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3,578,443

METHOD OF PRODUCING OXIDE-DISPERSION-STRENGTHENED ALLOYS

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ABSTRACT OF THE DISCLOSURE

A method is disclosed for producing an alloy having a fine uniformly dispersed hard refractory oxide material in a ductile matrix metal. The alloy is made from an alloy powder, the individual particles of which each contain the metal of which the refractory oxide is formed and the matrix metal, the oxide-producing reactive metal being one that has a much greater affinity for oxygen than the matrix metal and is soluble in the matrix metal. The powder particles are formed preferably into thin flakes, of the order of 5 microns or less thick, in a controlled oxygen containing environment to oxidize the surfaces of both the reactive metal and the matrix metal in a thin film. The alloy powder flakes produced are thin enough to allow oxidation of a substantial portion of the reactive metal and a portion of the matrix metal to some predetermined degree. The oxidized flakes are then placed in a neutral or inert environment at an elevated temperature to remain a sufficient time to allow the matrix oxides to react with the matrix and thereby to supply oxygen to the reactive metal to oxidize the reactive metal within the interior of the flakes. The flake powders, now free of matrix oxide or oxygen in solution, are compacted, heat is applied to bring the temperature of the compact to a hot working temperature while maintaining the inert environment, and the compact is extruded or otherwise hot worked to a wrought alloy form. Favorable results for some purposes have been obtained by reducing the surface matrix metal oxides without the internal oxidation step, and then following the further steps mentioned to provide the wrought alloy.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; U.S.C. 2457).

The present invention relates to alloys produced by powder metallurgy process and, more particularly, to alloys produced by combining one or more ductile matrix metals and a refractory oxide forming solute element.

Since the introduction of the SAP method (dispersion strengthened, sintered aluminum powder) in 1948, a great deal of effort has been expended in attempts to produce other alloys employing a ductile matrix metal with a refractory oxide material uniformly dispersed through the matrix to provide strength thereto. A number of the techniques employed to provide such alloys are discussed in Letters Patent 3,176,386 issued to Grant (one of the present inventors) et al., on Apr. 6, 1965. It is not necessary to repeat all the background information contained in the patent, but a brief discussion thereof is in order.

The refractory oxide forming element is added to the matrix metal generally to improve resistance to creep, yield strengths and high temperature stability thereof while retaining, as much as possible, the favorable characteristics of the matrix metal. For example, copper is one highly regarded matrix metal, but the addition of a refractory oxide, such as Al_2O_3 , to furnish the foregoing improved characteristics, degrades some of favorable

characteristics, e.g., electrical conductivity, and ductility. The degradation of the favorable characteristics increases non-linearly with increases in the amount of refractory oxide in the alloy, but the strength characteristics depend more upon the dispersion of the refractory. Thus the strength characteristics can be improved by having smaller-sized refractory oxide particles in the alloy, but uniformly dispersed throughout the alloy. Both reduction in the size of the refractory oxide and uniform dispersion are difficult to obtain and are, furthermore, costly to produce in the one prior-art process that shows promise in this respect.

Accordingly, an object of the present invention is to provide an improved process for preparing a wrought alloy of one or more ductile metals and a refractory oxide material, in which the percentage of refractory oxide material in the wrought alloy may be no greater than heretofore (and may be less), but in which the size of the refractory oxide particles distributed through the alloy is smaller than could heretofore be produced economically, thereby to provide improved strength characteristics with minimal degradation of the favorable characteristics of the matrix.

Such alloys have been prepared by a number of methods including: mechanical mixing of the matrix metal and refractory oxide in preparation for extrusion or the like, which results in a nonuniform alloy because of segregation of the refractory oxide; internal oxidation of equi-axed alloy powders, which is not adapted economically to give the desired strength characteristics without the mentioned degradation, and which places an important limitation on the types of alloy compositions which can be utilized; salt decomposition which fails to supply the expected alloys because the refractory oxide does not adhere to the matrix metal powder and, again, nonuniform distribution prevails in the end product; and a method wherein a salt solution of the matrix metal and one of the reactive metals of which the refractory is formed is subjected to a number of chemical steps which can result in sub-micron size matrix and refractory particles to provide a good end-product alloy but at a very high cost. It is, therefore, another object of the invention to provide a process for producing a wrought alloy having submicron size dispersion of a refractory oxide material in a ductile matrix at a production cost within reasonable limits.

Other and still further objects are discussed in the description to follow and are particularly pointed out in the appended claims.

By way of summary, the foregoing objects are attained by producing a wrought alloy having a fine uniformly dispersed hard refractory oxide material in a ductile matrix metal from an alloy powder, the particles of which each contain the metal of which the refractory oxide is formed and the matrix metals, the oxide-producing reactive metal being one that has a much greater affinity for oxygen than the matrix metal and is soluble in the matrix metal, in a process that comprises, forming the powder particles into thin flakes no greater than about five microns thick and preferably no greater than 0.5 micron thick in an oxygen containing environment to oxidize the surfaces of both the reactive metal and the matrix metal in a thin film. The powder flakes thereby produced must be thin enough to allow oxidation of a substantial portion of the reactive metal and a portion of the matrix metal. The oxidized flake powders are then placed in a neutral or inert environment for a sufficient time at a sufficiently elevated temperature to allow the matrix metal oxide to dissolve and to react with the reactive metal in depth to oxidize, internally, more of the reactive metal. The flake powders are then compacted in a neutral or inert atmosphere, sufficient heat being applied

to bring the temperature of the compact to a hot working temperature while protected against further oxidation. The compact is then worked to a wrought alloy form. In one form of the invention, the flakes are placed in a reducing atmosphere, for example, hydrogen, to reduce the matrix metal oxide, and the internal oxidation step is eliminated. As hereinafter noted, however, the additional utilization of internal oxidation provides higher-strength alloys.

The discussion to follow relates primarily to copper-aluminum oxide alloys wherein the alloy powders, from which the wrought alloy is made, comprises particles of copper and aluminum in solution. Typically, the alloy powders contain 2.5 to 16.0 atom percent of aluminum as the reactive metal, the remainder being copper as the matrix metal. The wrought alloy derived in the manner discussed herein typically contains 2.3 to 6.0 volume percent aluminum oxide (in the form Al_2O_3) uniformly dispersed in the copper matrix. Other matrix metals such as nickel, cobalt, iron molybdenum, tungsten, titanium, zirconium, niobium and tantalum and their alloys, and other reactive metals such as beryllium, silicon, thorium, titanium, zirconium, hafnium, yttrium, chromium and metals of the lanthanide and actinide series, can be used. Since, as mentioned, for the present process to perform as described, it is necessary that the reactive metal have a significantly greater affinity for oxygen than the matrix metal (the reactive metal should have a heat of formation of the oxide which is at least 30,000 cal. per gram atom of oxygen larger than the heat of formation of the oxide of the matrix metal), the last named matrix metals, i.e., titanium, zirconium, niobium and tantalum can be combined only with metals selected from the group consisting of metals of the lanthanide and actinide series plus beryllium, thorium and yttrium; and zirconium will function either as a matrix metal or a reactive metal, depending upon the other metal used in the combination. Furthermore, the reactive metal must be soluble in the matrix metal at room temperature no less than about one-half atom percent.

The copper-aluminum alloy powders employed are fine atomized or milled powders at the -100 micron size and preferably at the -44 micron size. The powders are comminuted by a comminuting technique referred to as the attritor grinding method to produce fine flakes of which the thickness dimension is the order of 0.2 to 0.5 micron (but may be up to 5 microns, depending upon desired results) and the length and width dimensions thereof are the order of 1 to 10 microns, but may be as large as 1000 microns. The 2.3 to 6.0 volume percent alumina for the flake material appears at the surface as evenly distributed areas of alumina and as fine dispersions within the copper matrix. Thus, the amount of aluminum exposed can be very carefully controlled by a choice of powder particle size and length of time that the powder is subjected to the attritor. A desirable refractory oxide thickness is 10 to 40 angstroms but it may be as thick as 200 angstroms. The maximum thickness of aluminum oxide possible at room temperature is about 200 angstroms; so the control of aluminum oxide obtainable by the concept herein disclosed is of considerable importance.

As previously mentioned, the present process makes possible alloys in which ductile metal is strengthened by an oxide dispersed more or less uniformly through the metal without lowering, inordinately other characteristics of the material. The results are attained by reducing the size of the individual refractory oxide particles below particle sizes heretofore commercially, economically possible. The refractory particles which appear in the wrought alloy are less than 100 to 500 angstroms which is fine enough to provide the strength characteristics desired without degrading to an unacceptable extent the other characteristics of the alloy.

The process will now be discussed generally, specific examples being included hereinafter. As a first step, atomized copper-aluminum alloy powders are subjected to at-

tritor action for a period of about six to ten hours (but this may be as high as 36 hours or longer as hereinafter noted) in ethanol to produce a flake product of thickness less than 0.5 micron and length and width dimensions the order of 1 to 10 microns from -44 micron starting powders; although the thickness dimension should never be greater than about 5 microns, and preferably no greater than 0.5 micron, the length and width dimensions may be as large as 1000 microns. The powder particles are oxidized during comminution to provide thin aluminum oxide films or film patches surrounded by copper oxide regions. The refractory oxide thickness is of the order of 10-40 angstroms, and may be as thick as 200 angstroms as before discussed. Non-flaked powders, as mentioned, present a minimum surface to volume ratio for air oxidation; the flakes, on the other hand, present maximum surface to volume ratio for oxidation and the surface can be enlarged or decreased by changing the ratio of flake thickness to the length and width dimensions thereof. Thus, it is necessary with the non-flaked (or regular shaped) material to have more initial aluminum or provide significantly smaller particle diameters than generally accepted as economically feasible to provide a desired strength of wrought alloy because an optimal amount of aluminum cannot be oxidized and/or the size of the oxide particles in the wrought alloy is far greater than by the present process. Furthermore, the time needed to oxidize is increased. Also, if the aluminum percentage in the powder alloy is increased too much, little or no surface oxide of the copper forms and the internal oxidation discussed herein cannot take place; in this connection it has been observed that during the formation of the surface oxide, the aluminum oxide covers a disproportionate portion of the particle surface.

The flakes are preferably internally oxidized in the manner discussed herein, but an acceptable product for many purposes is obtained by reducing the non-refractory oxide in a hydrogen atmosphere at an elevated temperature to produce the "A" series alloys hereinafter discussed. (Other known reduction methods, e.g. by vacuum, can be substituted for hydrogen reduction.) The reduced flake material is compacted in a can, evacuated, sealed and extruded at a hot-working temperature above about one-half the absolute melting temperature of the matrix metal, i.e., 740° C. for the Cu-Al alloys, but below about 800° C.-850° C. The resultant product contains a fine oxide dispersion of the refractory oxide in a ductile matrix, the oxide particles tending to be finer than about 200 angstroms. As is noted in the tables below, the extruded alloy has excellent room temperature strength properties, unusually good high temperature strength properties, and useful values of ductility.

By deliberately producing sub-micron thick flakes, a sufficiently large amount of the reactive metal is exposed at the surface to produce a significant and desirable amount of refractory oxide to serve as a dispersoid. Since the refractory oxide adheres tenaciously to the matrix metal there is no tendency for the two to separate or segregate in processing, as occurs in mixing processes. Since the flakes and the thin-film oxides are so thin, there is assurance of close spacing of fine refractory oxide particles in the wrought alloy to a much greater degree than when spheroidal particles or thick flakes are used.

In the "B" series alloys hereinafter discussed, the flakes are internally oxidized by a process now to be explained. The flakes in this process are not reduced by hydrogen initially, but are, rather, placed in a gas-tight container in a non-reactive environment (i.e. vacuum or an inert or neutral atmosphere), and the temperature is raised to about 600° C. to 850° C. (for the copper-aluminum alloys). The flakes remain in this neutral environment a sufficient time at this elevated temperature to allow copper oxides to dissolve and react with the dissolved aluminum in the flakes and in this fashion supply oxygen by diffusion in depth to provide internal oxidation of the

aluminum. Work done to date indicates that one hour is more than enough time to assure extensive internal oxidation of the very thin flakes and that, with proper temperature control, a few minutes is enough time. Internal oxidation done in the manner just discussed enables very precise control over the amount of oxygen available to react internally with the reactive metal, thus making it possible to predetermine the amount of refractory oxide in the finished product but, also, making it possible to assure complete freedom of the matrix metal from oxygen.

Should it be decided that more refractory oxide is desired than that which can be provided by the surface copper oxide on the flake powders, that oxygen can be added in a number of ways. One way is to add a given amount of oxygen to the non-reactive environment, at a reduced pressure, so that said oxygen will dissolve into the flake powders and be converted to Al_2O_3 . A second method is to add the oxygen as a mixture of hydrogen and water vapor, at a ratio which is oxidizing to the aluminum in solution, at the reaction temperature, but is not oxidizing to the copper.

A number of examples are included below of methods of preparation of alloys employing teachings of the present inventive concept. The examples are followed by tables giving details of the composition of the same alloys and strength characteristics thereof.

EXAMPLE 1

Copper-aluminum alloys, with varying amounts of aluminum in solid solution were dispersion hardened with varying amounts of gamma alumina using the technique of surface oxidation. Alloys of copper with 1, 3 and 1.5 weight percent aluminum were initially obtained in powder form; the size of the powders was such that all particles passed through a 325 mesh (44 micron) screen. These powders were then comminuted to a much smaller size using a device called an attritor which is a grinding device similar to a ball mill but an order of magnitude more efficient with regard to performing the grinding process. The capacity of the attritor was approximately 1 gallon. The powders in 500 g. batches were ground, using absolute ethanol as a surfactant, for two time periods, namely 6 and 10 hours. After grinding, the slurry of powder and ethanol was removed from the grinding device and allowed to settle for about 24 hours, after which the majority of the ethanol was decanted. The remaining alcohol was removed by placing the mixture in a vacuum desiccator and applying a vacuum until the powder was completely dry. The yield from this procedure was about 95% and the ground powder had a "tap" density of 10%–15% of theoretical.

Metallographic observations both by light and electron microscopy indicated that the ground particles were flake shaped, the length and width dimensions being 5 to 15 microns and the thickness 0.1 to 0.5 micron. At this point in the process, the surface of the produced powder flakes consists of a mixture of Al_2O_3 and Cu_2O or CuO , the relative amounts of which depend on the initial alloy composition and the final particle size distribution of the ground powder. In order to eliminate any copper oxide that was formed as a result of the oxidation of the surface of the flakes at room temperature, the powders were given a hydrogen reduction at 450° C. until no water was detected in the exit gas (using Karl Fisher reagent). At this point the reduction was stopped and the powders allowed to cool to room temperature, keeping the reduction tube thoroughly sealed to prevent re-oxidation of the powder flakes; the resultant product was composed of flakes of copper-aluminum alloys with a thin surface layer of aluminum oxide and with no copper oxide present.

Copper cans suitable for use as containers for the produced powders were prepared, being 8.0" long by 3.0" O.D., with an internal cavity 7.0" long by 2.5"

I.D. A system was designed to allow the loading of the powders from the reduction tube to the copper cans without re-exposure to oxygen, and subsequent compacting. The best way of accomplishing this is by means of a dry box. The sealed compacts in each instance were placed inside a mild steel "can" the dimensions of which were as follows: 8.0" long by 3.5" O.D. and 3.0" I.D.: the compacts fit closely into the cans. The bottoms of the cans were heli-arc welded, and the tops, with a mild steel evacuation tube, were also heli-arc welded to the cans, now containing the powder compacts. The compact assembly was thus ready for the final hot consolidation process which was, in this case, hot extrusion. Prior to extrusion, the assemblies were leak tested using a vacuum leak detector and then placed in a furnace at 538° C. under a dynamic vacuum of less than 1μ and allowed to out-gas. This is an important step in the process, since the aluminum oxide that forms on the surface of the flakes will normally contain water of hydration. The oxide will most probably be of the form $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (alpha monohydrate) or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (alpha or beta trihydrate). This "water of hydration" does not decompose rapidly until about 550° C.; holding at 538° C. in vacuum allows the decomposition of the hydrated alumina films and the transformation is to the much more stable structure of gamma Al_2O_3 . The treatment is thus important because it allows the removal of an instability of the system before final consolidation.

Final consolidation was accomplished by hot extrusion of the evacuated assembly at a temperature of 760° C.; this is safely below the gamma to alpha alumina transformation temperature. It is important that all consolidation and subsequent hot working temperatures be kept at or below about 850° C. in order to avoid the instability of the transformation of gamma alumina to delta or alpha alumina. The hot extrusion process allows several processes to take place; they can be listed as follows:

- (1) Full densification.
- (2) Break up and intimate mixing of thin surface films of Al_2O_3 with the alloyed matrix.
- (3) Imparting of a certain degree of cold work which is subsequently retained by the produced alloy.

EXAMPLE 2

Copper-aluminum alloys were ground in the attritor as in Example 1; however, after removing the excess alcohol, the procedure is somewhat different. Batches of the dried powders were placed in an air tight tube and the tube then flushed with argon gas for ½ hour. At this point, the tube was placed in a horizontal furnace and the temperature was raised to 750° C. The powders were allowed to internally oxidize in static argon at 750° C. for 1 hour. Reactions take place in the following way:

- (1) Reaction of surface copper oxide with the Cu-Al alloy. This provides dissolved oxygen in the alloy.
- (2) Reaction of dissolved oxygen with Al in solid solution in copper to produce Al_2O_3 .
- (3) Diffusion, penetration, and reaction of oxygen with Al to form Al_2O_3 still deeper into the powder.
- (4) Total utilization of all available oxygen to produce an equivalent amount of Al_2O_3 .

Following the internal oxidation procedure, the powder was removed from tube, transferred to a hydrogen reduction tube and hydrogen reduced, as in Example 1. The hydrogen reduction treatment guarantees that there is no copper oxide or oxygen in solution in the alloy, thereby assuring the production of a stable alloy.

Subsequent to the reduction treatment, the powders were compacted, evacuated, and hot extruded as in Example 1. Thus the oxides (Al_2O_3) that were produced in the example were a result of surface plus internal oxidation. In using this method, flakes of Cu-Al alloys were produced with some Al_2O_3 present on the surface of the flake and the rest generated by internal dispersion within the flake. A comparison between the "A" and "B" series alloys in

Table I shows the additional amount of Al_2O_3 obtained by using internal oxidation in conjunction with surface oxidation; and Tables II, III and IV show the effect of such internal oxidation upon the properties of the wrought alloy.

EXAMPLE 3

A copper, 20% nickel, 1% aluminum alloy was dispersion hardened with varying amounts of gamma and eta alumina using the surface oxidation technique. The alloy was prepared similarly to those described in Example 1, however, the intermediate and final surface conditions were somewhat different. After grinding, as in Example 1, for the 6 to 10 hours, and removing the ethanol grinding agent, the produced flakes powders contained on their surface mixtures of nickel oxide, aluminum oxide and some copper oxide. Thus the reducing procedure had to be such that all the nickel oxide on the surface and any copper oxide that was present were reduced to nickel and copper, respectively. This was accomplished by reducing in dry hydrogen at 550° C.-600° C. until no water was detected in the exit gas, as in Example 1. Compaction, degassing and final consolidation were carried out as in Example 1. The effect on grinding time on the final flake size is significant for these alloys and hence the alloy with the finer initial starting flake size possessed superior properties to the one with the coarser flake size. This example is significant since it shows that the surface oxidation method is applicable to suitably chosen ternary alloy systems, and could as well be applied to quaternary and even more complex alloy systems.

TABLE I.—COMPOSITIONS AND EXTRUSION RATIOS
[final compositions]

Alloy No.	Wt. percent		Atmospheric percent Al	Wt. percent Ni	Vol. percent Al_2O_3	Extrusion ratio
	Cu	Al				
A1.....	98.3	0.65	1.51	-----	2.3	12:1
A2.....	98.0	2.80	6.54	-----	2.9	22:1
A3.....	91.95	6.86	15.80	-----	4.5	22:1
A4.....	84.0	.33	.70	15.0	2.6	22:1
B1.....	98.3	0.58	1.35	-----	2.9	22:1
B2.....	95.4	2.65	6.18	-----	4.2	22:1
B3.....	91.4	6.89	16.00	-----	4.5	30:1
B4.....	84.3	0.06	.12	14.71	4.4	22:1

TABLE II.—ROOM TEMPERATURE TENSION PROPERTIES
FOR AS-EXTRUDED ALLOYS

Alloy	0.2% Y.S., p.s.i.	U.T.S., p.s.i.	Elongation, percent	Reduction area, percent
A1.....	46,200	49,700	19.8	22.6
A2.....	53,400	59,600	19.6	26.4
A3.....	83,100	92,600	7.5	10.5
A4.....	75,300	75,300	6.1	8.0
B1.....	68,300	70,500	12.0	17.8
B2.....	66,000	60,100	4.8	6.1
B3.....	83,900	88,600	4.6	2.1
B4.....	40,400	44,400	17.4	29.5

TABLE III.—STRESS FOR 100-HOUR LIFE AT 450 AND 650° C.
[tests in air]

Temp. ° C.	Alloy No.	Stress for 100-hour life, p.s.i.
450.....	A1	19,000
	A2	23,000
	A3	25,000
	A4	11,000
	B1	25,700
	B2	28,900
	B3	27,700
	B4	9,500
650.....	A1	8,500
	A2	13,500
	A3	14,800
	A4	5,500
	B1	13,800
	B2	15,400
	B3	16,900
	B4	4,500

TABLE I V.—RESULTS OF CREEP-RUPTURE TESTING
[all tests in air]

	Alloy	Temp., ° C.	Stress, p.s.i.	Rupture life, hours	Elongation, percent	Reduction area, percent
5	A1.....	450	22,500	0.36	4.6	5.1
			20,000	16.7	4.3	2.4
			18,000	454.6	2.5	2.4
10	A1.....	650	15,000	0.05	5.0	2.4
			12,500	2.02	3.3	2.4
			10,000	35.5	5.4	1.2
			9,000	60.2	-----	2.4
			8,000	380.0	3.3	3.9
15	A2.....	450	25,000	1.38	7.1	5.1
			24,000	16.3	6.2	3.9
			23,000	25.8	6.6	2.6
			22,500	373.6	4.4	2.4
20	A2.....	650	15,000	0.31	5.1	3.9
			14,000	16.4	3.3	3.9
			12,500	516.0	4.4	5.1
			-----	-----	-----	-----
25	A3.....	450	29,000	0.026	5.8	7.1
			28,000	0.24	20.4	23.4
			27,450	48.5	3.8	6.3
			25,000	82.5	6.4	13.9
30	A3.....	650	20,000	.127	5.7	7.8
			17,000	3.08	4.5	5.5
			15,000	40.7	5.1	11.7
			14,000	90.7	2.6	4.8
35	A3.....	850	10,000	0.003	24.2	33.2
			8,000	0.01	18.3	40.0
			4,000	15.3	-----	3.9
			-----	-----	-----	-----
40	A4.....	450	14,000	0.75	2.4	2.5
			12,000	4.5	2.0	3.7
			10,500	>1,010.0	1.0	-----
			-----	-----	-----	-----
45	A4.....	650	10,000	0.01	4.4	2.5
			7,000	0.75	3.0	1.5
			5,000	318.7	5.5	1.5
			-----	-----	-----	-----
50	B1.....	450	29,000	0.067	2.4	3.2
			27,000	6.6	2.7	2.4
			26,000	25.8	2.8	3.7
			25,500	182.5	3.0	1.5
55	B1.....	650	20,000	0.017	-----	2.4
			17,000	0.63	3.0	2.5
			15,000	14.3	-----	5.1
			-----	-----	-----	-----
60	B2.....	450	32,000	0.40	3.8	2.4
			30,000	3.0	5.5	3.2
			29,000	27.4	2.7	2.4
			27,000	704.0	3.6	1.5
65	B2.....	650	20,000	0.37	1.9	2.4
			18,000	4.2	3.8	2.4
			15,500	88.5	3.3	2.9
			13,000	91.8	-----	2.4
70	B3.....	450	30,000	0.8	10.0	12.0
			28,250	2.15	7.0	7.5
			26,500	16.4	6.7	10.0
			24,000	>289.0	1.6	1.5
75	B3.....	650	20,000	0.41	5.7	7.4
			19,000	1.05	6.3	6.6
			17,000	75.8	-----	1.5
			15,000	177.0	7.0	4.6
80	B4.....	450	16,000	0.33	5.2	2.4
			13,000	2.85	3.5	1.5
			10,000	69.5	2.4	1.5
			-----	-----	-----	-----
85	B4.....	650	9,000	0.078	4.1	1.5
			6,000	11.7	2.7	2.5
			5,000	66.1	-----	2.5
			-----	-----	-----	-----

The alloys described in the foregoing discussion resulted from grinding times in the attritor of from 6 to 10 hours. Work done in which grinding times are of the order of 36 hours has resulted in improved extruded alloys, which is attributed to the smaller flake sizes, both in thickness and other dimensions, that result from the added grinding. Optimal grinding times are a function of the alloy being produced. The resulting alloys by the method herein discussed generally contain the matrix metal with some reactive metal in solid solution and a finely dispersed second phase of the reactive metal oxide, the amount of reactive metal left in solid solution being determined by the amount thereof converted to an oxide.

A further advantage of the present process is that with reactive metals as Al, Si, Cr, for example, a significant residual amount of the reactive element is left in solution (balance used to produce the refractory oxide), and as

a result the alloy gains corrosion resistance. Thus alloys A3, B3, etc. were tested in air at 650° C. for up to 177 hours and showed only a thin surface film of oxide on the test specimen surface. With pure copper matrix, exposure at 650° C. is not practical. This advantage applies also to stainless materials, brasses, bronzes, Ni-aluminum, Co and Fe-aluminum materials, as well.

Modifications of the invention herein disclosed will occur to persons skilled in the art and all such modifications are considered to be within the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A method of producing a wrought alloy with a fine uniformly dispersed hard refractory oxide phase in a ductile matrix metal from an alloy powder the particles of which each contain the metal of which the refractory oxide is formed and the matrix metal, the oxide-producing reactive metal being one that has a much greater affinity for oxygen than the matrix metal and is soluble in the matrix metal, in a process that comprises forming the powder particles into thin flakes no greater than about five microns thick in an oxygen containing environment to oxidize the surface of both the reactive metal and the matrix metal in thin films, the powder flakes produced being thin enough to allow oxidation of a substantial portion of the reactive metal and a portion of the matrix metal, placing the oxidized flake powder in a non-reactive environment for a sufficient time at an elevated temperature to allow the matrix metal oxides to react with the reactive metal to supply oxygen in depth to oxidize internally more of the reactive metal, compacting the flake powders in a non-reactive environment, and applying sufficient heat to bring the temperature of the compacted material to a hot working temperature while protected against further oxidation, and working the compact to a wrought alloy form.

2. The method of claim 1 in which the particles of the alloy powder are less than about 10 microns thick, and the flakes are less than 5 microns thick, and the other flake dimensions may be as coarse as 1,000 microns.

3. The method of claim 1 in which the particles of the alloy powder are less than about 5 microns thick, and the flakes are less than 1 micron thick, and the other flake dimensions may be as coarse as 400 microns.

4. The method of claim 1 in which the hot-working temperature is above about one-half the absolute melting temperature of the matrix metal, and the working method is extrusion, rolling or forging.

5. The method of claim 1 in which predetermined amounts of an oxygen source are introduced to the flakes in the neutral environment.

6. The method of claim 1 in which predetermined amounts of an oxygen source are introduced to the flakes in the non-reactive environment prior to internal oxidation thereof and the environmental temperature is raised to provide an increase in the thickness of the surface oxide, the raised temperature being far below the elevated temperature at which internal oxidation occurs.

7. The method of claim 6 in which the oxidized matrix metal is reduced subsequent to being internally oxidized and prior to compacting.

8. The method of claim 1 in which the matrix metal is reduced in a hydrogen atmosphere subsequent to being internally oxidized and prior to compacting.

9. A method of producing a wrought alloy having a fine uniformly dispersed hard refractory oxide material in a ductile matrix metal from an alloy powder, the particles of which powder each contain the metal of which

the refractory oxide is formed and the matrix metal, the oxide-producing reactive metal being one that has a much greater affinity for oxygen than the matrix metal and is soluble in the matrix metal, in a process that comprises, forming the powder particles into thin flakes no greater than about five microns thick in an oxygen containing environment to oxidize the surfaces of both the reactive metal and the matrix metal in thin films, the powder flakes produced being thin enough to allow oxidation of a substantial portion of the reactive metal and a portion of the matrix metal, compacting the flake powders in a non-reactive environment and applying sufficient heat to bring the temperature of the compacted material to a hot working temperature while protected against further oxidation, and working the compact to wrought alloy form.

10. The method of claim 9 in which predetermined amounts of an oxygen source are introduced to the flakes in the non-reactive environment prior to compacting.

11. The method of claim 9 in which predetermined amounts of an oxygen source are introduced to the flakes in the non-reactive environment prior to compacting and the environmental temperature is raised to provide an increase in the thickness of the surface oxide.

12. The method of claim 11 in which subsequent to the introduction of the oxygen source and prior to compacting the matrix metal oxide is reduced.

13. A method as claimed in claim 9 in which the oxidized flake powder is placed in a non-reactive environment for a sufficient time and at a sufficiently elevated temperature to allow the matrix metal oxides to react with reactive metal within the flakes to supply oxygen in depth to oxidize internally more of the reactive metal.

14. A method as claimed in claim 13 in which said time and temperature are sufficient to enable substantially all the matrix oxides to be reduced by the reaction with the reactive metal.

15. A method as claimed in claim 14 in which the flake thickness is no greater than 0.5 micron.

16. A method as claimed in claim 9 in which the oxidized flake powder is placed in a room temperature non-reactive environment and a predetermined amount of oxygen is added thereto, the environmental temperature being shortly thereafter raised to provide an increase in thickness of the surface oxides, the temperature of the non-reactive environment being thereafter increased to a level sufficient to allow the matrix oxides to react with the reactive metal within the flakes to supply oxygen in depth to oxidize internally more of the reactive metal.

17. A method as claimed in claim 16 in which the matrix metal oxide is reduced subsequent to being internally oxidized and prior to compacting.

18. A method as claimed in claim 9 in which the matrix oxide is reduced prior to compacting.

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