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DISPERSION STRENGTHENED MOLYBDENUM

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This invention relates to dispersion strengthened metals and in particular to a method for dispersion strengthening refractory metals having a propensity of forming unstable oxide films when heated to elevated temperatures, such as molybdenum, tungsten and the like.

Design demands for aircraft and missile propulsion equipment require the use of materials with high strength at temperatures above 1800° F. which has led to emphasis in the development of the refractory metals. Molybdenum, with its high melting point (4730° F.), its exceptional thermal shock resistance and other advantages is of particular interest for these applications. Molybdenum alloys based on conventional alloy development such as solid solution hardening are currently in use or under development.

Dispersion strengthening has the advantage of promoting high temperature strength and stability unobtainable by other techniques. This is evidenced by increased recrystallization temperatures and the absence of intercrystalline failures in low strain rate tests at high temperatures. Dispersion strengthening is achieved by the dispersion of a hard, inert, stable phase, e.g. refractory oxide, in a metal matrix. This second phase should be of sub-micron size and uniformly dispersed. Storage of energy, obtained by a high strain rate deformation process, such as extrusion, produces a strong, stable material at high temperatures. The second phase is not prone to coalescence, as in age-hardened materials, and the particle size and distribution of the dispersoid remain to a large extent fixed.

One method of achieving oxide dispersion in a ductile metal matrix is to mix uniformly finely divided refractory oxide particles with a ductile metal powder, consilidate the mixture into a compact and then strain work the compact at an elevated temperature into a wrought metal shape to optimize the strength of the metal by the storage of energy therein. While this method has resulted in improved high strength materials, certain limitations were inherent in it, such as the tendency for the oxide particles to agglomerate to larger sizes which put a limit on the physical properties obtained.

Another method of achieving dispersion strengthening is through the process of internal oxidation. In this method, a sufficient amount of solute metal, e.g. aluminum, is added to a solvent or matrix metal, e.g. copper, to form a dilute solution thereof, the solute metal being one having a propensity to oxidize in preference to the matrix metal. By forming a powder of the alloy and by preferentially oxidizing the solute metal internally of the matrix metal at an elevated temperature to form a fine oxide dispersion throughout the matrix metal and then consolidating by hot working the powder to a wrought shape, improved high temperature stress-rupture properties are obtainable. In carrying out this process, time, temperature, oxygen pressure and solute metal concentration are important in achieving the desired strength properties. The internal oxidation temperature employed for such base metals as copper and nickel is in the neighborhood of about 850° C. which represents a homologous temperature for these metals of about 0.7 to 0.8 referred to their melting points on the absolute scale. Comparable homologous temperatures for molybdenum and tungsten in the neighborhood of about 0.7 would be

about 1800° C. for molybdenum and 2300° C. for tungsten. However, with respect to these refractory metals, such temperatures pose certain difficulties due to oxide instability whereby improper formation of solute oxide occurs leading to excessive volatilization and to agglomeration of matrix metal oxide along the grain boundaries.

It is known that molybdenum trioxide forms readily at elevated temperatures, volatilizes rapidly and melts at a low temperature of about 1460° F. For example, at 1100° F., molybdenum oxidizes very readily in air to form a loosely adherent scale. Tungsten behaves similarly and, thus, attempts to dispersion harden such metals by using the technique of internal oxidation have not been too successful. Either the solute metal oxide could not be controlled or considerable agglomeration of the matrix metal oxide would occur at the grain boundaries which adversely limited the physical properties of the metal. Although attempts have been made to dispersion harden such metals as molybdenum and tungsten by internal oxidation, none, as far as we are aware, has been too successful.

It is an object of our invention to provide a method for producing by internal oxidation dispersion strengthened metals having the normal propensity of forming at elevated temperatures an unstable oxide.

Another object is to provide a method for dispersion strengthening by internal oxidation a metal selected from the group consisting of molybdenum and tungsten and containing a preferentially oxidizable solute metal.

These and other objects will more clearly appear from the following description.

We have found a method of producing dispersion strengthened materials from such metals as molybdenum, tungsten and the like, normally characterized by the tendency of forming an unstable oxide at elevated temperatures. For example, we have found in the case of molybdenum that by working under conditions which avoid formation of the unstable molybdenum trioxide but favor the formation of the more stable molybdenum dioxide for internal oxidation purposes, an improved wrought metal product is obtainable.

In one embodiment of our invention, we achieve a dispersion strengthened alloy of molybdenum of improved physical properties by providing an ingot or other solid shape of molybdenum containing a solute metal, such as titanium, comminuting said metal in an oxygen containing environment, such as by machining, grinding, abrading or other comminuting means, so that a relatively stable flash oxide coating forms on the surface of the thus-formed particulate material, subjecting the particulate material to thermal treatment at an elevated temperature under conditions substantially non-oxidizing to molybdenum but adapted to promote the internal oxidation of the molybdenum matrix metal and form an oxide dispersion of titanium oxide by virtue of the oxygen available in the oxide coating and then consolidating and hot working said particulate material into a wrought metal shape under conditions substantially non oxidizing to the matrix metal.

As illustrative of one embodiment of the invention, the following example is given:

Example 1

A solid stock of vacuum cast molybdenum containing about 0.5% Ti and about 0.035% carbon and measuring about 1¼ inches in diameter and 12 inches long was used. The stock was turned on a lathe in an oxygen-containing atmosphere using a tungsten carbide cutting tool which was ground flat on top and set at just below the center line of the stock. The lathe speed was about 600 r.p.m. and the feed set at 0.0015 inch per revolution. A depth of cut of 0.002 inch was used.

Small, brittle, substantially elongated chips were obtained as short curls which were crumbled into smaller sizes passing 35 mesh by hammering. The particle distribution was as follows:

Mesh size:	Percent by weight
+35	0.25
−35 +60	43.35
−60 +100	47.80
−100 +200	6.05
−200 +325	1.60
−325	0.95

The particulate or chip material was introduced into a rubber tube supported within a two inch diameter perforated steel canister and rubber stoppered at one end. A second rubber stopper which contained a hypodermic needle running through it was inserted at the other end of the tube, vacuum was applied to the needle and the rubber tube evacuated for about five minutes after which the needle was removed and the evacuated assembly subjected to hydrostatic pressure at about 30,000 p.s.i. to form compacts of about 1.5 inches in diameter.

The compacts were then sintered in a hydrogen atmosphere at about 2700° F. during which a substantial portion of the oxygen in the oxide coating diffused into the matrix metal and reacted with the contained titanium to form a dispersion of titanium oxide. The compacts or billets thus sintered were about 50 to 60% dense and could be handled on a lathe and machined for preparation for extrusion.

The billets were heated in an induction coil in an argon atmosphere, coated with a glass and alcohol paste and then extruded at a temperature of about 3100° F. with a reduction ratio of about 3 to 1 at a ram speed of about 1200 inches per minute. Since the whole operation proceeded very quickly, no deleterious effects from oxidation on the resulting extrusion were found. The extruded rods were immediately placed in crushed mica to prevent oxidation before cooling. The total elapsed time from the start of heating until the extruded rod was placed in crushed mica did not exceed 2.5 minutes. The diameter of the extruded rod varied from about 0.86 inch to 0.88 inch.

The extruded rod was then turned on a lathe to a diameter of about 0.71 inch to remove any scabs and other surface defects and then re-extruded at 3100° F. at the same rate to a final diameter of about 0.4 inch, other conditions being also the same as the first extrusion. The final extrusion ratio of the material was in the neighborhood of about 10 to 1.

Stress rupture tests were conducted at 1800° F. on the foregoing alloy and compared to pure vacuum cast molybdenum, and also to the alloy as vacuum cast. The specimens tested were 0.16 inch in diameter, 2.1 inches long and had a gage length of 1.1 inches. The alloys were tested at 1800° F. in a creep testing rack at various stresses under non-oxidizing conditions and time-to-rupture data obtained at the various applied stresses. The results obtained at 1, 10 and 100 hours are as follows:

Time	Rupture Stress, p.s.i.		
	Vacuum Cast Mo	Vacuum Cast Mo—0.5 Ti	Extruded Chip
1	27,600	54,000	73,000
10	19,000	52,000	66,000
100	14,000	50,000	60,000

It will be noted from the above that the extruded chip material is markedly superior to the vacuum cast molybdenum and to the vacuum cast Mo—Ti alloy. Metallographic examination of the extruded chip material by electron microscopy at 20,000 magnification indicated the markedly improved strength property to be due to the presence of the solute oxide titania, as was evidenced by the presence of titania needles of about 0.4 micron in length and about 0.1 micron in width. Apparently the process of turning or chipping the bar stock so greatly increases the surface area of the material that there is enough oxygen, due to surface oxidation in air at room temperature, for use in promoting the internal oxidation of the titanium during the sintering treatment. It is believed that surface oxidation is favored by virtue of the fact that a clean fresh surface is produced at the moment of cutting whereby a flash oxide coating results. It will be appreciated that the heat of friction, which may be generated during the cutting, also aids in producing the desired oxide coating. The foregoing conditions appear to favor the formation of the relatively stable molybdenum dioxide as opposed to the very unstable highly volatile molybdenum trioxide.

In a comparison test, molybdenum alloy chips were surface oxidized by heating in air at 1200° F. for 50 minutes. The chips were then subjected to a diffusion internal oxidation treatment by heating at 2700° F. in argon for 100 hours. An extruded product similarly produced from the foregoing treated material indicated the extruded product to be brittle. A metallographic analysis by the electron microscope revealed the formation of molybdenum dioxide of over 2.0 microns in size in the grain boundaries as well as sub-micron particles of titania within the grain. The presence of the grain boundary oxide of molybdenum caused embrittlement of the alloy. The preferred method described hereinabove avoided the grain boundary oxide.

Similar adverse results were obtained with another process of oxidation in which the alloy chips were substantially oxidized by heating in air at 1200° F. for 50 hours and then subjected to a reducing treatment in hydrogen at 2700° F. for 100 hours to remove the excess oxygen while leaving throughout the mass a dispersion of titania. A billet produced from this material was similarly extruded but was observed to be brittle due to the presence of molybdenum dioxide particles in the grain boundaries.

Example 2

Improved results were also obtained with a molybdenum alloy containing about 1.5% Ti. A bar stock of this alloy was prepared by powder metallurgy by means of the high temperature diffusion of elemental powders in a reducing atmosphere.

As in Example 1, the alloy was similarly chipped by turning to produce minus 35 mesh material and subjected to the same processing steps to produce a dispersion strengthened extruded billet. Stress rupture results obtained at 1800° F. are given as follows:

Time, Hrs.	Rupture Stress, p.s.i.		
	Mo	Mo—1.5 Ti	Extruded Chips
1	27,000	30,000	76,000
10	19,000	25,500	62,000
100	14,000	21,500	55,000

It will be noted that the internally oxidized extruded chip material is likewise markedly superior over the pure molybdenum, as well as the alloy from which it was produced. In a test conducted on the internally oxidized alloy loaded at a stress of 30,000 p.s.i., the alloy did not fail after 200 hours.

The foregoing pattern of strengthening was also noted in an alloy containing 0.5% Cb.

Example 3

An arc cast alloy of molybdenum containing 0.5% Cb was provided from which chips of minus 35 mesh were similarly prepared as in Examples 1 and 2 and subjected to the same processing steps to produce a dispersion

strengthened extruded billet. Stress rupture data were similarly obtained at 1800° F. At a stress loading of 52,000 p.s.i., the extruded chip material did not fail after 350 hours while the arc cast material failed on loading in less than one hour.

The extruded chip material in Examples 1, 2 and 3 exhibited elongation values at failure falling within the range of about 12 to 20%, while reduction in area ranged from about 30 to 45%. In the case of the alloys dispersion-strengthened by methods other than the invention, the values were substantially below these due to the prevailing brittle structure.

It is apparent from the foregoing that our method enables the production of improved high strength wrought molybdenum products heretofore not obtainable by prior methods of dispersion strengthening. Apparently, the type of oxide coating on the particles is an important consideration. Thus, besides the requirement that the oxide should be rather stable, it is preferred that the oxide thickness, depending on the shape and specific surface of the powder and the volume loading of the disperse oxide phase desired in the final product, should not exceed about 0.3 micron and more preferably not exceed 0.1 micron. For example, the preferred oxide thickness for the purpose of effecting internal oxidation of the base metal may range from about 0.005 to 0.1 micron.

As will be appreciated, the amount of surface oxide will generally depend upon the specific surface of the particulate metal. We have found that for our purposes, the specific surface should exceed 50 cm.^{2}/gr. and may range up to about 8,000 cm.^{2}/gr. We prefer the specific surface of the particulate base metal be at least about 100 cm.^{2}/gr. As a working maximum, a specific surface not exceeding about 2000 cm.^{2}/gr. is preferred. The thickness of the oxide coating will generally be inversely related to the specific surface of the particles. For example, the greater the surface area, the smaller will be the thickness of the surface oxide to achieve a particular oxide loading.

In achieving the desired specific surface, mechanical reduction is preferably employed in an oxidizing environment. As stated herein, mechanical methods of reduction may comprise machining, grinding, drilling and the like. Maximum surface may be produced by such methods by forming flaky or small plate-like particles. Thus, the particle size of one shape might appear to be large compared to a spherical particle of smaller diameter but yet have greater exposed surface than the spherical particle. For example, in producing flat particle shapes by machining, generally a roughened surface is obtained characterized by a fairly large specific surface. Thus, a particle of molybdenum might have one dimension corresponding to 200 microns but be thin enough to exhibit a specific surface in excess of 100 cm.^{2}/gram. On the other hand, a spherical powder of molybdenum to yield a specific surface in excess of 100 cm.^{2}/gram would have to be restricted to a smaller dimension below about 50 microns. Thus, in order to increase the oxide loading of the matrix base metal, particles produced by machining may be further mechanically reduced in a ball mill in an oxidizing atmosphere. Where a large specific surface is desired, e.g. above 500 cm.^{2}/gram, it may be desirable to carry out the mechanical reduction in an argon atmosphere characterized by a low partial pressure of oxygen so as to control the extent of the surface oxidation. Because particles of different shapes can be employed to yield a desired specific surface, we prefer to define our mechanically reduced metal powder in accordance with its specific surface rather than in particle size units per se.

The amount of oxide coating will depend to some extent on the amount of solute metal present or the volume loading desired in the metal. We prefer the amount of solute metal should not exceed that amount which will give a maximum oxide loading in the matrix metal of about 10 v./0 (volume percent). The preferred minimum loading would be at least about 0.1 v./0. More preferably, the

oxide loading may range from about 0.1 to 6.0 v./0. Of course, it is appreciated that not all of the contained solute metal need be oxidized.

While the solute metal from which the dispersed oxide is produced may comprise Ti or Cb, it will be appreciated that other solute metals may be employed whose propensity for forming the oxide is greater than that for the matrix metal. Examples of such solute metals are Mg, Ce, La, Th, Be and preferably those whose negative free energy of formation of oxide referred to 25° C. is at least about 85,000 calories per gram atom of oxygen and more preferably at least about 95,000.

As stated hereinbefore, the matrix metals to which the invention is applicable are those having a propensity of forming unstable oxide films when heated to an elevated temperature, e.g. at temperatures above 200° C., but, like for example molybdenum and tungsten, capable of forming stable oxide films under certain conditions. Such matrix metals will generally have a melting point over 2000° C. and be capable of forming a stable oxide film having a melting point above 1200° C. In addition, the oxides formed by such matrix metals should be characterized by a negative free energy of formation per gram atom of oxygen referred to 25° C. not exceeding about 75,000 calories per gram atom of oxygen. When the foregoing conditions are met, we find that we can dispersion strengthen such matrix metals to provide improved physical properties by alloying with the matrix metal a solute metal whose oxide has a negative free energy of formation of at least about 85,000 calories per gram atom of oxygen, mechanically reducing or comminuting the alloy under conditions to provide a thin, stable oxide coating of the matrix metal on the particulate material, subjecting the particulate material to a thermal heat treatment at an elevated temperature under non-oxidizing conditions to promote internal oxidation of the material and then hot working the thus-treated material into a wrought metal shape. Of course, the particulate material may be surface oxidized by heating in an oxygen-containing atmosphere provided it is done at a temperature which favors the formation of the stable oxide.

In providing a dispersion strengthened tungsten alloy, having a dispersion of titania therethrough, an amount of the solute metal titanium is added and a bar stock produced therefrom which is thereafter comminuted by machining or other suitable method such as drilling, grinding and the like, in an environment conducive to promoting an oxide coating on the particles. Thereafter the particulate material would be similarly treated as in Example 1 to internally oxidize the tungsten and thereafter extruded at a temperature of about 3000° F. to form a wrought metal tungsten product having a uniform dispersion of titania throughout the matrix thereof.

While the invention has been directed to the treatment of the matrix metal in substantially the elemental state, it will be appreciated that the invention is also applicable to alloys based on the matrix metal, provided that the negative free energy of formation of the oxides of the elements added does not exceed about 75,000 calories per gram atom of oxygen. For example, in the case of molybdenum, tungsten and other metals, the alloying element might comprise tungsten in the case of molybdenum or molybdenum in the case of tungsten or other elements having melting points exceeding 1300° C. Such alloying elements when added to the matrix metal may range up to about the solid solution limit in the respective phase diagram but not exceed about 20% by weight of the alloy composition. Where the matrix metal is based on an element or an alloy thereof, the processing of the metal will be substantially the same.

Generally speaking, the particle size of the disperse oxide will not exceed about 1 micron and preferably will range from about 0.01 to 0.1 micron.

Although the present invention has been described in conjunction with preferred embodiments, it is to be un-

derstood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. A method of producing by internal oxidation a dispersion strengthened wrought metal product from a matrix metal selected from the group consisting of Mo, and W and molybdenum-base and tungsten-base alloys containing an alloying constituent in an amount ranging up to the solid solution limit of the respective phase diagram but not exceeding 20% by weight of the alloy and capable of forming a stable oxide but which has a normal propensity of forming an unstable oxide when heated under oxidizing conditions to an elevated temperature which comprises, providing a solid stock of said matrix metal containing solute metal ranging in an amount corresponding up to about 10 v./0 of solute metal oxide equivalent whose negative free energy of formation at 25° C. is at least about 85,000 calories per gram atom of oxygen, comminuting by mechanically reducing said solid stock in an oxygen-containing atmosphere, whereby an oxide film is provided on the comminuted matrix metal obtained, subjecting the particulate matrix metal to thermal treatment at an elevated temperature under substantially non-oxidizing conditions sufficient to promote the internal oxidation of said matrix metal, whereby its surface oxide is converted to an internal dispersion of solute metal oxide and then hot working said thermally treated matrix metal under substantially non-oxidizing conditions into a wrought metal shape, whereby said matrix metal is characterized by improved high temperature strength properties.

2. The method of claim 1 wherein the comminuted matrix metal has a specific surface ranging from about 50 cm.^{2}/gram to 8,000 cm.^{2}/gram.

3. A method of producing by internal oxidation a dispersion strengthened wrought metal product from a matrix metal selected from the group consisting of Mo and W and molybdenum-base and tungsten-base alloys containing an alloying constituent in an amount ranging up to the solid solution limit of the respective phase diagram but not exceeding about 20% by weight, said matrix metal capable of forming a relatively stable oxide but which has a normal propensity of forming an unstable oxide when heated to an elevated temperature which comprises, providing a solid stock of said matrix metal containing solute metal ranging in an amount corresponding up to about 6 v./0 of solute metal oxide whose negative free energy of formation at 25° C. is at least about 85,000 calories per gram atom of oxygen, mechanically reducing said solid stock in an oxygen-containing atmosphere to form comminuted matrix metal having a specific surface ranging from about 100 cm.^{2}/gram to 2000 cm.^{2}/gram, whereby an oxide film is provided on the comminuted matrix metal obtained, subjecting the particulate matrix metal to thermal treatment at an elevated temperature under substantially non-oxidizing conditions sufficient to promote the internal oxidation of said matrix metal, whereby substantially its surface oxide is converted to an internal dispersion of solute metal oxide and then hot working said thermally treated matrix metal under substantially non-oxidizing conditions into a wrought metal shape, whereby said matrix metal is characterized by improved high temperature strength properties.

4. A method of producing by internal oxidation a dispersion strengthened wrought metal product from a molybdenum-base matrix metal having a normal propensity of forming an unstable oxide which comprises providing said matrix metal containing an amount of a refractory oxide-forming solute metal whose propensity for forming an oxide is greater than that for the matrix metal and is characterized by a negative free energy of formation at about 25° C. of at least about 85,000 calories per gram atom of oxygen, the amount of solute metal not exceeding an amount corresponding to up to about 10 v./0 of its oxide, mechanically reducing said matrix metal in the presence of an oxygen-containing atmosphere thereby to form a comminuted matrix metal having flash layer of oxide coating thereon, subjecting said comminuted matrix metal to a thermal treatment at an elevated temperature under substantially non-oxidizing conditions to promote the internal oxidation of said matrix metal and form a dispersion of refractory oxide therethrough and then hot working said alloy into a wrought metal shape under substantially non-oxidizing conditions.

5. The method of claim 4 wherein the specific surface of the comminuted molybdenum-base metal ranges from about 50 cm.^{2}/gram to 8000 cm.^{2}/gram.

6. A method of producing by internal oxidation a dispersion strengthened wrought metal product from molybdenum matrix metal having a normal propensity of forming an unstable oxide which comprises providing said molybdenum matrix metal containing an amount of a refractory oxide-forming solute metal whose propensity for forming an oxide is greater than that for molybdenum and is characterized by a negative free energy of formation at about 25° C. of at least about 85,000 calories per gram atom of oxygen, the amount of solute metal not exceeding an amount corresponding up to about 10 v./0 of its oxide, mechanically reducing said matrix metal in the presence of an oxygen-containing atmosphere to produce comminuted metal having a specific surface ranging from about 50 cm.^{2}/gram to 8000 cm.^{2}/gram thereby to form a flash layer of oxide coating thereon, subjecting said comminuted metal to a thermal treatment at an elevated temperature under substantially non-oxidizing conditions to promote the internal oxidation of matrix metal and form a dispersion of refractory oxide therethrough and then hot working said alloy into a wrought metal shape under substantially non-oxidizing conditions.

7. The method of claim 6 wherein the refractory oxide forming metal is titanium.

8. The method of claim 7 wherein the amount of titanium does not exceed an amount corresponding up to about 6 v./0 of its oxide.

9. The method of claim 6 wherein the refractory oxide forming metal is columbium.

10. The method of claim 9 wherein the amount of columbium does not exceed an amount corresponding up to about 6 v./0 of its oxide.

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