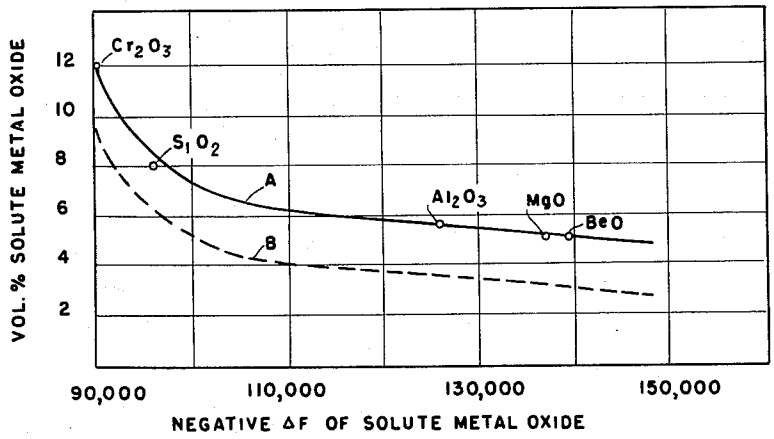
April 20, 1965 N. J. GRANT ETAL 3,179,515

DISPERSION STRENGTHENED METALS

Filed April 27, 1960 4 Sheets-Sheet 1

FIG. 1



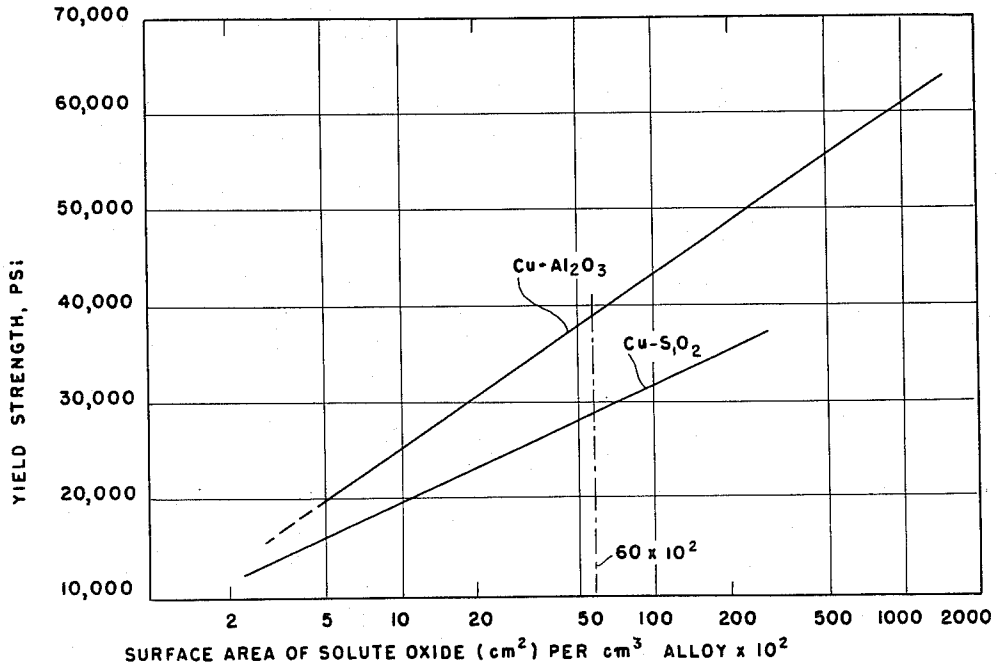


FIG. 2

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DISPERSION STRENGTHENED METALS

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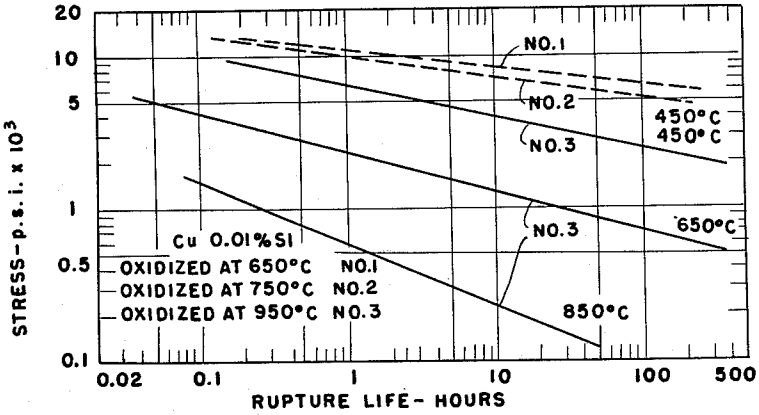


FIG. 3

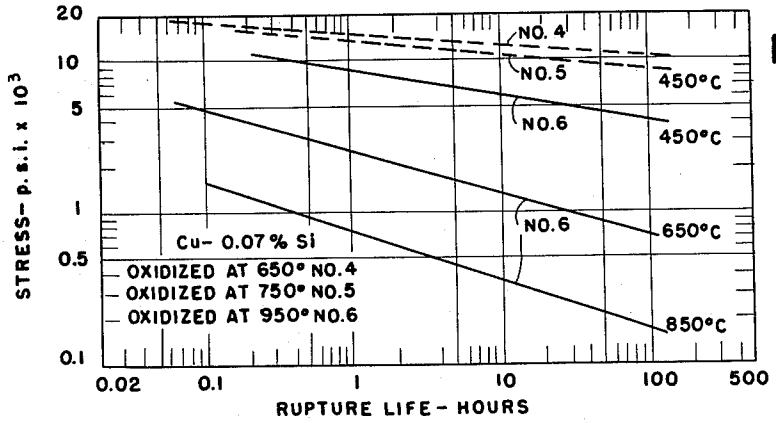


FIG. 4

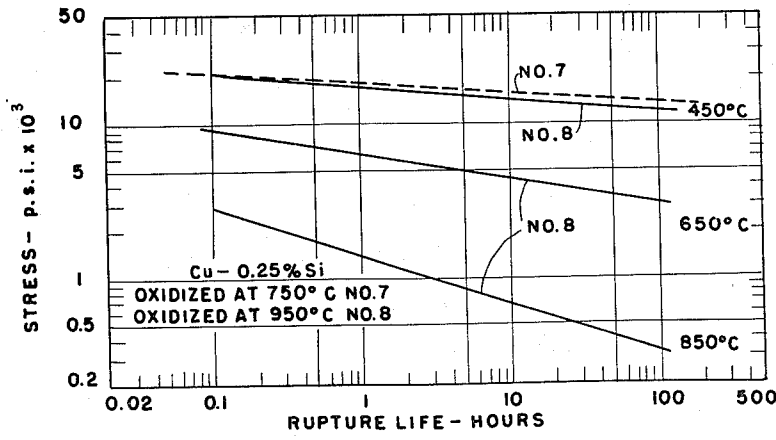


FIG. 5

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DISPERSION STRENGTHENED METALS

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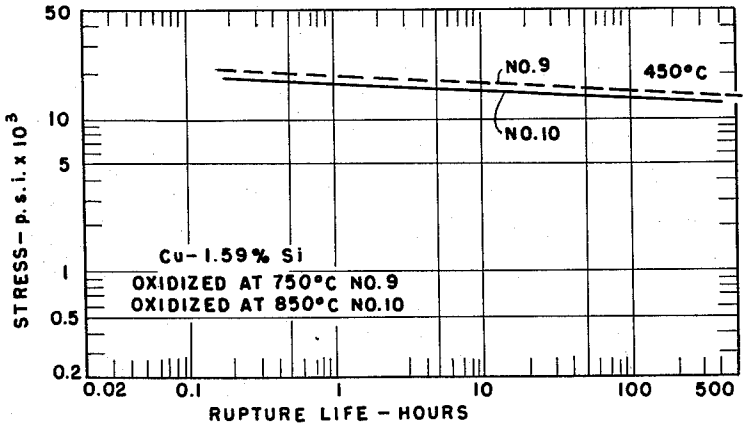


FIG. 6

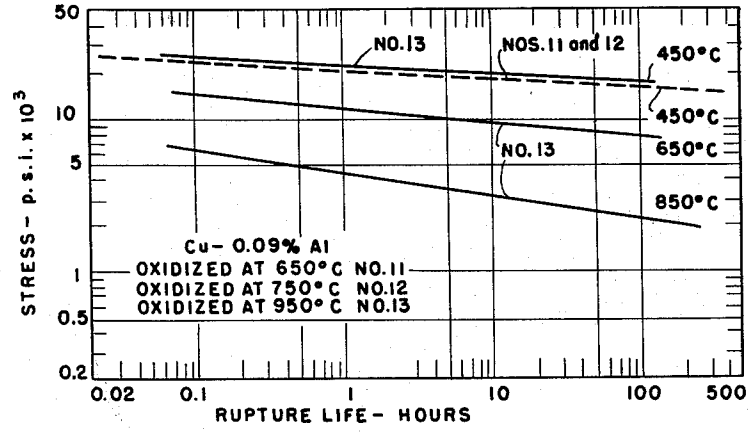


FIG. 7

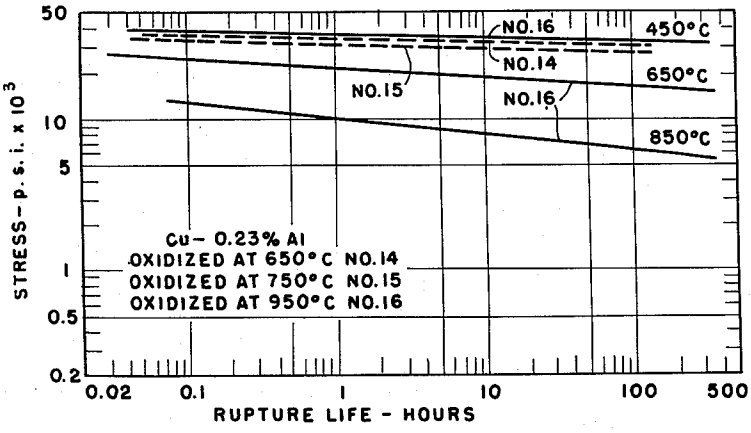


FIG. 8

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DISPERSION STRENGTHENED METALS

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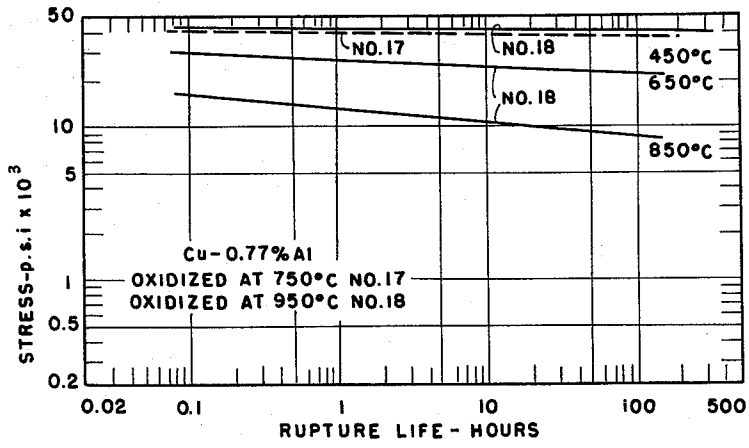


FIG. 9

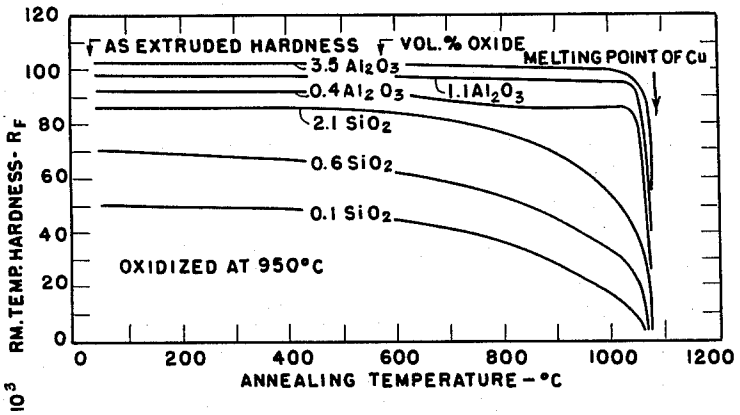


FIG. 10

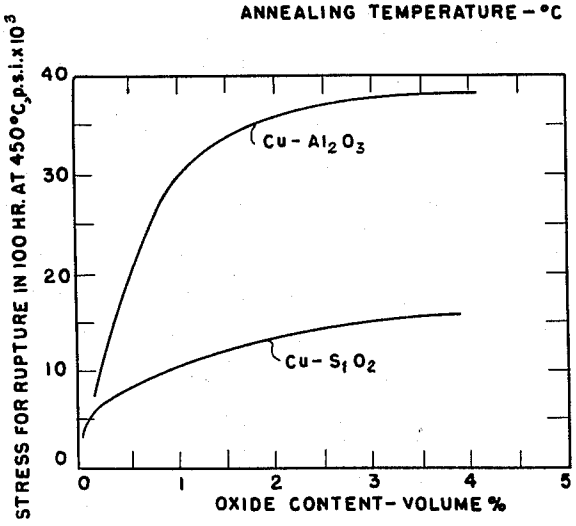


FIG. 11

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United States Patent Office 3,179,515 Patented Apr. 20, 1965

3,179,515

DISPERSION STRENGTHENED METALS

Nicholas J. Grant, 10 Leslie Road, Winchester, Mass., and Oliver Preston, Menlo Park, Calif.; said Preston assignor to said Grant

Filed Apr. 27, 1960, Ser. No. 25,100
2 Claims. (Cl. 75—206)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalty thereon or therefor.

The present invention relates to dispersion strengthened metals which are further strengthened by storage of energy characterized by resistance to softening and creep at elevated temperatures and in particular to metals containing a uniform dispersion of a hard refractory oxide phase in the sub-micron size range.

The general problem of the strengthening of metals for elevated temperature use by means of a highly dispersed second phase has received wide attention in recent years since the introduction of SAP in 1946 (dispersion strengthened sintered aluminum powder). Most of the methods employed to take advantage of the results achieved by SAP depended primarily on the technique of powder metallurgy.

The most direct method, employed with varying degrees of success, involved the simple mechanical mixing of desired inert hard phase (e.g., refractory oxide) and metal powders by either dry or wet ball-milling, followed by compacting and extruding as in the case of producing copper alloys dispersion hardened with Al_2O_3. However, this method had its limitations in that in working in the sub-micron range of particle size of inert hard phase, it was difficult to obtain the desired degree of dispersion due to a tendency for the fine particles to agglomerate and form stringers in the finally extruded product produced from the powder mixture. As a result the expected optimum strength characteristics were not always obtainable. Attempts were made to utilize the phenomenon of internal oxidation to produce the hard phase, this being done by producing an alloy from a matrix metal, such as copper, containing an easily oxidizable solute metal, such as silicon or aluminum, comminuting the alloy followed by the selective oxidation of the contained solute metal into a dispersed hard phase and then consolidating the thus-treated powder into a wrought metal product. While this technique generally resulted in a further improvement of physical properties, optimum properties were not always obtainable due to difficulty in achieving proper control of the particle size and distribution, and to the excessively long treatment times involved.

Our invention overcomes the foregoing difficulties and enables the production of dispersion strengthened metals of markedly improved physical properties by utilizing the technique of internal oxidation under conditions which enable the controlling of particle size of the dispersoid over a sub-micron size range consistent with yielding optimum results in subsequent deformation and fabrication.

It is the object of this invention to provide a method for effecting optimum dispersion hardening and strengthening and a product characterized by improved physical properties at both room and elevated temperatures.

Other objects will more clearly appear from the following description when taken in conjunction with the drawings wherein:

FIG. 1 shows graphically the maximum amount of solute metal oxide preferably employed in the matrix metal as determined by the corresponding negative free energy of formation of the solute oxide when producing the solute metal oxide by internal oxidation of the starting matrix alloy;

FIG. 2 depicts a semi-log plot showing the relation between yield strength of the extruded alloy and the total surface area of the solute metal oxide present in a cubic centimeter of the hardened alloy;

FIGS. 3 to 9 illustrate graphically the creep-rupture properties of the alloys at various temperatures;

FIG. 10 shows annealing curves illustrating the resistance of the alloys to softening at temperatures up to the melting point of copper; and

FIG. 11 depicts graphically the stress to produce 100-hour rupture life at 450° C. for extruded copper alloys as a function of oxide content.

Broadly speaking, in carrying our invention into practice, we find that we can produce a dispersion of a hard, insoluble slip-inhibiting, grain and sub-boundary migration inhibiting phase in a matrix or solvent metal over a controlled average particle size of up to about 800 Angstrom units (A.) average diameter, e.g., 60 to 800 A., or, assuming the dispersed particles to approximate spheres, then over an average radius of the particles of about 30 to 400 A. We find that when dispersed hard particles are controlled over the foregoing size range, markedly improved strength properties are obtained. We also find the improvement particularly effective when the average particle diameter preferably ranges from about 60 to 300 A., or, assuming spherical particles, an average radius of about 30 to 150 A.

For the purposes of our invention, the introduction of the hard insoluble phase is achieved by internally oxidizing a matrix or solvent metal in particulate form, having alloyed therewith a refractory oxide-forming solute metal whose propensity for forming the oxide is substantially greater than that of the matrix metal. In other words, the matrix metal should be relatively noble compared to the refractory oxide-forming metal. Such matrix metals are preferably defined as those having a melting point above 800° C. and whose negative free energy of formation of the oxides at about 25° C. ranges up to about 70,000 calories per gram atom of oxygen. A refractory oxide-forming metal having a greater propensity for forming the oxide than the matrix metal includes those having a negative free energy of formation with oxygen of at least about 90,000 calories per gram atom of oxygen, e.g., within the range of 90,000 to about 150,000 calories, and generally over 110,000 calories.

Examples of matrix metals include silver, gold, copper, platinum, palladium, nickel, cobalt, iron and alloys based on one or more of these metals. Stating it broadly, the matrix metals may be selected from copper group, platinum group and iron group metals so long as the negative free energy of formation of the oxides ranges up to about 70,000 calories per gram atom of oxygen. Alloys based on the copper group, or the platinum group or iron group metals are included so long as the alloys will be more noble than the solute metal with respect to reaction with oxygen.

Examples of refractory oxide-forming metals include silicon, aluminum, magnesium, calcium, strontium, barium, beryllium, zironcinum, titanium, hafinium, columbium, tantalum, chromium, thorium, rare earth metals such as cerium, yttrium, lanthanum, neodymium, etc., and other metals which combine chemically with oxygen to form refractory oxides having melting points of 1600° C. and above.

As illustrative of the approximate free energies of formation of some of the matrix metal oxides as com-

pared to some oxides produced from refractory oxide-forming metals, reference is made to Table I as follows:

Table I

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

[1] Free energy of formation in calories per gram atom of oxygen at about 25° F.
[2] Alpha alumina.
[3] Heat of formation. Free energy is a little lower than this value.

Regarding the platinum group metals, platinum oxide is known to have a negative free energy of formation below 20,000 calories per gram atom of oxygen while the value for palladium oxide is below 17,000 calories.

The amount of solute metal alloyed with the matrix metal will vary according to the amount of disperse oxide desired in the matrix metal, the maximum amount of solute metal employed being related to the absolute negative free energy of formation of its oxide. Where the negative free energy of formation is less than about 105,000 or 110,000 calories per gram atom of oxygen, the maximum amount of solute metal that may be employed to produce the desired dispersion by internal oxidation will be greater than the maximum which need be employed when the absolute negative free energy is above 110,000 calories per gram atom.

For example, if nickel is the matrix metal and chromium is the solute metal, the preferred maximum of chromium alloyed with nickel would be that equivalent to produce 12% by volume of Cr_2O_3, Cr_2O_3 having a negative free energy of formation in the neighborhood of about 90,000 calories at about 25° C. For the purposes of this invention, we prefer to limit the maximum of chromium alloyed with the matrix metal to that amount equivalent to not more than 10 vol. percent Cr_2O_3, because of density requirements of the alloy and other reasons.

Similarly, where silicon is used as the solute metal with copper as the matrix metal, its preferred maximum would be equivalent to a SiO_2 content of about 10 vol. percent SiO_2 having a negative free energy of formation of about 96,200 calories. For best results, we prefer the amount of silicon alloyed with the matrix metal not exceed that amount equivalent to 6 vol. percent SiO_2, because of density requirements of the alloy and other reasons.

Where aluminum is used as the solute metal, because its oxide (Al_2O_3) has a negative free energy of formation of about 125,590 calories, the preferred maximum should not exceed that amount equivalent to about 6 vol. percent Al_2O_3, and preferably not exceeding 4 vol. percent essentially 100% density being achieved at these values.

The reason for the foregoing limits is that if too much solute metal is present in the alloy for its particular negative free energy of formation of the oxide, the oxide formed during the oxidation treatment is not prone to be distributed uniformly throughout the matrix metal.

With respect to the above, reference is made to FIG. 1 which depicts the relation between the solute metal oxide in the matrix metal and the corresponding negative free energy of formation of the solute oxide. As shown in FIG. 1, the amount of solute metal oxide in the matrix metal formed by internal oxidation should preferably not exceed the limits indicated by curve A and more preferably not exceed the limits indicated by curve B. Generally, the amount of solute metal oxide employed, depending upon the particle size, will be at least about 0.1 vol. percent and range up to the limit imposed by curve A, and preferably up to the limit imposed by curve B.

In producing the oxide dispersion, an alloy of the matrix and solute metals of desired composition is prepared and the alloy then converted to the particulate form by atomizing, machining, grinding, ball milling and the like followed by internal oxidation. The particle size of the alloy may be less than 20 mesh, and preferably less than 325 mesh (minus 44 micron). This depends on the matrix metal or alloy and the particular solute and its concentration. Where the starting alloy in the particulate form is Cu-Al, the oxygen may be caused to diffuse into the alloy particle to oxidize the Al by utilizing an oxidizing treatment comprising first oxidizing the alloy in air to produce a thin coating of Cu_2O followed by heating the oxidized alloy particles under inert conditions, e.g., inert atmosphere or at sub-atmospheric pressure, to decompose the Cu_2O to diffuse oxygen into the copper matrix for reaction with Al. Where the starting alloy is Ni-Si, the internal oxidation may be achieved by heating the alloy in the presence of a mixture of Ni-NiO, the oxygen pressure being determined by the presence of Ni and NiO, and the temperature.

In order to obtain the desired particle size of the disperse oxide within the matrix metal, we have found that the oxidation temperature employed depends upon the oxygen solubility of matrix metal and the absolute value of the free energy of formation of the solute metal. The higher the negative free energy of formation of the oxide of the solute, the higher the temperature one can employ to maintain the desired fineness of the oxide, and conversely, the lower the negative free energy of formation of the oxide of the solute, the lower the internal oxidation temperature to achieve the desired fine oxide particle size of less than 800 A. diameter. Thus, for free energies of formation falling within the range of about 90,000 to 150,000 calories per gram atom of oxygen, lower oxidizing temperatures are preferred at the lower range to obtain the desired particle size. The difference in free energy of formation between the matrix metal oxide and the solute metal oxide appears to be important. For example, where the difference in free energy of formation substantially exceeds 60,000 calories, the temperature of oxidation does not to any great degree affect the obtaining of the desired average particle size. Generally, the particle size obtained will range up to about 300 A. average diameter. Where the difference does not substantially exceed 60,000 calories, the lower is the temperature required to obtain small particle size. We have found as a general proposition that where the absolute negative free energy of formation of the solute metal oxide exceeds 120,000 or 125,000 calories per gram atom of oxygen, the average particle size (average diameter) of the dispersoid will range from about 60 to 300 A.

As illustrative of the difference in the free energy of formation between some matrix metal oxides and solute metal oxides, attention is directed to Table II:

Table II

Solvent metal oxide	ΔF	Solute metal oxide	ΔF	Difference in ΔF
Ag_2O	−2,586	SiO_2	−96,200	−93,614
		ZrO_2	−122,200	−119,614
		Al_2O_3	−125,590	−123,004
		BeO	−139,000	−136,414
Cu_2O	−34,980	SiO_2	−96,200	−61,220
		ZrO_2	−122,200	−87,220
		Al_2O_3	−125,590	−90,610
		BeO	−139,000	−104,020
CoO	−51,000	SiO_2	−96,200	−45,200
		ZrO_2	−122,200	−71,200
		Al_2O_3	−125,590	−74,590
		BeO	−139,000	−88,000
NiO	−58,400	SiO_2	−96,200	−37,800
		ZrO_2	−122,200	−63,800
		Al_2O_3	−125,590	−67,190
		BeO	−139,000	−80,600
Fe_2O_3	−59,800	SiO_2	−96,200	−36,400
		ZrO_2	−122,200	−62,400
		Al_2O_3	−125,590	−65,790
		BeO	−139,000	−79,200

It will be noted from Table II that where silver is used as the matrix metal, the differences in the free energy of formation between the oxide of silver and the oxides of Si, Zr, Al and Be are quite large, i.e., ranging substantially above the aforementioned 60,000 calories preferred minimum difference and even above 90,000 calories. Because of this, dispersoids formed in silver or silver alloy matrix by internal oxidation will generally have a fine particle size.

Where the matrix metal is copper, the difference in the negative free energy of formation of Cu_2O and the oxide of silicon is 61,220 calories. As this difference is in the neighborhood of about 60,000 calories, care must be taken to correlate the temperature of oxidation with the amount of solute metal present, the temperature of oxidation being lower for lower amounts of solute to achieve fine particles. Unless care is taken in instances where the difference in negative free energy of formation is not great, particle sizes in excess of 800 A. diameter may be obtained. Thus, it will be noted in Table II, that the iron group matrix metals Co, Ni and Fe show low differences in negative free energy of formation between their oxides and SiO_2 in which case such metals will be prone to exhibit large SiO_2 particles, unless care is taken in using the correct oxidation temperature. However, in such instances oxidation times may be uneconomically long.

The foregoing will be better appreciated in the light of the following examples in which alloys of copper containing varying amounts of silicon as well as copper containing varying amounts of aluminum were prepared and tested in accordance with the inventive concept.

A series of dilute alloys of Cu-Si and Cu-Al were prepared in a range of compositions calculated to give approximately from 0.1 to 12 volume percent of dispersed refractory oxide by internal oxidation. The alloys were prepared by vacuum melting in the form of chill-cast bars one inch in diameter by eight inches long. The bars were cold swaged to 50% reduction, sealed in a helium filled steel container and annealed for 50 hours at 1000° C. for homogenization.

The homogenized bars were then reduced to chips on a milling machine and then rod milled to form a size fraction passing through a 20-mesh screen, this size fraction thereafter being used for internal oxidation treatment.

The method adopted for internal oxidation of the alloy powders involved the surface oxidation of the powders to form a surface coating rich in Cu_2O (and also containing some solute oxide) by heating a given amount of powder in a measured amount of oxygen at about 450° C. The oxygen from the surface oxide was then diffused into the sample by heating at the desired temperature under substantially inert conditions. This method was found adequate for obtaining up to about 3% by volume of solute oxide within the matrix metal. Where larger amounts of solute oxide were desired, this was accomplished by repeating the step of surface oxidation followed by diffusion of oxygen into the matrix as aforementioned, the number of repeated steps depending upon the amount of solute metal to be oxidized. Preferably, the kind of solute, amount, and particle size should be balanced to accomplish this in one such treatment.

As an example of one method employed in effecting the internal oxidation of the alloy powder, the surface oxidized powder is sealed in a tube by flattening of the ends. The tube is placed in a large muffle furnace held at the desired temperature, e.g., 650° C. to 950° C., for a time, determined by pilot tests, sufficient to obtain a uniform dispersion of solute metal oxide in each of the matrix metal particles.

The internally oxidized matrix metal powder is thereafter hydrogen reduced at an elevated temperature, e.g., 450° C. for one hour, to free the surface of each particle of oxygen and then packed by vibration in a copper container to achieve a pack density of about 50%. The container is evacuated and sealed and made ready for direct extrusion.

Of course, it will be appreciated that the foregoing method is by way of illustration and that many variations of accomplishing the same result may be substituted. For example, the internal oxidation could also be achieved by treating the alloy powder at a low partial pressure of oxygen (e.g., sub-atmospheric pressure) at which copper does not readily oxidize and the solute metal oxidized by diffusion of the oxygen into the matrix metal powder. However, we prefer in carrying out our invention to utilize the first method described as we find that this method is more economical and lends itself to ease of control and readily reproducible results.

The two types of alloys used to illustrate the invention (Cu-Si and Cu-Al) contained 0.01, 0.07, 0.25, 1.59% by weight of silicon and 0.09, 0.23 and 0.77% by weight aluminum, respectively. These alloys were ultimately converted into powder passing 20 mesh, surface oxidized as aforesaid and internally oxidized at temperatures of about 650, 750, 850 and 950° C. for a time sufficient to convert all of the contained solute metal in its corresponding oxide dispersion. After the internal oxidation treatment, the powders were cleaned by hydrogen reduction and then extruded as aforementioned at 760° C., using a ram speed of about 55 inches per minute to give an extrusion ratio of about 28 to 1. Rods of approximately 0.25 inch diameter by four feet in length were obtained from the alloys.

It has been established that extrusion ratios greater than 8 to 1 are necessary to develop the optimum properties in these alloys, even at low oxide content. At higher oxide contents the extrusion ratio is increased to at least 15 to 1 and preferably higher.

The oxide compositions correlated with the original analysis of the alloys are given in Table III as follows:

Table III

Alloy No.	Wt. percent Si	Vol. percent SiO_2	Wt. percent Al	Vol. percent Al_2O_3
1	0.01	0.1		
2	0.01	0.1		
3	0.01	0.1		
4	0.07	0.6		
5	0.07	0.6		
6	0.07	0.6		
7	0.25	2.1		
8	0.25	2.1		
9	1.59	12.0		
10	1.59	12.0		
11			0.09	0.4
12			0.09	0.4
13			0.09	0.4
14			0.23	1.1
15			0.23	1.1
16			0.23	1.1
17			0.77	3.5
18			0.77	3.5

The desired internal oxidation was readily obtained over the temperature range of 650° C. to 950° C. for the alloys with the lower solute content. However, in the case of the alloy containing 1.59 weight percent Si (equivalent to 12 vol. percent SiO_2) a surface film rich in silica formed at 950° C. which hampered internal oxidation, while at 750 and 850° C. the same alloy was successfully internally oxidized. An attempt to internally oxidize a copper alloy containing 2.59% Al (equivalent to about 10.5 vol. percent Al_2O_3) over the temperature range studied presented difficulties. These tests showed that the extent of internal oxidation was governed by the amount of solute metal to be oxidized as well as the negative free energy of formation of the solute metal oxide. Where the amount of solute metal is relatively high, for example, an amount which would form over 10 vol. percent solute metal oxide, internal oxidation tends to be impeded by the formation of a surface film of the solute oxide. When this condition prevails, the temperature of oxidation should be at the low end of the temperature range employed.

As stated hereinbefore and illustrated by FIG. 1, we have found that where the absolute negative free energy of formation of the oxide at about 25° C. is less than about 95,000 calories per gram atom of oxygen, the maximum amount of solute metal would be that equivalent to about 8 to 10 volume percent of solute metal oxide, while for free energy values above 95,000 calories and, preferably, above 120,000 calories, the maximum amount of solute metal would be that equivalent to about 4 to 6 volume percent.

The determination of the particle size of the dispersed phases was obtained by solvent extraction by dissolving the matrix metal in a 20% nitric acid solution, this being accomplished quantitatively by suspending a weighed sample in the acid by means of a dialysis bag. After complete solution of the copper, the bag was transferred to distilled water and washed by dialysis. Upon completion of washing, the residue was dried, collected and weighed. The extracted residues were identified from the diffraction pattern obtained on a spectrogoniometer and the particle sizes determined by X-ray line broadening using the method of Scherrer (C. S. Barrett: Structure of Metals, 2nd ed., McGraw-Hill [1952] 157). The particle sizes obtained with each temperature of oxidation are given as follows:

Table IV

Alloy No.	Vol. percent SiO_2	Vol. percent Al_2O_3	Oxidation temp., ° C.	Particle radius A.
1	0.1		650	330
2	0.1		750	420
3	0.1	1	950	1,000
4	0.6		650	250
5	0.6		750	350
6	0.6		950	630
7	2.1		750	260
8	2.1		950	310
9	12.0		750	215
10	12.0		850	175
11		0.4	650	100
12		0.4	750	150
13		0.4	950	150
14		1.1	650	55
15		1.1	750	47
16		1.1	950	60
17		3.5	750	60
18		3.5	950	83

Assuming the oxide phase to comprise spheres, the various sizes above are indicated in terms of the average radius of the spheres.

It will be noted from Table IV that insofar as the Cu-Si alloys are concerned, the average radius of the SiO_2 particles tend to exceed substantially 175 A., depending on the amount of silicon in the alloy and the temperature of oxidation used. Thus, in forming 0.1 vol. percent of SiO_2, considerably larger particles were formed at the higher temperature range (e.g., 1000 A. radius at 650° C.). However, as the amount of silica in the alloy increases, the size of the SiO_2 produced by internal oxidation decreases accordingly except that for each composition the particle sizes vary with the temperature of oxidation used. On the other hand, where aluminum is employed as the source of the oxide phase (Al_2O_3), much finer particles are obtained, generally not exceeding 150 A. radius. This is probably explained by the fact that the free energy difference between Cu_2O and SiO_2 is in the neighborhood of about 60,000 calories while that for Cu_2O and Al_2O_3 is substantially above 60,000, i.e., above 90,000 calories. Thus, in order to obtain fine SiO_2 particles, temperature of oxidation is an important consideration while in the case of Cu-Al alloys, fine particles may be obtained over substantially a broad temperature range.

By working within a particle size range of up to about 800 A. average diameter and, preferably, over the range of about 60 to 300 A. average diameter, markedly improved strength properties at both room and elevated temperatures are obtainable. Using yield strength as an indication of an alloy's ability to resist creep, we have been able to increase the yield strength of pure copper from 8,000 p.s.i. (0.2% offset) to as high as 65,000 p.s.i. (0.2% offset) for extruded copper containing 3.5 vol. percent of Al_2O_3. Even after annealing this alloy for one hour at 1000° C. (about 80° below its melting point), a yield strength of 59,200 p.s.i. was still maintained, this illustrating the ability of the alloy to resist very high annealing temperatures. Table V is illustrative of the improved yield strength obtained with each composition.

Table V

Alloy No.	Vol. percent oxide	Yield, p.s.i., 0.2% offset	Percent elong.	Particle radius A.	Free mean path (microns)
1	0.1	19,900	33	330	54.3
2	0.1	17,900	40	420	69.5
3	0.1	15,300	41	1,000	166.5
4	0.6	29,100	28	250	5.8
5	0.6	26,600	30	350	8.1
6	0.6	20,700	38	630	14.4
7	2.1	34,400	16	260	1.65
8	2.1	27,500	25	310	1.98
9	12.0	29,000	5	215	0.21
10	12.0	25,800	9	175	0.17
11	0.4	42,800	23	100	3.12
12	0.4	40,800	22	150	4.81
13	0.4	45,200	22	150	4.70
14	1.1	55,800	20	55	0.81
15	1.1	54,500	16	47	0.66
16	1.1	58,200	19	60	0.56
17	3.5	63,800	13	60	0.21
18	3.5	65,100	13	83	0.31

Improved resistance to creep at elevated temperatures is also indicated as will be evident from the 100-hour creep rupture data obtained on the series of alloys at 450° C. as shown in Table VI.

Table VI

Alloy No.	Vol. percent oxide	100-hour rupture life, p.s.i.	Percent elongation	Particle radius A.	Free mean path (microns)
1	0.1	6,300	1	330	54.3
2	0.1	5,200	4	420	69.5
3	0.1	2,400	6	1,000	166.5
4	0.6	10,500	3	250	5.8
5	0.6	8,800	7	350	8.1
6	0.6	4,000	4	630	14.4
7	2.1	13,500	4	260	1.65
8	2.1	12,000	2	310	1.98
9	12.0	15,000	3	215	0.21
10	12.0	13,000	3	175	0.17
11	0.4	15,500	4	100	3.12
12	0.4	15,500	4	150	4.81
13	0.4	17,000	2	150	4.70
14	1.1	30,000	3	55	0.81
15	1.1	27,000	2	47	0.66
16	1.1	31,000	2	60	0.56
17	3.5	36,500	2	60	0.21
18	3.5	38,000	2	83	0.31

The foregoing table shows that significant increases in both room temperature and high temperature strength properties are obtainable. Strength increases with increasing oxide content up to 3.5% oxide, the rate of increase being much higher at the lower oxide content. This was indicated with as little as 0.1 vol. percent of silica, With the highest oxide content, e.g., 12 vol. percent silica, the strength dropped off to values below that obtained with the intermediate alloys. This decrease in strength was accompanied by lower density in the extruded product and a much less uniform distribution of the oxide. These results tend to indicate that where silica is involved, its preferred maximum should not exceed about 8 vol. percent. Likewise, with respect to Al_2O_3 and other refractory oxides having absolute negative free energies of formation above 120,000 calories per gram atom of oxygen, the preferred maximum should not exceed 6 vol. percent, and preferably not exceed 4 vol. percent.

Included in the data of Tables V and VI is the mean free path of the oxide determined for each composition. These data indicate that for improved properties the mean free path should be below 5 microns and preferably below 1 micron, for example 0.2 micron.

It will be noted that the foregoing tables also show quite significantly that strength varies inversely with particle size, other things being equal. In the silica alloys, the oxide particle size over the composition range of 0.1 to 2.1 vol. percent varied from an average radius of 250 to 1000 A. as against 47 to 150 A. for the Al_2O_3 alloys over the range of 0.4 to 3.6 vol. percent.

Since the strength exhibited by the alloys is apparently dependent upon the particle size of the oxide and the volume fraction of the oxide phase per unit volume of hardened alloy, it would appear, therefore, that a relation would exist for the alloy between the total surface area of the oxide particles in a unit volume of the matrix metal (surface parameter) and the strength achieved through dispersion hardening, for example yield strength. Where the average diameter of the disperse phase is expressed in centimeters, the surface parameter may be expressed as cm.^{2} per cubic centimeter of hardened alloy using the formula:

$$A=\frac{6f}{D}$$

where:

A=cm.^{2}/cubic centimeter of alloy
f=the volume fraction of the solute metal oxide
D=diameter of solute metal oxide particle expressed in centimeters

By using the foregoing relation, both volume fraction and particle diameter are expressed together by one term as illustrated in Table VII which correlates yield strength with the surface parameter expressed by the foregoing equation:

Table VII

Alloy No.	f	Particle radius, cm.	Surface parameter cm.^{2}/cc. of alloy	Y.S., p.s.i.
1	0.001	330×10^{-8}	9.10×10^{2}	19,900
2	0.001	420×10^{-8}	7.15×10^{2}	17,700
3	0.001	1000×10^{-8}	3.00×10^{2}	15,800
4	0.006	250×10^{-8}	72.00×10^{2}	29,100
5	0.006	350×10^{-8}	51.00×10^{2}	26,600
6	0.006	630×10^{-8}	28.40×10^{2}	20,700
7	0.021	260×10^{-8}	242.00×10^{2}	34,400
8	0.021	310×10^{-8}	205.00×10^{2}	27,500
11	0.004	100×10^{-8}	120.00×10^{2}	42,800
12	0.004	150×10^{-8}	80.00×10^{2}	40,800
13	0.004	150×10^{-8}	80.00×10^{2}	45,200
14	0.011	55×10^{-8}	600.00×10^{2}	55,800
15	0.011	47×10^{-8}	700.00×10^{2}	54,500
16	0.011	60×10^{-8}	550.00×10^{2}	58,200
17	0.035	60×10^{-8}	1750.00×10^{2}	63,800
18	0.035	83×10^{-8}	1270.00×10^{2}	65,100

It will be appreciated that for optimum strengthening, the diameter of the oxide particles should be small but volume fraction should not be too large. Where volume fraction tends to be too large, skin formation of the solute oxide is favored, thus hampering uniform dispersion of the oxide throughout the matrix metal. Hence, by keeping the diameter of the oxide particle small, e.g., less than 150 A. and even less than 100 A., then volume fraction of the oxide can be kept small, e.g., below 5 or 4%.

It will be noted from FIG. 2 that when the yield strength is plotted against the logarithm of the surface parameter average straight lines are obtained for silica- and the alumina-containing alloys, which when extrapolated to zero surface area (to pure copper), indicate a yield strength value for pure copper in the neighborhood of about 8,000 to 9,000 p.s.i. which compares favorably to the value of 8,000 p.s.i. actually obtained for pure copper.

For particle radii of 30 to 400 A. (60 to 800 A. diameter) and volume percent of the disperse oxide phase ranging from 0.05 to 10%, the surface parameter to achieve the desired results may range from 60×10^2 to $10{,}000\times10^2$ cm.^{2} per cubic centimeter of hardened alloy. We prefer that the particle radius be maintained below 150 A. and in the range of about 30 to 150 A. (60 to 300 A. diameter) for oxide compositions ranging from 0.1 to 4 volume percent, the surface parameter for such compositions ranging from about 60×10^2 to 4000×10^2 cm.^{2} per cubic centimeter of hardened alloy. We have found that where the particle size is controlled over the aforementioned size ranges, optimum results are indicated

for disperse oxide phases in the neighborhood of about 4 volume percent. This is illustrated by actual test data for alloys of Cu-Al_2O_3 and Cu-SiO_2 shown in FIG. 11.

In order to appreciate the extent to which the elevated temperature creep properties of the alloys are improved by means of the invention, reference is made to FIGS. 3 to 9 which show the silica- and alumina-hardened alloys tested in creep rupture at 450° C., 650° C. and 850° C. The test bars with a gauge section of 0.160 inch diameter and 1.0 inch long were prepared by machining from the extruded rods.

FIG. 10 shows the interesting property of the extruded alloys to resist softening by annealing. The alumina strengthened alloys are particularly resistant to softening, with little or no annealing occurring up to just below the melting point of copper. Thus, dispersion strengthened alloys produced in this way have the advantage over the more conventional alloys of retaining their work hardened structure over broad temperature ranges, even above normal annealing temperatures approaching the melting point of the pure copper.

We have found that while sub-micron oxide particles over the range of 30 to 400 A. average radius can be obtained by other processes, we prefer to use internal oxidation as the means of producing fine particles as we find we obtain the best results with this method. For example, an alumina-containing alloy was prepared by mixing sufficient aluminum nitrate with 500 grams of minus 325 mesh copper powder to be equivalent to 1.1 vol. percent of Al_2O_3. This was achieved by dissolving the nitrate in minimum amount of methanol necessary to completely wet the copper powder. After mixing by spatulation, the charge was held under vacuum at 65° C. for 24 hours to remove the methanol and the bulk of water of crystallization. This permitted the heating of the mixture to the decomposition temperature of the nitrate without melting it. The mixture was canned and heated for one hour in vacuum at 450° C. to decompose the nitrate. This was followed by sintering in hydrogen at 750° C. for four hours, machining the compact and then extruding to the desired dimension. The alloy which contained 1.1 vol. percent Al_2O_3 was determined to have a particle size of about 60 A. radius. It exhibited a 100-hour rupture life at 450° C. under a stress of 5,600 p.s.i. as compared to a 100-hour rupture life at a stress of about 31,000 p.s.i. of a similar composition of the same particle size prepared by internal oxidation. In other words, while the Al_2O_3 particles in both had the same average radius of 60 A., the material produced by internal oxidation was markedly superior in that it could withstand over five times the stress for 100 hours. Apparently, this difference was due to imperfect oxide distribution of the alumina produced in situ by nitrate decomposition.

One of the unique aspects of strengthening of copper and similar metals by means of a dispersed oxide phase, in contrast with the more conventional methods of solid solution strengthening or precipitation hardening, is that a significant increase in strength is possible while retaining a substantially pure metal matrix with virtually no alloying element remaining in solid solution. This has the advantage of giving markedly higher strength without too much loss in electrical or thermal conductivity or corrosion resistance. Furthermore, our extrusion experiments have shown that the hot working properties of the dispersion strengthened alloys are not measurably different from those of the pure metal, and machinability remains practically unimpaired. By means of the invention, these alloys which exhibited optimum strength properties retained about 60% of the electrical and heat conductivity of pure copper. To illustrate the vast improvement obtained by the invention, alloy No. 18 is compared with pure copper and two of the well known commercial alloys in Table VIII:

Table VIII

	Pure copper	Alloy No. 18	70 Ni-30 Cu	Type 304 stainless
Y.S. (p.s.i.)	8,000	65,000	35,000	34,000
T.S. (p.s.i.)	32,000	76,000	80,000	85,000
Percent Elong	55	13	40	63
Percent R.A	70	31	65	76
Modulus (10^6 p.s.i.)	17	23	26	28
Electrical cond. (percent of Cu)	100	60	3.5	2.5
Thermal cond. (percent of Cu)	100	60	6.5	5.3
Density (g./cc.)	8.96	8.75	8.23	7.93

It will be noted that the alumina strengthened copper (3.5 vol. percent Al_2O_3) not only compares quite favorably with the Ni-Cu alloy and type 304 stainless on the basis of tensile properties but also even exhibits markedly superior yield strength in combination with substantially higher thermal and electrical conductivity.

Of great importance is the increase of modulus of elasticity to 23 million p.s.i., 6 million greater than recorded for pure copper.

While examples given herein are concerned with the treatment of copper, it will be appreciated that the treatment with or without variations thereof may be applied to other metals, such as nickel. Thus, in strengthening nickel, alloys of up to 3.5 weight percent Cr or up to 1.5 weight percent Al in nickel are cast, homogenized, machined into fine chips, ball milled to powder of less than 44 microns and then internally oxidized at 700 or 800° C. in an oxidizing environment created by a mixture of nickel and nickel oxide. After complete internal oxidation of the powders, the powders are briefly treated at 650° C. in hydrogen to remove surface oxygen. The powders are then compacted at a hydrostatic pressure of 35,000 p.s.i., machined into a right cylinder about 1.25 inch diameter by 2 inches long, canned in a nickel container, heated to about 1000° C. and extruded. The extrusion ratio is from 16 to 25 to 1, preferably greater than 20 to 1 to attain maximum density.

Alloys containing up to about 8 vol. percent of oxide have been produced in this way and showed strength improvements over pure nickel at 815° C. by a factor of 6 times for a 100 hour rupture life.

In producing a dispersion strengthened alloy containing chromium as an alloying ingredient, such as an alloy comprising 85% Fe and 15% Cr, we would first produce dispersion strengthened iron powder which we would then mix with chromium, consolidate the mixture to a compact, subject the compact to a sintering heat treatment and then extrude it. Assuming the dispersion hardener to be Al_2O_3, an alloy of iron and aluminum would first be produced containing an amount of aluminum equivalent to 4 vol. percent Al_2O_3. The alloy would then be converted to powder of about minus 100 mesh. The iron powder would thereafter be subjected to internal oxidation by heating in a controlled partial pressure of oxygen at the desired temperature, between about 600° C. and 1450° C. until complete internal oxidation of the solute aluminum is achieved. The necessary oxygen pressure may be obtained with an Fe-FeO mixture, by sub-atmospheric means, or by partial surface oxidation as previously described. The powder would then be hydrogen reduced at about 750° C. to remove any excess oxygen.

The clean internally oxidized powder is then mixed with minus 10 micron chromium powder, compacted at 50,000 lbs./sq. in., subjected to a sintering and diffusion heat treatment at a temperature of about 800° C. The sintered compact is then encased in a sheath of iron and extruded at a temperature of about 1000° C. at an extrusion ratio of about 20 to 1 to produce an alloy of Fe-Cr dispersion hardened with Al_2O_3. The particle size of the dispersoid would be in the range of about 60 to 800 A. average diameter in view of the fact that the

difference in free energy of formation between the oxide of iron and that of aluminum would be sufficient to enable the obtaining of such small sub-micron sizes.

It becomes apparent that the invention not only provides a method for producing dispersion strengthened metals in which the disperse hard phase is controlled over narrow limits of sub-micron size range but also provides as a composition of matter a substantially ductile matrix metal powder having dispersed therethrough fine particles of a hard refractory oxide of melting point above 1600° C. In addition, the invention also provides wrought metal product produced from dispersion strengthened metal powders.

While the 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: 90% copper and 10% nickel; 80% copper and 20% nickel; 70% copper and 30% nickel; 70% copper and 30% gold; 65% copper, 30% gold and 5% 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 the requisite amount of refractory oxide formers can be internally oxidized at temperatures ranging from about 500° C. to 1000° C.

Examples of iron group alloys include: steels, 64% iron and 36% nickel; 31% nickel, 4 to 6% cobalt, and the balance iron; 54% iron and 46% nickel; 90% iron and 10% molybdenum or tungsten; 90% nickel and 10% molybdenum or tungsten.

Heat resisting alloys having a base of one or more of the iron group metals nickel, iron and cobalt may also be dispersion strengthened. However, where such alloying agents as chromium are employed, it is preferred that such agents be not added until the iron group metal powder containing the refractory oxide-forming metal has been internally oxidized.

With respect to platinum group alloys, the following are examples: 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, and others. As to these non-ferrous alloys containing refractory oxide-forming metal, we prefer to treat them similarly to the copper group alloys.

Generally speaking, the temperatures employed to effect internal oxidation must be at least sufficient to oxidize the refractory oxide-forming metal alloyed with the ductile matrix metal. Broadly speaking, such oxidizing temperatures may range up to about 90% of the melting point of the metal and preferably within the range of about 45% to about 90% of the melting point of the metal subject to internal oxidation.

In the case of copper or copper-base alloys, such oxidizing temperatures may range from about 500° C. to 950° C., depending upon the solute metal alloyed therewith and its negative free energy of formation of its oxide relative to that for copper oxide. Thus, if silicon is used as the oxide former, the oxidation temperature should be at the lower range thereof to insure oxide particles within the desirable range of size.

In the case of platinum or platinum-base alloys, such oxidizing temperatures may range from about 700° C. to about 1500° C. Because of the extremely low negative free energy of formation of platinum oxide, very small particle sizes are obtainable over a wide temperature range.

As for metals and alloys of the iron-group, the oxidizing temperatures may range from about 500° C. to 1200° C.

In setting up the environment to effect internal oxidation, we have found that certain conditions should prevail. One may preoxidize the powders at a controlled oxygen pressure at relatively low temperature (500° C. to 800° C.) until a specific gain in weight is recorded which is just sufficient to oxidize the solute element to oxide, followed by heating under inert conditions to promote internal oxidation which then is followed by hydrogen reduction at 400 to 700° C. to clean the surface. One may also expose the alloy powder to mixtures of $Fe\text{-}Fe_2O_3$ or Ni-NiO or Co-CoO, etc. which at each temperature will result in an appropriate oxygen pressure to carry on the internal oxidation process. In still other instances, one may expose the alloy powders to a mixture of H_2 and H_2O, the mixture resulting in an oxygen pressure which depends on the temperature. The resultant oxygen at low pressure then internally oxidizes the solute metal. If carburization is not a problem a $Co\text{-}CO_2$ system may also be used.

To permit the shortest possible treatment time and to minimize the tendency to form large particles in the grain boundaries, the internal oxidation temperature should be as high as possible consistent with the desired oxide particle size. Smaller alloy powder particles also aid in this respect. In this connection we prefer to use alloy particles of less than 50 microns or even less than 10 microns in size as we have found that because such sizes contain fewer grain boundaries than the much coarser particles, a finer particle of the oxide is assured and a more uniform distribution thereof obtained.

For optimum results, the oxygen partial pressure should be as high as possible without forming an undue amount of the solvent metal oxide. This means that the oxygen partial pressure should be maintained close to the decomposition pressure of the matrix metal oxide at the particular temperature of the internal oxidation treatment. Furthermore, the rate of delivery of oxygen, as well as its partial pressure, must be maintained at a suitable level, particularly at the early stages of the process where the reaction rate is highest. If, for example, the necessary atmosphere is to be produced by subatmospheric treatment, then both partial pressure and flow rate must be controlled at the desired level by obtaining the proper balance between leak rate and pumping speed in the system.

In producing a wrought metal product by extrusion from the prepared dispersion hardened metal powder, the prepared powder may or may not be consolidated prior to hot working depending upon the type of metal to be extruded. For example, in the case of copper, we found that ordinary vibrational packing within a copper sleeve without any further treatment to be sufficient in preparing a billet for extrusion. When the material is of such a nature that ordinary vibration packing of the powder is not sufficient we prefer that the mixture be consolidated to an apparent density of at least about 65%, and preferably to at least 80%, before it is hot worked. While the mixture may be cold pressed, it will be understood that hot pressing can also be employed. In cold pressing a compact to at least 65% apparent density, the pressure applied may range from 15 to 50 tons per square inch. When hot pressing a compact preparatory to extrusion, the temperature may range from about 650° C. to 1250° C. in a protective environment at pressures ranging up to about 40 tons per square inch. Generally, lower pressure would be employed at higher temperature levels.

When extruding the compact, protective conditions should be used, such as encasing the compact in an air tight, evacuated, welded container, for example a sheath of copper or iron or nickel. Extrusion pressures may range from about 40 to 250 tons per square inch over a temperature range of about 800 to 1250° C., depending

on the particular metals involved, for extrusion ratios ranging from about 20 to 1 to 30 to 1.

The invention enables the production of high strength wrought metal products characterized by structural stability and by the ability to retain high strength properties at elevated temperatures. In addition, the invention is also applicable to the production of metal articles having improved strength properties at elevated temperatures in combination with relatively high heat conductivity and electrical conductivity. Examples of metal structures are heat exchangers, turbine buckets of iron or iron alloys and other metals for use in steam and gas turbines, furnace structures where resistance to creep at elevated temperatures is an important consideration, boiler tubing for carrying superheated steam and many other applications too numerous to mention.

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 the appended claims.

What is claimed is:

1. As a composition of matter, a metal powder comprising a ductile matrix metal whose oxide has a negative free energy of formation at 25° C. ranging up to about 70,000 calories per gram atom of oxygen, the matrix metal having dispersed substantially uniformly therethrough by internal oxidation about 0.1 to 4 v/o of fine particles of a hard refractory solute metal oxide of average diameter ranging up to about 800 Angstroms and a surface parameter determined by the formula $6f/D$ as surface area of solute metal oxide per cubic centimeter of matrix metal ranging from about 60×10^2 to 4000×10^2 cm.^{2}, where f equals the volume fraction of the disperse phase and D equals the average diameter of said oxide phase in centimeters, the negative free energy of formation of said oxide phase exceeding 120,000 calories per gram atom of oxygen at 25° C., the difference in negative free energy between the matrix metal and solute metal oxides being at least 60,000 calories per gram atom of oxygen at 25° C.

2. A method of introducing a hard slip and grain boundary-subboundary inhibiting phase of average diameter ranging up to 800 Angstroms into a matrix metal of melting point above 800° C., an oxide of which has a negative free energy of formation at 25° C. ranging up to about 70,000 calories per gram atom of oxygen, which comprises providing said metal in particulate form having alloyed therewith an amount of solute metal whose oxide is substantially stable at elevated temperatures and has a negative free energy of formation at 25° C. exceeding 120,000 calories per gram atom of oxygen, the difference in the negative free energy between the oxide of the matrix metal and that of the solute metal being at least 60,000 calories, said amount of solute metal corresponding to an amount of solute metal oxide ranging from 0.1 to 4 v/o, and subjecting said powder to an internal oxidation treatment at an elevated temperature ranging from about 45% to 90% of the melting point of the matrix metal to form a solute metal oxide dispersed through said particulate matrix metal, the oxidation temperature employed for obtaining the desired range of dispersoid being related to the difference in negative free energy between the matrix metal and the solute metal oxides and to the amount of solute metal present, the oxidation temperature being lower as the difference in negative free energy approaches 60,000 calories and as the solute metal content approaches the lower end of the composition range, whereby the disperse phase will have a surface parameter ranging from 60×10^2 to 4000×10^2 cm.^{2} as determined by the formula $6f/D$, where f equals the volume fraction of the disperse phase and D equals the average diameter of said oxide phase in centimeters.

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