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MOLYBDENUM POWDER FOR USE IN
SPRAY COATING

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ABSTRACT OF THE DISCLOSURE

A free flowing molybdenum powder for use in molten metal spray guns and made up of separate particles containing voids; and the method of making such powder which consists in melting the oxide of the metal, breaking the molten metal oxide up into separate substantially spherical droplets which are then allowed to solidify separately and reducing the resulting solidified particles with hydrogen to remove the oxygen in such a manner that the particles do not sinter together. The reduced metal particles are of a size range that will pass a 150 mesh screen and be retained on a 325 mesh screen. The molybdenum may contain minor quantities of other metal elements or oxides but they are optional.

The present invention relates to a powder of molybdenum or certain molybdenum base alloys which may be used to form molten sprayed coatings and to a method of making such a powder and such coatings.

For various reasons it is desirable to provide coatings of molybdenum or certain molybdenum base alloys. For example, the ways of machine tools and the piston rings of internal combustion engines are advantageously coated with molybdenum. An alloy of 70% molybdenum and 30% tungsten can be used to coat parts of zinc die casting machines where resistance to attack by molten zinc is desired. In the past the preferred method of forming such coatings has been by the use of an oxyacetylene flame molten metal spray gun in which the molybdenum is fed to the gun in the form of wire. Molten metal spray guns equipped with powder feed mechanisms are known and used for spraying other metals and would be advantageous for use in spraying molybdenum since they save the cost of producing molybdenum wire, but in the past all attempts to use an oxyacetylene powder-fed gun for spraying molybdenum have been unsuccessful.

It is an object of this invention to provide a novel physical form of molybdenum powder which may be used with success to form a sprayed coating using a conventional powder-fed oxyacetylene flame spray gun or similar equipment employing other gases to form the flame.

Another object of the invention is to provide a novel method of making a molybdenum powder which is useful for the purpose mentioned.

Another object is to provide a novel method of forming metal coatings of molybdenum and molybdenum base alloys.

In accordance with the present invention, it is found that a molybdenum powder suitable for use as the supply for an oxyacetylene flame molten spray gun has a particle size, shape and structural character which satisfies certain critical requirements. Thus, the particles must be large enough to avoid excessive oxidation during the travel of the molten droplet toward the surface to be coated and to retain enough heat to avoid solidification prior to contact with that surface. In addition, the particles must be small enough in mass to melt in the flame in the fleeting moment they pass through that flame en route to the surface. Applicant has found that solid particles of molybdenum which are large enough to satisfy the

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first requirement are too large to meet the second requirement, and it is for that reason prior attempts to use powdered molybdenum have failed. This is particularly true if the particles are of the generally spherical shape required for good flowability. Accordingly, the particles must also satisfy a third requirement, namely, that they be porous so that each particle contain less metal than a solid molybdenum particle of the same general shape and overall dimensions, so that less heat is required to melt the particle than would be required if the particle were solid, and less time required for the heat to penetrate to the inner portion of the particle. For this purpose, the term porous simply means that the particles contain voids which may or may not open to the outside surface.

In addition to the foregoing requirements, it is highly desirable, if not essential, that the powder be free flowing to facilitate feeding of the powder to the gun nozzle. This means that the powder particles should be of a limited range of size and substantially spherical in form.

All of the foregoing requirements are met by a powder consisting of appropriately shaped porous particles having a size range which will pass a 150 mesh screen and be retained on a 325 mesh screen (Tyler sieves), although better results are obtained if the largest particles will pass a 200 mesh screen and the best results are obtained with powders which will pass a 200 mesh screen and be retained on a 250 mesh. Particles which will pass a 150 mesh screen and be retained on a 325 mesh screen will have a nominal size of more than 43 and less than 104 microns. The more restricted size range which will pass the 200 mesh and be retained on the 250 mesh will have a nominal particle size of more than 61 and less than 74 microns. Satisfactory results have been obtained with a powder, 60% of which consisted in particles that would pass a 250 mesh screen and be retained on a 325 mesh screen and the balance of a size that would pass a 200 mesh screen and be retained on a 250 mesh screen.

In referring in this specification and the appended claims to the size range of the powder particles, it should be understood that while it is preferred to have no particles of a size outside the range specified, minor quantities of particles outside the size range specified may be tolerated. Thus, as much as 2% by weight may be smaller than 325 mesh and as much as 2% may be of a size which would pass a 100 mesh screen but be retained on a 150 mesh screen.

The degree of porosity required for satisfactory results may be designated in several ways. Thus, it is that degree of porosity which results when the powder is made by the method hereinafter described. Another method of measuring density is by a combination of particle size range and tap density. Tap density is the weight per given volume of powder of a particular size measured by placing a given weight of dry powder in a cylindrical graduate and reading the volume occupied by the powder after the graduate has been tapped gently ten times on a yielding surface, such as a rubber pad. By this method, satisfactory results may be obtained with powders having the following sizes and tap densities.

Particle size microns:

	Tap density grams per cubic centimeter
61-74	2.00-3.00
43-61	2.75-3.75
43-74	2.40-3.40

¹ (A 50-50 mixture of the above samples.)

The character and density of the particles may also be indicated by measuring their apparent density by relating weight to the volume displacement in methanol. If the powder is dropped slowly into methanol in such a

manner as to avoid entrapment of air between the particles and the initial volume displacement measured promptly, a density figure may be obtained which reflects to some degree the magnitude of the large voids within the particles because the methanol does not fill those voids until after the particles have been gently agitated in the methanol for some time. During such agitation, the escape of air will be noted, indicating that the voids are being filled with the methanol. After evolution of air ceases, the apparent density will be substantially increased, as indicated in the following table:

Test	Mesh range	Density, gm./cc.	Percent of theoretical Mo density
1-----	-200+250	7.2	71
2-----	-250+325	7.6	74
3-----	-200+250	8.8	86
4-----	-200+250	9.7	95
5-----		9.8	96

The density information was obtained in tests 1 and 2, above, by measuring the change in volume as soon as the powder was deposited in the methanol and entrained air had risen to the surface. In test 3 the change in volume was measured after the powder had been gently agitated in the methanol for two minutes. In test 4 the measurement was made after the agitation had been continued to the point that no further air evolved. Test 5 was made like test 1 except that the powder was first ground with a mortar and pestle about thirty minutes, that being sufficient to fracture all of the spherical particles. In all five of the above tests the powder used was pure molybdenum.

From the foregoing data and the microscopic examination of sections through the powder particles, it appears that each particle has one or more large interior voids which are surrounded by a skin of fairly solid material, but that all or many of the voids communicate to the outside surface of the particle through small openings; and it is through these small openings that the methanol seeps to fill the voids.

The flowability of the powder depends to a large degree upon the shape of the particles. To obtain the best results, the particles should be substantially spherical in form. Flowability may be measured by a standard Hall flow meter or by measuring the angle of repose. A satisfactory powder will have a flow time of not more than 42 seconds, and preferably not more than 38 seconds as determined on a standard Hall flow meter using the standard testing procedure covered by specification B 213-48 of the American Society for Testing Materials. The orifice used was calibrated with 150 mesh Turkish emery, which gave a flow time of 40.6 seconds.

Flowability may also be measured by measuring the angle of repose of the dry powder mass. Satisfactory powders will have an angle of repose of not more than 45 degrees to the horizontal, and preferably not more than 40 degrees.

It will be understood that in characterizing the particles as substantially spherical, it is meant that they approximate spherical form to such an extent that they roll freely and do not interlock with each other or pack together in such a manner as to preclude free flowing of the powder. For the purposes of this invention the particles are sufficiently spherical if the resulting powder has the flow characteristics set forth above.

The material of which the powder is made may be substantially pure molybdenum (i.e., molybdenum plus unavoidable impurities), or molybdenum containing deliberately added alloying elements. Tungsten in an amount up to about 30% may be present. Other elements such as cobalt, nickel and iron in a total amount not exceeding 10% may be present. The material may also contain small quantities of the oxides of other elements, such as titanium, zirconium, chromium, columbium, thorium, silicon, aluminum, sodium, potassium and magnesium, provided the total of all such oxides does not exceed about

2%. Such oxides are useful to inhibit grain growth or enhance strength.

In accordance with the present invention, powders made up of substantially spherical particles of molybdenum and certain of its alloys are made by melting an oxide of the metal, breaking the liquid oxide into separated droplets or spherical liquid particles and allowing them to solidify separately in that form. The resulting solid particles of the metal oxide are then reduced with hydrogen at elevated temperatures under conditions which will preserve their form and separate identity. The reduced powder consists of substantially spherical particles of the metal which are admirably suited for use in powder feed molten spray equipment and which are substantially free of oxygen unless small quantities of oxides that cannot be reduced by hydrogen are present or are deliberately added. The size of the particles may be controlled in part by the droplet-forming procedure, but subsequent screening is usually required to restrict the mass to a more limited range of sizes than may be obtained by control of the droplet-forming process alone.

The present process is applicable to molybdenum and also an alloy of molybdenum and tungsten containing not less than about 70% molybdenum and preferably an alloy of about 70% molybdenum and 30% tungsten. Tungsten trioxide is soluble in molten molybdenum trioxide and both can be reduced by hydrogen. Minor amounts of other metals may be present in combination with the molybdenum or the molybdenum and tungsten. Thus, the oxides of one or more of the metals cobalt, iron or nickel, whose oxides are soluble in molten molybdenum and tungsten oxides and are reducible by hydrogen, may be present. The preferred total quantity of cobalt, iron and nickel is less than 10% by weight in the reduced material. The molten oxide may also include small quantities of oxides of metals which cannot be reduced by hydrogen, such as the oxides of titanium, zirconium, chromium, columbium, thorium, silicon, aluminum, sodium, potassium and magnesium, provided the total of all such oxides does not exceed 2%.

In the practice of the process, relatively pure oxides of the metals employed may be melted in any desired manner, preferably by induction heating or by radiant heating in a crucible. A graphite crucible is preferred for this purpose. Molybdenum trioxide (MoO_3) melts at about 1500 degrees Fahrenheit. While tungsten trioxide (WO_3) melts at about 2700 degrees Fahrenheit, it will dissolve in molten MoO_3 at a much lower temperature. At the temperature required to melt a mixture of oxides which contain sufficient molybdenum trioxide to form an alloy containing 70% or more molybdenum, no significant sublimation or deoxidation occurs when the molten oxides are melted in a graphite crucible. However, to minimize sublimation, it is preferred to use a graphite cover on the crucible.

If the final alloy is to contain both molybdenum and tungsten, it is advantageous to melt the molybdenum trioxide first and then dissolve the tungsten trioxide in the molten oxide bath since by that means the entire bath may be melted at a lower temperature. This will result automatically if the oxides of the two metals are placed in the crucible at the same time and then heated. A solution containing the oxide proportions that will produce an alloy of 70% molybdenum and 30% tungsten is liquid at about 1660 degrees Fahrenheit.

The molten oxide is then converted to discrete droplets or spherical liquid particles and allowed to solidify in that form by any means heretofore used for the purpose of forming small solid spheres from a liquid phase. For example, this can be carried out in a shot tower or by a gas atomizing gun or by blasting the molten oxide into a bath of water or by an atomizer of the rotating disc or vibrating reed type. The operation is carried out in such a manner that the liquid particles solidify while they are suspended in air or some other gaseous medium or in a

liquid such as water. In each of these procedures the usual means may be employed for controlling the approximate size of the resulting solid particles to the end that they be of a size suited for molten spray equipment. For this purpose particles which are too small or too large for the purpose intended may be removed by screening.

One specific procedure which has been employed with success to form spheres of pure molybdenum trioxide involved the use of a graphite crucible have a $\frac{3}{8}$ " opening in the bottom through which a stream of molten oxide flowed into a fast-moving downward stream of air. The crucible opening was closed during the melting operation by a carbon rod which extended from above the molten material downwardly to the opening. Immediately below the crucible the stream of liquid oxide entered a 2" internal diameter collar which was $1\frac{1}{2}$ " long and was provided with three axially spaced circumferential rows of air inlet openings which extended inwardly through the wall of the collar and inclined downwardly at an angle of about 30 degrees to the axis of the collar. The axis of the collar was vertical and passed through the center of the drain opening of the crucible. Air at 80 p.s.i. was supplied to the air inlet passageways of the collar. The resulting spherical oxide particles were collected in a 6-foot diameter tank which was 14 feet deep and open at the top, the top edge of the tank being located just below the collar.

With this type of equipment the size of the particles can be controlled to some degree by adjusting the air pressure and the size of the air inlet holes, but screening is usually necessary to eliminate particles which are too small or too large for the purpose intended. The particles are preferably screened to the desired size while in the form of the oxide to eliminate any excessively small particles which would interfere with the subsequent reduction step and also since the rejected particles are economically recovered by remelting. Because of the shrinkage which occurs during subsequent reduction to the metallic state, an oxide powder which will pass a 100 mesh screen and be retained on a 270 mesh screen will produce a reduced powder that will pass a 150 mesh screen and be retained on a 325 mesh screen.

The solidified spherical particles which are largely MoO_3 but contain some partially reduced oxide (probably MoO_2), are reduced with hydrogen in accordance with the conventional procedures employed in reducing molybdenum or tungsten oxide powders except that care should be exercised to avoid a temperature high enough to melt or sinter the spherical particles together. In the case of molybdenum oxide powders which were produced in the above-described manner, the powder was reduced by hydrogen in two stages. In the first stage 200 grams of oxide powder were placed in molybdenum boats to a depth of approximately $\frac{3}{8}$ " and pushed through an Inconel tube in a direction counter to the direction of flow of hydrogen. The tube was heated in three separate zones along the length of the tube by resistance wire windings. The temperature in the first zone was maintained at 810° F., the second at 950° F. and the third at 1120° F. and the boats were pushed through the tube at such a rate that they were in each zone for one hour for a total of three hours. The hydrogen flow through the tube continued throughout the period at the rate of 24 cubic feet per hour and the residual hydrogen burned at its discharge. During this first stage the MoO_3 was reduced to MoO_2 which has a higher melting point and this will not sinter at the higher temperatures required to complete the reduction.

At the end of the first stage the boats were passed directly into a second tube which was heat to 2200° F. The boats were pushed through the second tube in a direction counter to the flow of hydrogen at the rate of 28" per hour. The hydrogen flow rate was 47 cubic feet per hour. The total time at elevated temperature in the second stage was 6 hours, following which the powder

was cooled to a temperature of about 200° Fahrenheit in a stream of hydrogen and then removed to the atmosphere. By this procedure the oxygen content of the powder was reduced to approximately .01%. The spherical powder particles tend to stick together slightly, but if the temperatures are controlled in the manner indicated to avoid sintering of the trioxide spheres before conversion to the dioxide, the finally reduced contents of the boats may be gently broken up into the discrete spheres. It will be understood that the times and temperatures herein given may be varied in accordance with well known principles without materially changing results.

The spheres are porous due to the fact that they are reduced after they are formed. The spheres have one or more internal voids, many of which do not open to the outer surface. These are believed to be due to shrinkage of the inner material after the outer surface has been reduced and thereby hardened.

Spheres produced as above described may be sprayed by a conventional molten metal spray gun employing a gas flame of any suitable type. In addition, such powders may be sprayed by a plasma spray gun. For this purpose, the preferred powder size range is one which will pass a 200 mesh screen but be retained on a 325 mesh screen. The so-called plasma gun employs an electric arc combined with a high speed jet of gas through a very fine orifice. The gas stream carries the metal powder particles through the arc. The gas may be hydrogen or an inert gas such as argon. While this equipment may also be used on molybdenum and molybdenum base alloys, the oxy-acetylene gas gun is preferred for molybdenum spraying because of its much greater production capacity.

The expression "consisting essentially of" a certain specified metal or metals, which appears in the appended claims, means that the specified metal or metals are the sole constituents of the final composition other than the usual impurities and minor quantities of elements which do not impair the usefulness of the powder for flame spraying.

The proportions given herein are by weight.

What is claimed is:

1. A metallic powder consisting essentially of molybdenum and from zero to about 30% tungsten, from zero to not more than 10% total of material from the group consisting of cobalt, iron and nickel and from zero to not more than 2% total of oxides of metals which cannot be reduced by hydrogen, said powder being formed of separate porous particles of a size which will pass a 150 mesh screen and be retained on a 325 mesh screen, the shape of said particles being such as to impart to the powder that degree of flowability which will result in an angle of repose of not more than 40 degrees to the horizontal.

2. A metallic powder consisting essentially of molybdenum and from zero to about 30% tungsten, from zero to not more than 10% total of material from the group consisting of cobalt, iron and nickel and from zero to not more than 2% total of oxides of metals which cannot be reduced by hydrogen, said powder being formed of separate porous particles of a size which will pass a 150 mesh screen and be retained on a 325 mesh screen, and said particles having an approximately spherical form which will impart free flowing characteristics to the dry powder mass.

3. A metallic molybdenum powder consisting of separate particles each produced by solid state hydrogen reduction of a solid substantially spherical particle of molybdenum oxide.

4. A metallic molybdenum powder consisting of separate porous substantially spherical particles of size which will pass a 200 mesh screen and be retained on a 250 mesh screen.

5. A free flowing porous metallic molybdenum powder consisting of separate particles which are of a size that will pass a 150 mesh screen and be retained on a 325

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mesh screen, said powder having an angle of repose of less than 45 degrees to the horizontal.

6. The process of forming a free flowing metal powder consisting essentially of molybdenum which comprises melting an oxide of the metal, breaking the liquid oxide up into droplets, allowing said droplets to solidify separately in substantially spherical form and reducing the resulting powder particles with hydrogen under elevated temperature conditions that will produce a powder substantially free of combined oxygen without causing the original particles to lose their separate identity.

7. The process of claim 6 further characterized by the fact that the metal oxide is melted in a graphite crucible.

8. The process of claim 6 further characterized by the fact that the resulting metal contains a quantity of tungsten not exceeding 30% of the total and by the fact that the molybdenum oxide is first melted in a container at a temperature below the melting point of tungsten oxide and the tungsten oxide thereafter dissolved in the molybdenum oxide to produce a solution of the two oxides.

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9. The process of claim 6 further characterized by the fact that the resulting reduced powder contains not more than 2% of oxides of metals that cannot be reduced by hydrogen, which oxides were dissolved in the molten molybdenum oxide.

10. The process of claim 6 further characterized by the fact that the oxide powder which would pass a 270 mesh screen is eliminated from the powder mass and only the powder that is sufficiently coarse to be retained on a 270 mesh screen is subjected to the reducing operation.

11. The process of claim 9 further characterized by the fact that the metal oxide is melted in a graphite crucible.

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