

[54] OXYREACTION STRENGTHENING OF METALS

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[51] Int. Cl. B22f 3/24

[58] Field of Search 75/206, 200; 148/126

[56] References Cited

UNITED STATES PATENTS

3,326,676	6/1967	Rubel et al.	75/206
3,475,159	10/1969	Hansen	75/206
3,551,992	1/1971	Maykuth et al.	75/206

OTHER PUBLICATIONS

Blickensderfer et al., Bureau of Mines Report of In-

vestigations, June 1971, No. RI7521, "A New Internal Oxidation Process for Strengthening Tungsten", U.S. Dept. of Interior.

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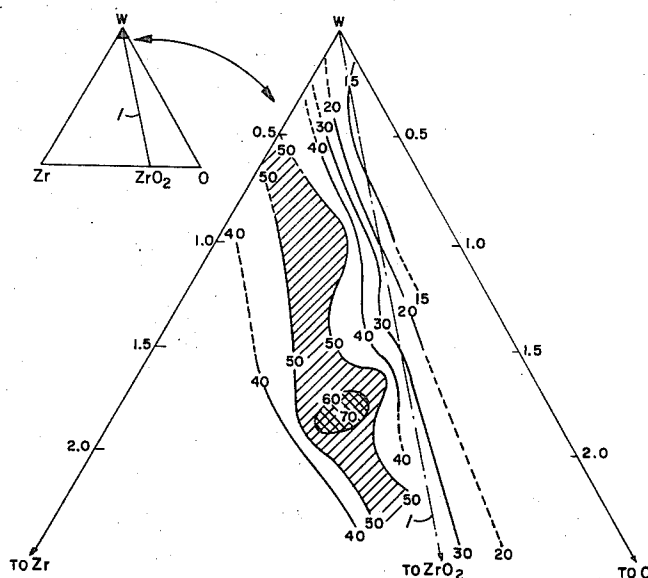
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[57] ABSTRACT

Oxyreaction strengthening of base metals and their alloys is accomplished by a powder metallurgical technique in which a base metal powder containing oxygen is blended with a reactive metal powder, and then pressed, sintered, densified if desired, and held below the sintering temperature to form an ultrafine dispersion of reactive metal oxide throughout the base metal. Preferred base metals include the Periodic Table metals of Groups 1B, VIB, and VIII while preferred reactive metals include silicon, aluminum and Periodic Table elements of Group IVB.

16 Claims, 2 Drawing Figures



OXYREACTION STRENGTHENING OF METALS

BACKGROUND OF THE INVENTION

It is known to strengthen or otherwise modify the properties of a metal or alloy by incorporating therein finely divided oxide particles. The oxide particles may comprise an oxide of the metal itself, an oxide of another metal or even an oxide of a non-metal. A number of techniques have been developed and practiced on a commercial scale to produce such oxide strengthened or stabilized metals and alloys. As a general rule, powder metallurgy methods are used and all methods have in common the production of hard, insoluble oxide particles in the metal. Usually working is required to consolidate the metal or alloy into a fully dense structure and to strengthen the metal by generating dislocations around the oxide particles. Each method has its own particular advantages and disadvantages depending upon the particular alloy system selected.

In one method, surface oxidation is used to produce a thin oxide film on the surface of ultrafine base metal or alloy particles. The metal powder is then compacted, sintered and formed into useful shapes by techniques such as extrusion. This method, unfortunately, is restricted to those metals or alloys which form a thin, tightly adherent, refractory film. This requirement severely limits the number of metals or alloys which may be strengthened by this method. Moreover, particle size of the metal should be less than 1 micron in diameter or thickness and the compact produced requires extensive working to achieve maximum strengthening. The "SAP" (stabilized alumina powder) aluminum alloys exemplify materials prepared by this method.

Decomposition of inorganic salts on a metal powder is another method for producing ultrafine oxide particles. For example, low temperature decomposition of a thorium nitrate coating on nickel particles results in formation of submicron sized particulate deposit of thoria or nickel powder. This method is most effective using thoria as the strengthening oxide but thoria is radioactive and its use is limited accordingly.

Preferential reduction of one of a mixture of oxides is another method used to produce dispersed ultrafine oxide particles. From a mixture of oxides, such as NiO and Al_2O_3 , one can reduce the oxide having the lowest free energy of formation, NiO , at low temperatures. Unfortunately, particles of the dispersed phase strengthener, in this case Al_2O_3 , tend to agglomerate.

Another method commonly used is internal oxidation. A suitable system consists of a dilute solid solution in which the solute metal has a much higher free energy of oxide formation than does the base metal. Oxygen is allowed to diffuse into the alloy and reacts with the solute to precipitate fine oxide particles. An example of this method is the internal oxidation of copper-aluminum powders to produce fine alumina particles within the alloy grains. However, diffusion rates along grain boundaries are usually more rapid than diffusion through the grain resulting in concentration of oxide along grain boundaries which leads to segregated structures. Use of very fine, prealloyed particle tends to circumvent this problem but production of such fine prealloyed powder is not presently an economical method. Also, because of diffusion limitations, some alloys cannot be internally oxidized to form a uniform

dispersion of fine oxide particles throughout the powder.

Still another common method is the mechanical blending of fine metal powders and oxide particles. To obtain optimum properties, the metal powders should be on the order of 1 micron in size and the oxide particles much smaller.

None of these conventional processes are applicable to all of the common metal and alloy systems and all tend to have the problem of segregation of oxide particles. Generally, the finer the size and the greater the difference in density between the matrix metal and the oxide particles, the greater is the susceptibility for segregation. Two other disadvantages predominate in high-temperature strengthening of metals or alloys by the above methods. One is that the materials must be subjected to a large amount of cold, plastic working to achieve maximum strengthening. Another disadvantage is that the oxides cannot be taken into solution within the matrix metal at high temperature to promote workability and then reprecipitated at a lower temperature to strengthen the material.

SUMMARY OF THE INVENTION

We have discovered a powder metallurgical process for the oxyreaction strengthening of metals and alloys in which ultrafine oxide particles are deposited in a dispersed fashion throughout a formed metal shape by ageing heat treatment or by use at elevated temperatures after the normal sintering step. The sintered compact may be further densified by techniques such as extrusion prior to, or as a part of, the ageing heat treatment. A base or matrix metal powder, containing small amounts of oxygen, is blended with a small proportion of a more reactive metal powder and the mixture is compacted and sintered. The reactive metal reacts with most of the oxygen in the base metal to form relatively coarse reactive metal oxides. A portion of the reactive metal and oxygen diffuses through the base metal grains as well as along grain boundaries to form solutes with the base metal and/or unresolved reactive metal-oxygen structures. During post-sintering or post-densification heat treatments or use at elevated temperatures, ultrafine reactive metal oxide particles form throughout the base metal. Size of the reactive metal oxide particles formed within the base metal grains is typically on the order of 0.05 to 0.2 microns.

Preferred base metals include Periodic Table metals of Groups IB, VIB and VIII and their alloys. Reactive metals appropriate for use are characterized by a free negative energy of formation of the oxides substantially greater than that of the base metal; by a significant solid state solubility within the base metal at sintering temperatures and by stability of their respective oxides at high temperatures. In addition, it is preferred that the reactive metal have the capability of solution-strengthening the base metal. Silicon, aluminum, and Periodic Table elements of Group IVB are preferred reactive metals.

Metals and alloys strengthened by our process show superior tensile strength and stress-rupture properties, particularly at high temperatures, compared to conventional oxide strengthened or stabilized metals. ZOW (zirconium-oxygen-tungsten) alloys and MOZ (molybdenum-oxygen-zirconium) alloys produced by our process, for example, show exceptional strength

and stress-rupture properties at temperatures in the range of about 1,200° to 1,900°C.

Hence it is an object of our invention to provide a method for the oxyreaction strengthening of metals.

Another object of our invention is to provide a method for forming ultrafine metal oxide particles dispersed throughout a base metal matrix.

Yet another object of our invention is to produce metal compositions having dispersed therein ultrafine particles of a second metal oxide.

DETAILED DESCRIPTION OF THE INVENTION

In the drawings:

FIG. 1 is a ternary plot of the effect of zirconium and oxygen on the tensile strength of ZOW alloys at 1,650°C.

FIG. 2 is a plot showing the tensile properties of ZOW alloys over the temperature range of 20° to 1,920°C.

Our invention comprises a powder metallurgy technique for the oxyreaction strengthening of metals and the production of alloys by use of that technique. In a most preferred mode of operation, our process combines the advantages of dispersion strengthening as well as solution strengthening. By blending a reactive metal powder with an oxygen-containing base metal or alloy powder prior to pressing, sintering, and (optionally) densifying, we cause to develop during subsequent heat treatments or use at elevated temperatures an ultrafine dispersion of reactive metal oxides. We prefer to add to the blend an amount of reactive metal powder in excess of that required to completely react with the oxygen contained in the base metal oxide. Excess reactive metal diffuses into the base or matrix metal and contributes to the properties of the base metal by solution strengthening.

Our process differs from those of the prior art in that ultrafine oxide particles are formed during the ageing heat treatment or use at elevated temperature after blending, sintering, and possibly densifying the base and reactive metal powder blends. Previous methods typically are dependent upon adding tiny oxide particles during the blending procedure or upon forming oxides within or on the surface of metal powders prior to blending. We can control the size and distribution of oxide particles within the alloy by regulating the oxygen and reactive metal content of the powder blend and the sintering and ageing temperature and time. In previous methods, control of oxide particle size is largely dependent upon the size of oxide particles added to the starting base metal powder.

We can prevent agglomeration of ultrafine oxide particles, a problem which plagues previous techniques, by control of ageing heat treatments. Base metal or alloy particles exceeding 1 micron in size may be used in our process and in some cases the larger particles are actually preferred. Many previous methods require base metal having a 1 micron or smaller particle size. These finer metal powders are generally more expensive. Preparation of ultrafine oxide particles for addition to a base metal powder, required by many prior art techniques, is eliminated in our method. Finally, base metal particles containing oxygen in small amount not only can be used but are desirable in our process.

Base metals useful in our process include generally those in Groups IB, VIB and VIII of the Periodic Table and their alloys. Particularly preferred base metals are

tungsten, molybdenum, and their alloys. Oxygen content of the base metal powders must be within the range of about 0.01 to 2.0 percent by weight and preferably is in the range of 0.05 to 0.5 percent. Many commercially available metal powders have an oxygen content in the range of a few hundred to a few thousand parts per million and in some instances these powders may be used without further treatment. Somewhat higher oxygen contents may be desired and the metal powders may be further oxidized by exposure to air or oxygen at moderately elevated temperatures. Particle size of the base metal powders should be small but is not critical. For example, commercially available tungsten powders having a mean particle size ranging from less than 1 to more than 5 microns gave essentially equivalent results.

Reactive metals useful in our process must fulfill several requirements. First, the reactive metal must have a negative free energy of oxide formation substantially greater than that of the base metal, or in the case of an alloy, substantially greater than any of the alloy components. Second the oxide or oxides of the reactive metal must be stable at high temperatures. It is also necessary that the reactive metal be soluble, at least to some extent, within the base metal at sintering temperatures. It is preferred that the reactive metal display solubility levels comparable to those of oxygen within the base metal at sintering temperatures. Lastly, the reactive metal should be capable of solution-strengthening the base metal at low concentration levels. We particularly prefer zirconium and hafnium as reactive metals for use with tungsten and molybdenum base metals.

The reactive metals may be blended with base metals in the form of an elemental powder having a particle size comparable to that of the base metal. It is preferred, however, that the reactive metal be added in the form of an intermetallic compound. Most preferred intermetallic compounds are those which comprise the reaction product of the reactive metal with the base metal. For example, we prefer to use the compounds ZrW_2 and HfW_2 for the oxyreaction strengthening of tungsten and the compounds $ZrMo_2$ and $HfMo_2$ for the oxyreaction strengthening of molybdenum. Intermetallic compounds are preferred primarily because of their ease of preparation and handling. Such compounds are simple to synthesize and typically are brittle but nonreactive in ordinary environments. A powder of any desired size range may be easily prepared by conventional grinding techniques.

Amount of reactive metal blended with the base metal must be sufficient to react with all of the oxygen contained in the base metal. It is preferred to add reactive metal in excess of that required to react with all the base metal oxygen. Excess reactive metal then goes into solution within the base metal during sintering and enhances the physical properties of the base metal by solution strengthening. A preferred range of reactive metal addition is from about 125 percent to about 300 percent of that required to completely react with the oxygen contained in the base metal.

We utilize conventional techniques for blending base metal and reactive metal powders and for pressing the powder blends into shaped forms or compacts. Dry blending techniques may be used but we prefer to wet-mill the powders using rod or ball mills and fluids such as distilled water. Compacts may be formed by vibratory packing the blended powders into a die followed by iso-

static pressing. Other conventional pressing techniques may be used as well.

The pressed compacts are then sintered at temperatures which are relatively high but substantially below the melting point of the base metal. For example, compacts comprising tungsten as the base metal were sintered at temperatures ranging from 1,500° to 2,400°C with good results. Sintering time required depends upon the amounts of reactive metal and oxygen present, their diffusion rates, the density of the compacts and upon the sintering temperature. In general, sintering time will range from about 1 to about 24 hours. Sintering atmosphere must have a low oxidizing potential and may conveniently comprise wet or dry hydrogen, inert gases, or a vacuum.

We believe the oxyreaction strengthening mechanism to occur in several overlapping stages or steps. Initially, the reactive metal combines with the base metal oxygen, and some reaction may occur between the sintering atmosphere and the base metal oxygen. Reactive metal oxide particles form at the prior sites of the reactive metal particles and later coalesce into relatively large masses, on the order of a few microns in size. The remaining reactive metal and oxygen diffuse through the structure along diverse local concentration gradients and produce a sparse dispersion of submicron oxide particles by internal oxidation. As equilibrium is approached, some reactive metal and oxygen remain in solution or as unresolved reactive metal-oxygen-matrix metal structures. Continued sintering produces sparse, ultrafine oxides. Subsequent to sintering, ageing or strain ageing heat treatments or simple usage at elevated temperatures produce extensive precipitation and growth which results in a relatively dense dispersion of reactive metal oxide particles having a particle size ranging from less than about 0.01 to about 0.2 microns.

Formation of the ultrafine reactive metal oxide dispersion is accomplished generally in a procedure which may be described as a precipitation heat treatment. As has been set out previously, the precipitation heat treatment may comprise a heat ageing step or, in appropriate cases, may consist of normal usage at elevated temperatures. Temperatures required for the precipitation heat treatment depend upon the base metal and reactive metal system but will be below, usually substantially below, normal sintering temperatures. However, the temperature must be sufficiently high to produce precipitation and growth of reactive metal oxide particles from the dissolved reactive metal and oxygen in the base metal. Time required to precipitate and develop a dense dispersion of ultrafine reactive metal oxide particles depends to some degree upon the treatment temperature but is generally in the range of about 2 to 24 hours.

Precipitation heat treatment conditions appropriate for use with any particular matrix metal-reactive metal system may be determined in a routine fashion. This may be accomplished by subjecting samples of the alloy to a heat treatment at varying temperatures for selected time periods and examining the so-treated samples with an electron microscope to determine the degree of development of the ultrafine reactive metal oxide dispersed phase. For example, precipitation heat treatment of ZOW alloys may be accomplished at temperatures above about 1,400°C and below about 2,000°C.

Referring now to FIG. 1, this ternary plot shows the effect of zirconium and oxygen on the tensile strength of ZOW (zirconium-oxygen-tungsten) alloys at 1,650°C. Contours are in 1,000's psi. Note that zirconium and oxygen are plotted in atomic percent. For small amounts of those elements in tungsten, atomic % zirconium is divided by 2.0 to obtain weight % while atomic % oxygen is divided by 10.2 to obtain weight %. The plot is based on tensile tests from 54 specimens which were synthesized and sintered over a range of conditions. The results show that oxygen alone had a deleterious effect on the hot tensile strength. Zirconium alone up to levels of about 0.6 atomic % produced a marked increase in tensile strength but with additional Zr content the strength decreased. Highest strength alloys were formed when both zirconium and oxygen were present in amounts within the range 0.8 to 1.0 atomic %. This range would correspond to 0.4-0.5 weight % zirconium and 800-1,000 ppm by weight oxygen.

All of the relatively high strength compositions lay on the Zr rich side of the tie line 1 extending from the W apex to ZrO_2 . Based on this evidence, it was concluded that tensile strengthening occurred both from the effect of Zr combined as ZrO_2 and from excess Zr in solution. Polished specimens of a number of different alloy compositions were examined by electron microscope. Most observations were made by preparing replicas with the two-stage, plastic-carbon technique, or from direct extraction carbon replicas. Resolution was limited to about 100 Å or 0.01 micron. Zirconium dioxide was found to occur in relatively coarse particles several microns in diameter, which were not believed to contribute to strengthening, and in the form of small particles less than about 0.3 microns in size. Particles as small as the limit of resolution, 0.01 micron, were observed and it is believed that even smaller particles existed. The smaller particles were well dispersed throughout the tungsten grains and these were considered to be largely responsible for strengthening of the alloy.

FIG. 2 is a plot of tensile properties of selected ZOW alloys over the temperature range 20° to 1,920°C. Strain rate was 0.02 in. per minute and specimens were in the stress-relieved condition. The abrupt decrease in tensile strength between 1,650° and 1,920°C is attributed to recrystallization which was found to occur in this temperature range.

The following examples more fully illustrate specific embodiments of our invention.

Example 1

In many instances, the oxygen content of commercially available base metal powders may be somewhat lower than that desired for use in our process. For example, samples of commercial tungsten powders displayed a range of oxygen content from about 200 to 3,400 ppm depending upon particle size and manufacturer. Most samples ranged from 200 to 500 ppm.

Oxygen content of tungsten powders may be increased in a controlled fashion by heating in air at moderately elevated temperatures. Tungsten powder having a particle size of 5.4 microns and an initial oxygen content of 421 ppm was heated in air at 215°C for 40 hours. At the end of this time, the oxygen content was 920 ppm. A second sample of the same tungsten powder was heated in air at 265°C for 40 hours. At the end of this time, oxygen content was 2,235 ppm.

Example 2

The zirconium-tungsten intermetallic compound, ZrW₂, was prepared by arc melting tungsten powder (previously hydrogen reduced at 1,000°C for 4 hours) with thin strips of crystal bar zirconium in the proportion of 82g tungsten to 18g zirconium. The ZrW₂ buttons thus produced were solution heat treated and pulverized under argon in a steel mortar and pestle, and further reduced by rod milling either in the dry state or in alcohol. No free zirconium was present in the ZrW₂ powder. Similar techniques may be used to produce other intermetallic compounds including those of zirconium-molybdenum.

Example 3

ZOW alloy billets were prepared by the following general procedure. The required amount of tungsten powder, containing small amounts of combined oxygen, was mixed with ZrW₂ powder by wet rod milling using distilled water for about 4 hours. After this time, the slurry was allowed to settle, water was decanted off and the powder was dried. After drying, the powder cake was broken up, passed through a 200 mesh screen, and then tumbled for about 30 minutes. The blended powder was vibratory packed in a die and was isostatically pressed and then sintered. Sintering temperatures used ranged from 1,500° to 2,400°C. Sintering times ranged from 2 to 22 hours in either a flowing hydrogen or vacuum atmosphere.

The sintered compacts were machined into 1 1/4 in. diameter billets and densified by extruding to 1/2 in. diameter rod at temperatures between 1,600° and 2,200°C by a high-energy-rate forming machine. After being stress-relieved at 1,350°C for 15 minutes under

ment at 1,650°C for various times but under no stress. At this temperature between 2 1/2 to 7 hours was required to develop the observable dispersion of ultrafine zirconium oxide particles. At the end of 20 hours at this temperature, some growth of the oxide particles was observed.

Example 5

Another ZOW alloy, containing 0.4 weight % zirconium and 865 ppm oxygen, was prepared by the procedure set out in Example 3. The pressed compact was sintered at 2,000°C for 16 hours and was then densified by extruding to a 1/2 in. diameter rod. Electron microscope examination of the extrusion revealed relatively large zirconium oxide stringers but no evidence of an ultrafine zirconium oxide dispersion.

After heat ageing the sample for 20 hours at 1,400°C, a number of very fine precipitates began to appear. Heating for 20 hours at 1,600°C resulted in further development of the dispersed ultrafine precipitate. 4 hours of heating at 2,000°C resulted in the dissolution of much of the dispersed ultrafine phase. After one hour of heating at 2,250°C, only a few sparsely distributed ultrafine oxide particles remained.

Example 6

A number of additional ZOW alloy specimens were prepared by the procedure of Example 3 and were densified by extrusion as before. Instead of being subjected to a heat ageing treatment after extrusion, these specimens were tested to determine stress-rupture properties at 1,650°C. As well as determining physical properties, these tests were considered to simulate usage of the alloy at elevated temperatures. Illustrative data from these tests are set out in Table I which follows.

TABLE I

Sample designation	Sintering			Analyses		Test temp. °C	Creep stress psi	Creep life hr.	Elongation %	Reduction in area %
	Time hr.	Temp. °C	Atmosphere	Zr wt. %	O ppm					
135A	16	2000	vacuum	0.37	660	1650	20,000	10	19	17
134	16	2000	vacuum	.37	490	1650	15,000	24	10	12
131	16	2000	vacuum	.44	695	1650	10,000	100	11	11
92	16	2000	wet H ₂	.49	690	1650	10,000	142	17	14
59	6	2400	vacuum	.49	805	1650	10,000	87.5	8	6
57	6	2400	vacuum	.44	1075	1650	10,000	96.8	7	8

an argon atmosphere, the rods were slowly cooled and were then prepared for physical testing and analysis. Some specimens were used to determine tensile properties and representative data from these tests are presented as FIG. 2.

Example 4

A ZOW alloy billet was prepared by the procedure set out in Example 3. This compact contained 0.47 weight % zirconium and 1,075 ppm oxygen. It was sintered for 16 hours at 2,000°C and an additional 6 hours at 2,400°C. Electron microscope observation revealed the presence of relative coarse zirconium oxide particles dispersed in the base metal matrix but no evidence of an ultrafine zirconium oxide dispersion.

The billet was divided into a number of smaller specimens which were then subjected to a heat ageing treat-

The results obtained show our ZOW alloys to be far superior to the W-ZrO₂ alloys (8 vol. % ZrO₂) of Quatinetz et al (Quatinetz et al., Studies of Tungsten Composites Containing Fibered or Reacted Additives, Nat. Aeronautics and Space Administration, NASA TN D-2757, April 1965, 34 pp) and much better than commercial W-3.7 vol. percent ThO₂ tested under identical conditions. At a given stress, the ZOW alloy has about four times the life of the W-3.7 vol. percent ThO₂ alloy.

Example 7

A ZOW alloy extrusion, prepared by the procedure set out in Example 3, was examined by microprobe analysis to determine zirconium distribution. Nominal zirconium content was 0.36 weight % and the compact was sintered for 16 hours at 2,000°C before extrusion. Results obtained are set out in the following table.

TABLE II

Location	Zr (as solute or microprecipitate), wt. pct.	Zr (as ZrO ₂ over 1 micron), wt. pct.	Zr (total) wt. pct.
From surface:			
50 microns	0.17	0.21	0.38
200 do.	.17	.21	.38
1,000 do.	.16	.09	.25
One-half way to center	.18	.07	.25
Center	.17	.21	.38
Average	.17	.16	.33

The zirconium was found to be about evenly divided between relatively coarse ZrO₂ and solute or microprecipitate ZrO. The microprobe could not distinguish between Zr as a solute or as microprecipitate ZrO₂.

Example 8

Another series of alloys were prepared by the same general procedure as outlined in Example 4 except that hafnium, added as HfW₂, was used as the reactive metal rather than zirconium. Physical testing of the samples produced the following results:

TABLE III

Sample designation	Analyses Hf, wt. %	O, ppm	Tensile strength psi	Yield strength 0.2% offset, psi
9	0	100	15,100	12,800
10	0.20	140	17,100	15,300
11	.40	135	47,700	42,400
12	.60	145	55,100	49,400
13	.80	235	43,400	41,300

All of these samples were sintered for 16 hours at 2,000°C in a vacuum atmosphere. All of the strength tests were performed at 1,650°C. In addition the stress-rupture life of several samples was determined. These tests were performed at 1,650°C, at a stress of 10,000 psi, and showed a maximum life of 22 hours at a Hf level of 0.4 weight %. These properties are definitely superior to the properties for W-HfO₂ alloys reported by Barth (Review of Recent Developments in the Technology of Tungsten, Battelle Memorial Institute, DMIC Memo 139, Nov. 24, 1961, p. 6) while the maximum stress-rupture life is comparable to commercial W-3.7 vol. % ThO₂ alloys.

Example 9

A series of molybdenum-base (MOZ) alloys were prepared by the general procedure outlined in Example 3. A 3-micron molybdenum powder, containing about 3,000 ppm oxygen, was blended with varying amounts of a 1-micron ZrMo₂ powder. These various blends were pressed into compacts at 30,000 psi, sintered at 1,800°C for 5 hours, extruded as ½ in. rod at 900°C and then tensile tested at a temperature of 1,200°C. Results obtained are set out in the following table:

TABLE IV

Sample designation	Zr, wt. %	Yield strength psi	Tensile strength psi	Elongation %	Reduction in area %
19	0.46	14,600	15,600	20	39
21	.69	15,500	16,800	19	32
23	.93	16,000	16,900	21	32
25	1.28	18,400	19,400	28	47
27	1.61	53,400	57,500	25	66
29	1.90	63,800	69,000	21	59
31	2.51	74,000	77,700	5	10

We claim:

1. A powder metallurgical process for the oxyreaction strengthening of metals which comprises: mixing a oxygen containing base metal powder chosen from the group consisting of metals of Groups IB, VIB and VIII of the Periodic Table and their alloys, and having an oxygen content in the range of 0.01 to 2.0 weight percent with a reactive metal powder, the reactive metal being chosen from the group consisting of silicon, aluminum and elements of Group IV B of the Periodic Table and

- having a free energy of oxide formation greater than that of the base metal, the amount of reactive metal being in excess of that required to react with all of the oxygen contained in the base metal; pressing the mixed powders to form a compact of predetermined shape, sintering the compact in an atmosphere selected from the group consisting of wet hydrogen, dry hydrogen, inert gases and vacuum at temperatures below the melting point of the base metal to form relatively coarse reactive metal oxide particles and to solubilize in the base metal a portion of the reactive metal and oxygen, and subjecting the sintered compact to a precipitation heat treatment at a temperature below the sintering temperature for a time sufficient to form a dispersion of very finely divided reactive metal oxide particles throughout the base metal.
2. The process of claim 1 wherein the sintered compact is further densified prior to the precipitation heat treatment.
3. The process of claim 1 wherein the base metal is chosen from the group consisting of tungsten and molybdenum and their alloys.
4. The process of claim 3 wherein the reactive metal is chosen from the group consisting of zirconium and hafnium.
5. The process of claim 4 wherein the oxygen content of the base metal is in the range of 0.05 to 0.5 weight percent.
6. The process of claim 5 wherein the base metal comprises tungsten and wherein the reactive metal is selected from the group consisting of zirconium and hafnium.
7. The process of claim 6 wherein the compact is sin-

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tered at a temperature in the range of 1,500° to 2,400°C for a time in the range of 1 to 24 hours.

8. The process of claim 7 wherein the sintered compact is densified and is thereafter subjected to a precipitation heat treatment at a temperature within the range of about 1,400° to 2,000°C but below the sintering temperature for a time in the range of 2 to 24 hours.

9. The process of claim 7 wherein the sintered compact is densified and formed into a useful shape and is thereafter subjected to a precipitation heat treatment comprising normal use at a temperature within the range of 1,400° to 2,000°C but below the sintering temperature.

10. The process of claim 7 wherein the reactive metal is in the form of an intermetallic reactive metal-base metal compound.

11. The process of claim 10 wherein the intermetallic compound is ZrW_2 .

12. The process of claim 10 wherein the intermetallic compound is HfW_2 .

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13. The process of claim 11 wherein zirconium is blended with the tungsten base metal powder in an amount ranging from 125 to 300% of that required to completely react with the oxygen combined with the tungsten.

14. The process of claim 5 wherein the base metal comprises molybdenum and wherein the reactive metal is selected from the group consisting of zirconium and hafnium.

15. The process of claim 14 wherein the reactive metal is zirconium.

16. An oxyreaction strengthened ZOW alloy containing 0.4 to 0.5 weight percent zirconium and 800 to 1,000 ppm oxygen by weight, the balance comprising tungsten; substantially all of said oxygen being chemically combined with zirconium and dispersed throughout the tungsten in the form of very small oxide particles with the balance of the zirconium being dissolved in the tungsten.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,821,036 Dated June 28, 1974

Inventor(s) MARK I. COPELAND ET AL

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

On the cover sheet, item [75] should read:

--[75] Inventors: Mark I. Copeland, Corvallis;
William L. O'Brien, Albany; and
Robert Blickensderfer, Corvallis,
all of Oregon.--

Signed and sealed this 29th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

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Signed and sealed this 29th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents