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Dunham

[54] TUNGSTEN ALLOY PRODUCTS

- [75] Inventor: **Thomas E. Dunham**, Cleveland Heights, Ohio
- [73] Assignee: General Electric Company, Schenectady, N.Y.
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- [51]
 Int. Cl.
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 Field of Search
 29/182, 182.5; 75/207,
 - 75/206

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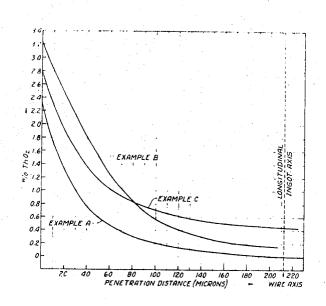
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[57] ABSTRACT

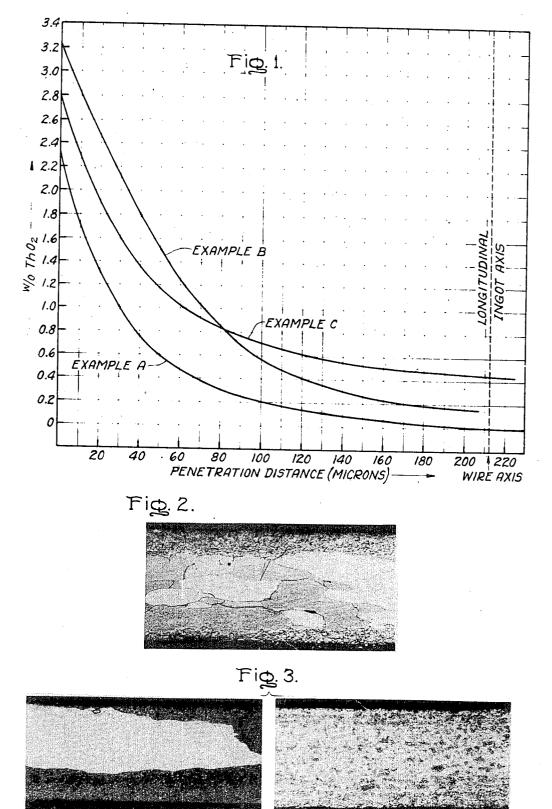
Dispersion alloy products of tungsten are disclosed containing grain-growth promoting additives uniformly distributed in the tungsten matrix along with a concentration gradient of thoria particles. The thoria particles are distributed in the tungsten matrix so as to provide a compositional gradient which diminishes continuously with increasing distance from the exterior surface of the product to the product interior. In certain cases upon recrystallization of a wire product fabricated with the dispersion alloy material, there is also formed a central core of relatively large tungsten crystals and a shell of smaller more equiaxed crystals near the exterior surface portion of the particular product. In other embodiments, large interlocked grains were formed throughout the wire. Methods of producing these dispersion alloy products are also disclosed.

18 Claims, 3 Drawing Figures



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3,802,851



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TUNGSTEN ALLOY PRODUCTS

BACKGROUND OF THE INVENTION

Thoriated tungsten materials commonly are used in two different types of applications, namely, as lamp filaments in shock and vibration resistant lamps and as electron sources in such items as power tubes, discharge lamps and welding electrodes. While the known materials perform adequately in some of the above applications, there are shortcomings associated with them 10 so that some need for an improved material exists in both areas of use. For the product application of lamp filaments, the conventional thoriated tungsten materials having a uniform distribution of thoria particles throughout the tungsten matrix are effective in increas- 15 ing the recrystallization temperature of tungsten and, in addition, offer some restraint to grain boundary motion at lamp-operating temperatures thereby stabilizing a small grain size. Unfortunately, in obtaining a higher recrystallization temperature from the thoria addition, 20 there is a drawback in that the resulting small tungsten grain structure is not creep resistant and is subject to lamp filament sag and other maladies common to small grain size materials. While some lamp designs can tolerate the low creep resistance of the conventional tho- 25 riated tungsten material in order to obtain the benefits of enhanced shock resistance and vibration-damping characteristics, there is still a distinct need for a creep resistant wire having a high recrystallization temperature for use in high efficiency rough service electrical 30 lamps.

The electronic applications mentioned above are predicated on the inherent instability of ThO2 in tungsten at elevated temperatures. When thoria reduction occurs, thorium atoms diffuse to the surface and effec- 35 tively lower the work function of the surface thereby providing an efficient electron source. Electronic applications which put the most severe demands on thoriated tungsten materials are those which utilize small diameter wires as grids and electron sources in high ⁴⁰ power rectification tubes. In these applications, dimensional stability of the coiled or wound part is required at extremely elevated temperatures above the recrystallization temperature of tungsten. Significant problems encountered with such utilization of the conventional thoriated tungsten materials are difficulty in fabricating the small diameter wire needed and poor creep resistance above the recrystallization temperature.

It would be desirable in both of the foregoing product 50 applications, therefore, to provide a dispersion alloy product of tungsten having greater structural stability at elevated temperatures than the known materials.

SUMMARY OF THE INVENTION

55 It has now been discovered that a dispersion alloy product of containing grain-growthtungsten promoting additives as disclosed in U.S. Pat. No. 1,410,499 and thoria with the thoria concentration being varied in accordance with liquid diffusion princi-60 ples hereinafter defined provides a novel material which is both easier to fabricate into wire and other forms than is the conventional thoriated tungsten material and which further exhibits greater stability and creep resistance upon recrystallization than said con-65 ventional W-ThO₂ materials. More particularly, a dispersion alloy product of tungsten containing the graingrowth-promoting additives and thoria with the maxi-

mum concentration of thoria being located at the exterior surface of said dispersion alloy product and with said thoria concentration continuously diminishing with increasing distance to the interior portion of the dispersion alloy product provides all of the foregoing desired advantages.

In accordance with one aspect of the invention, a liquid diffusion process is employed to impregnate a porous compact of tungsten particles containing a uniform distribution of the grain-growth-promoting additives. By way of example, the tungsten powder compact was prepared by treating blue tungsten oxide powder (approximately WO_{2.9}) with aqueous solutions of potassium silicate and aluminum chloride and then reducing the chemically treated oxide to metallic tungsten by heating in hydrogen. The pressed compact of tungsten particles containing the grain-growth-promoting additives and having an interconnected pore structure was first presintered at 1,200°C in hydrogen and then soaked in water until all pores were essentially filled. The water-filled compact was then immersed in a water solution of thorium nitrate for various time periods depending upon the thickness of the thoriated tungsten alloy shell desired in the final alloy product. Removal of the solvent was accomplished by drying the impregnated compact which was then processed by conventional presintering and sintering operations. The end result is a sintered material having a continuously diminishing concentration gradient of thoria in the direction of the central core of the porous compact. The maximum thoria concentration is produced at the exterior-most surface portion of the porous compact with said concentration continuously diminishing as the distance increases to the center core of the porous compact in accordance with operating principles of liquid diffusion. Upon recrystallization of wires produced by swaging and wire drawing, different metallurgical structures could be obtained depending on the thermal treatment and the specific ThO₂ gradient present in the wire.

In a preferred embodiment of the present invention, the thoria concentration uniformly decreases from the surface to a very small value near the central axis so that a portion of the interior of the ingot contains essentially no ThO₂. Mechanically working the sintered product at high temperatures, such as by forging, swaging and wire drawing, converts the crystalline structure into a fibrous elongated grain structure. The graingrowth-promoting additives produce exaggerated grain growth in the central core compared with tungsten crystals not containing such additives. On the other hand, the presence of increasing amounts of thoria particles in the surface portion of the dispersion alloy product is effective in restraining grain growth of the tungsten crystals and providing smaller size tungsten crystals at this location when certain thermal treatments are given the material. Such a tungsten grain structure at the core of the wire is effective in minimizing sag which is primarily a creep process as well as the further problem of offsetting which is due to slip in grain boundaries forming large angles with the longitudinal working direction. The composite crystalline structure of the tungsten matrix in the final product should also be obtainable although possibly to a lesser degree in a dispersion alloy product containing other types of additives.

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In a different preferred embodiment of the present invention, it is possible to obtain a more creep or sag resistant structure when recrystallization takes place by achieving a ThO₂ concentration profile such that there is a decreasing concentration of ThO₂ from the surface to the interior of the product of at least 10 percent. More particularly, since the recrystallized tungsten grain size and recrystallization temperature for the dispersion alloy product are influenced by the thoria content, it becomes readily apparent that a high degree of 10 control can be exercised over the final crystalline structure with modifications of the diffusion technique. By using different combinations of the presintered ingot porosity, the diffusion time, the solution concentration of the thorium compound, and the concentration of the 15 grain-growth-promoting additives in the original compact, it becomes thereby possible to vary the tungsten crystal size upon recrystallization in the final product from a relatively large grain size internal core with a surrounding shell of small grain size to a more uniform 20 large grain size throughout the cross section. The recrystallized tungsten grain size and distribution are also dependent upon the heat treatment schedule employed to obtain the final product.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph depicting concentration gradients of ThO₂ in three different 14 mil wires prepared in accordance with the present invention. These data were obtained using a point-by-point analysis by the electron 30beam microprobe technique. These curves are most useful in illustrating the existence of gradients as well as the difference between the concentration gradients in three different preparations.

FIG. 2 is a photomicrograph of a longitudinal section 35of one type of 14 mil wire obtained by practice of the present invention. Magnification is at 100 times.

FIG. 3 illustrates the effect of heating rate on the recrystallized structure of another type of 14 mil wire product obtained by practice of the present invention. 40Magnification is at 100 times.

DESCRIPTION OF THE PREFERRED **EMBODIMENTS**

45 Basically, the liquid diffusion process practiced in the present invention comprises soaking a porous compact of tungsten having uniformly dispersed therein graingrowth-promoting additives disclosed in U.S. Pat No. 1,410,499 with an inert liquid solvent of a soluble tho-50 rium compound until the pore structure of said compact is essentially filled with the solvent and thereafter immersing the solvent-filled compact in a liquid solution of the thorium compound for a sufficient time period to permit liquid diffusion of the dissolved thorium 55 compound into at least a portion of the solvent contained in the pores of the compact. The compact is then removed from the solution after a predetermined amount of liquid diffusion has taken place and all solvent is removed to retain a concentration gradient of $_{60}$ the thorium compound in the pores of the composite formed. By "inert liquid solvent" is meant a solvent for the thorium compound which can be removed by drying or heating the liquid-filled compact without leaving a residue in the pore structure or undergoing any signif-65 icant chemical reaction with the tungsten material. In modifications of the above-described liquid diffusion process, there can be added a second soluble additive

in the same liquid solvent for the thorium compound or a different solvent can be used to fill the pore structure than is employed to dissolve one or more additives. When a first liquid solvent is used to saturate the compact while a second liquid solvent is used to prepare the additive solution, it follows that the concentration gradient of additive in the porous compact after removal of solvent can be controlled by liquid diffusion principles applicable to diffusion of the additive from said second liquid solvent into the first liquid solvent.

Specific examples describing preparation of dispersion alloy products according to the present invention will now be given.

EXAMPLE A

A pressed compact measuring 17 mm \times 22 mm in cross section was prepared having a tungsten composition which contained small residual amounts of Al, K and Si in accordance with the teachings of the aforementioned U.S. Pat. No. 1,410,499. The presintered ingot weighing approximately 1.7 kg was soaked in distilled water until the interconnected pore structure of the compact was saturated and the liquid-filled ingot thereafter immersed in an aqueous $Th(NO_3)_4$ solution 25 having a concentration of 260 grams ThO₂ per liter of solution. The liquid diffusion process was interrupted after approximately 4 hours by removing the compact from the thorium nitrate solution. The compact was next dried slowly in a vacuum oven at approximately 400°F, which removed all solvent from the pores of the compact while retaining a concentration gradient of the thorium additive as specified in Table I below. The thorium additive-containing compact was next subjected to a conventional presintering operation at approximately 1,200°C in hydrogen which converted the thorium nitrate in the pores to thorium oxide (thoria) and thereafter sintered at approximately 2,400°C in hydrogen for approximately 2 hours to produce a densified thoriated tungsten composition in accordance with the present invention having a density of approximately 90 percent of the theoretical value.

Test specimens were obtained from sintered products produced in accordance with this example as well as in following Examples B and C in order to measure the thoria concentration gradient and observe the crystalline structures. The test specimens were examined by a known autoradiograph technique and all found to have a visible concentration gradient of the thoria additive with maximum concentration being located at the exterior-most surface portion of the sintered compact. All thoria concentrations continuously diminished with increasing distance to the center portion of the compact along radii extending from its surface to the axis. Further comparisons of W-ThO₂ materials made via the liquid diffusion process with conventionally made W-ThO₂ materials were made. The thoria particles in the thoriated tungsten dispersion alloy products produced in accordance with the present invention were found to be uniformly smaller in size range without any significant agglomeration of thoria particles that was found when the products were produced from practice of conventional powder metallurgy techniques.

Table I summarizes some data pertaining to ingots prepared in accordance with Examples A, B and C of the present invention. These data were obtained using standard X-ray fluorescence techniques. Corner and axis values were obtained from small ¼-inch cube sam-

ples taken at these locations. The bulk value was obtained from a ¼-inch cross-sectional slice.

Wt. % Thoria (±0.05)				
Example	Corner	Axis	Bulk	•
A B C	0.62 0.97 0.93	<0.08 0.41 0.67	0.44 0.81 0.93	10

TABLE I

It can be noted from Table I that a concentration gradient of thoria exists which decreases from surface to center such that in each case there is at least 10 percent by weight thoria at the central axis than at the surface of each sintered compact.

The sintered compact of Example A was rolled, swaged and drawn to 14.6 mil wire in accordance with conventional tungsten working practice. The approximate thoria concentration gradient in the prepared wire is reported in the accompanying FIG. 1 graph for all compositions of Examples A-C as determined by conventional microprobe measurement. Again, it can be noted from FIG. 1 that in each instance from the surface to the longitudinal axis of the wire there is at least a 10 percent less thoria concentration at the central axis than at the wire surface.

The Example A wire was also subjected to recrystallization by passing an electric current through the wire $_{30}$ in a hydrogen atmosphere. More particularly, the wire was subjected for a 6-minute time period to approximately 70 percent of the fusion amperage which produced a large tungsten grain structure exhibiting sag or high temperature creep resistance far superior to either 35 pure tungsten or conventional thoriated tungsten wire of the same size. Upon subjecting a different specimen of the Example A wire to recrystallization at 1 minute up to 80 percent of the fusion amperage and thereafter maintaining the same electric current for an additional $_{40}$ 6-minute time period, there was obtained in some cases a tungsten grain structure as shown in the photomicrograph of FIG. 2. Observation of the photomicrograph illustrates a fine grain tungsten structure at the surface portion of the wire with a large grain structure of tung- $_{45}$ sten in the central core region. In addition to having applicability as a configurationally stable electron source at high temperatures, this structure should exhibit improved performance as an incandescent filament in an electric lamp. The small surface grain structure allows 50 the filament in a lamp to absorb shock and vibration at high temperatures, while the larger grain interior structure provides resistance to filament sag.

EXAMPLE B

55 A presintered compact having the same initial tungsten composition disclosed in Example A and containing the same solvent was impregnated by liquid diffusion with the same aqueous thorium nitrate solution for a time period of approximately 30 hours. The thorium-60 containing compact was also given the same heat treatment disclosed in Example A. A comparison of the values reported in Table I above for the dispersion alloy products obtained upon sintering the Examples A and B finds the longer diffusion time to effectively increase 65 the thoria concentration both at the surface and central axis of the compact. The sintered compact was next processed to 14.6 mil wire as described in Example A,

and the approximate thoria concentration profile of the wire products is shown in FIG. 1.

A comparison was made of recrystallization behavior for the wire prepared in this example compared with a control sample of the same size wire prepared from unthoriated tungsten but containing the same concentration of grain-growth-promoting additives. More particularly, the samples were heated by electric current in hydrogen for one minute up to 70 percent or to 80 per-10 cent of the fusion amperage and thereafter held for an additional 6 minutes at the same heating current. A large grain tungsten structure was produced in the Example B wire (FIG. 3a) exhibiting excellent sag resistance comparable to the control wire containing no 15 thoria for both the 70 and 80 percent current settings. In additional experiments, the 6-minute recrystallization temperature of the Example B wire was found to be significantly higher by approximately 300°C than that obtained with the control wire. If the heating time to 70 or 80 percent fusion amperage is very short (approximately 1 second), a small grain structure seen in FIG. 3b can be obtained. That such a change in heating rate could result in the significant change in grain size noted in FIG. 3 and that the large grain tungsten structure was obtained in the presence of small ThO₂ particles comprising about 0.8 percent by weight of the alloy was not expected.

EXAMPLE C

A presintered compact of tungsten containing the same concentration of grain-growth-promoting additives was prepared as described in the previous examples. The compact was immersed in distilled water, and the solvent soaked ingot then placed in an aqueous thorium nitrate solution having a concentration of approximately 520 grams thoria per liter of solution. The liquid diffusion time for this example was 4 hours which provided a thoria concentration gradient in the sintered ingot as reported in Table I above. The sintered compact was processed into 14.6 mil wire in the same manner described in the preceding examples. The approximate thoria concentration gradient in the wire is reported in FIG. 1.

The recrystallization behavior of the Example C wire was quite similar to that for Example B wire under the same electrical heating conditions. Specifically, for a one-minute rise time to 70 or 80 percent fusion amperage in hydrogen, the Example C wire recrystallizes to a large grain tungsten structure which is sag-resistant. The temperature at which this occurs for 6-minute isochronal anneals is approximately 400°C above that for a control wire of the same size containing only the same concentration of the grain-growth-promoting additives but containing no thoria. Very fast heating rates cause a small grain size to develop analogous to that shown in FIG. 3b. It will be apparent from all of the foregoing recrystallization results that a desirably higher recrystallization temperature can be obtained by practice of the present invention while still achieving desired sag resistance from a relatively large tungsten grain size in the recrystallized product.

It can also be appreciated from the foregoing description of exemplary embodiments employed to form the novel dispersion alloy products of the present invention that various modifications in the liquid diffusion technique and the products obtained therefrom can provide even further improved results. For example, still other 5

soluble additives can be incorporated with a thorium compound in a common solvent to permit co-diffusion of the additives. Consequently, it is intended to limit the present invention only to the scope of the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A dispersion alloy product of tungsten containing grain-growth-promoting additives and thoria with the maximum concentration of thoria being located at the 10 exterior surface portion of said dispersion alloy product and with said thoria concentration continuously and uniformly diminishing with increasing distance to the interior portion of the dispersion alloy product, thereby establishing a concentration gradient of thoria having 15 no sharp compositional variation along said gradient.

2. A product as in claim 1 wherein the growthpromoting additives comprise potassium, silicon and aluminum compounds.

3. A product as in claim 1 wherein the thoria concen- 20 tration is at least 10 percent less at the center of the product than at the exterior surface.

4. A filament as defined in claim 1.

5. An electric lamp including an incandescible filament as defined in claim 4.

6. A recrystallized dispersion alloy product of tungsten containing grain-growth-promoting additives and thoria with a central core of sag-resistant tungsten crystal grains and a surface portion of vibration-damping tungsten crystals having a smaller average size than the 30 persed in at least a portion of the pores such that a contungsten crystals in the central core, said thoria being dispersed in the dispersion alloy product with a maximum concentration being located at the exterior surface portion of the dispersion alloy product and with said thoria concentration continuously and uniformly 35 diminishing with increasing distance to the interior portion of the dispersion alloy product thereby establishing a concentration gradient of thoria having no sharp compositional variation along said gradient.

7. A product as in claim 6 wherein the growth- 40promoting additives comprise potassium, silicon and aluminum compounds.

8. A product as in claim 6 wherein the thoria concentration is at least 10 percent less at the center of the 8

product than at the exterior surface.

9. A filament as defined in claim 6.

10. An electric lamp including an incandescible filament as defined in claim 9.

11. A dispersion alloy product of tungsten containing grain-growth-promoting additives and thoria with said thoria concentration continuously and uniformly diminishing with increasing distance to the interior portion of the porous body thereby establishing a concentration gradient of thoria having no sharp compositional variation along said gradient, said dispersion alloy product having a recrystallized tungsten grain structure with the size and shape of the individual tungsten grains being dependent upon the rate of reheating the dispersion alloy product after said product has been

mechanically worked at elevated temperatures. 12. A product as in claim 11 wherein the growth-

promoting additives comprise potassium, silicon and aluminum compounds.

13. A product as in claim 11 wherein the ThO_2 concentration is at least 10 percent less at the center of the product than at the exterior surface.

14. A filament as defined in claim 11.

15. An electric lamp including an incandescible filament as defined in claim 13.

16. A porous metal body having an interconnected pore structure of tungsten containing grain-growthpromoting additives which includes thoria particles discentration gradient is established with the maximum thoria concentration being located at the exterior surface portion of said porous body and with said thoria concentration continuously and uniformly diminishing with increasing distance to the interior portion of the porous body so that no sharp compositional variation exist along said concentration gradient.

17. A porous metal body as in claim 16 wherein the growth-promoting additives comprise potassium, silicon and aluminum compounds.

18. A porous metal body as in claim 16 wherein the thoria concentration is at least 10 percent less at the center of the product than at the exterior surface. *

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