:				
Acetylene, p.s.i./flow.....	12/36	12/36	14/39	14/39
Oxygen, p.s.i./flow.....	16/27	16/27	19/26	19/26
Spray distance.....	8*	8*	10*	10*
Carrier gas.....	(1)	(1)	(2)	(2)
Air cooling, p.s.i.....	(3)	15	15	10
Results:				
Hardness, 15W ⁴	-45±10	-10±5	5±5	35±5
Density, g./cc.....	3.60	3.85	4.10	4.30
Erosion resistance, volume loss, cc.....	0.120	0.030	0.024	0.020
Abradability, inches, thickness loss.....	0.060	0.015	0.011	0.008

¹ Oxygen.

² Air.

³ None.

⁴ 15 kg. load, 1/8" ball, Superficial Hardness Tester.

In order to obtain the density, the coatings were sprayed on 1-inch- by 1-inch- time 1/8-inch-thick flat pieces of mild steel. These coatings were ground flat and weighted. Then almost 0.03 inch of the coating thickness were ground off and the specimen weighted again. The difference in weight over the volume gave, fairly accurately, the density of the coating.

The erosion resistance tests were carried out by spraying the coatings on 1-inch by 2-inch by 1/8-inch mild steel plates prepared by blasting with alumina grit (Metcolite "F"), upon which the erosion tests were carried out for one minute. The test coatings were blasted at a 45° angle with Al₂O₃ type particles propelled by compressed air. The distance between the nozzle and the coating was about 4 inches. The weight loss was converted into volume using density. For the abrasability test the specimen were 1-inch by 3-inch plates coated to 0.05 inch and ground flat. The tests were conducted on a scribe test machine which moves a stylus back and forth on the coating to cut a scratch using a 0.35-inch-wide pointed probe and a 1,650-gram load on the probe. The tests were run for one minute each and the thickness loss measured.

With Coating B the metal matrix was continuous whereas with Coating A the boron nitride was in the continuous phase. The B-type coating had a metallurgical structure that gave a high erosion resistance with less abrasability. Similarly, Coating C and D had a more continuous metal phase than Coating B and this tended to make a hard matrix and erosion resistant coating.

Example III

Eight weight percent of a diatomaceous earth is clad on a cobalt alloy (25.5 Cr, 10.5 Ni, 7.5 W, 0.5C, balance cobalt) using the same cladding method as above described. The size of the alloy powder is -200 + 325 mesh. The diatomaceous

earth has a size of less than one micron. Three percent aluminum flake powder having a size of 0.2 microns thick and 1 micron long is also added to the mixture. The binder used is as in Example I.

The coating produced from this powder is capable of withstanding temperatures up to 1,800° F.

Example IV

A 3 percent weight carbon, having a size of less than 1 – 3 microns is clad onto an aluminum powder of –170 + 325 mesh using organic silicate as the binder. This is combustion flame sprayed to produce a self lubricating and abradable coating.

Example V

Talc $Mg_3Si_4O_{10}(OH)_2$ is clad onto an aluminum bronze powder of –270 + 15 microns using a resinuous binder. This powder will produce a self lubricating bronze coating suitable for bearing applications.

Example VI

Fifteen weight percent titanium oxide 0.1 micron to 1 micron is clad on a titanium alloy (6 Al. 4 V) 100 to 325 mesh using polyvinyl alcohol as a binder and water for solvent. If this is plasma flame sprayed on titanium alloy shafts used in jet engines it provides a wear resistance bearing surface which is lightweight and capable of high temperature operation.

Example VII

An aluminum oxide powder (10 weight percent) 2 microns to 5 microns is clad onto an aluminum powder 270 to 400 mesh and combustion flame sprayed on steel to give an abrasion and corrosion resistance protective coating.

Example VIII

Similarly, tungsten carbide particles (10 weight percent) 2 to 7 microns are clad onto Metco 15E self-fluxing alloy (1 C, 4 Si, 17 Cr, 3.5 B, 4 Fe, balance Ni). This will provide a very dense, hard, wear-resistance coating.

Example IX

Silicon carbide particles (5 weight percent) 5 to 10 microns are clad onto copper powder –170 + 325 mesh and combustion flame sprayed on brake disks. This provides a wear and fade resistant, thermally conductive coating for automobile brakes.

What is claimed is:

1. A flame spray powder comprising finely-divided core particles of a metal bonded to and coated with discrete particles of a ceramic that remains in solid phase at least 100° above the fusing temperature of said metal, said ceramic having an

average particle size less than 25 percent of the average particle size of said metal core and leaving exposed on the average in the range of 5 to 75 percent of the surface area of the metal core as determined by the PLMG method.

2. The powder of claim 1 having a particle size in the range of –100 mesh to 3 microns and wherein in the range of 10 to 50 percent of the surface of said core particles is exposed by said discrete particles which amount to in the range of 1 to 30 volume percent of the volume of the core particles.

3. The powder of claim 1 wherein said discrete particles are bonded to said core particles with a resinuous binder, said binder amounting to in the range of 0.05 to 5 volume percent of the volume of said core particles.

4. The powder of claim 1 wherein said metal is a nickel-chromium and said ceramic is boron nitride.

5. The powder of claim 1 wherein said discrete particles additionally include a material selected from the group comprising metals and ceramics and having an average particle size of less than 25 percent of the size of said metal core particles, the additional material being present in an amount in the range of 0.5 to 15 percent of the volume of the amount of said metal.

6. The powder of claim 5 wherein said metal is a cobalt-nickel-chromium alloy, said ceramic is a diatomaceous earth and said additional material is aluminum.

7. The powder of claim 1 wherein said metal and ceramic particles have a globular to generally spherical shape.

8. A flame sprayed composition obtained by passing a metal-ceramic powder through a flame spray gun and melting at least the metal component thereof; and thereafter impinging the heated powder against a receptor surface, said powder comprising finely-divided core particles of a metal bonded to and coated with discrete particles of a ceramic that remains in solid phase at least 100° F. above the fusing temperature of said metal, said ceramic having an average particle size less than 25 percent of the average particle size of said metal and leaving exposed on the average in the range of 5 to 75 percent of the surface are thereof as determined by the PLMG method.

9. The composition of claim 8 wherein said ceramic is in the continuous phase and said composition is relatively soft and abradable.

10. The composition of claim 8 wherein said metal is in the continuous phase and said composition is relatively hard and erosion resistant and not too abradable.

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