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CARBIDE FLAME SPRAY MATERIAL

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This invention relates to a novel carbide flame spray material. The invention more particularly relates to a carbide flame spray powder for plasma flame spraying and to a process for spraying the same.

In flame spraying a heat-fusible material is heat-softened or melted in the heating zone of the flame spray gun and propelled in this condition against the surface to be coated.

While it was known to produce flame spray coatings containing high melting point carbides, such as tungsten carbide, tantalum carbide, zirconium carbide, titanium carbide, or the like, these carbides were usually bonded in a matrix, such as cobalt or nickel, and it was generally not feasible or practical to produce coatings of pure or crystalline carbides which were not bonded in such a matrix. The conventional flame spray guns utilizing a combustion flame, such as an oxy-acetylene flame, in most cases, did not produce a high enough temperature to satisfactorily spray such carbides. Even when attempting to produce such coatings by plasma flame spraying, utilizing a plasma flame spray gun which produced a sufficiently high temperature, satisfactory coatings were not obtained, and the same were generally badly oxidized, poorly bonded, and lacked particle coherence. While these difficulties could be partially avoided by effecting the spraying in an inert atmosphere, such as an inert gas chamber, spraying in this manner is very difficult, expensive, and generally not practical, except in a laboratory. Thus, it has not been possible to produce flame spray coatings of carbides without a binder or matrix which would be considered satisfactory for practical applications, or on a commercial basis.

One object of this invention is a novel, flame spray powder which allows the production of high melting, wear-resistant carbide coatings, by plasma flame spraying without the above mentioned difficulties.

A further object of this invention is a process for producing high melting, wear-resistant carbide coatings, without a matrix by plasma flame spraying.

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

In accordance with the invention I have discovered that a certain specific combination of high melting metal carbides may be plasma flame sprayed to produce high temperature and wear-resistant coatings without the prior art difficulties.

The flame spray powder in accordance with the invention comprises particles of substantially pure carbides of tantalum, hafnium and zirconium. The tantalum is present in amount of about 20–90 and preferably 75–85 atomic percent based on the total of the three metals. The hafnium is present in amount of about .5 to 95 and preferably .5 to 25 atomic percent of the total of the hafnium and zirconium, the zirconium making up the balance. carbon content of the carbides may range betwen 15 and 65 atomic percent, and preferably between 45 and 55 atomic percent, and most preferably 50 atomic percent. While the carbides of the three metals may be in the form of individual particles of each of these metal carbides in the proportions indicated, each of the powder grains preferably contains each of the three metal carbides in the proportions indicated. Thus, each of the powder particles may be formed from compacted and/or sintered subgrains of the individual metal carbides. Most preferably, in accordance with the invention, the individual powder particles are formed of what may be referred to as a solid solution of the carbides of the tantalum, hafnium and zirconium.

The term "solid solution" designates a homogenous, solidified mixture of the carbides, with the carbides mutually dissolved, or one or more of the carbides dissolved in the others.

Solid solution carbides may be formed in a number of ways. Thus, for example, mixtures of the metal oxides, in their proper proportion, and sufficient carbon (for reduction of the oxides and carburization of the resultant metals) are thoroughly blended and pressed by powder metallurgy techniques into convenient forms. These compacted forms are then sintered under a reducing atmosphere. At the required temperature, reduction of the metal oxides and carburization of the reduced metals occurs, resulting in a solid solution of the metal carbides whose proportions in the solid solution are determined by the proportions of metal oxides used. It is also possible to use chemically co-precipitated oxides, instead of oxide mixtures, as starting materials.

Alternatively solid solutions may be formed by heating metal powder mixtures with carbon for simultaneous carburization with formation of the solid solution. This method, however, requires high purity metal powders which are expensive.

The above-described methods may also be combined such that an oxide of one of the metal components and a pure metal are mixed with sufficient carbon for reduction of the one oxide and carburization of the entire metal content.

Still further, pre-formed carbide powders may be blended in their proper proportion and heated under potective gas cover or in vacuum to a required temperature, usually between 2900° F. and 4000° F. for a time required for the diffusion of the carbides.

Also hydrides of the desired metals may be mixed with sufficient carbon and heated to a suitable temperature at which the hydrogen in the hydrides is evolved and the resultant high purity metals are carburized and the solid solution is formed.

In accordance with one embodiment of the invention, the powder particles are formed of compacted or sintered subgrains, some of which are tantalum carbide and the balance of which are a solid solution carbide of zirconium and hafnium. Compacted and sintered particles are formed for example by mixing fine powders of the individual constituent carbides, compacting, lightly sintering, and then reducing to powder sized for spraying. The constituent carbides or solution carbides are formed by any of the methods described above.

In all cases the powder should have a particle size ranging between −100 mesh (U.S. Standard screen scale) and +5 microns, and preferably between −230 mesh and +10 microns. The powder may also be compacted and/or bonded into the form of a wire, as for example, with a plastic binder such as a polyethylene binder, for spraying in a wire or rod type gun, and the term "powder" as used herein and in the claims includes the same in this form.

The powder is sprayed in accordance with the invention, using a conventional plasma flame spray gun, as for example of the type described in U.S. Patent 2,960,594, and the spraying is effected in a manner conventional and well known in the art for plasma flame spraying. The spraying may be effected on any substrate surface or base, as for example, a steel base. Coatings having a layer thickness from .001" to .03" thick and greater may be formed without difficulty. The coatings have an extremely high melting point of about 7000° F. and thus are extremely useful for high temperature applications involving neutral or reducing atmosphere. The coatings are further-

more extremely hard and wear-resistant. The coatings may, for example, be used for bearing applications where extreme wear-resistance is needed, and may be used wherever protection against high temperature and/or erosion is desired, as for example in rocket throats. In many instances, as for example for rocket applications, the same may be used in an "as sprayed" condition. If a finishing is necessary or desired, the coatings may be ground-finished with a diamond wheel and lapped, if desired. The coatings may also be used on cutting tools or knives, and thus for example a very thin coating used in an "as sprayed" condition on a knife blade will help maintain a good cutting edge.

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

EXAMPLE 1

Carbide powders of tantalum, zirconium, and hafnium in the correct proportion and of a particle size of less than approximately 325 mesh are intimately mixed in a ball mill and then pressed into compacts of a convenient size. The compacts thus formed are heated in a high frequency vacuum furnace at around 3800° F. for three hours or more, until complete diffusion has taken place. The compacts of solid solution carbides are then crushed and subsequently milled to powder and classified to the desired particle size range. The milling to the desired particle size range, after initial crushing, may be accomplished either in a ball mill, or in a jet-mill in which the powder is carried in a gaseous carrier at high velocities in two opposing jets.

A pure solid solution carbide material is thus formed containing tantalum, hafnium and zirconium, with 80 atomic percent tantalum based on the total of tantalum, hafnium and zirconium, and 1 atomic percent hafnium based on the total of hafnium and zirconium, and 50 atomic percent carbon based on the total. The material was ground and screened to a particle size between −230 mesh and +10 microns.

The powder was sprayed, using a Metco type 2MB plasma flame spray gun operated at 400 amps. and 60 volts at a spray distance of 3". Argon was used as the carrier gas, being fed at a pressure of 100 lbs. p.s.i. and a flow rate of 18 standard cu. ft. per hour. Argon and hydrogen were fed to the gun as the plasma-forming gas, the Argon being fed at a pressure of 100 lbs. p.s.i. and a rate of 100 standard cu. ft. per hour, and the hydrogen at a pressure of 50 lbs. p.s.i. at a rate of 25 standard cu. ft. per hour. The powder was sprayed at a rate of approx. 5 lbs. per hour. The substrate surface was a mild, low carbon, cold-rolled steel, which had been surface-ground clean. Prior to the spraying the surface was pre-heated to a temperature between 300 and 350° F. and was held at a maximum of 400° F. during the spraying. A coating was deposited to a thickness of .010". The sprayed solid solution carbide was self-bonding to the smooth substrate surface, and the coating deposited was of excellent quality. The average particle hardness was $KHN_{50}2900$, which compares to a typical hardness of $KHN_{50}2400$ for pure, unsprayed tungsten carbide. The deposited coating showed excellent wear-resistant and temperature-resistant properties.

EXAMPLE 2

Example 1 was repeated except that the base was not pre-heated. An excellent, high-temperature, wear-resistant coating was formed.

EXAMPLE 3

Example 1 was repeated except a solid solution carbide containing 80 atomic percent of tantalum, based on the total tantalum, hafnium, and zirconium, and 21 atomic percent of hafnium based on the total of hafnium and zirconium was used. The results were similar to those obtained in Example 1.

EXAMPLE 4

A mixture consisting of 80 atomic percent tantalum carbide powder and powders of hafnium and zirconium carbides in which the hafnium carbide is 21 atomic percent based on these two carbides, is compacted and heat treated in the same manner as described for Example 1. However, instead of heating the compacts for sufficient time at temperature for complete solid solution to occur, the compacts are heated only for such time that the formation of the solid solutions is enough to bind the particles of the compacts together. At this point, the compacts are more easily reduced to powder, and each powder particle consists of a mixture of the three carbides. The particles are sprayed in the same manner as described in Example 1. The completion of the formation of the solid solution occurs in the flame and the particles are deposited as homogenous particles of the solid solution of tantalum, zirconium, and hafnium carbides.

EXAMPLE 5

Example 4 is repeated except the powder is formed by compacting a mixture of 80 atomic percent tantalum carbide and a solid solution hafnium-zirconium carbide in which the hafnium is 21 atomic percent based on the total of hafnium and zirconium.

EXAMPLE 6

Example 1 was repeated but the spraying was effected on the following basis: high carbon steel, stainless steel, aluminum, nickel-chromium alloy.

EXAMPLE 7

The powder of Example 1 may be incapsulated in molten polyethylene and extruded from the melt in the form of a wire for use in a wire type gun. The carbides may, in addition to being sprayed alone, be sprayed in conjunction or admixture with other conventional spray materials, as for example self-fluxing spray weld alloys and powders (see U.S. Patent 2,936,229).

While the invention has been described in detail with reference to certain specific embodiments and examples, 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 particles each consisting of substantially pure carbides of tantalum, hafnium and zirconium, said tantalum being present in amount of about 20–90 atomic percent of the total of said three metals, said hafnium being present in amount of about .5 to 95 atomic percent of the total of hafnium and zirconium, said carbides containing 15–65 atomic percent of carbon.

2. A flame spray powder according to claim **1** in which said tantalum is present in amount of 75–85 atomic percent of the total of said three metals, said hafnium is present in amount of about .5 to 25 atomic percent of the total hafnium and zirconium, and said carbon is present in amount of about 45–55 atomic percent.

3. A flame spray powder according to claim **2** in which said particles have a particle size between −100 mesh and +5 microns.

4. A flame spray powder according to claim **1** in which said particles have a particle size between −230 mesh and +10 microns.

5. A flame spray powder according to claim **1** in which said particles are in the form of aggregates each said aggregate containing sub-grains of carbides of tantalum, hafnium and zirconium.

6. A flame spray powder according to claim **1** in which said particles are in the form of aggregates each said aggregate containing sub-grains of tantalum carbide

and subgrains of a solid solution carbide of zirconium and hafnium.

7. A flame spray powder comprising particles consisting of a solid solution carbide of tantalum, hafnium and zirconium, said tantalum being present in amount of about 20–90 atomic percent of the total of said three metals, said hafnium being present in amount of about .5 to 95 atomic percent of the total of hafnium and zirconium, said carbides containing 15–65 atomic percent of carbon.

8. A flame spray powder according to claim 7 in which said tantalum is present in amount of 75–85 atomic percent of the total of said three metals, said hafnium is present in amount of about .5 to 25 atomic percent of the total of hafnium and zirconium, and said carbon is present in amount of about 45–55 atomic percent.

9. A flame spray powder according to claim 8 in which said particles have a particle size between −100 mesh and +5 microns.

10. A flame spray powder according to claim 7 in which said particles have a particle size between −230 mesh and +10 microns.

11. In a flame spray process in which a heat-fusible material is heated to at least heat-softening temperature in a plasma flame and sprayed against the surface to be coated, the improvement which comprises effecting said spraying with a flame spray powder comprising particles consisting of substantially pure carbides of tantalum, hafnium and zirconium, said tantalum being present in amount of about 20–90 atomic percent of the total of said three metals, said hafnium being present in amount of about .5 to 95 atomic percent of the total of hafnium and zirconium, said carbides containing 15–65 atomic percent of carbon.

12. Improvement according to claim 11 in which said flame spray powder contains said tantalum in amount of 75–85 atomic percent of the total of said three metals, hafnium in amount of about .5 to 25 atomic percent of th total of hafnium and zirconium, and carbon in amount of about 45–55 atomic percent.

13. In a flame spray process in which a heat-fusible material is heated to at least heat-softening temperature in a plasma flame and sprayed against the surface to be coated, the improvement which comprises effecting said spraying with a flame spray powder comprising particles consisting of a solid solution carbide of tantalum, hafnium and zirconium, said tantalum being present in amount of about 20–90 atomic percent of the total of said three metals, said hafnium being present in amount of about .5 to 95 atomic percent of the total of hafnium and zirconium, said carbide containing 15–65 atomic percent of carbon.

14. Improvement according to claim 13 in which said flame spray powder contains said tantalum in amount of 75–85 atomic percent of the total of said three metals, said hafnium in amount of about .5 to 25 atomic percent of the total of hafnium and zirconium, and said carbon in amount of about 45–55 atomic percent.

15. A substrate having a flame spray coating formed of sprayed particles, which particles consist of substantially pure carbides of tantalum, hafnium and zirconium, said tantalum being present in amount of about 20–90 atomic percent of the total of said three metals, said hafnium being present in amount of about .5 to 95 atomic percent of the total of hafnium and zirconium, said carbides containing 15–65 atomic percent of carbon.

16. A substrate having a flame sprayed coating according to claim 15 in which said tantalum is present in amount of about 75–85 atomic percent of the total of said three metals, and said hafnium is present in amount of about .5 to 25 atomic percent of the total of hafnium and zirconium, and said carbon in amount of about 45–55 atomic percent.

17. A substrate having a flame sprayed coating formed of sprayed particles, which particles consist of substantially pure, solid solution carbide of tantalum, hafnium and zirconium, said tantalum being present in amount of about 20–90 atomic percent of the total of said three metals, said hafnium being present in amount of about .5 to 95 atomic percent of the total of hafnium and zirconium, said carbide containing 15–65 atomic percent of carbon.

18. A substrate having a flame sprayed coating according to claim 17 in which said tantalum is present in amount of about 75–85 atomic percent of the total of said three metals, and said hafnium is present in amount of about .5 to 25 atomic percent of the total of hafnium and zirconium, and said carbon in amount of about 45–55 atomic percent.

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