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METHOD OF INTRODUCING HARD PHASES INTO METALLIC MATRICES

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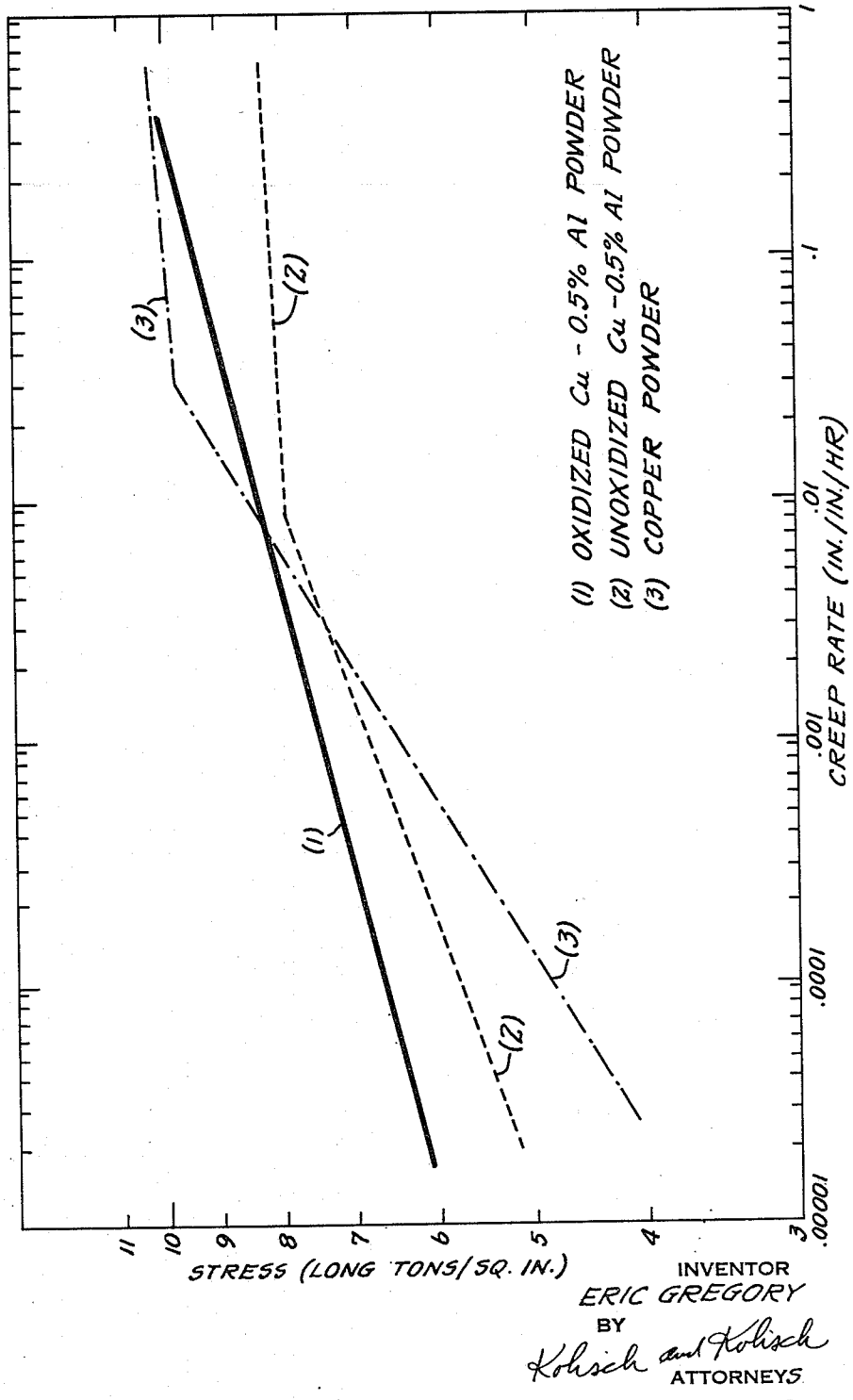

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METHOD OF INTRODUCING HARD PHASES INTO METALLIC MATRICES

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The present invention relates to the production of a reinforced metal product and, more particularly, to a method of introducing a hard refractory oxide phase into a ductile metal matrix.

It is known that high temperature strength properties of certain ductile metals can be improved by the addition to the metals of a discrete hard phase, e.g. Al_2O_3, which increases the metal's resistance to deformation and enables it to sustain high stress at elevated temperatures for prolonged periods of time. Wrought aluminum products produced from fine aluminum powders exhibit such improved properties in comparison to aluminum products made by conventional casting. This is because aluminum powders are generally characterized by a surface oxide coating which remains in the final product as finely dispersed hard particles of Al_2O_3. These particles behave as slip inhibitors and it is largely this characteristic that stiffens the metal or alloy and raises its resistance to applied stress at elevated temperatures. The disperse hard phase acts as a deterrent to recrystallization and grain growth and thus inhibits or decreases the metal's tendency to weaken and soften at elevated temperatures.

There have been recent trends to employ this disperse phase hardening mechanism in stiffening heat resistant alloys, for example an alloy containing 80% nickel and 20% chromium. A given amount of hard phase, e.g. titanium carbide powder, is added to the foregoing type alloy in the powder form and the two mechanically mixed to obtain a uniform distribution of one in the other. The mixture is consolidated into a compact and then hot worked at an elevated temperature into a desired shape. The fine dispersion of the carbide stiffens the matrix of the alloy and confers additional resistance to deformation at high stresses at elevated temperatures. In order to obtain full benefit, the hard phase must be substantially insoluble in the matrix of the alloy, otherwise the alloy will lose its stiffness and soften due to the solution of the hard phase in the matrix metal.

One of the disadvantages of the foregoing method of introducing hard phases into the matrix was the tendency for mechanically mixed materials to segregate. Because of this effect, it was not always consistently possible to maintain a perfect mixture. Even when the powders were blended under the best possible mixing conditions, there was still the problem of segregation during storage, handling, processing, pressing, etc. If the powders were stored for any length of time and subjected inadvertently to extraneous vibration usually prevailing in buildings maintaining large presses, reciprocating vacuum pumps, and other heavy industrial machines and equipment, the powders would tend to segregate due to marked differences in densities and, unless the powders were remixed, the final product would be affected due to nonuniform distribution of the slip-inhibiting phase in the final product.

The present invention overcomes the foregoing difficulties by providing a method for insuring uniformity of the final product by enabling the production of a metal powder in which substantially each particle contains a slip-inhibiting phase associated with it as a disperse phase.

It is, therefore, an object of the present invention to provide a method of introducing a hard disperse phase into

a ductile metal powder prior to consolidating the powder into a solid shape, thereby insuring a uniform distribution of said hard phase throughout the final product.

These and other objects will more clearly appear from the following description when taken in conjunction with the drawing in which FIG. 1 depicts curves comparing the physical properties of an internally oxidized material, the same material not oxidized, and straight copper.

The introduction of the hard phase is achieved by "internally oxidizing" a ductile matrix metal powder having alloyed therewith a refractory oxide-forming metal whose oxide is substantially stable at elevated temperatures. By the term internally oxidizing is meant the introduction of oxygen through diffusion into and through the powder particle structure from the surrounding atmosphere during the special heat treatment. The matrix metal should be relatively noble compared to the refractory oxide-forming metal contained therein. Examples of such metals for the purposes of this invention are silver, gold, copper, platinum, palladium, nickel, cobalt, iron, and alloys based on one or more of these metals, etc. Such metals may be selected broadly from the copper group, platinum group, and iron group metals.

Examples of refractory oxide-forming metals include silicon, aluminum, magnesium, beryllium, zirconium, titanium, thorium, rare earth metals such as cerium, lanthanum, neodymium, etc., and similar metals which combine chemically with oxygen to form hard, refractory oxides having melting points of about 1500° C. and above.

The so-called ductile metals are also defined broadly as those metals having a melting point of at least about 750° C. and whose oxides have a negative free energy of formation at 25° C. below 70,000 calories per gram atom of oxygen. For the purposes of this invention, the refractory oxide-forming metal has a negative free energy of formation with oxygen of over 90,000 calories per gram atom of oxygen, and generally over 120,000.

The following table compares approximate values of free energies of formation of some noble metal oxides with some refractory oxides at 25° C.:

Noble Metal Oxide	ΔF [1]	Refractory Oxide	ΔF [1]
Ag_2O	−2,586	SiO_2	−96,200
CuO	−30,400	TiO_2 [2]	−101,400
Cu_2O	−34,980	ZrO_2	−122,200
CoO	−51,000	Al_2O_3 [3]	−125,590
NiO	−51,700	MgO	−136,130
FeO	−58,400	BeO	−139,000
Fe_2O_3	−59,000	ThO_2	[4]−146,000

[1] Free energy of formation in calories per gram atom of oxygen.
[2] Rutile.
[3] Alpha alumina.
[4] Heat of formation. Free energy is a little lower than this value.

Platinum oxide has a negative free energy of formation below 20,000 calories per gram atom while the value for palladium oxide is below 17,000 calories.

Since the amount of the refractory oxide-forming metal alloyed with the more noble matrix metal is usually small, for example in amounts of up to about 5% by weight, generally from about 0.05 to 2.5%, the matrix metal is also prone to oxidize during the oxidizing treatment. Depending upon composition, temperature and oxygen partial pressure, the refractory oxide will form within the alloy powder particle in the form of fine particles. In addition, the powder particles may be covered by a surface scale oxide of the more noble matrix metal, provided the matrix metal oxide is stable. Generalizing in the case of silver, the oxide Ag_2O is relatively unstable because of its rather low negative free energy of formation, while in the case of iron, the oxide Fe_2O_3 is comparatively more stable because of its higher negative free energy.

If the matrix metal oxide is allowed to remain on the surface of the powder after the oxidation treatment, and the powder then used to form solid shapes by powder metallurgical techniques, the resulting product will not exhibit the results desired at elevated temperatures as the matrix metal oxide is relatively unstable at elevated temperatures, has a higher solubility in the matrix metal at such temperatures and is prone to react with stronger oxide formers contained therein. Therefore, it is important that the formation of matrix metal oxide either be inhibited or, if it forms, removed by a subsequent operation prior to forming solid shapes from the treated powder.

The conditions for the formation of a stable dispersion of refractory oxide compound RO in a more noble metal N or, by diffusing element O into solid solution N and R are as follows:

(1) O must diffuse more rapidly in the more noble metal solvent N than solute R does, otherwise a surface layer RO will be formed.

(2) The free energy of formation of the compound RO must be much more negative than that of compound NO.

When gases are soluble in metals, they generally diffuse far more quickly than do metallic solute elements and, therefore, they are ideally suited to the formation of a dispersed phase by this method. In general noble metals, e.g. silver, alloyed with a small percentage of a metal having a high affinity for oxygen, e.g. aluminum, are very suitable for internal oxidation.

A large difference between the free energy of formation of the oxide of the solute and the oxide of the solvent favors the formation of small particles. Thus, the particles formed on the oxidation of silver-aluminum alloys are far smaller than those obtained in silver-silicon, which, in turn, are smaller than those formed in copper-silicon alloys under the same conditions.

The particle size is affected by the rate of diffusion of the solute metal outwards relative to that of the oxygen inwards. When the two rates are equal either an external scale or a continuous inner oxide film is formed and when the oxygen diffuses only slightly faster than the solute the resulting particles are large. Factors which alter the difference between these diffusion rates will change the size of the particles and the tendency to form continuous films.

For silver alloys it was found that increasing the temperature of oxidation, other factors being constant, increases the average particle size and the tendency to form inner oxide films. Increasing the concentration of the solute has a similar effect.

The importance of some of the above variables were shown by preliminary experiments on a wire specimen of silver alloy containing 0.13% silicon. This was vacuum annealed at 900° C. to obtain a large stable grain size and the specimens were heated in air at 650° C., 750° C. and 850° C. Oxidation at 650° C. led to the production of a dispersed phase throughout but at 850° C. an inner oxide film was formed very close to the surface. When the oxidation was carried out at 750° C. the inner oxide film was still present and in this case close to the center of the wire. Material which had been vacuum annealed at 675° C. and had a fine grain size could not be oxidized throughout at 650° C. in air owing to the formation of an inner oxide film. This may have been due to the faster diffusion of silicon along the grain boundaries compared with bulk diffusion through the grains. Fine grained material having a much greater grain boundary area than the coarse grained, will allow the silicon to diffuse outwards more quickly and favor the formation of continuous films.

Increasing the oxygen partial pressure over silver alloys increases the concentration gradient of oxygen, decreases the particle size of the disperse hard phase, and reduces the probability of forming continuous films, the fine grained and coarse grained materials were both oxidized throughout at all temperatures between 675° C. and 850° C. by heating in oxygen.

A complete explanation of such effects must take into account the overall rate of movement of the oxidation front and how this is influenced by changes in (*a*) the oxygen rate of penetration with depth and (*b*) the rate of migration of aluminum as influenced by changes in concentration gradient as oxidation occurs.

The oxidation of massive metal, such as a wire of a copper alloy containing small mounts of solute aluminum, had its limitations in improving the physical properties of the alloy wire. It was not always possible to obtain adequate internal dispersion of hard phase, e.g. Al_2O_3. This was true in instances where the alloy had a high aluminum concentration gradient relative to that of oxygen as might prevail in a copper alloy containing about 1% aluminum. Such an alloy oxidized in air, other conditions being equal, was more prone to form an internal oxide film below the metal surface comprising substantially Al_2O_3 which inhibited further diffusion of oxygen into the interior of the metal wire which usually gave rise to large areas deficient in disperse hard phase. Because of this, the full benefits of the hard phase-forming element could not be utilized adequately and thus there was a limit as to the amount of solute metal that could be tolerated in a particular solvent metal.

The present invention overcomes the foregoing difficulty by using internally oxidized, finely divided powder as the starting material (for example, particle size preferably below 300 microns, and more preferably below 150 microns). As long as there is some internal oxidation, the final product resulting from the treated finely divided powder will have generally a more uniform dispersion of hard phase throughout its cross section than in the case of an internally oxidized wire. An important feature of using metal powders is that more of the solute phase-forming metal can be tolerated in the alloy powder than in massive metal, and thus greater benefits property-wise can be realized.

As illustrative of the invention, the following examples are given:

Example I

A finely divided alloy powder (minus 300 microns) containing 0.5% aluminum and the balance copper was internally oxidized in air at a temperature of about 1000° C. for a few minutes (below ten minutes). The oxidized powder had a surface scale enriched in copper oxide and a small amount of internal oxidation. The material was then heated in an inert atmosphere of nitrogen at 900° C. for about one hour. During this heating the surface oxide decomposed and acted as a source of oxygen which diffused into the powder particles to form Al_2O_3 with the aluminum, most of the surface oxide being reduced to pure copper. Some copper oxide remained on the surface and this was reduced by heating the powder to 600° C. in an atmosphere of hydrogen. The powder was then cold compacted in a confining die at a pressure of about 30 tons per square inch, thereafter heated to 900° C., placed in a cold die mold, and a pressure of 30 tons per square inch applied immediately. The billet thus formed was hot extruded at a temperature of about 900° C. at an extrusion ratio of about 20 to 1 under a pressure of about 50 tons per square inch. The stress rupture and creep properties were obtained and compared to similar properties obtained for pure copper (note FIG. 1).

FIG. 1 shows the relationship between creep rate and stress for the internally oxidized material (1), the same material in the unoxidized condition (2), and material made from straight copper powder (3).

The internally oxidized material (1) comprising 0.5% aluminum and the balance copper was produced in accordance with Example I. The unoxidized material (2) was produced from the same powder lot as (1) except the

oxidation step was omitted while (3) was produced from straight electrolytic copper powder. All three powders were fabricated similarly into solid shapes. It will be seen that at low stresses the internally oxidized material has considerably improved creep resistance over those of the other two materials. Also it is significant that the latter [(2) and (3)] show instability breaks associated with recrystallization. This is absent in results of the internally oxidized material (1), showing the stability resulting from the presence of the finely dispersed phase.

Example II

A finely divided alloy powder (minus 300 microns) containing 0.5% silicon and the balance copper was internally oxidized in air at a temperature of about 925° C. for about one hour. The oxidized powder had a surface scale enriched in copper oxide and a small amount of internal oxidation. The material was then heated in an inert atmosphere of nitrogen at 925° C. for two hours. During this heating, the surface oxide decomposed and acted as a source of oxygen which diffused into the powder particles to form SiO_2 with the silicon, most of the surface oxide being reduced to pure copper. Some copper oxide remained on the surface and this was reduced by heating the powder to 750° C. in an atmosphere of hydrogen for about five minutes. The powder was then cold pressed in a confining die at a pressure of about 40 tons per square inch, thereafter heated to 900° C., placed in a cold die mold and a pressure of 40 tons per square inch applied immediately. The resulting compact was then hot extruded at a temperature of about 900° C. at an extrusion ratio of about 20:1 under a pressure of about 50 tons per square inch. The extruded material had a yield strength of about 19,700 p.s.i. as compared to a similarly extruded material of electrolytic copper powder which exhibited a lower yield stress of 12,600 p.s.i.

A finely divided powder comprising 1% zirconium and the balnace nickel may be similarly treated by subjecting said powder (e.g. minus 150 microns) to oxidation in air at 950° C. for about one hour followed by heating for several hours at 1000° C. in a nitrogen atmosphere to promote the internal oxidation of the powder via the decomposition of the nickel oxide forming the surface scale. A substantial amount of the contained zirconium is thus converted to fine particles of ZrO_2. The powder is thereafter subjected to the reducing action of hydrogen, or other reducing gas, to remove the last traces of nickel oxide from the surface, after which the resulting internally oxidized powder is compacted as in Examples I and II and hot extruded into a desired shape.

Where a nickel-chromium alloy is desired hardened by ZrO_2, e.g. 80% nickel and 20% chromium, the chromium is not added until the ZrO_2 has been formed otherwise the presence of the large amount of chromium would interfere with the internal oxidation mechanism. First, an internally oxidized powder of Ni—Zr (e.g. 1% zirconium) would be produced as described above and the powder then mixed with powdered chromium, compacted, subjected to an alloying heat treatment and then hot shaped, e.g. by extrusion to the desired configuration.

The present invention is also applicable to the grain stabilization of platinum and platinum alloys or metals of the platinum group such as iridium, osmium, palladium, rhodium and ruthenium and to alloys in which at least one of these metals forms the principal ingredient. Such metals stabilized by the present invention enable their use at elevated temperatures as furnace heating elements, etc. Such refractory oxide formers as thorium (to form thoria), silicon (to form silica), aluminum (to form alumina), etc., may be added in amounts up to 5%, preferably from 0.05% to 2.5%.

In producing platinum stabilized with thoria, an alloy powder of platinum and thorium of about minus 150 microns is first produced containing for example, about 0.75% thoria. The powder is first subjected to internal oxidation in air at about 800° C. for about half an hour. Since platinum like silver is relatively stable and does not oxidize to any great extent it need not be subjected to a reducing treatment but may be directly compacted into a slug and thereafter hot extruded into the desired shape.

It is apparent from the foregoing that a method of introducing a hard phase into a matrix metal is provided comprising starting with a powder of said matrix metal having alloyed therewith a small amount of refractory oxide-forming metal having a greater oxide-forming propensity than the more noble matrix metal, subjecting said powder to internal oxidation by heating at an elevated temperature below the melting point of said noble matrix metal under oxidizing conditions and then hot forming said oxidized powder to produce a solid shape of said ductile matrix metal having dispersed therethrough fine particles of a hard refractory oxide. Where part of the matrix metal is oxidized along with part of the refractory oxide-forming metal to form some disperse refractory oxide phase and a surface scale of matrix metal oxide, the powder is additionally treated after the oxidation step by heating it to an elevated temperature, e.g. 900° C., under inert conditions, e.g. in an atmosphere of nitrogen gas, for a time sufficient for the surface oxide to decompose and provide oxygen for diffusion into the underlying metal to form said refractory oxide by reaction with the contained refractory oxide-forming metal. The excess matrix metal oxide remaining at the surface is then reduced by heating in a reducing atmosphere (e.g. hydrogen) at an elevated temperature, thereby resulting in a metal powder having a reduced metal surface but containing internally thereof finely dispersed refractory oxide.

The invention also provides a novel method for the production of a susbtantially ductile metal powder having dispersed therethrough fine particles of a refractory oxide, e.g. selected from the group consisting of SiO_2, Al_2O_3, MgO, BeO, ZrO_2, TiO_2, ThO_2, and rare earth metal oxides.

The invention further provides as a composition of matter a substantially ductile relatively noble metal powder having dispersed therethrough fine particels of a hard refractory oxide of melting point above 1500° C., such as defined above, wherein the ratio of the relatively noble metal to the refractory oxide-forming metal substantially combined as the oxide is preferably at least about 19 to 1 and higher.

While the ductile copper group, iron group and platinum group metals have been given as examples of matrix metals that can be dispersion hardened by the novel process of the invention, it will be appreciated that alloys based on these metals can be similarly treated.

Examples of copper group alloys are: 95% copper and 5% zinc; 90% copper and 10% zinc; 60% copper and 40% zinc; 71% copper, 28% zinc and 1% tin; 65% copper, 17% zinc and 18% nickel; 90% silver and 10% copper; up to 15% nickel and the balance silver; 70% gold and the balance palladium; 69% gold, 25% silver and 6% platinum, etc. These alloys as powders containing up to 5% by weight of refractory oxide formers can be internally oxidized at temperatures ranging from about 500° C. to 1000° C., in an atmosphere at least oxidizing to the refractory oxide former.

Examples of iron group alloys include: certain steels; 64% iron and 36% nickel; 31% nickel, 4 to 6% cobalt, and the balance iron; 54% iron and 46% nickel; 99% nickel and the balance cobalt; 68% nickel and 32% copper, etc.

Heat resisting alloys based on the iron group metals may also be treated providing such alloying agents as chromium are not added until the iron group metal powder containing the refractory oxide-forming metal has been internally oxidized.

The foregoing iron group alloys as powders containing preferably up to about 5% by weight of refractory oxide

formers may be internally oxidized at a temperature of about 500° C. to 1300° C. in an atmosphere oxidizing to the refractory oxide former. Such an atmosphere could comprise oxygen, air or other oxygen containing gaseous media.

Examples of platinum group alloys are as follows: platinum-rhodium alloys containing up to 50% rhodium; platinum-iridium alloys containing up to 30% iridium; platinum-nickel containing up to 6 or 10% nickel; platinum-palladium-ruthenium containing 77% to 10% platinum, 13 to 88% palladium, and 10 to 2% ruthenium; alloys of palladium-ruthenium containing up to 8% ruthenium; 60% palladium and 40% silver, etc. These alloys with refractory oxide-forming metal would be treated similarly as the copper group alloys.

Generally speaking, the oxidizing temperatures must be at least sufficient to oxidize the refractory oxide-forming metal. Such temperatures will range from 500° C. and up, preferably 600° C. and up.

An important advantage of the invention is that it provides a method for producing a sinterable, internally oxidized powder.

The composite powder produced in accordance with the invention is first consolidated before it is hot worked or extruded. It is preferred that the mixture be consolidated to an apparent density of at least about 65%, preferably as near as 90% as possible, before it is hot worked. While in general it would be preferred that the mixture be cold pressed, it will be appreciated that hot pressing can also be employed. In producing a compact of at least 65% apparent density by cold pressing, the pressure applied may range from 15 to 50 tons per square inch. When hot pressing is employed, the temperature will usually range from about 650° C. to 1250° C. at pressures ranging up to about 40 tons per square inch, lower pressures being employed at higher temperature levels. Where high compacting pressure in conjunction with high temperature is employed the billet is heated separately, placed in a cold die and immediately hot compacted. When hot pressing is conducted, it should be carried out under protective conditions, e.g. in a reducing atmosphere, an inert atmosphere or even at subatmospheric pressure.

Likewise, when the compact is extruded, the conditions also should be protective to the materials forming the compact. Encasing the compact in an air tight, evacuated, welded container, for example a sheath of iron or nickel, is one method of protecting the materials in the compact from oxidation, etc. Depending on the situation, extrusion pressure may range from about 40 to 250 tons per square inch over a temperature range of about 800 to 1250° C. for extrusion ratios ranging from about 14 to 1 and 20 to 1.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood 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 appended claims.

I claim:

1. A method of introducing a hard slip inhibiting phase into a substantially ductile, matrix metal of melting point above 750° C., an oxide of which has a negative free energy of formation at 25° C. below 70,000 calories per gram atom of oxygen, which comprises providing a powder of said matrix metal of minus 300 microns in size having alloyed therewith up to about 5% by weight of a refractory oxide-forming metal selected from the group consisting of Si, Al, Mg, Be, Zr, Ti, Th and rare earth metals each of whose oxides is substantially stable at elevated temperatures and is characterized by a negative free energy of formation at 25° C. of over 90,000 calories per gram atom of oxygen and has a melting point over about 1500° C., subjecting said powder to oxidation by heating it at an elevated temperature at least about 500° C. but below the melting point of said matrix metal in an oxidizing atmosphere subjecting said oxidized powder to additional heating in an inert atmosphere at an elevated temperature at least about 500° C. to decompose matrix metal surface oxide and provide additional oxygen for diffusion into the powder to convert further refractory oxide-forming metal into disperse oxide phase, heating said treated powder to an elevated temperature below the melting point of the metal powder in a reducing atmosphere to reduce excess matrix metal oxide remaining on the surface of the powder, consolidating said reduced powder to a substantially solid compact and hot extruding said compact to a desired shape, whereby said shape is characterized by a uniform dispersion throughout of fine particles of a hard refractory oxide.

2. A method of introducing a hard slip inhibiting phase into a substantially ductile, matrix metal powder of melting point above 750° C., an oxide of which has a negative free energy of formation at 25° C. below 70,000 calories per gram atom of oxygen, which comprises providing said metal powder of minus 300 microns size having alloyed therewith up to about 5% by weight of a refractory oxide-forming metal selected from the group consisting of Si, Al, Mg, Be, Zr, Ti, Th and rare earth metals each of whose oxides is substantially stable at elevated temperatures and is characterized by a negative free energy of formation at 25° C. of over 90,000 calories per gram atom of oxygen, subjecting said powder to oxidation by heating it at an elevated temperature at least about 500° C. but below the melting point of said matrix metal in an oxidizing atmosphere subjecting said oxidized powder to additional heating in an inert atmosphere at an elevated temperature at least about 500° C. to decompose matrix metal surface oxide and provide additional oxygen for diffusion into the powder to convert further refractory oxide-forming metal into disperse oxide phase, heating said treated powder to an elevated temperature below the melting point of the metal powder to reduce excess matrix metal oxide remaining on the surface of the powder, whereby a substantially ductile metal powder is produced characterized by a dispersion throughout of fine particles of a hard refractory oxide.

3. The method of claim 2 wherein the refractory oxide-forming metal is employed in amounts ranging from about 0.05% to 2.5% by weight of the alloy composition.

4. A method of introducing a hard slip inhibiting phase into a substantially ductile, matrix metal of melting point above 750° C. an oxide of which has a negative free energy of formation at 25° C. of below about 70,000 calories per gram atom of oxygen, which comprises providing a powder of said matrix metal of minus 300 microns in size having alloyed therewith up to about 5% by weight of a refractory oxide-forming metal whose oxide is substantially stable at elevated temperatures and is characterized by a negative free energy of formation at 25° C. of over 90,000 calories per gram atom of oxygen and has a melting point of over about 1500° C., subjecting said powder to oxidation by heating it at an elevated temperature but below the melting point of said matrix metal in an oxidizing atmosphere to form a matrix metal oxide coating thereon, subjecting said oxidized powder to additional heating in an inert atmosphere at an elevated temperature sufficient to decompose said matrix metal surface oxide and provide oxygen for diffusion into the powder to form a disperse refractory oxide phase with said contained refractory oxide-forming metal, heating said treated powder at an elevated temperature below the melting point of the metal powder in a reducing atmosphere to reduce excess matrix metal oxide remaining on the surface of the powder, whereby a substantially ductile metal powder is produced characterized by a dispersion throughout of fine particles of a hard refractory oxide.

5. The method of claim 4 comprising the additional step of consolidating said reduced powder into a compact and hot forming said compact to a desired shape, whereby said shape is characterized by a substantially uniform dispersion throughout of fine particles of a hard refractory oxide.

6. The method of claim 4 wherein the refractory oxide-forming metal ranges from about 0.05% to 2.5%.

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