Sept. 5, 1967 E. S. HODGE ETAL 3,340,053

GAS-PRESSURE BONDING

Filed Nov. 23, 1965 2 Sheets-Sheet 1

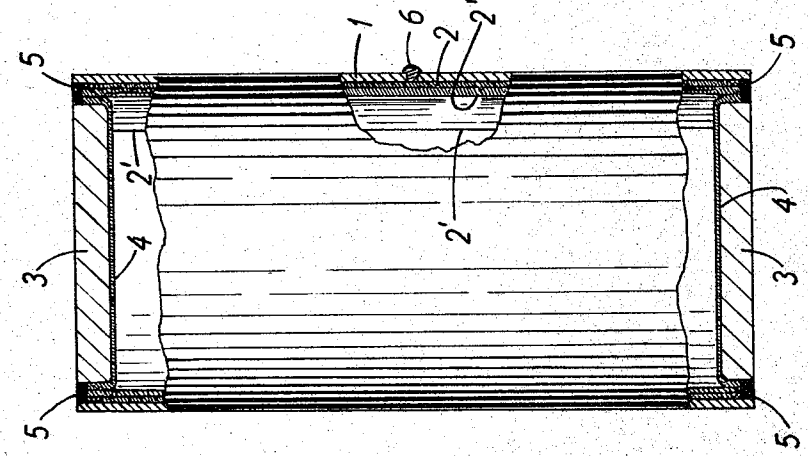


FIGURE 1.

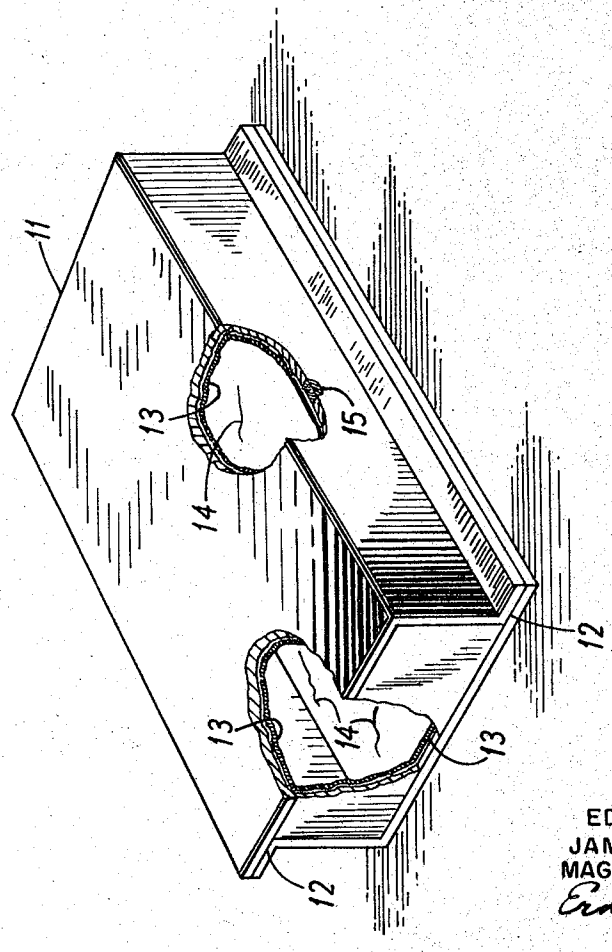


FIGURE 2.

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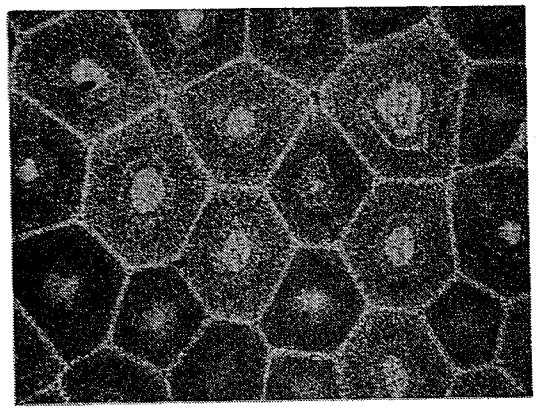


FIGURE 3.

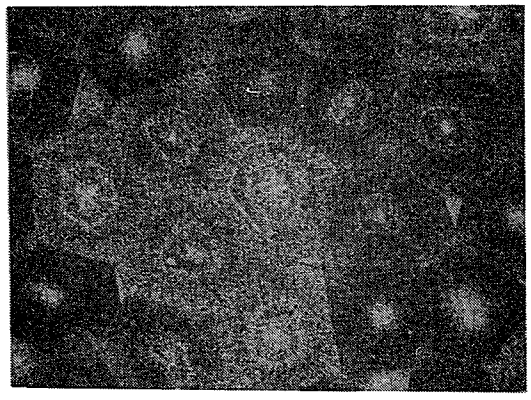


FIGURE 4.

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3,340,053

GAS-PRESSURE BONDING

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5 Claims. (Cl. 75—208)

ABSTRACT OF THE DISCLOSURE

This invention relates to the preparation of tungsten metal shapes by gas-pressure bonding. More particularly, the invention relates to gas-pressure bonding of tungsten metal shapes in a specially constructed container, said container comprising a gas-impervious casing and a gas-impervious inner liner.

In gas-pressure bonding of tungsten metal particles, molybdenum has heretofore been considered the most suitable container material. Although molybdenum containers are generally usable, the containers often rupture, due to distortion, when it is attempted to bond tungsten metal particles to substantially full density. Avoidance of container failure by employing molybdenum of greater thickness substantially increases the expense of bonding. Further, molybdenum containers have the disadvantages of being difficult to form and weld. It has been found that titanium is more ductile, formable and weldable than molybdenum. However, when titanium containers are employed in gas-pressure bonding of tungsten metal particles, the resulting tungsten shapes are heavily contaminated with titanium.

We have now discovered that tungsten shapes, free of contamination, may be prepared employing a container comprising a gas-impervious casing composed of a member of the group consisting of titanium, tantalum, niobium and mixtures thereof and a gas-pervious inner liner composed of a member of the group consisting of molybdenum, tungsten and mixtures thereof.

The specially constructed container of this invention has been found to possess numerous advantages. First of all, tungsten metal particles may be bonded to substantially full density without container rupture. Moreover, the container is easier to form and weld than conventional molybdenum containers. Finally, the container using a titanium casing is less expensive than molybdenum containers since the cheaper titanium replaces part of the more expensive molybdenum otherwise required. Further, it has been unexpectedly found that the titanium, tantalum or niobium casing acts as a getter for detrimental gases evolved during the bonding procedure, thereby substantially reducing intergranular recrystallization. As a result, the tungsten metal shapes formed in the present container are fine grained shapes having superior physical properties and may be worked, as by rolling, swaging, etc., to products of exceptional strength and hardness.

As indicated above, the gas-impervious casing of the container of this invention is composed of a member of the group consisting of titanium, tantalum, niobium and mixtures thereof. It is intended that the titanium, tantalum and niobium include alloys containing at least 95% of these metals with other components, such as iron, carbon, etc. Further, the gas-pervious inner liner is composed of a member of the group consisting of molybdenum, tungsten and mixtures thereof. It is intended that the molybdenum and tungsten include alloys containing at least 95% of these metals with other components, such as rhenium, boron, sodium, potassium, thoria, silica, etc. Particularly outstanding results are obtained using a container comprising a gas-impervious casing composed of titanium and a gas-pervious inner liner composed of molybdenum.

In order to achieve the gettering action of the casing, the inner liner must be pervious to gas. In other words, there must be access for gas diffusion, as through open seams or cracks in the inner liner. The seams or cracks, however, must be small enough so as to prevent casing material from coming into contact with the tungsten metal particles. This may be accomplished by various means including, but not limited to, providing an inner liner comprising overlapping layers of metal foil or providing a molded inner liner which contains cracks created by imperfect molding or by deliberate fracture of the liner. Generally speaking, the inner liner is at least about 4 mils thick. Use of liners of lesser thickness has been found to frequently cause spalling or end cracking of the tungsten metal shapes. For the sake of economy, it is preferred, however, that the inner liner be no more than 30 mils thick.

The casing must, of course, be gas-tight, i.e. impervious to the diffusion of gas, for successful operation of the gas-pressure bonding process. Generally speaking, the casing is about 20 to 40 mils thick. Greater thicknesses can be used but tend to become uneconomical. In order to prevent attack of the casing by oxygen and hydrogen which are frequently present in inert gases used for gas-pressure bonding purposes, it is preferred to employ an outer wrapper of molybdenum which envelops the casing. The outer wrapper is generally about 2 to 10 mils thick, preferably about 2 to 3 mils thick, the preferred thickness being adequate to prevent the wrapper from breaking.

In general, the tungsten metal shapes are prepared by packing tungsten metal particles in the container, evacuating and gas-tight sealing the container and then subjecting the evacuated and sealed container to inert gas pressure, time and temperature requisite to deform the container to cause it to flow inwardly to compact, deform and bond the tungsten metal particles into a shape of desired densification. It is possible, depending upon the pressure, time and temperature conditions, to prepare shapes of predetermined density ranging from porous shapes, as from 70% of theoretical density, up to substantially dense shapes, i.e. 99+% of theoretical density.

Although the tungsten metal particles generally employed are discrete, substantially spherical tungsten metal particles, particles having other than substantially spherical form can be used. The preferred tungsten metal particles are taught in copending patent application of John M. Blocher, Jr., and John H. Pearson, Ser. No. 298,515, filed July 5, 1963, now Patent No. 3,234,007. These tungsten metal particles are of substantially spherical form and consist of a microstructure of columnar tungsten grains having width and thickness of about 1/10 to 2 microns radially oriented from a seed of tungsten metal, said microstructure having a density of at least 95% of theoretical and undergoing less than about 20% recrystallization upon being subjected to temperature of about 2900° F. for about three hours.

In preferred practice of the gas-pressure bonding process, substantially spherical tungsten metal particles, such as the tungsten metal particles prepared according to copending application Ser. No. 298,515, are isostatically gas-pressure bonded to provide the desired tungsten metal shape. Isostatic gas-pressure bonding of materials is described to some extent in Canadian Patent 680,160. During isostatic gas-pressure bonding, the individual particles are formed into tungsten metal shapes of desired predetermined size and configuration, cored or otherwise, as rods, bars, billets and the like. These tungsten metal shapes, with or without prior removal of the container material, may be readily worked by conventional metallurgical techniques, as by rolling, swaging, forging, draw-

ing, spinning and the like, to form products having exceptional physical properties. Container material may be removed during or after completion of the working.

The principal steps comprising the gas-pressure bonding operation involve placing the tungsten metal particles inside the lined container, packed as by mechanical vibration to a desired extent, for example, to a bulk density of 65% or more of theoretical. The packed container is evacuated and then sealed, and the evacuated and sealed packed container is subjected to inert gas pressure, time and temperature requisite to deform the container to cause it to flow inwardly to compact and bond the packed particles into a shape of desired densification. The inert gas is one which, considering the conditions and container materials employed, will have a suitable heat conductivity and will not penetrate the gas-tight casing. The bonding operation involves deformation and plastic flow of the individual tungsten metal particles to decrease interstitial volume and increase area of contact between discrete particles, accompanied and followed by development of metallurgical bond between contacting particles.

Typically in preparing the tungsten shapes there is employed as a compressing gas an inert gas such as helium, argon or the like at pressures which may range from as low as about 1000 pounds per square inch up to 50,000 pounds per square inch and higher, while maintaining the container and contents at a suitable temperature for plastic flow of tungsten metal consistent with maintenance of the container in gas-tight condition. Such temperature should be sufficient to cause plastic flow of the tungsten metal but should not be as high as the melting point of the casing material. Suitable temperatures, considering inherent limitations of the container and pressure, can be in the range of about 2000° to 3500° F., and the time necessary may vary from several minutes to several hours or longer. The particular pressure, temperature and time all influence the density of the produced tungsten shape. Generally speaking, formation of larger shapes generally requires somewhat higher pressure, temperature and time conditions.

It is believed that the gettering action of the casing takes place primarily during the period in which gas pressure is increased and the container and contents are heated to reach final gas-pressure bonding conditions. At latter stages of the bonding process, the inner liner tends to bond together so as to be gas-impervious. Accordingly, in certain instances, it may be desirable for the container and contents to be brought to an intermediate pressure and temperature and held there for a short time before reaching the final pressure and temperature parameters.

The container is stripped from the gas-pressure bonded shape by mechanical removal, such as grinding, and/or by chemical means, such as chemical dissolution. In the case of the preferred molybdenum-lined titanium container, the titanium casing may be pickled off in 50% hydrofluoric acid, or alternatively, removed by grinding, machining, etc. The molybdenum liner may be removed by grinding, chipping, machining, etc., or alternatively, pickled off in 50% nitric acid. If desired, for example, in the preparation of a sheet bar which is to be rolled, the molybdenum may be retained on the bar to act as an oxidation barrier in protecting the tungsten surface during rolling. Any part of the outer wrapper of molybdenum which may adhere to the casing can be readily removed by scraping or filing.

In the drawings:

FIGURE 1 is a partial half section elevational view of a molybdenum-lined titanium cylindrical container of the present invention.

FIGURE 2 is a perspective view, partially cut away, of a sheet bar container of this invention comprising a titanium casing and an inner molybdenum liner.

FIGURE 3 is a photomicrograph of a cross-section of a tungsten metal shape prepared using a conventional molybdenum container.

FIGURE 4 is a photomicrograph of a cross-section of a tungsten metal shape prepared using a molybdenum-lined titanium container of this invention.

FIGURES 1 and 2, which have not been drawn to scale, show representative containers within the scope of the present invention for making cylindrical and sheet bar shapes. It is to be understood that complex shapes may be made by varying the container design in ways known to those skilled in the art.

The container shown in FIGURE 1 is employed for making tungsten metal rods, billets and the like. The container has a gas-impervious titanium cylindrical casing **1**, preferably about 20 to 40 mils thick, and an inner molybdenum liner **2**, preferably about 4 to 10 mils thick. The inner liner is installed around the periphery of casing **1** by overlapping molybdenum foil of 1 mil thickness. The overlap is illustrated at **2'**. The liner so installed is pervious to gas evolved during the bonding operation but does not permit the titanium casing to intrude into the tungsten metal particles. Due to the gas perviousness of liner **2**, gas evolved during the bonding process is gettered by the titanium casing. Titanium plates **3**, preferably about 20 to 40 mils thick, are provided with a molybdenum liner **4**, installed in similar manner to liner **2**, and are welded to casing **1** at **5**. Opening **6** is provided in the side of casing **1** in order to provide for evacuation of the container prior to bonding. The opening, as shown, is plugged with titanium rod applied after evacuation, preferably by electron beam welding. Casing **2** is enveloped by an outer wrapper (not shown) of molybdenum foil, preferably about 2 to 3 mils thick, secured by molybdenum wire. In operation, the tungsten metal particles to be bonded are placed in an open end of the container, and the open end is then sealed by welding. The container is evacuated through opening **6**, which is filled with titanium rod after evacuation, as described above.

The container shown in FIGURE 2 is employed for producing sheet bars of tungsten metal. In this container, a gas-impervious titanium casing **11** is provided, preferably about 20 to 40 mils thick, said casing having overlapping edges **12** in order to permit flexibility of the casing during the bonding operation. An inner liner **13**, preferably about 10 to 30 mils thick, inserted within casing **11**, is composed of molybdenum and contains one or more cracks **14** which permit gas to permeate the inner liner without allowing the titanium casing to intrude into the tungsten metal particles. The cracks may be formed by imperfect molding or may be made by intentional cracking. Opening **15** in casing **11** is provided for evacuation of the container and, after evacuation, is plugged, as shown, with titanium rod, applied preferably by electron welding. Casing **11** is enveloped by an outer wrapper (not shown) of molybdenum foil, preferably about 2 to 3 mils thick, secured by molybdenum wire. In operation, the tungsten metal particles are placed in the inner molybdenum liner which has one of its ends unsealed. The unsealed end is then sealed by welding. The inner liner containing the tungsten particles is inserted through an open end of casing **11**, that opening then being sealed by welding. The dimensions of the casing and inner liner are such as to provide as tight a fit as possible when the liner is placed in the casing. The container is then evacuated through opening **15**, and the opening plugged with titanium rod, as described above.

FIGURES 3 and 4 illustrate the metallurgical microstructure of tungsten metal shapes at a magnification of 60 times, after gas-pressure bonding using a conventional molybdenum arc cast container and a molybdenum-lined titanium cylindrical container of the type shown in FIGURE 1, respectively. Both of the tungsten metal shapes were prepared from substantially spherical tungsten particles of the aforementioned copending patent application. The shapes were made by isostatic gas-pressure bonding, using 10,000 pounds per square inch of helium pressure at temperature of about 2900° F. for about three hours in the case of the molybdenum container, and 10,000

pounds per square inch of helium pressure at temperature of about 2800° F. for about three hours in the case of the molybdenum-lined titanium container. The shape obtained using the molybdenum container had a density of 98.5 to 99% of theoretical, whereas the shape prepared using the molybdenum-lined titanium container had a density of over 99% of theoretical. It is seen, therefore, that use of a container of this invention enabled obtainment of a shape of higher density at a lower bonding temperature than use of a conventional molybdenum container.

The photomicrograph of FIGURES 3 and 4 shows that substantially no intergranular recrystallization appears in the tungsten metal shape prepared using the molybdenum-lined titanium container, whereas intergranular recrystallization appears in the tungsten metal shape made using the conventional molybdenum container.

Tungsten metal shapes showing substantially no intergranular recrystallization are similarly obtained using containers in which tantalum or niobium is substituted for the titanium casing or tungsten is substituted for the molybdenum liner.

Due to the elimination of intergranular recrystallization, the tungsten metal shapes produced in accordance with the present invention exhibit superior physical properties. More specifically, the shapes show a considerably reduced degree of recrystallization upon being used in high temperature applications.

Numerous ways of diminishing intergranular recrystallization are set forth in the aforementioned copending patent application. These methods, however, are more complicated than use of the container of the present invention.

Since various changes and modifications may be made in this invention without departing from the spirit thereof, the invention is deemed to be limited only by the scope of the appended claims.

We claim:

1. In a process for the preparation of a tungsten metal shape which comprises:

(1) packing tungsten metal particles in a container,
(2) evacuating and gas-tight sealing the container, and
(3) subjecting the sealed container to inert gas pressure, temperature and time requisite to cause the container to deform inwardly to compact, deform and metallurgically bond the tungsten metal particles into a tungsten metal shape,

the improvement which comprises employing a container comprising a gas-impervious casing consisting essentially of a member of the group consisting of titanium, tantalum, niobium and mixtures thereof and a gas-pervious inner liner consisting essentially of a member of the group consisting of molybdenum, tungsten and mixtures thereof.

2. The improvemet according to claim 1 wherein the casing is about 20 to 40 mils thick and the inner liner is about 4 to 30 mils thick.

3. The improvement according to claim 1 wherein the container comprises a gas-impervious casing composed of titanium and a gas-pervious inner liner composed of molybdenum.

4. The improvement according to claim 3 wherein the casing is about 20 to 40 mils thick and the inner liner is about 4 to 30 mils thick.

5. The improvement according to claim 3 wherein the container is provided with an outer wrapper composed of molybdenum.

No references cited.

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