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REPLY TO
ATTN OF: GP

TO: USI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for
Patent Matters

SUBJECT: Announcement of NASA-Owned U. S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code USI, the attached NASA-owned U. S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U. S. Patent No. : 3474709

Government or Corporate Employee : Government

Supplementary Corporate Source (if applicable) : n/a

NASA Patent Case No. : LE-03940

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:
Yes No

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of Column No. 1 of the Specification, following the words "... with respect to an invention of . . ."

Dorothy J. Jackson
Dorothy J. Jackson
Enclosure

Copy of Patent cited above

Oct. 14, 1969

M. QUATINETZ ET AL

3,472,709

METHOD OF PRODUCING REFRACTORY COMPOSITES CONTAINING TANTALUM
CARBIDE, HAFNIUM CARBIDE, AND HAFNIUM BORIDE
Filed March 25, 1966

N71-26153 5070



FIG. 1

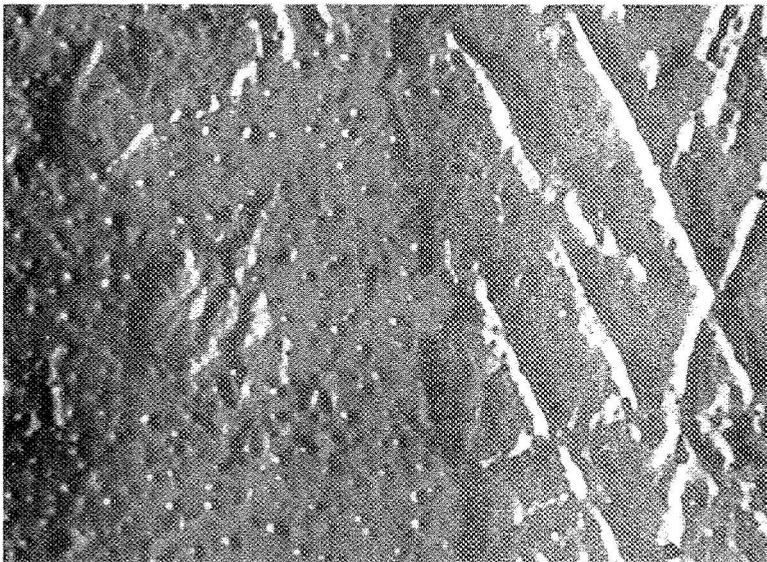


FIG. 2

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3,472,709

**METHOD OF PRODUCING REFRACTORY COM-
POSITES CONTAINING TANTALUM CARBIDE,
HAFNIUM CARBIDE, AND HAFNIUM BORIDE**
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U.S. Cl. 148—126

4 Claims

ABSTRACT OF THE DISCLOSURE

Powders of refractory compounds are uniformly distributed throughout powders of a refractory metal matrix. The resulting mixture is densified by heat and pressure. Solution treatment follows in which a portion of the refractory compound is dissolved into a matrix to form a solid solution which is subsequently uniformly reprecipitated throughout the microstructure.

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

Background of the invention

This invention is concerned with the production of high strength refractory metals that are stable at high temperatures. More particularly, the invention relates to the incorporation of refractory compounds and micro-constituents into a refractory metal matrix.

Refractory compounds and micro-constituents are incorporated into a refractory metal matrix conventionally by melting refractory metals and simultaneously adding reactive metals and interstitial compounds to the molten matrix material. Upon consolidation of cast billets or ingots and subsequent working a rejection of particles of refractory compounds that strengthen the matrix occurs. The methods employed for making refractory materials are quite similar to those used for superalloys and non-ferrous metals which involve casting, mechanical working, and heat treatment. Other methods utilize pre-alloyed powders which react to produce precipitates, intermetallic compounds, or carbides, and in some cases, refractory compounds are produced.

To illustrate the conventional procedure of the prior art, a metal solvent (X) is melted with soluble metals (A) and (B), or (X) may be melted alone with (A) and (B) being added subsequent to melting. The resulting melt is a liquid solution of the solvent (X) with (A) and (B) in solution. A precipitate of an (AB) compound may form on cooling this type of material. However, very frequently (A) and (B) segregate in either the grain boundaries or the dendritic interstices. Sometimes (A) and/or (B) combine with (X) to form other components or phases that segregate. This type of segregation is termed ingotism.

Any of the prior art methods which involves the conventional melting and casting of refractory metals to produce precipitates or other configurations of refractory compounds embedded in a metallic matrix has an inherent disadvantage noted in all cast and wrought products. This is the segregation of alloying constituents and micro-constituents as a result of the casting. Segregation of these constituents, as well as of alloying elements which takes place during the casting, is a result of the previously described phenomenon termed ingotism.

Another disadvantage is the greater impurity contents occur in the dendritic interstices and the grain boundaries. Subsequently, upon mechanical working and processing, micro-constituents and alloying elements that segregate during casting are stringered, elongated, sometimes fragmented, but are rarely homogeneously distributed.

In an effort to solve these problems, powder metallurgy techniques have been proposed to obtain greater uniformity of microstructures. While the problem of ingotism is avoided by these powder metallurgy techniques and the process of precipitation is most often uniform and well carried out, the usual procedure in reacting these types of powders does not permit the incorporation of large quantities of products into the matrix. Inherent in both the pre-alloyed method and in the casting concept is the fact that the quantities of refractory compounds produced by reaction or by dissolution and precipitation are limited.

According to the present invention these types of compounds can be incorporated in the material in any given or desired amount up to the saturation point. By way of illustration, powders of an (AB) compound formed from (A) and (B) are distributed throughout a powdered matrix (X). The mixture is compacted and densified to form a fine uniform distribution of (AB) in (X). The composite may be heated to a high temperature either during or subsequent to fabrication so that a part or all of the (AB) dissolves into (X) and forms a partial or total solid solution in (X). That portion of the compound (AB) that dissolves into solution may subsequently be precipitated more uniformly throughout the microstructure by heat treating and aging processes. Also, the material may be worked subsequent to the dissolution of (AB), and the working with aging uniformly or advantageously distributes a fine precipitate of (AB) throughout the structure. The residual undissolved particles of (AB) in themselves also add dispersion strength to the composite.

The invention utilizes a powder metallurgical process in which refractory compounds or oxides are mechanically mixed with refractory metal powders, with or without attrition or grinding. This is followed by a densification procedure which includes cold compaction and sintering or hot pressing. Mechanical working at elevated temperatures that either dissolves portions of the refractory compounds or oxides added to the mix or that causes the oxides or refractory compounds to react with the refractory metal matrix powder can be utilized. In general, consolidation and densification of the product pertains to billets that would subsequently be processed by other methods, such as extrusion. The mechanical processing further densifies and consolidates the product while producing nucleation sites within the product thereby permitting subsequent precipitation of some of the dissolved constituents to occur in the nucleation sites so produced. The residual undissolved refractory compound particles also add dispersion or fiber strength to the compounds.

It is, therefore, an object of the present invention to provide an improved process for making refractory metal base alloy composites in which a quality of refractory compounds is added to a metallic matrix in excess of what is possible by conventional casting or pre-alloyed powder methods.

Another object of the invention is to control the degree and homogeneity of alloying reactions in which the particle size and distribution of matrix and additive powers are controlled by incorporating small or large particles of refractory compounds into a matrix of small or large powders thus varying the ratios of the particle sizes of the different constituents.

A further object of the invention is to provide an improved alloy by utilizing an initial mechanical distribution

which prearranges in a controlled fashion particle spacing where the incorporated or added particle is a compound.

Still another object of the invention is to provide an alloy having a better homogeneous distribution than that obtained with conventional pre-alloyed powder metallurgy approaches.

Still a further object of the invention is to provide an improved method of making an alloy which eliminates the steps of casting, comminution and reconsolidation which are required in conventional pre-alloyed powder metallurgy techniques.

These and other objects and advantages of the invention will be apparent from the drawing and the specification which follows.

microns in average diameter while the refractory compounds were nominally 4 to 7 microns in diameter.

The powders used to prepare the composites were weighed and placed in a container partially filled with glass beads. Mixing occurred as the container was rotated at relatively slow speed, and the powders rolled gently without sliding or clinging to the sides of the container.

The powders for the first three billets shown in Table II were cleaned in a tower with a stream of hydrogen at a temperature of 1500° F. for a period of six hours prior to compaction to reduce any tungsten oxide present. The cleaning tower was heated slowly to maintain the moisture evolved below 1000 p.p.m. and to prevent localized sintering. The hydrogen flow rate was between 5 and 15 cubic feet per hour.

TABLE II.—TUNGSTEN BILLET COMPOSITION, PROCESSING AND TESTING

Additive	Percent	Composition		
		Extrusion		Test Results
		Maximum extrusion pressure, lb./sq. in.	Ram speed, in./sec.	Type of strength-ening
				Stress/p.s.i. 100 hr. 1lf
Vacuum-sintered billets				
1..... Zirconia.....	8.0	183.0	5.0 Fiber.....	4,700
2..... Yttria.....	8.0	106.2	10.0do.....	4,750
3..... Hafnia.....	10.0	106.0	10.0do.....	6,000
Hydrogen-presintered billets				
4.....	0	115.7×10 ⁶	8.6do.....	4,250
5..... Thoria.....	8.0	89.8	4.0 Fiber.....	7,000
6..... Hafnium nitride.....	8.0	172.6	6.6do.....	12,000
7..... Tantalum carbide.....	8.0	173.6	9.0 Reaction.....	13,000
8..... Hafnium carbide.....	8.0	197.6	4.0do.....	17,00
9..... Hafnium boride.....	8.0	131.7	9.8do.....	17,50

In the drawings:

FIGS. 1 and 2 are electro micrographs of a test specimen illustrating the reprecipitation of a refractory metal compound which was added in accordance with the present invention to a high temperature refractory matrix.

To illustrate the features of the invention, refractory composite specimens were prepared by adding powders having a wide range of melting temperatures and reactivities to tungsten. Composites comprising tungsten with 8 or 10 volume percent of oxide or refractory compounds were extruded into bar stock. All the billets were extruded at a temperature of 4200° F. and a reduction ratio of 8:1.

Oxides in the form of zirconia, yttria, hafnia, and thoria were used as additives. These additives were fibered during extrusion into bar stock.

The refractory compounds added were hafnium boride, nitride and carbides as well as tantalum carbide. Photomicrographs of the composites showed the hafnium nitride was also fibered during the extrusion process. The other refractory compounds were deformed to a small extent and reacted with the tungsten.

The powders used in preparing the billets are shown in Table I. The compositions of the billets and their processing are listed in Table II.

The hafnium boride in Table I contained 2.9 percent zirconium, titanium, and carbon while the hafnium contained 3 percent zirconium. The hafnium carbide contained 4.6 percent zirconium, titanium, and boron.

TABLE I.—BILLET MATERIALS

Material	Nominal purity, weight percent	Particle size, microns	Melting point, ° F.	Density, g./cc.
Tungsten.....	99.96	1.2	6,170	19.30
Oxides:				
Zirconia.....	98.80	2.0	4,892	5.49
Yttria.....		1.7	4,370	4.84
Hafnia.....	99.92	1.9	5,090	9.68
Thoria.....		2.1	5,522	10.03
Refractory compounds:				
Hafnium boride....	93.3	6.8	5,880	11.20
Hafnium nitride....	96.6	4.6	5,990	14.00
Hafnium carbide....	95.4	4.2	7,039	12.70
Tantalum carbide..	99.85	5.0	7,020	14.65

With regards to particle size nominally 1 micron tungsten powder was used. The oxides were nominally 2 to 7

All the powders were compacted isostatically at 30,000 p.s.i. at room temperature. The powder was packed initially in a rubber mold set in a metal tube so that after processing and sintering the billet required a minimum of machining for canning and extruding.

Two distinct sintering schedules were used. The first three billets were sintered for two hours at a pressure of less than 5×10^{-4} torr and at a temperature of 3500° F. These billets were again sintered in vacuum at 4200° F. for a period of two hours. With regards to the remaining billets, the compacts were given a two hour presintering in hydrogen at 2600° F. which was followed by a two hour sintering in vacuum at 4200° F. to obtain improved density.

Billets 1, 2 and 3 were extruded in a tantalum can having a wall thickness of 0.09 inch. A 0.25 inch-thick-wall pressed and sintered molybdenum can was used to extrude the remaining billets. A temperature of 4200° F. was utilized with a reduction ratio of 8:1 and ram speeds from four to ten inches per second. The billets were extruded in a conventional 1000 ton vertical extrusion press.

The composites shown in Table II were canned in containers of the softer materials, tantalum and molybdenum, to provide adequate lubrication at the high temperature of 4200° F. A variety of metals or other materials, such as oxides, glass, graphite and rubber were used as container lubricants. The extrusion die was also coated with oxides.

A nearly isostatic condition in which the extruding pressure was distributed uniformly about each billet was obtained by using the soft metal canning material. Less expensive molybdenum cans produced by powder metallurgy techniques were found to be a satisfactory substitute for the more expensive tantalum. The billets were protected from contaminations by the cans. In this manner, the extrusion capability for tungsten billets was extended to higher reduction ratios of 16:1 and higher temperatures of approximately 4200° F.

Stress-rupture tests of the extruded materials were conducted in a vacuum of 5×10^{-6} torr at different stress levels at 3000° F. A number of tests were also conducted at 2500°, 3400°, 3500°, and 3800° F.

Photomicrographs of the stress-rupture specimens and

of the extruded bars were prepared and examined. Fiber length-diameter ratios were determined and correlated with the stress-rupture life of the composites. Step-load creep tests were run with a few composites to evaluate rapidly their strength potential and to obtain suitable stresses for short-time stress-rupture tests.

Photomicrographs of transverse and longitudinal sections of the extruded material showed that the oxides were the most effectively fibered. From the microstructures it was noted that the extent of elongation varied with the degree of deformation throughout the extruded bar. The elongation was greater at the center than at the nose of the bar and greater at the edge than in the middle. The photomicrographs of the oxide composites showed that substantial fibering was obtained with zirconia, yttria, and hafnia. The thoria was not elongated as much as the other oxides.

Examination of the tungsten-refractory-compound composites showed that the refractory compounds had reacted with the tungsten. Experimental evidence of reactions was obtained in the case of W-TaC and W-HfB₂ composites where the elongation of the additives was relatively small. In the case of the tantalum carbide composite, there was reaction in the nose of the bar and elongation toward the middle of the bar.

The electron micrographs shown in FIGS. 1 and 2 were prepared at an original magnification of 31,800 from the nose portion of the extruded W-TaC composite. These figures show the extremely small tantalum carbide particles formed by the solutioning and reprecipitation of the 5 micron particles listed in Table I. FIGS. 1 and 2 show these tantalum carbide particles to be 0.05 micron. In addition, an X-ray analysis of the tungsten-hafnium boride composite showed the presence of a W₂B phase produced by the reaction of the HfB additive with the W matrix.

Stress-rupture tests were run at 3000° F. The stress for a 100 hour rupture life for each of the composites was obtained from these tests. These stresses are listed in the last column in Table II to provide a ready comparison of the strengths of the various composites. Table II shows the superiority of the reacted composites over the fibered composites.

While tungsten was used as the matrix metal in the composites tested, refractory compounds can be added to other refractory matrices such as Cb, Ta and Mo as well as to lower melting matrices, such as superalloys, in the same manner. Other methods of incorporating the refractory compounds in a matrix or metal include chemical coprecipitation, electroplating, electrophoretics, ultrasonics, and vaporization with condensation. Also, mechanical processes including rolling, swaging, forging, drawing and explosive deformation can be used instead of extrusion to work the composite. Explosive deformation techniques can also be utilized to consolidate the composites initially.

What is claimed is:

1. A powder metallurgy method of adding a refractory compound to a metallic matrix for producing a metal base alloy composite with improved microstructure uniformity comprising the steps of
 - mixing particles of a refractory compound selected from the group consisting of tantalum carbide, hafnium carbide, and hafnium boride with particles of a tungsten matrix,
 - densifying the mixture with heat and pressure to form a composite, and
 - solution treating the composite to dissolve at least a portion of the refractory compound up to the saturation point into a matrix thereby forming a solid solution therein and to reprecipitate the refractory compound uniformly throughout the micro-structure.
2. A method of producing a metal base alloy composite as claimed in claim 1 including extruding the composite subsequent to the dissolution of the refractory compound into the matrix thereby inducing nucleation to improve the distribution of said compound throughout the structure.
3. A method of producing a metal base alloy composite as claimed in claim 2 including
 - cold compacting the mixed particles of the refractory compound and the particles of tungsten to form the composite,
 - sintering the composite, and
 - extruding the composite.
4. A method of producing a metal base alloy composite as claimed in claim 3 including
 - mixing 8 to 10 volume percent of the refractory compound with tungsten, and
 - extruding the composite at about 4200° F.

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