ABSTRACT

Disclosed are methods and compositions for forming dispersion-strengthened metal products by the in situ internal oxidation of an alloy powder of a solute metal in a matrix metal. The matrix metal is relatively noble with respect to the solute metal so that the solute metal will be preferentially oxidized. The oxidant for the internal oxidation of said alloy powder is a mixture of a heat-reducible (i.e., reducible by the solute metal with heat) metal oxide (the metal moiety of which is different or the same as the matrix metal that is present in the alloy) present in proportion sufficient for substantial oxidation of all of said solute metal to solute metal oxide; and a hard, refractory metal oxide (the metal moiety of which is different from or the same as the solute metal present in the alloy). The alloy powder and the oxidant are intimately mixed and heated in an inert atmosphere for internal oxidation. Upon internal oxidation, the composite residue of spent oxidant comprises an in situ heat-reduced metal intimately associated with the refractory metal oxide, and such residue is coalesced with the rest of the mass by hot working.

18 Claims, 3 Drawing Figures
Fig. 3
1

DISPERSION STRENGTHENING OF METALS BY
INTERNAL OXIDATION

The present invention relates to dispersion strengthening of ductile matrix metals by the in situ formation of a hard, refractory oxide phase therein by the technique known as internal oxidation. Dispersion strengthened metal products such as copper dispersion strengthened with aluminum oxide have many commercial and industrial uses where high temperature strength and high electrical conductivity and/or heat conductivity are desired or required. Such uses include frictional brake parts such as linings, facings, drums and the like and other machine parts for frictional applications; contact points for resistance welding electrodes; electrodes generally, electrical switches and electrical switch gears, transistor assemblies, wires for solderless connections, wires for electrical motors and many other related applications. Dispersion strengthened products of this invention are useful in the above and other applications.

In the past, it has been recognized that strength and hardness can be imparted to a solid solution alloy of a ductile matrix metal, having relatively low negative heat or free energy of oxide formation, and a solute metal having a relatively high negative heat or free energy of oxide formation, by heating the alloy under oxidizing conditions so as to preferentially oxidize the solute metal to cause the in situ precipitation of hard, refractory solute metal oxide particles in the matrix metal without substantial oxidation of the matrix metal. This technique is known as the in situ internal oxidation of the solute metal to the solute metal oxide or more simply “internal oxidation”. In internal oxidation, the matrix metal is relatively noble compared to the solute metal so that the solute metal will be preferentially oxidized.

In the past, attempts have been made to dispersion strengthen alloys by internal oxidation in various ways. For instance, U.S. Pat. No. 3,026,200 shows the surface oxidation of alloy powder followed by a heat treatment in an inert atmosphere to diffuse the oxygen from the surface of the alloy and to preferentially oxidize the solute metal to solute metal oxide within the alloy. This method requires the precise control of the conditions for oxidation of the alloy powder.

U.S. Pat. No. 3,399,086 discloses the internal oxidation of copper-aluminum alloy in plate or strip form using copper oxide as the oxidant, through an oxidation-reduction chemical mechanism. The copper oxide is reduced and gives up its oxygen for the preferential oxidation of the alloy aluminum to form dispersed particles of aluminum oxide dispersed within the copper matrix. Internal oxidation of alloy powder is not discussed, so the problem of oxidant powder removal from alloy powder is not a factor.

U.S. Pat. No. 3,184,835 discusses the internal oxidation of copper-beryllium or copper-aluminum alloys wherein the oxidant is a sintered and milled (110 mesh) mixture consisting of 50 percent copper oxide and 50 percent aluminum oxide. The use of the sintered mixture as the oxidant is said to minimize adhesion of the oxidant residue to the internally oxidized alloy. The sintered oxidant residue is physically separated from the internally oxidized alloy powder before the powder is formed into a dispersion strengthened metal product.

U.S. Pat. No. 3,179,515 discloses the internal oxidation of alloys by surface oxidizing a powdered alloy and then diffusing the oxygen into the powder particles to preferentially oxidize the solute metal to solute metal oxide. This patent shows that internal oxidation can be achieved by treating the alloy powder at a controlled partial pressure of oxygen at which copper does not readily oxidize whereas the solute metal is oxidized mainly by diffusion of oxygen into the alloy. Particle size and surface parameters of the solute metal oxide are said to be critical to product performance.

British Patent 654,962 shows a method of internally oxidizing silver, copper and/or nickel alloys containing solute metal by oxygen diffusion to increase the hardness of the alloy by more than 30 percent.

All of these prior art methods either require a delicate control over the partial pressure of oxygen during internal oxidation or the removal of oxidant residue after the internal oxidation reaction is complete. When an oxidizing gas is used as an oxidant, elaborate processing and control equipment must be provided and maintained. When the oxidant is an oxide of the matrix metal or another metal the reduced oxide metal often sinters during the oxidizing reaction and produces agglomerates that must be separated and removed before the metal powder can be further processed. Furthermore, any oxidant residue that remains in the internally oxidized powder in these prior art processes forms defects due to compositional variations when said metal shapes are eventually formed. The present invention provides a unique solution to this problem in providing for the complete assimilation of the oxidant residue into metal articles formed from the internally oxidized alloy powder.

The above and other advantages will be more easily understood from the following description and drawings where

FIGS. 1, 2 and 3 are graphs showing how the electrical conductivity, ultimate tensile strength and hardness vary with composition and annealing treatment according to the present invention.

In achieving the objects of the present invention, one feature provides for the internal oxidation of solute metal to solute metal oxide in a powdered alloy of a matrix metal and solute metal wherein the matrix metal has a negative free energy of oxide formation per gram atom of oxygen at 25°C ranging up to 70 kilocalories per gram atom of oxygen at 25°C; and the negative free energy of formation of said solute metal oxide exceeds the negative free energy of formation of said matrix metal oxide by at least 60 kilocalories per gram atom of oxygen at 25°C in the presence of and in intimate admixture with an oxidant comprising a pulverulent, in situ, heat-reducible metal oxide having a negative free energy of oxide formation per gram atom of oxygen ranging up to 70 kilocalories per gram atom of oxygen at 25°C. In intimate interpersions with discrete particles of hard, refractory metal oxide, the negative free energy of formation of said hard, refractory metal oxide exceeding the negative free energy of formation of said heat-reducible metal oxide by at least 60 kilocalories per gram atom of oxygen at 25°C. The heat-reducible metal oxide can contain the same or different metal moiety that is present as the matrix metal in the alloy. Similarly, the hard, refractory metal oxide that is present in a proportion and particle size adapted for dispersion strengthening the oxidant residue resulting
from internal oxidation can be the same or different metal oxide that results from the internal oxidation of the solute metal to the solute metal oxide in the alloy.

The pulverulent, in situ heat-reducible metal oxide in the oxidant is in substantial stoichiometric proportion for internal oxidation of all the solute metal to solute metal oxide in said alloy. After internal oxidation, the oxidant residue comprises uniformly distributed agglomerates consisting of particles of in situ oxidized alloy powder which after internal oxidation comprises matrix metal containing dispersed particles of refractory oxide. According to this present technique, the oxidant is neither presintered nor is the oxidant residue separated from the internally oxidized alloy powder as in U.S. Pat. No. 3,184,835. When the internally oxidized alloy powder and the oxidant residue are eventually consolidated by hot working to form a solid metal workpiece, the oxidant residue itself dispersion strengthens to form an integral part of the resulting workpiece.

Preferably, the in situ heat-reducible metal oxide in the oxidant contains the same metal moiety as the matrix metal in the alloy powder; and preferably, the hard, refractory metal oxide in the oxidant contains the same metal moiety as the solute metal in the alloy powder. In one particular commercially important embodiment of this preferred practice, the oxidant contains substantially the same proportion of matrix metal moiety and solute metal moiety as are present in the alloy powder. Thus upon eventual coalescence of the internally oxidized mixture of alloy and oxidant residue into a workpiece, the oxidant residue itself is of substantially the same composition as the internally oxidized alloy and becomes dispersion strengthened therewith.

Another feature of the present invention resides in a metal powder composition based upon an alloy of matrix metal and solute metal about 0.01 to 5 percent by weight, adapted for coalescence upon hot working to form dispersion-strengthened metal articles, said composition comprising particles of internally oxidized alloy of a matrix metal whose oxide has a negative free energy of formation at 25°C, ranging up to about 70 kilocalories per gram atom of oxygen, the matrix metal having dispersed substantially uniformly throughout by internal oxidation fine particles of a hard, refractory solute metal oxide, the negative free energy of formation of said solute metal oxide exceeding the negative free energy of oxide formation of said matrix metal by at least 60 kilocalories per gram atom of oxygen at 25°C. Said particles of internally oxidized alloy being blended with an oxidant residue mixture comprising discrete particles of in situ heat-reduced metal having a negative free energy of oxide formation at 25°C, ranging up to 70 kilocalories per gram atom of oxygen and discrete particles of hard, refractory solute metal oxide having a negative free energy of oxide formation exceeding the negative free energy of formation of said heat-reduced metal by at least 60 kilocalories per gram atom of oxygen at 25°C. Preferably, the heat-reduced metal oxide in the oxidant residue is of the same metal moiety as the matrix metal in the internally oxidized alloy. Most preferably, the proportion of matrix metal and hard, refractory metal oxide in said oxidant residue is substantially the same as the proportion of matrix metal and solute metal oxide in said internally oxidized alloy.

The matrix metals in the alloy and in situ, heat-reduced metal in the oxidant residue are defined broadly as those metals having a melting point of at least about 200°C and whose oxides have a negative free energy of formation at 25°C of from 0 to 70 kilocalories per gram atom of oxygen. Suitable metals of this class for practicing the present invention include the following:

<table>
<thead>
<tr>
<th>Matrix metal and in situ heat-reduced metal</th>
<th>Heat-reducible metal and matrix metal oxide</th>
<th>Approximate negative free energy of formation of oxide at 25°C in kilocalories per gram atom of oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>FeO</td>
<td>59</td>
</tr>
<tr>
<td>Cobalt</td>
<td>CuO</td>
<td>52</td>
</tr>
<tr>
<td>Nickel</td>
<td>NiO</td>
<td>51</td>
</tr>
<tr>
<td>Copper</td>
<td>CuO</td>
<td>33</td>
</tr>
<tr>
<td>Cadmium</td>
<td>CuO</td>
<td>55</td>
</tr>
<tr>
<td>Thallium</td>
<td>TiO</td>
<td>40</td>
</tr>
<tr>
<td>Germanium</td>
<td>GeO2</td>
<td>58</td>
</tr>
<tr>
<td>Lead</td>
<td>SnO</td>
<td>60</td>
</tr>
<tr>
<td>Antimony</td>
<td>SnO2</td>
<td>62</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi2O3</td>
<td>40</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>MoO3</td>
<td>60</td>
</tr>
<tr>
<td>Tungsten</td>
<td>WO3</td>
<td>59</td>
</tr>
<tr>
<td>Rhenium</td>
<td>Re2O7</td>
<td>45</td>
</tr>
<tr>
<td>Indium</td>
<td>In2O3</td>
<td>65</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag2O</td>
<td>3</td>
</tr>
<tr>
<td>Gold</td>
<td>Au2O</td>
<td>0</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Ru2O7</td>
<td>25</td>
</tr>
<tr>
<td>Palladium</td>
<td>PbO</td>
<td>15</td>
</tr>
<tr>
<td>Osmium</td>
<td>OsO3</td>
<td>20</td>
</tr>
<tr>
<td>Platinum</td>
<td>PtO</td>
<td>0</td>
</tr>
<tr>
<td>Rhodium</td>
<td>Rh2O3</td>
<td>17</td>
</tr>
</tbody>
</table>

In the above table, matrix metal of the alloys and in situ heat-reduced metal of the oxidant residue are shown to be of the same class of metals. Similarly, the corresponding heat-reducible metal oxides in the oxidant and matrix metal oxides are listed as the same class of metal oxides.

In practicing the present invention, a matrix metal and a solute metal alloyed by conventional techniques such as melting the metals under inert or reducing conditions. The matrix metal of the alloy can be a single matrix metal of a combination of two or more matrix metals which themselves form an alloy. Accordingly, the term “matrix metal” includes a plurality of matrix metals so alloyed. Similarly, the solute metal includes a single solute metal or a combination of two or more solute metals which form solid solution alloys with the matrix metal. The alloy composition comprises 0.01 percent to about 5 weight percent of the solute metal with the balance of the alloy being matrix metal with or without other conventional additives in minor proportions to improve abrasion resistance, hardness, conductivity and other selected properties.

The alloy is then comminuted by atomization or other conventional size reduction techniques such as grinding or ball milling to form a particulate alloy having an average particle size of less than about 300 microns, usually less than about 150 microns and preferably less than about 44 microns. Optionally, the comminuted alloy powder is then annealed according to conventional procedures to increase the grain size since one of the problems associated with internal oxidation of alloys is the tendency for the solute metal oxide to concentrate at the powder grain boundaries. This is undesirable because it can cause early failure under stress at these grain bounda-
ries. It is, therefore, often desirable to reduce the grain boundary area in the alloy powder; and this is done by annealing the powder to form a larger grain size of at least about ASTM Grain Size Number 6 as measured by ASTM Test E-112. For copper-aluminum alloys which are one of the more commercially important embodiments of the present invention, annealing treatment at 1,600°F. for one hour in an inert atmosphere such as argon produces grain size of at least about ASTM Grain Size Number 6 by ASTM Test E-112.

The oxidant for internally oxidizing the above alloy powder is a mixture of an in situ heat-reducible metal oxide (this term includes materials capable of providing such metal oxide under internal oxidation conditions) and a hard, refractory metal oxide. The heat reducible metal oxide in the oxidant is in substantially stoichiometric proportion for internally oxidizing all of the solute metal in said alloy.

In any particular combination of matrix metal and solute metal in the alloy to be internally oxidized, the matrix metal must be relatively noble with respect to the solute metal so that the solute metal will be preferentially oxidized. This is achieved by selecting the solute metal such that its negative free energy of oxide formation at 25°C. is at least 60 kilocalories per gram of oxygen greater than the negative free energy of formation of the oxide of the matrix metal at 25°C. Generally, such solute metals have a negative free energy of oxide formation per gram atom of oxygen of over 80 kilocalories and generally over 120 kilocalories. The approximate negative values of free energy of formation of several suitable solute metal oxides at 25°C. are:

<table>
<thead>
<tr>
<th>Solute metal oxide and hard, refractory metal oxide</th>
<th>Approximate negative free energy of oxide formation at 25°C., in kilocalories per gram atom of oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon oxide</td>
<td>96</td>
</tr>
<tr>
<td>Titanium oxide</td>
<td>101</td>
</tr>
<tr>
<td>Zirconium oxide</td>
<td>122</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>126</td>
</tr>
<tr>
<td>Beryllium oxide</td>
<td>139</td>
</tr>
<tr>
<td>Thorium oxide</td>
<td>146</td>
</tr>
<tr>
<td>Chromium oxide</td>
<td>83</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>136</td>
</tr>
<tr>
<td>Manganese oxide</td>
<td>87</td>
</tr>
<tr>
<td>Nickel oxide</td>
<td>83</td>
</tr>
<tr>
<td>Tantalum oxide</td>
<td>92</td>
</tr>
<tr>
<td>Vanadium oxide</td>
<td>99</td>
</tr>
</tbody>
</table>

In the above table, the solute metal oxide in the alloy and hard, refractory metal oxide in the oxidant are shown to be the same class of metal oxides.

The metal moiety of the heat-reducible metal oxide in the oxidant preferably is the same metal as matrix metal present in the alloy to be internally oxidized, although the heat-reducible metal oxide moiety can be different to achieve specific performance requirements in the final product.

For instance, alloy matrix metal/oxidant heat-reducible metal oxide combinations include:

<table>
<thead>
<tr>
<th>Alloy Matrix Metal</th>
<th>Oxidant Heat-Reducible Metal Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Cobalt oxide, nickel oxide, copper oxide</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cobalt oxide, nickel oxide, copper oxide</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Cobalt oxide, nickel oxide, copper oxide</td>
</tr>
</tbody>
</table>

Similarly, the hard, refractory metal oxide in the oxidant preferably is the same as the solute metal oxide formed in the alloy during internal oxidation of the alloy, although the refractory metal oxide in the oxidant can be different from the solute metal oxide in the internally oxidized alloy.

For instance, solute metal oxide/oxidant hard, refractory metal oxide combinations include:

<table>
<thead>
<tr>
<th>Alloy Solute Metal Oxide</th>
<th>Oxidant Hard, Refractory Metal Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Al₂O₃, BeO, ZrO₂, ThO₂</td>
</tr>
<tr>
<td>BeO</td>
<td>Al₂O₃, BeO, ZrO₂, ThO₂</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Al₂O₃, BeO, ZrO₂, ThO₂</td>
</tr>
<tr>
<td>ThO₂</td>
<td>Al₂O₃, BeO, ZrO₂, ThO₂</td>
</tr>
</tbody>
</table>

To achieve the proper proportion of oxidant, about 0.1 to about 10 parts by weight of oxidant are employed per 100 parts of alloy to be internally oxidized. The exact proportions depend on the solute metal to be oxidized, its concentration in alloy and oxygen content of oxidant.

In a commercially important embodiment, the matrix metal is copper and the solute metal is aluminum in the alloy; and the oxidant contains copper oxide as the in situ, heat-reducible metal oxide and aluminum oxide as the hard, refractory metal oxide. The copper oxide in the oxidant is present in substantially stoichiometric proportions for internally oxidizing all of the aluminum metal to aluminum oxide in the alloy powder. During internal oxidation of the preferred embodiment, the in situ, heat-reducible copper oxide in the oxidant gives up its oxygen to the aluminum metal in the alloy. This reduces the copper oxide to copper in the oxidant which by virtue of its intimate mixture with aluminum oxide in the oxidant becomes dispersion strengthened during subsequent coalescence upon hot working. The stoichiometry of the oxidant is predetermined so that the composition of the oxidant residue and internally oxidized alloy are substantially identical after internal oxidation. This represents a substantial advance over the prior art techniques where matrix metal oxide alone is used as the oxidant and reverts to matrix metal which must be removed, or where the mixture of matrix metal oxide and refractory oxide, because of unfavorable particle size and homogeneity, does not produce acceptable properties.

The ratio of the average particle size diameters of the alloy particles to the oxidant particles should be at least about 2:1 and usually between about 5:1 and about 30:1 or even higher if practical to provide desirable inter-particle contacts for efficient chemical reaction and to maximize the homogeneity of the final product. This particle size differential permits the oxidant particle to surround the alloy particle thus providing for sufficient solid-state reaction during the internal oxidation period. Generally the oxidant particles are micron or submicron in particle size.

There are several methods of forming oxidant suitable for the present invention. In one method, an oxygen-forming salt of a refractory metal is applied to and decomposed on a particle of a heat-reducible metal oxide in the micron or submicron range. In the case of the copper-aluminum system, for instance, submicron cuprous/cupric oxide particles are treated with an aqueous solution of aluminum nitrate so as to form a uniform coating. The particles are dried and heated to decompose the aluminum nitrate to form cuprous/cupric oxide particles having uniform coating of aluminum oxide thereon. The amount of aluminum nitrate added to the cuprous/cupric oxide particles is predetermined
according to the aluminum oxide content desired in the final product.

In another method, oxide-forming compounds of refractory metal and metals of heat-reducible metal oxides are simultaneously coprecipitated from solution of their salts. In the copper-aluminum system for example, copper and aluminum hydroxides or carbonates are precipitated from a solution of their nitrates by adding ammonium hydroxide or carbonate respectively. The hydroxide and carbonate salts are then decomposed to their respective oxides by heating.

In a third method, a physical blend of micron or sub-micron particles of heat-reducible metal oxide and refractory oxide particles can be intimately blended in a blending device to form the oxidant.

The amounts of such oxidants that are to be added to the alloy are determined by the stoichiometric amount of oxygen required to oxidize the solute metal completely. For most applications, this is in the range of 0.1 to 10 parts oxidant per 100 parts of alloy. The percent of hard, refractory metal oxide in the oxidant is then calculated to produce that desired in the oxidized residue which also equals that desired in the final product.

In the following examples, all parts are by weight and all temperatures are in °F unless stated otherwise.

EXAMPLE 1

Part A — Preparation of the Alloy Powder
Electrolytic tough-pitch grade copper rod are melted in an inert refractory crucible in an induction-heating furnace under reducing conditions at about 2,300°F. Metallic aluminum shavings are introduced into the molten copper in the proportion of 0.33 percent by weight of the resulting molten metallic mass.

The molten solution of aluminum in copper is then super-heated to 2,400°F, atomized through an atomizing aperture in a jet of nitrogen (alternatively other inert gases or water or steam can be used as the atomizing fluid) to yield an atomized copper-aluminum alloy powder which substantially all passes a 100-mesh U.S. Sieve indicating that the average particle size is less than about 146 microns.

The atomized and screened alloy powder is annealed at a temperature of about 1,600°F. about an hour in an inert argon atmosphere to yield a grain size in the annealed powder of at least about ASTM Grain Size 6 according to ASTM Test E-112. Preferably, the grains are as large as possible to minimize grain boundary area in the powder. The alloy powder is then ready for use in combination with the oxidant.

Part B — Preparation of the Oxidant
One hundred parts of commercially available cuprous oxide (Cu₂O) with an average particle size of about 1 to 2 microns is mixed with 41 parts of a 20 percent aqueous solution of Al(NO₃)₃·9H₂O to form a slurry of cuprous oxide in aluminum nitrate solution. The solution of aluminum nitrate is slurried with cuprous oxide particles, and the stirring is continued with mild heating at 200°F until the water has evaporated and the mixture is almost dry. The mixture is then heated at a temperature of about 500°F, for ½ hour to decompose the aluminum nitrate into aluminum oxide. The resulting agglomerate is then ground to form fine oxidant powder which passes a 325-mesh sieve. The resulting oxidant powder comprises 99.44% Cu₂O and 0.56% Al₂O₃ by weight.

Part C — Preparation of the Internally Oxidizable Alloy Powder-Oxidant Mixture
The alloy powder of Part A is thoroughly mixed with the oxidant powder of Part B in the proportion of 2.12 parts of oxidant to 100 parts of alloy powder. The mixing is accomplished in a ball-mill, although a conventional V-cone blending device can alternatively be used.

Part D — Internal Oxidation of the Alloy Powder-Oxidant Mixture to form the Internally Oxidized Metal Powder Composition
The alloy powder-oxidant mixture of Part C is then charged to an internal oxidation vessel which is then sealed. The oxidation vessel is copper or copper-lined steel to avoid contamination of the alloy powder-oxidant mixture during oxidation.

The alloy powder-oxidant mixture is then brought to a temperature of about 1,750°F and maintained at this temperature for about 30 minutes to effectuate internal oxidation of the alloy powder. Alternatively, the internal oxidation can be carried out on a continuous basis using a continuous belt furnace maintained under an inert atmosphere.

At the end of the 30-minute internal oxidation period, substantially all of the aluminum in the alloy powder has been oxidized to Al₂O₃ and substantially all of the cuprous oxide in the oxidant has been reduced to metallic copper. The particles of internally oxidized alloy comprise 99.37 percent by weight of copper plus minor amounts of impurities and 0.63 percent by weight of Al₂O₃. The oxidant residue comprises 99.37 percent copper particles and 0.63% Al₂O₃ particles. The overall internally oxidized metal powder composition comprises 98.21 percent internally oxidized alloy powder and 1.79 percent oxidant residue.

Part E — Reduction of the Internally Oxidized Metal Powder Composition
The internally oxidized metal powder composition of Part D is then placed in a reducing atmosphere of hydrogen at a temperature of about 1,500°F for one hour to reduce any residual copper oxide.

Part F — Thermal Coalescence or Consolidation of the Internally Oxidized Metal Powder Composition
The internally oxidized and reduced metal powder composition of Part E are then charged under an inert argon atmosphere to a thin-walled copper can having a diameter of about 7 inches and equipped with a vent tube. The can and its contents are heated to about 1,600°F, and the vent tube sealed. Alternatively instead of using the inert gas atmosphere, the vent tube can be attached to a vacuum pump; and the can is evacuated while the temperature of the can is brought to 1,600°F to remove any occluded gas from the powder. After evacuation at a pressure of 1 × 10⁻⁵ mm of Hg for 60 minutes at 1,600°F, the vent tube is sealed and disconnected from the vacuum pump.

The sealed can is brought to 1,700°F and then placed in a ram-type extrusion press and is extruded to form extrudate in the shape of cylindrical bar stock having a diameter of about 1.25 inches. This corresponds to an extrusion ratio of about 31:1 (i.e., the ratio of the cross-sectional area of the can to the ratio of the cross-sectional area of the extrudate).

The bar stock comprises about 99.37 percent copper having dispersed throughout 0.63 percent (or about 1.5 percent by volume) of Al₂O₃ particles and has a density of about 99.2 percent of the theoretical density. The
bar stock has an electrical conductivity of 88% IACS* (*International Annealed Copper Standard — A copper wire 1 meter long weighing 1 gram, having a resistance of 0.15328 ohms. at 20°C. has a conductivity of 100% IACS. (see Kirk-Othmer: Encyclopedia of Chemical Technology, Second Edition, Volume VI, Interscience Publishers, Inc. 1965 p. 133.)) a tensile strength of about 72,000 psi, an elongation of 19 percent using ASTM Test E-8 (for a test specimen 0.16 inch diameter and 0.65 inch gage length) and a Rockwell hardness of about 72 units on the B scale. All property measurements reported in the example are conducted at room temperature. The bar stock is substantially and does not possess the compositional defects that normally result when the spent oxidant is present in the dispersion-strengthened workpiece.

The bar stock is suitable for use as is, or it can be cold worked by swaging, forging, rolling, wire drawing, cold extrusion or cold drawing to form workpieces having particular tensile strengths according to conventional cold working techniques.

For instance, when the bar stock is reduced to 50 percent in cross-sectional area by coldswaging, the tensile strength is 80,000 psi, the elongation is 13 percent and Rockwell B hardness is 84 units and conductivity is 86 percent IACS.

This swaged material with a Rockwell B hardness of 84 units and prepared by the procedure of Example 1 is annealed along with a commercial copper-chromium alloy (0.9% Cr) at various temperatures for 1 hour in argon. The hardness values obtained by annealing in an annealing furnace for 1 hour at the various temperatures and cooling to room temperature after annealing at each temperature are shown in FIG. 1. In another experiment these same two materials are annealed together at 1,000°F in argon. At various time intervals samples are removed from the annealing furnace, cooled at room temperature and tested for hardness. The results are shown in FIG. 2. The results shown in FIGS. 1 and 2 show the superior resistance to softening on heating of the dispersion-strengthened workpieces of this invention.

**EXAMPLE 2**

The procedures of Example 1 are repeated except that in Part F the 7 inch diameter copper can is replaced by a 1.25 inch diameter copper can. The extrusion is carried out at an extrusion ratio of 30:1 yielding a 0.250 inch diameter rod. Such rod has an electrical conductivity of 86.7% IACS, a tensile strength of about 73,000 psi and an elongation of 19.8 percent in a gage length of 0.650 inch.

**EXAMPLE 3**

The material of Part B of Example 1 is fed into a thin-walled copper can of 1.25 inch diameter and extruded at an extrusion ratio of 45:1 to yield a rod of 0.206 inch diameter. This rod has an electrical conductivity of 89% IACS and when swaged and drawn to 0.010 inch diameter wire and heat treated at 500°C for ½ hour in helium yields an ultimate tensile strength of 84,000 psi, yield strength of 71,200 psi and an elongation of about 5 percent in 10 inches.

**EXAMPLE 4**

The procedures of Example 2 are repeated except that the compositions of the alloy powder in Part A and the oxidant in Part B is modified so that the alloy powder and the oxidant each contain the equivalence of 0.22 weight percent aluminum to produce extruded copper bar stock containing 0.42 weight percent (or 1 volume percent) Al₂O₃.

The electrical conductivity of the bar stock is 91% IACS, the tensile strength is 70,000 psi, elongation is 21 percent and the Rockwell B hardness is 68 units. The bar stock is substantially uniform and does not possess the compositional defects normally associated with in situ, reduced copper oxide.

**EXAMPLE 5**

The procedures of Example 2 are repeated except that the compositions of the alloy powder in Part A and the oxidant in Part B are modified so that the alloy powder and the oxidant each contain the equivalence of 0.66 weight percent aluminum to produce extruded copper bar stock containing 1.26 weight percent (or 1 volume percent) Al₂O₃.

The electrical conductivity of the bar stock is 78% IACS, the tensile strength is 85,000 psi, elongation is 19 percent and the Rockwell B hardness is 89 units. The bar stock is substantially uniform and does not possess the compositional defects normally associated with in situ, reduced copper oxide.

FIG. 3 shows a plot of properties against aluminum or aluminum oxide content of workpieces as extruded in rod form as described in this Example 5 and the preceding Examples 3 and 4.

**EXAMPLE 6**

The procedures of Example 1 are repeated except that the alloy powder of Part A has a particle size passing a U. S. standard sieve of 80 mesh but is retained on a 325-mesh sieve. On the basis of the sieves employed, the particle size varies between 44 and 75 microns. The internally oxidized powder is used to compact test bars at 45 psi having a size of 0.394 in. × 0.394 in. × 2.96 in. These test bars are preheated in an atmosphere of 92% N₂ — 8% H₂ at 1,700°F. for 10 minutes and forged using a 200 ton drop hammer and a 28 inch vertical drop rather than extruded as in Example 1, Part F. The resulting drop-forged bars are 0.35 inch square in cross-section.

The bars are then cold forged at room temperature to form 0.31 inch diameter bars which represents a 38 percent reduction in cross-section.

The resulting test bars have a Vicker's hardness (at 15 gram load) of 149 Kg/mm², a tensile strength of 67,700 psi and an elongation of 4.3 percent. The test samples are then annealed for 1 hour at 1,500°F. in argon after which the Vicker’s hardness is 139 Kg/mm², tensile strength is 60,200 psi with an elongation of 5.7 percent.

**EXAMPLE 7**

The procedures of EXAMPLE 6 are repeated except that the alloy powder has a particle size passing a U. S. standard sieve of 325 mesh. This means that the average particle is less than 44 microns. The test sample has a Vicker's hardness of 153 Kg/mm², a tensile strength of 75,600 psi and an elongation of 6.2 percent. After annealing in argon at 1,500°F. for 1 hour, the Vicker's hardness is 153 Kg/mm², the tensile strength is 68,000 psi and the elongation is 8.8 percent.
Examples 6 and 7 illustrate that the smaller alloy particles after internal oxidation produce better hardness, higher tensile strength and better elongation properties in the dispersion-strengthened product.

Examples 8 through 17 further illustrate the dispersion strengthening of matrix metals with various solute metal oxides by internal oxidation. Where solubility permits, the solute metal concentration in the alloy is selected to provide approximately 5 percent by volume of the solute metal oxide. In cases where the solubility of the solute metal is not sufficient to provide 5 percent by volume of the solute metal oxide, the solute metal concentration in the alloy is adjusted to maximum solubility at room temperature. In all of the following Examples 8 through 21, the alloy powder passes through a U. S. standard sieve of 100 mesh, the pulverulent oxidant is an intimate suspension of the stated metal oxides having an average particle size of about 1 to 5 microns and the alloy powder-oxidant mixture is internally oxidized by the method described in Parts D, E and F of Example 1. In the metal oxides presented in the following examples, copper is at a valence of 1, nickel is at a valence of 2, iron is at a valence of 3, silver is at a valence of 1, zirconium is at a valence of 4, molybdenum is at a valence of 6 and beryllium and magnesium are at a valence of 2.

EXAMPLE 8

Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 98.87 percent copper and 1.13 percent aluminum with 9.38 parts of pulverulent oxidant comprising 9.2 parts of copper oxide and 0.18 parts of aluminum oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar copper-aluminum alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 9

Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 99.37 percent copper and 0.63 percent beryllium with 10.26 parts of pulverulent oxidant comprising 10.10 parts of copper oxide and 0.16 parts beryllium oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar copper-beryllium alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 10

Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 99.90 percent copper and 0.10 percent zirconium with 0.319 parts of pulverulent oxidant comprising 0.318 parts of copper oxide and 0.001 parts of zirconium oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar copper-zirconium alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 11

Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 98.86 percent nickel and 1.14 percent aluminum with 4.76 parts of pulverulent oxidant comprising 4.68 parts of nickel oxide and 0.08 parts of aluminum oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar nickel-aluminum alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 12

Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 99.8 nickel and 0.2 percent beryllium with 1.687 parts of pulverulent oxidant comprising 1.680 parts of nickel oxide and 0.007 parts of beryllium oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar nickel-beryllium alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 13

Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 99.8 percent nickel and 0.2 percent zirconium with 0.328 parts of pulverulent oxidant comprising 0.327 parts of nickel oxide and 0.001 parts of zirconium oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar nickel-zirconium alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 14

Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 98.72 percent iron and 1.28 percent aluminum with 3.864 parts of pulverulent oxidant comprising 3.800 parts of iron oxide and 0.065 parts of aluminum oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar iron-aluminum alloy which has not been internally oxidized. Furthermore, the dispersion-
sion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 15
Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 99.55 percent iron and 0.45 percent beryllium with 2.724 parts of pulverulent oxidant comprising 2.700 parts of iron oxide and 0.024 parts of beryllium oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar iron-beryllium alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 16
Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 99.04 percent silver and 0.96 percent aluminum with 12.70 parts of pulverulent oxidant comprising 12.48 parts of silver oxide and 0.22 parts of aluminum oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar silver-aluminum alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 17
Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 98.84 percent silver and 1.16 percent magnesium with 11.30 parts of pulverulent oxidant comprising 11.10 parts of silver oxide and 0.20 parts of magnesium oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures and after annealing as compared to bar stock of a similar silver-magnesium alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

Examples 18 and 19 illustrate the dispersion strengthening of alloys of matrix metals (rather than a single matrix metal) by internal oxidation using the method of Examples 8 through 17.

EXAMPLE 18
Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 72.54 percent copper, 26.33 percent nickel and 1.13 percent aluminum with 4.75 parts of pulverulent oxidant comprising 4.67 parts of nickel oxide and 0.08 parts of aluminum oxide. The matrix composition of the resulting dispersion-strengthened bar stock is 70.6 percent copper metal and 29.4 percent nickel metal. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar copper-nickel-aluminum alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

EXAMPLE 19
Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 60.00 percent nickel, 19.55 percent molybdenum, 20.00 percent iron and 0.45 percent aluminum with 1.207 parts of pulverulent oxidant comprising 1.200 parts of molybdenum oxide and 0.007 parts of aluminum oxide. The matrix composition of the resulting dispersion-strengthened bar stock is 59.5 percent nickel metal, 21.0 percent molybdenum metal and 19.5 percent iron metal. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar nickel-molybdenum-iron-aluminum alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece.

Examples 20 and 21 illustrate the dispersion strengthening of alloy of matrix metals and solute metals with an oxidant containing a hard, refractory oxide that is different from the solute metal oxide.

EXAMPLE 20
Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 98.87 percent copper and 1.13 percent aluminum with 9.34 parts of pulverulent oxidant comprising 9.20 parts of copper oxide and 0.14 parts of beryllium oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to bar stock of a similar copper-aluminum alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant is present in the dispersion-strengthened workpiece, although the dispersed oxides are dissimilar.

EXAMPLE 21
Dispersion-strengthened metal bar stock is formed by the above-described method by oxidizing 100 parts of a powdered alloy of 99.8 percent nickel and 0.2 percent zirconium with 0.329 parts of pulverulent oxidant comprising 0.327 parts of nickel oxide and 0.002 parts of aluminum oxide. The resulting dispersion-strengthened bar stock has increased tensile strength and hardness at elevated temperatures or after annealing as compared to the bar stock of similar nickel-zirconium alloy which has not been internally oxidized. Furthermore, the dispersion-strengthened bar stock does not have the disadvantages that normally result from compositional variations when the spent oxidant
is present in the dispersion-strengthened workpiece, although the dispersed oxides are dissimilar.

Having thus described the invention, what is claimed is:

1. A process for dispersion-strengthening of metal by internal oxidation comprising:
   providing a powdered alloy having an average particle size of less than 300 microns comprising a matrix metal and a solute metal, said matrix metal having a negative free energy of oxidation at 25°C of up to 70 kilocalories per gram atom of oxygen, said solute material having a negative free energy of oxide formation exceeding the negative free energy of oxide formation of said matrix material by at least about 60 kilocalories per gram atom of oxygen at 25°C;
   providing an oxidant comprising an intimate interdispersion of in situ heat-reducible metal oxide and a finely divided hand refractory metal oxide, said heat-reducible metal oxide having a negative free energy of formation at 25°C of up to 70 kilocalories per gram atom of oxygen, said refractory metal oxide having a negative free energy of formation exceeding the negative free energy of formation of said heat-reducible metal oxide by at least about 60 kilocalories per gram atom of oxygen at 25°C;
   combining into an intimate mixture at least about 0.1 weight parts of said oxidant per 100 weight parts of said alloy, said oxidant having the heat-reducible metal oxide present in at least stoichiometric proportion for complete internal oxidation of all of said solute metal in said alloy;
   internally oxidizing said alloy mixed with said oxidant by heating said alloy to oxide the solute metal of said alloy and to form a residue of said oxidant; and thermally coalescing said internally oxidized alloy and said oxidant residue into dispersion-strengthened metal stock.

2. The process of claim 1 wherein the ratio of the average particle diameter of the alloy particles to the average particle diameter of the oxidant particles is at least about 2:1.

3. The process of claim 1 wherein the metal moiety of said in situ heat-reducible metal oxide is the same metal as said matrix metal.

4. The process of claim 3 wherein the metal moiety of said hard, refractory metal oxide is the same metal as said solute metal.

5. The process of claim 4 wherein the metal moiety of said heat-reducible metal oxide and the metal moiety of said hard, refractory metal oxide are in substantially the same proportion as the proportion of matrix metal and solute metal in said alloy.

6. The process of claim 1 wherein said solute metal is present in said alloy in the proportion of 0.01 to 5 percent by weight of said alloy.

7. The process of claim 1 wherein said powdered alloy has an average particle size of less than about 150 microns.

8. The process of claim 7 wherein said powdered alloy has an average particle size of less than about 44 microns.

9. The process of claim 6 wherein the ratio of the average particle diameter of the alloy particles to the average particle diameter of the oxidant particles is between about 5:1 and about 30:1.

10. The process of claim 1 wherein said matrix metal is copper and said solute metal is aluminum.

11. The process of claim 5 wherein said matrix metal is copper and said solute metal is aluminum.

12. The process of claim 1 wherein about 0.1 to 10 weight parts of said oxidant are mixed with 100 weight parts of alloy.

13. The process of claim 1 including the step of reducing said alloy mixed with said oxidant with reducing gas after the step of internally oxidizing the same.

14. A dispersion-strengthened metal produced by internally oxidizing a mixture of 100 weight parts of a powdered alloy with at least about 0.1 weight parts of an oxidant, said powdered alloy having an average particle size of less than 300 microns and comprising a relatively noble matrix metal having a negative free energy of oxide formation at 25°C of up to 70 kilocalories per gram atom of oxygen and a solute metal having a negative free energy of oxide formation exceeding that of said matrix metal by at least about 60 kilocalories per gram atom of oxygen at 25°C, said oxidant comprising an intimate mixture of heat-reducible metal oxide having a negative free energy of formation at 25°C of up to 70 kilocalories per gram atom of oxygen and finely divided refractory metal oxide having a negative free energy of formation exceeding the negative free energy of formation of said heat-reducible metal oxide by at least about 60 kilocalories per gram atom of oxygen at 25°C, said heat-reducible metal oxide present in at least stoichiometric proportions for complete oxidation of all of said solute metal in said alloy;
   comprising: a dispersion-strengthened metal mixture of oxidized solute metal, relatively noble matrix metal, residue of heat-reducible metal oxide, and hard refractory metal oxide, said mixture adapted to be thermally coalesced whereby said hard refractory metal oxide dispersion strengthens said residue of heat-reducible metal oxide to form dispersion-strengthened metal stock.

15. The dispersion-strengthened metal mixture in claim 14 wherein said metal mixture is thermally coalesced and said residue of heat-reducible metal oxide is dispersion strengthened by said hard refractory metal oxide.

16. The dispersion-strengthened metal in claim 14 produced by internally oxidizing a mixture of 100 weight parts of said powdered alloy with from about 0.1 to 10 weight parts of said oxidant, and said metal moiety of said residue of heat-reducible metal oxide is the same moiety as said relatively noble matrix metal.

17. The dispersion-strengthened metal in claim 16 wherein the metal moiety of said hard refractory metal oxide is the same metal moiety as said oxidized solute metal.

18. The dispersion-strengthened metal in claim 16 wherein the metal moiety of said relatively noble matrix metal is copper and the metal moiety of said oxidized solute metal is aluminum.

* * * * *
CERTIFICATE OF CORRECTION

Patent No. 3,779,714 Dated December 18, 1973

Inventor(s) Erhard Klar; Anil V. Madkarni

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 60, for "110" should read --100--; Column 4, line 19, insert --Tin--; Column 8, line 67, for "99.2" should read --99.3--; Column 10, line 42, before "forged" insert --drop--; Column 12, line 61, for "3,864" should read --3,865--; Column 13, line 62, for "72.54%" should read --72.54%--; Column 15, line 19, for "hand" should read --hard--; Column 16, line 54, after "same" insert --metal--.

Signed and sealed this 17th day of September 1974.

(SEAL)

Attest:

McCoy M. Gibson Jr. C. Marshall Dann
Attorneying Officer Commissioner of Patents
UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,779,714 Dated December 18, 1973

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