June 27, 1967 E. S. HODGE ETAL 3,328,139

POROUS TUNGSTEN METAL SHAPES

Filed Feb. 26, 1965 5 Sheets-Sheet 1

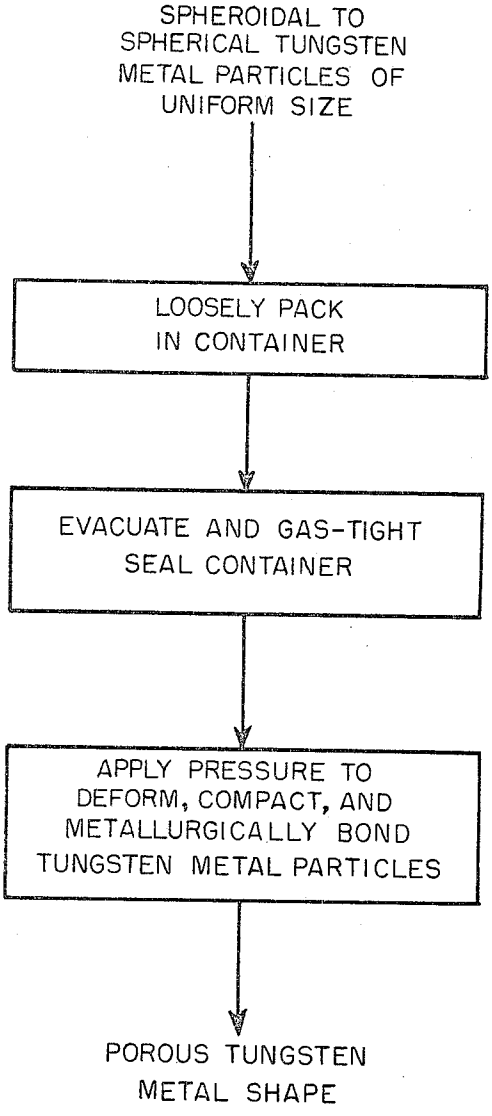


FIGURE 1.

INVENTORS
EDWIN S. HODGE
BY JAMES H. PETERSON
Ernest A. Polin
ATTORNEY

June 27, 1967 E. S. HODGE ETAL 3,328,139

POROUS TUNGSTEN METAL SHAPES

Filed Feb. 26, 1965 5 Sheets-Sheet 2

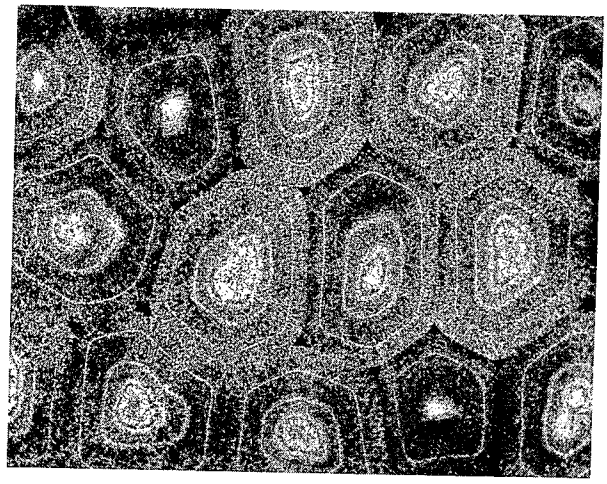


FIGURE 2.

INVENTORS
EDWIN S. HODGE
JAMES H. PETERSON
BY
Ernest A. Polin
ATTORNEY

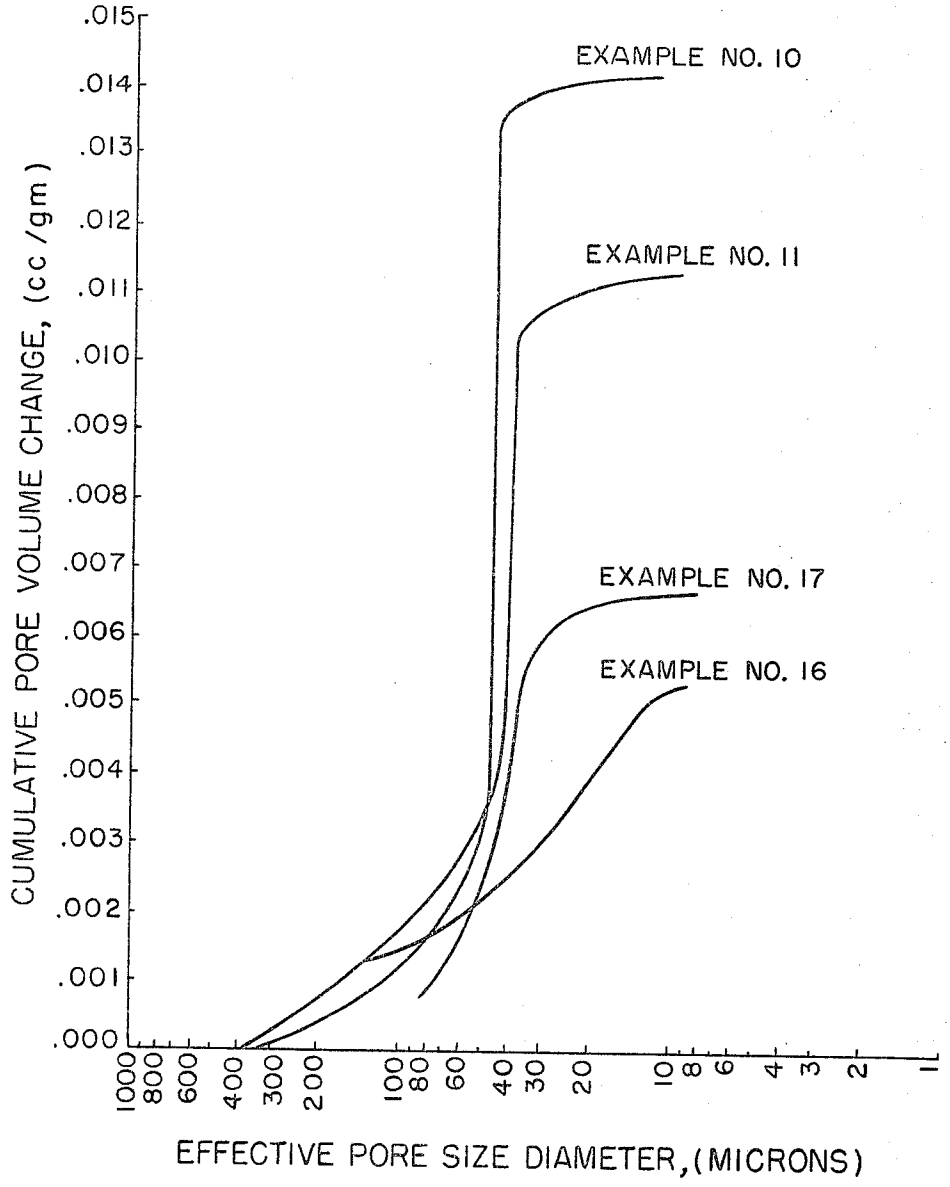


FIGURE 3.

INVENTORS
EDWIN S. HODGE
JAMES H. PETERSON
BY Ernest A. Polin
ATTORNEY

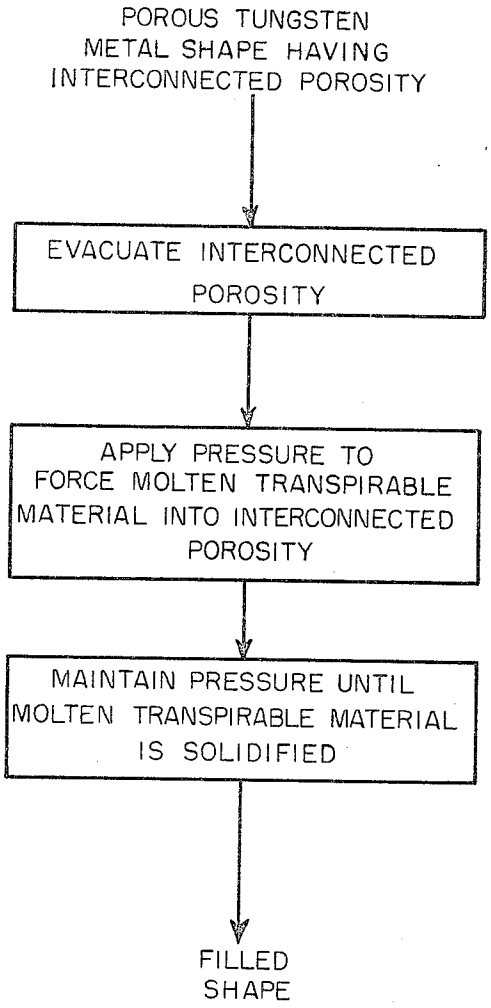


FIGURE 4.

INVENTORS
EDWIN S. HODGE
JAMES H. PETERSON
BY Ernest A. Polin
ATTORNEY

June 27, 1967 E. S. HODGE ETAL 3,328,139

POROUS TUNGSTEN METAL SHAPES

Filed Feb. 26, 1965 5 Sheets-Sheet 5

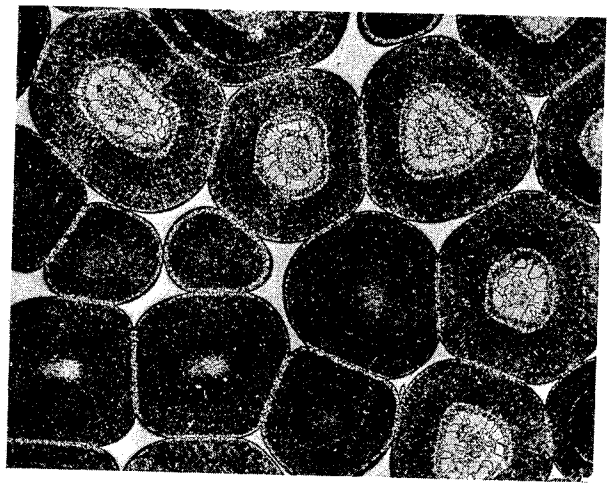


FIGURE 5.

INVENTORS
EDWIN S. HODGE
JAMES H. PETERSON
BY
Ernest A. Polin
ATTORNEY

United States Patent Office 3,328,139
Patented June 27, 1967

3,328,139

POROUS TUNGSTEN METAL SHAPES

Edwin S. Hodge and James H. Peterson, Columbus, Ohio, assignors, by mesne assignments, to the United States of America as represented by the United States Atomic Energy Commission

Filed Feb. 26, 1965, Ser. No. 435,549
2 Claims. (Cl. 29—182)

This invention relates to porous tungsten metal shapes and their preparation. In particular, it relates to synthetically produced permeable tungsten metal shapes possessed of an effective porosity within about 5 to 30 percent of the bulk volume of the shape. More particularly, the invention concerns gas-pressure bonded tungsten metal shapes of predictable and controlled-ordered interconnected porosity, these shapes having their porosity substantially completely filled with a solid transpirable material, and methods of preparation of such shapes.

Porous tungsten shapes having an interconnected pore structure are useful for infiltration with transpirable material (e.g., silver, copper, or other like material), and the resulting filled products are particularly useful in transpiration cooling applications, such as rocket nozzles and missile linings and claddings. Under high temperatures, the tungsten matrix of such filled products provides strength and conformity of structure while the lower melting transpirable material evaporates from the tungsten matrix and in so doing cools the tungsten matrix. Tungsten shapes possessed of predictable and controlled-ordered interconnected porosity permit production of desirable filled products having controlled transpiration rates and durations particularly suited for various applications.

An object of the invention is to provide tungsten shapes of predictable controlled-ordered interconnected porosity.

Another object is to provide a process for preparation of metallurgically bonded tungsten shapes of predictable controlled-ordered interconnected porosity.

Another object is to provide tungsten shapes of predictable controlled-ordered interconnected porosity having their porosity filled with a solid transpirable material.

Still another object is to provide a process for preparation of such filled tungsten shapes.

All these and other objects will be apparent from that which follows.

A porous tungsten metal shape of the invention consists essentially of a total void volume and a matrix or network of substantially uniform sized, discrete, polyhedral-shaped, tungsten metal particles metallurgically bonded at areas of particle contact to provide a density of about 70 to 95 percent of the theoretical density of tungsten metal. The total void volume of the porous tungsten metal shape consists essentially of a network of connected substantially uniform volume individual voids or pores distributed substantially uniformly throughout the matrix or network of metallurgically bonded discrete, polyhedral-shaped tungsten metal particles. The total void volume or absolute porosity of the porous tungsten metal shape falls within about 5 to 30 percent of the bulk volume of the shape with the absolute porosity of each shape substantially equal to its effective porosity. The effective porosity is that portion of total void volume constituted by interconnected voids or pores.

In general, the porous tungsten metal shape is prepared by loosely packing discrete spheroidal to spherical tungsten metal particles of a substantially uniform size in an enveloping container, evacuating and gas-tight sealing the container, and then subjecting the evacuated and sealed container to isostatic inert gas pressure, time, and temperature requisite to deform the container material

to cause it to flow inwardly to compact, deform, and bond the packed tungsten metal particles into a porous shape of the desired densification and interconnected porosity. From observing the teachings which follow hereafter, it is possible to prepare porous shapes of predetermined density with any desired effective pore size.

A filled tungsten shape of the invention consists essentially of a matrix of polyhedral-shaped, metallurgically bonded, tungsten metal particles having interconnected interstitial voids or pores between the bonded particles filled substantially completely throughout with an interconnected network of a transpirable material. The matrix of metallurgically bonded tungsten particles makes up from about 70 to 95 percent of the filled tungsten shape, and the interconnected network of transpirable material makes up the balance of the filled tungsten shape. The transpirable material in the filled tungsten shape characteristically always is of a melting point lower than tungsten metal, and generally is of a melting point below about 3000° F. and above 400° F. Generally the transpirable material in the filled tungsten shape is a lower melting metal, such as silver, copper manganese, beryllium, lithium, indium, tin, zinc, their alloys, and the like, although other metals and alloys and other transpirable materials, such as inorganic salts and organic compounds, also will be apparent and suitable.

In general, a filled tungsten shape of the invention is prepared by evacuating the interconnected porosity of a porous tungsten metal shape and then, while its effective porosity is evacuated, applying pressure to molten transpirable material to cause the same to completely fill the interconnected porosity and maintaining this pressure during solidification of the transpirable material.

In the drawings:

FIG. 1 is a block diagram flow sheet detailing the principal steps comprising the process for preparation of the porous tungsten metal shape.

FIG. 2 is a photomicrograph of a cross-section of a porous tungsten metal shape illustrating its uniform porosity and its metallurgically bonded, substantially polyhedral-shaped particles.

FIG. 3 is a plot of the effective pore sizes against the cumulative pore volume changes for several porous tungsten metal shapes.

FIG. 4 is a block diagram flow sheet detailing the principal steps comprising the process for preparation of the filled tungsten shape.

FIG. 5 is a photomicrograph of a cross-section of a filled shape consisting of the porous tungsten shape having its substantially uniform interconnected porosity substantially completely filled with a transpirable material, such as copper.

With reference to the drawings:

As a starting material for the invention there are employed relatively uniform-sized, discrete, spheroidical to spherical, tungsten metal particles. Particulare forms of relatively pure tungsten metal are available commercially. If the particulate tungsten metal lacks a spheroidal to spherical form, the particles can be spherulized by processes, such as flame spraying melting and plasma jet techniques, known to the art for converting metal particles to spheroidal to spherical form. Conventional separating and classifying methods for particulate materials can be used to classify such tungsten particles into useful fractions of relatively uniform size.

Although such aforedescribed spheroidal to spherical tungsten metal particles of relative uniform size are a useful starting material, the preferred and most desirable tungsten metal particles for the starting material are taught in a copending patent application. In this copend-

ing application of John M. Blocher, Jr. and John H. Pearson, Serial No. 298,515, filed July 5, 1963, under the title "Tungsten and Its Production," now Patent No. 3,234,007, there are taught novel spheroidal to spherical tungsten metal particles of high purity and their production. These novel tungsten metal particles of spheroidal to spherical form consist of a microstructure of columnar tungsten grains having width and thickness of about 1/10 to about 2 microns, radially oriented from a seed of tungsten metal, said microstructure of tungsten having a Knoop hardness of above about 900 KHN, a density of at least 95 percent the theoretical density of tungsten, and being subject to less than about 20 percent recrystallization upon being subjected to temperature of about 2900° F. for about 3 hours.

While taught with particularity in the copending application, the tungsten particles are generally produced by reduction of tungsten hexafluoride in its vapor phase in the presence of an excess in a fluidized bed of tungsten metal seed particles at a temperature sufficiently high to effect reduction of the tungsten hexafluoride to metallic tungsten. The produced tungsten metal deposits uniformly upon the tungsten metal seed, producing as the reaction progresses, a particulate product having tungsten metal seed as a core and a growing matrix of newly formed tungsten. Depending upon the seed size, reaction conditions and duration, etc. there readily are prepared spheroidal to spherical tungsten particles of purities of 99.8 percent and higher in desired particles of uniform size from two or three times the average diameter of the seed up to one hundred or several hundred times the seed diameter having controlled diameters of say 10 to 10,000 microns.

In practice of the process of the invention, spheroidal to spherical tungsten metal particles of a substantially uniform size, such as the novel particles prepared according to the teachings of the aforementioned pending application Serial No. 298,515 followed, if desired, by classification into fractions of selected size range, are isostatically gas-pressure bonded to provide the porous tungsten metal shape. Isostatic gas-pressure bonding of materials together, although a relatively recent development, is described to some extent in Canadian Patent No. 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, such as rods, bars, billets, and the like.

The principal steps comprising the process of preparation for the porous tungsten metal shape can be noted from the block diagram flow sheet of FIG. 1. In general, such particles are placed in a gas-tight envelope, such as a thin-walled container of a suitable material of predetermined shape and dimensions, loosely packed as by mechanical vibration to a desired extent, for example, to a bulk density of about 65 percent or more of the theoretical density of tungsten, the packed container evacuated and then sealed, and then the evacuated and sealed packed container subjected to inert gas pressure, time, and temperature requisite to deform the container material to cause it to flow inwardly to compact and bond the packed particles into a shape of the desired densification and interconnected porosity. By employing spheroidal to spherical tungsten metal particles of a substantially uniform size, such particles loosely packed in the container make up a starting mass having uniform permeability. By employing isostatic gas-pressure bonding, such a mass is uniformly compacted with the particles uniformly deformed and bonded to each other in a manner whereby the resulting porous shape is possessed of a controlled-ordered interconnected porosity. The inert gas is one which, considering the conditions and container material employed, will have a suitable heat conductivity and will not penetrate the gas-tight envelope. The bonding process involves deformation or plastic flow of the individual tungsten particles to decrease interstitial volume and increase area of contact between discrete particles, accompanied and followed by development of metallurgical bond between contacting particles. The container then is stripped from the gas-pressure bonded shape therein by mechanical removal, such as grinding, or a chemical means, such as chemical dissolution, as desired.

The relatively uniform pore openings connecting the substantially uniform volume pores in the porous shape can be noted from FIG. 2, which is a photomicrograph at a magnification of 75 times of a cross-section through a representative porous shape of the invention. This shape was prepared from spheroidal to spherical tungsten metal particles produced by the fluidized-bed tungsten hexafluoride process taught in the aforementioned pending patent application. The initial spheroidal to spherical particles employed averaged in size about 450 microns with over 80 percent of all employed particles within the range of ±20 percent of the average size. As is apparent from FIG. 2, the cores of these particles are of a much coarser grain structure than the surrounding tungsten, the surrounding tungsten having been deposited by the hexafluoride process on seed particles of commerical tungsten. The porous shape was made by the aforedescribed isostatic gas-pressure bonding process using 10,000 p.s.i. of helium pressure on a molybdenum container containing essentially the spheroidal to spherical tungsten metal particles at a temperature of about 2600° F. for about 3 hours. The porous shape had a density of about 95 percent of the theoretical density of tungsten metal and an effective pore size estimated to be about 20 microns. As shown in FIG. 2, the initial spheroidal or spherical form of the particles has been altered to a substantially polyhedral shape.

The preparation of the porous and filled shapes of the invention is unique in that the final dimensions, controlled uniformly ordered interconnected porosity and strength of the shapes are so accurately predictable that useful articles are obtained which require little or no machining or other processing (except possibly removal of the container material and excess transpirable material).

Typically in preparing the permeable tungsten metal shapes, there is employed as a compressing gas, inert gases such as helium or argon or the like, at pressures which may range from as low as about 1000 p.s.i. up to 50,000 p.s.i. and higher, while maintaining the container and contents at a suitable temperature for plastic flow of tungsten metal, consistent with the maintenance of the integrity of the encasing container as a gas-tight unit. 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 tungsten metal. Suitable temperatures, considering inherent limitations of the enveloping 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. Of course, the particular pressure, temperature, and time all influence the apparent density and the effective pore size of the produced tungsten metal shape.

Common to available tungsten metal particles, except those novel tungsten particles taught in the aforementioned patent application Serial No. 298,515, is an initial relatively coarse grain structure and/or additional grain coarsening or recrystallization upon being subjected to those temperatures and times required for isostatic gas-pressure bonding. In many applications for the permeable tungsten metal shapes, and also for the filled shapes, and in particular in those applications where high strength and/or high transition temperatures are a requirement, it is desirable to avoid, or at least to minimize, recrystallization or grain coarsening and to provide shapes with tungsten metal of extremely fine grain structure.

One unique property of the novel spheroidal to spherical tungsten metal particles, taught in the aforementioned copending patent application Serial No. 298,515, is an unusual resistance to recrystallization or grain coarsening

upon being subjected to high temperatures for limited periods of time. Because of such a unique resistance to recrystallization or grain coarsening, these novel spheroidal to spherical tungsten metal particles are preferred starting materials and are exceptionally useful in practice of the invention. Only by harsh or unusual treatment can such novel particles be made to recrystallize throughout to a coarse grained structure. The requisite temperatures and times for substantial coarse grain formation thereof are significantly much higher temperatures and longer times than those which create substantially complete grain coarsening within commonly available tungsten metal particles. Isostatic gas-pressure bonding of the novel tungsten metal particles can be accomplished without significant grain coarsening of individual particles. Depending on the particular preparation of the novel tungsten particles, they may possess some tendency to recrystallize and to grain coarsen under some isostatic gas-pressure bonding parameters. For example, where the tungsten seed of the novel particles comprises commonly available tungsten metal particles, there is a tendency for some grain coarsening to occur in the seed cores and to extend outward into the newly deposited tungsten metal surrounding the seed cores during preparation of a porous shape by isostatic gas-pressure bonding. Also with some novel particles, grain coarsening will initiate at the peripheral surfaces of individual particles and extend radially inwardly at certain gas-pressure bonding parameters. However, as will be apparent from that which follows, such grain coarsening initiating at the seed cores, initiating at the peripheral surfaces, or forming throughout the novel spheroidal to spherical tungsten metal particles can be avoided, or at least minimized to insignificant amounts, by appropriate pretreatments thereof and/or by following appropriate isostatic gas-pressure bonding techniques and parameters.

Choice of container material and bonding parameters are important to minimize recrystallization and grain coarsening in the commonly available tungsten metal particles and to avoid or minimize recrystallization and grain coarsening in the preferred novel spheroidal to spherical tungsten metal particles. Typically, molybdenum, iron, zirconium, niobium, tantalum, titanium, nickel, and the like, are useful container materials for encapsulating tungsten metal particles for the gas-pressure bonding of the same into the permeable tungsten metal shapes. Some materials are more useful than others, and some container materials at certain bonding parameters and/or in conjunction with certain other materials are exceptionally useful. Some limitations governing the container materials are illustrated as follows:

The flow characteristics of each container material places a maximum useful bonding temperature limitation on each or else the container will rupture. Additionally a zirconium container can alter strength of the prepared porous shape by formation of a zirconium-tungsten intermetallic at bonding areas of individual particles during gas-pressure bonding. Likewise by employing a container wholly of tantalum, and particularly at temperatures in excess of about 2600° F., traces of tantalum contamination will be found on the peripheral surfaces of the metallurgically bonded tungsten metal particles. With containers wholly of tantalum, lower bonding temperatures decrease the tantalum contamination of the formed permeable shape. Likewise applying inert gas compacting pressure to the container concurrently with bringing the container and contents to binding temperature and applying of a significant portion of the compacting pressure prior to reaching bonding temperature, each serve to diminish and make negligible any such tantalum contamination.

The preferred container material is molybdenum metal. Molybdenum metal containers at normal gas-pressure bonding parameters appear to be free from any significant promotion of recrystallization throughout the employed tungsten metal particles. Molybdenum containers at normal gas-pressure bonding parameters appear not to contaminate the produced permeable shapes, even with traces of molybdenum, and permit shapes of optimum tensile strength to be obtained.

Other aforementioned container materials also are suitable with the inherent flow characteristics of each limiting the maximum bonding temperature which can be used. In general, one applies the compacting gas pressure concurrently with the heating of the container and its contents to bonding temperature, so as to avoid rupturing the container. As in the case of molybdenum, with the other aforementioned container materials there may be noted grain coarsening or recrystallization of the particles and especially so at bonding temperatures above normal. While somewhat lower than normal bonding pressures will diminish recrystallization promotion by a container material, higher compacting pressures are required for equivalent densification, resulting in decreased strength of the metallurgical bond between the particles.

A number of ways exists to diminish, and in some instances eliminate grain coarsening and recrystallization effects and other detrimental effects of container material. While tantalum as a sole material for the container is of limited utility, there can be produced an excellent porous tungsten metal body by employing a small piece or strip of tantalum metal in conjunction with container material, such as molybdenum. In this procedure, a piece of tantalum metal, preferably not in excess of about 1 percent of the total weight of the employed tungsten metal particles, is placed in the container along with the tungsten particles and bonded as such into a surface of the produced shape. This piece of tantalum metal then later can be machined from the produced porous tungsten metal shape. For some reason, not fully understood at present, the use of such a piece of tantalum metal provides higher densification without increasing bonding parameters, diminishes grain recrystallization or coarsensing effects, increases the strength of the produced porous shape, and apparently does not contaminate the shape with noticeable traces of tantalum on the peripheral surfaces of the metallurgically bonded tungsten metal particles.

Another way to diminish, and in some instances eliminate, recrystallization and grain coarsening effects initiating at the peripheral surfaces of the tungsten metal particles during isostatic gas pressure bonding, is to subject the to-be-employed particles to a particular vacuum heat treatment prior to gas-pressure bonding of the same into a porous shape. Such a particle treatment should be for between ½ and 2 hours, desirably about 1 hour, in a substantial vacuum at a suitable temperature of at least about 2450° F., with up to about 2700° F. being a useful temperature and with even higher temperatures sometimes useful when the particles being vacuum heat treated do not undergo significant recrystallization or grain coarsening from the treatment. Heat treatments at higher and lower temperatures than the aforestated suitable temperatures apparently do not impart to the treated particles an equivalent resistance to peripheral grain coarsening. Likewise particle heat treatments other than in a substantial vacuum, for example in air or a hydrogen atmosphere, fail to impart the equivalent resistance to peripheral grain coarsening. While not fully understood at this time as to what may be happening through this particular vacuum heat treatment, it may well be that some trace material promoting grain coarsening may be removed from the particle's surface by the treatment. Whatever the explanation may be, it is not intended to limit this facet of the invention to any one particular explanation or mechanism. Surprisingly once the to-be-employed particles have undergone the particular vacuum heat treatment, they need not be gas-pressure bonded together immediately into a porous shape, but can be stored under ambient conditions for some time and still retain substantial benefits of the vacuum heat treatment.

Another way to diminish, and in some instances eliminate, recrystallization and grain coarsening effects initiat-

ing at the peripheral surfaces of the tungsten metal particles during isostatic gas-pressure bonding, is to subject the to-be-employed particles to particular chemical treatments prior to gas-pressure bonding of the same into a porous shape. An especially useful chemical treatment for the to-be-employed tungsten metal particles is to immerse them first in a dilute aqueous inorganic acid solution, second in a dilute aqueous caustic solution, and then thoroughly to wash with water and dry. Useful inorganic acids are nitric acid, hydrochloric acid, hydrofluoric acid, and the like, and various mixtures of these inorganic acids. The preferred caustic is sodium hydroxide, although other caustic materials such as potassium hydroxide and the like may be used. The immersion times in the dilute aqueous inorganic acid solution and the dilute aqueous caustic solution need only be sufficient to assure thorough contact of the particle's surfaces and most generally is only a few seconds duration and less than one minute, although much longer immersion times are not detrimental. The washing is with pure water and should be sufficient to remove all traces of the immersion solutions. The drying may be performed in dry air with or without heat being used to accelerate the drying. These chemically treated particles also need not be gas-pressure bonded immediately into a permeable shape, but can be stored under ambient atmospheric conditions for some time and still retain the benefits of the chemical treatment.

Still other pretreatments of the to-be-employed tungsten metal particles are of value. Of particular utility is to subject the to-be-employed tungsten particles to both the aforedescribed chemical and vacuum heat treatments prior to gas-pressure bonding.

The following Table I tabulates illustrative examples of preparation of the porous tungsten metal shapes by isostatic gas-pressure bonding. In Table I there is presented the factual information of the particle size of the employed tungsten metal particles, of the particularly employed gas-pressure bonding parameters, and of the apparent density of the resulting permeable tungsten metal shape.

TABLE I

Ex. No.	Tungsten Metal Particles,[1] Average Size (μ)	Gas Pressure Bonding Parameters				Permeable Shape, Apparent Density (Percent)
		Container	Pressure (p.s.i.)	Temp. (° F.)	Time (Hours)	
1	210	Mo	1,500	2,800	3	73.5
2	210	Mo	2,000	2,800	1	73.7
3	210	Mo	3,150	2,800	3	76.8
4	330	Mo	1,500	2,800	3	77.9
5	330	Mo	2,000	2,800	1	79.5
6	330	Mo	3,150	2,800	3	84.0
7	330	Mo	10,000	2,900	3	94.3
8	450	Mo	<1,500	2,900	3	[2] 80
9	450	Mo	1,500	2,800	3	82.3
10	450	Mo	1,700	2,800	3	82.5
11	450	Mo	2,000	2,800	1–3	87.5
12	450	Mo	3,150	2,800	3	91.2
13	650	Mo	1,500	2,800	3	85.2
14	650	Mo	2,000	2,800	1	87.0
	650	Mo	3,150	2,800	3	90.8
15	[3] 450	Mo	10,000	2,900	3	91.6
16	[4] 450	Mo+Ta strip	10,000	2,300	3	[5] 91
17	450	Mo+Ta strip	10,000	2,300	3	[5] 88
18	[6] 400	Mo	10,000	2,900	3	[2] 80
19	[4 6] 400	Mo	10,000	2,900	3	[2] 72
20	450	Fe	2,500	2,700	3	80
21	[3] 450	Fe	2,500	2,700	3	73.5
22	450	Fe	5,000	2,700	3	92
23	[4] 450	Fe+Ta strip	10,000	2,300	3	93.5
24	450	Fe+Ta strip	10,000	2,300	3	93.5
25	450	Fe	15,000	2,100	1	78
26	450	Fe	15,000	2,500	3	89.7
27	450	Ti	2,500	2,800	3	92
28	450	Ti	15,000	2,500	3	89.2
29	450	Zn+Ta strip	10,000	2,300	3	86.5
30	450	Zn	15,000	2,500	3	88.6

[1] Unless noted otherwise, all tungsten metal particles were spheroidal to spherical; were produced from WF_6 by the process disclosed in the aforementioned U.S. application Serial No. 298,515; and over 80% of the particles in each example were within a range of ±20% of the specified average size in microns of diameter.
[2] Estimated by comparison with specimen of known apparent density.
[3] Annealed at about 3,270° F. for about 2 hours in vacuum.
[4] Annealed at about 2,700° F. for about 2 hours in vacuum.
[5] Approximate.
[6] Tungsten metal particles produced from WCl_6 by process disclosed in U.S. Patent No. 3,020,148.

Permeability is that property of a porous material which characterizes the ease with which a fluid will flow through the material under an applied pressure gradient and throughout is expressed in measured units of darcys as defined by Darcy's Law. Characteristic of each porous tungsten metal shape is a uniform permeability which stems from uniform and controlled-ordered interconnected porosity. Individual void or pore volumes are distributed substantially uniformly throughout the shape with each connected to other void or pore volumes so that all are interconnected. The volume of each individual void or pore equals or at least closely approximates that of other individual voids or pores in the shape. The geometric configuration or boundary of an individual void or pore volume is determined by the unbonded surfaces of the polyhedral-shaped, tungsten metal particles which circumscribe the particular void or pore volumes. The openings which connect each void or pore volume to other void or pore volumes are quasi-hypocycloidal shaped openings. In the more porous shapes these pore openings constitute quasi-hypocycloidal shaped openings of four and three cups. As shape porosity decreases, the proportion of three-cupped quasi-hypocycloidal shaped openings becomes increasingly greater so that in the porous tungsten metal shapes of least porosity, all openings closely approximate quasi-hypocycloidal shaped openings of three cups. The openings into individual void or pore volumes are smaller in size than cross-sections through the pore volumes which they connect and are largely determinative of the permeability of the porous tungsten metal shape. In transpiration cooling applications of the filled shape, the openings into the individual void or pore volumes largely determine the transpiration rate, although the greater pore volumes control the duration of transpiration.

For determination of pore size and distribution, the method of Ritter and Drake (Industrial Engineering

Chemistry—Analytical Edition, 17 (1945), 782–791) has been used. In this method, pressure is applied to mercury and the pressure required to fill a given pore is a measure of the size of the pore. As pressure is increased, the amount of mercury flowed into the pores increases at a rate proportional to the differential pore volume due to pore entrances of size corresponding to the instantaneous pressure. Thus for each porous shape, a given pressuring curve permits a determination of the pore size distribution and the size of pore openings. In this method, it is assumed that the pore volumes and openings thereto are of circular cross-section. While this assumption is not correct for the porous tungsten metal shapes of the invention, the measured data remain useful for in the pores of non-circular cross-section of these shapes the order of magnitude and shape of distribution of the measured radii do not appreciable differ. From data obtained by this method there is determined the radius of the opening into a pore which, as in the present shapes where a plurality of openings into each pore exist, is the calculated radius of the largest opening into the core. Throughout the specification and claims where reference is made to "effective pore size" there is meant this calculated radius (r), or diameter (d), wherein $d=2r$, from experimental determinations by method of Ritter and Drake.

In the herein described determinations of effective pore size for the porous tungsten metal shapes, the employed apparatus was a modification of that described by Ritter and Drake in their aforementioned reference with the modifications being those primarily necessary to permit measurements to be made without use of a high-pressure bomb.

In FIG. 3 there are plotted cumulative pore volume changes against the effective pore sizes for several porous shapes set forth as examples in Table I. The pore volume sizes are expressed in terms of cc./g. of the porous shape. The data for the plots of FIG. 3 were determined by the aforementioned method of Ritter and Drake, and the effective pore size is expressed as the diameter in microns. As shown by the plots, it is possible to produce bodies with pore sizes concentrated in a narrow range. As the apparent density of the shapes increases, the spread in pore size tends to widen.

The effective pore size in the permeable shape depends, at least in part, on the size of the spheroidal to spherical particles from which the shape is prepared and the apparent density of the shape. By suitable variance of the size of the spheroidal to spherical particles and/or the apparent density of the shape into which they are bonded, one can prepare porous shapes with any of numerous different combinations of effective pore size and apparent density. With shapes prepared of particles of substantially the same size, the effective pore size decreases as the density increases. As an illustration thereof, when the shape is prepared from particles of which at least 80 percent are between about 420 to 480 microns diameter, there can be prepared a family of porous shapes with apparent densities ranging from as low as about 73 percent to 95 percent with effective pore sizes ranging from as low as about 60 microns for the more porous shapes to less than 20 microns for the least porous shapes. For example, such a shape of an apparent density of about 73 percent has an effective pore size of about 60 microns, a shape of an apparent density of about 80 percent has an effective pore size of about 48 microns, a shape of apparent density of about 84 percent has an effective pore size of about 40 microns, a shape of an apparent density of about 89 percent has an effective pore size of about 30 microns, and a shape of an apparent density of about 94 percent has an effective pore size of about 20 microns, and in each of such shapes at least about two-thirds of the pores equal or closely approximate the effective pore size. When porous shapes of equivalent effective pore size are produced from smaller size particles, their apparent densities are less than those of corresponding shapes of equivalent pore size prepared from larger size particles. Thus, there can be prepared a family of porous shapes of diminishing density and of like effective pore size. For example, such shapes of an effective pore size of about 48 microns can be provided with an apparent density of about 70 percent by preparation from about 330 micron diameter particles, also with about 80 percent apparent density by preparation from about 460 micron diameter particles, and also with an apparent density of about 93 percent by preparation from about 650 micron diameter particles, etc. When a porous shape of a specific particular apparent density is desired, this particular apparent density can be provided with any preselected effective pore size within a broad range of pore sizes through appropriate choice of the size of the tungsten particle from which the shape is produced. Thus, there can be prepared a family of porous shapes of a like apparent density and of a diminishing effective pore size. For example, such shapes prepared to an apparent density of about 80 percent, have an effective pore size of about 11 microns by preparation from about 100 micron diameter particles, and also an effective pore size of about 25 microns by preparation from about 210 micron diameter particles, also an effective pore size of about 35 microns by preparation from about 330 micron diameter particles, also an effective pore size of about 48 microns by preparation from about 460 micron diameter particles, also an effective pore size of about 70 microns by preparation from about 650 micron diameter particles, etc.

Permeability measurements have been made on porous tungsten metal shapes of several of the examples tabulated in Table I. In these measurements, cylindrical specimens of known cross-sectional area and length were used. The percent of theoretical density was redetermined for each specimen and is reported as the ratio of true volume (i.e., the volume enclosed by its outer surface excluding the volume of its open pores) to the apparent volume (i.e., the volume enclosed by its outer surface including its open pores). The true volume was measured by air pycnometer and the apparent volume from dimension measurements. Porosity is reported in percent with the percent of porosity plus the percent of theoretical density for each specimen totaling 100 percent. Each specimen was thoroughly cleaned by flushing with alcohol at 60 to 300 p.s.i., followed by ultrasonic cleaning in trichloroethylene and then flushing under pressure with the particular test fluid to be used for the permeability determination, until the fluid runs clear. The test fluids used were 14, 35, and 50 percent glycerol-water solutions having viscosities of 1.292, 2.60, and 5.041 centipoises, respectively, with these fluids of these viscosities selected to bracket viscosities of many molten metals. Each specimen was mounted in a stainless steel jacket and the specimen's side walls sealed by a plurality of Teflon chevron gaskets forced tightly thereagainst. A particular test fluid at a preset pressure was then passed lengthwise through the specimen. Records were made of the volume of fluid passing through the specimen along with the time interval therefor and from this recorded data and the dimensions of the specimen the fluid flow rate was calculated. The highest pressure run on each specimen was made first. Flow rate data was obtained on each specimen with each of the three different viscosity glycerol-water solutions at differential pressures up to 300 p.s.i. A plot of flow rate versus differential pressure yields a family of relatively straight lines with the slopes of the lines being determined by the viscosity of the test fluid used. If the total flow rate data for each specimen and all three viscosity solutions are combined so that the product of unit flow rate and the viscosity is plotted versus differential pressure, the relationship resolves itself to a single line of constant slope and meets the requirements for laminar flow consistent with Darcy's Law. Their slope provides a characteristic property value which is a measure of permeability and is expressed in darcys. From data derived from the permeability measurement procedure de-

scribed above, the permeabilities illustrative of several examples set forth in Table I are given in the following Table II.

TABLE II

Table I Example Number	Average Particle Size, Microns	Density, Percent Theoretical	Porosity, Percent	Permeability, Darcys
7	330	94.6	5.4	0.06
8	450	80.1	19.9	17.2
10	450	84.2	15.8	5.75
11	450	88.2	11.8	1.67
12	450	90.6	9.4	0.96
13	650	90.1	9.9	3.24

Because of predictable plastic deformation properties resulting in close dimensional control during preparation, very little to no machining usually is required of the porous shapes for most applications. Thus, material losses are minimized. However, if desired, the porous tungsten metal shapes can be machined, ground, electro-polished, chemical polished, or otherwise processes to desired dimensions. As a general rule, porous shapes of apparent densities even as low as about 70 to 75 percent can be machined, ground, and the like by appropriate selection of conditions and techniques known to the art, although greater care should be employed with the more fragile lower density shapes than when working with those porous shapes approaching 95% the theoretical density of tungsten metal.

In general, to prepare the filled tungsten metal shape, a permeable tungsten metal shape possessed of interconnected porosity is impregnated with a molten transpirable material. To assure complete filling of all of the interconnected porosity and freedom from unfilled interconnected voids, pressure may be employed to drive molten transpirable material into evacuated interconnected voids of the permeable shape, and applied pressure is maintained while the molten transpirable material solidifies. The principal steps comprising the process of preparation of the filled tungsten metal shape can be noted from the block diagram flow sheet of FIG. 4. Complete filling of the interconnected porosity is assured by the applied and maintained pressure. The applied pressure provides a filling force in addition to any existing wetting or capillary action of the molten transpirable material with the tungsten metal matrix of the permeable shape and further permits filling of the permeable shape with molten transpirable materials which do not significantly wet tungsten metal. Shrinkage voids, which can occur during solidification, are eliminated within the filled tungsten metal shape by maintaining pressure during solidification of the molten transpirable material. As solidification occurs, the imposed pressure continues to force transpirable material into any voids tending to be caused by shrinkage of the transpirable material as it solidifies. Thus by the above general method, there is obtained a substantially complete filling of the interconnected porosity of a permeable tungsten metal shape with a transpirable material. As a significant result of this complete filling, the solidified transpirable material filling the interconnected porosity reduces the notch sensitivity at bond junctions between individual tungsten particles metallurgically bonded together in the matrix or network making up the permeable tungsten metal shape. Flowing from this reduction in notch sensitivity for the substantially completely filled shapes, there is provided a significant increase in tensile strength for such so-produced filled tungsten metal shapes when compared to the tensile strength of the unfilled permeable tungsten metal shape.

In one embodiment for substantially completely filling of a permeable tungsten metal shape with a transpirable material, a process akin to isostatic gas-pressure bonding is employed. A permeable tungsten metal shape possessed of interconnected porosity is placed along with a slight excess, normally about 10 percent by weight, of that amount of transpirable material (e.g., silver), desirably in a particulate form or thin sheet form, within a disposable thin-walled enveloping container. The container and its contents of the permeable shape and transpirable material are evacuated and the evacuated container sealed to make the same gas-tight. The container may be of such materials aforementioned as useful in preparation of the permeable shape by the isostatic gas-pressure bonding process. The sealed evacuated container then is subjected, as in an autoclave, to an appropriate temperature and pressure of an inert gas so as to cause melting of the transpirable material within the container and a collapsing of the container walls to an extent to force molten transpirable material completely throughout the interconnected porosity of the permeable shape. The temperature then is lowered to below the solidification temperature of the transpirable material while the inert gas pressure is continued to be imposed on the now-collapsed, yet still sealed gas-tight, container until solidification of the transpirable material has taken place. Whereupon the inert gas pressure can be released, the sealed container removed from the autoclave, and the container and excess transpirable material machined from or in another suitable manner removed from the filled tungsten shape.

In another embodiment for substantially complete filling of a permeable tungsten metal shape with a transpirable material, the following procedure is carried out. In a suitable apparatus, such as an autoclave, there is placed the permeable tungsten shape and an open vessel containing transpirable material in excess of that required to completely fill the permeable tungsten metal shape. The autoclave is evacuated, and the transpirable material heated to place the same in molten state. The permeable shape then is immersed completely in the molten transpirable material so that molten transpirable material completely covers the permeable shape with no surface of the permeable shape exposed. The autoclave then is pressurized by introducing an inert gas therein and inert gas pressure exerted upon the surface of the molten transpirable material to force transpirable material into the interconnected porosity of the immersed permeable shape. This inert gas pressure is maintained upon the transpirable material while it is cooled until after the transpirable material solidifies. Whereupon the inert gas pressure is released, the vessel and its contents removed from the autoclave, and the vessel and excess transpirable material machined from or in other manner removed from the filled tungsten shape.

Common to each of the above techniques, and essential to the preparation of the tungsten metal shape completely filled with transpirable material, is an imposition of pressure during the filling and the maintenance of pressure during solidification. Also common to these techniques is that the permeable tungsten metal shape has its interconnected porosity evacuated before molten transpirable material is forced therein. Useful temperatures for preparing the filled tungsten shape depend in part on the particular transpirable material. The useful minimum temperature always is in excess of that temperature at which the particular transpirable material melts and becomes molten. The useful maximum temperature should not exceed that temperature whereat the transpirable material appreciably vaporizes, and more generally the maximum temperature should not be so high as to cause a significant grain coarsening or recrystallization of the tungsten metal of the shape. Useful pressures can range widely. Where the employed temperature is such that the transpirable material is quite molten and free flowing, lower pressures can be employed then where the molten material is just above its melting point. Generally the pressure employed is at least 200 p.s.i., more normally 4000 p.s.i. or more, with the useful maximum pressure limited only by the strength

of the apparatus or autoclave in which the filled tungsten metal shape is prepared.

The following Table III tabulates illustrative examples of preparation of tungsten metal shapes filled with various transpirable materials by the aforedescribed process embodiments.

TABLE III

Ex. No.	Permeable Shape		Infiltration Parameters				
	No.	Apparent Density (percent)	Container	Infiltrant	Temp. (° F.)	Pressure (p.s.i.)	Time (Hrs.)
31	5	79.5	Iron [1]	Mg	1,400	10,000	1
32	10	82.5	Iron [1]	Ag	1,850	10,000	1
33	10	82.5	Iron [1]	Ag	2,000	7,000	1
34	9	82.3	Iron [2]	Ag	2,000	7,000	1

[1] Technique involving inert gas pressure applied to disposable gas-tight container enveloping the permeable tungsten metal shape and transpirable material, and maintaining pressure on the container during solidification of the transpirable material.

[2] Technique involving inert gas pressure applied to molten transpirable material having the permeable tungsten metal shape immersed completely therein, and maintaining pressure on the transpirable material during its solidification.

EXAMPLE

Spheroidal to spherical tungsten metal particles of an average particle size of 420 microns were produced by the fluidized-bed tungsten hexafluoride process taught in the aforementioned pending patent application. These particles were then isostatically gas-pressure bonded in a molybdenum container at a pressure of 1300 p.s.i. and a temperature of 2800° F. for 3 hours to provide a porous tungsten metal shape of the invention. This porous shape had a density of about 79 percent of the theoretical density of tungsten metal.

The porosity of this porous shape was then substantially completely filled with copper by evacuating the interconnected porosity thereof and completely immersing the evacuated porous shape in a bath of molten copper of about 2200° F. Inert gas pressure of 7000 p.s.i. was then im posed on the molten copper bath and this pressure maintained while the molten copper was allowed to cool and solidify. Whereupon excess copper was machined from the porous shape with the resulting product being a copper-filled tungsten metal shape of the invention.

This copper-filled tungsten metal shape was then machined to a rocket nozzle configuration and test fired. The firing conditions were:

Environment—unsymmetrical dimethyl hydrazine-inhibited red fuming nitric acid fuel	
Weight ratio of oxygen to fuel	2.6
Flame temperature, ° F.	5000
Chamber pressure, p.s.i.	525
Firing time, sec.	10.5
Original nozzle throat diameter, inch	0.412

Transpiration of the copper took place to a substantially uniform depth inwardly from the surfaces exposed to the hot exhaust gases of the firing, and the fired rocket nozzle insert was devoid of cracks after firing. Examination of the microstructure of metallurgically bonded tungsten metal particles making up the tungsten metal matrix of the rocket nozzle insert revealed that only the first several granules in the high heat flux area showed any recrystallization and grain coarsening. No recrystallization was noted further in from the surface exposed to the hot exhaust gases of the firing.

Various embodiments, changes, and modifications will be apparent, from the foregoing description and examples, to those skilled in the art. All such embodiments, changes, and modifications that fall within the true spirit of the invention are intended to be included with the invention limited only as set forth in the appended claims.

We claim:

1. A porous tungsten metal shape of a density of about 70 to 95 percent of the theoretical density of tungsten metal, which shape is characterized by substantially uniform permeability throughout and which shape consists essentially of discrete substantially uniform sized polyhedral-shaped tungsten metal particles metallurgically bonded at areas of contact to other particles into a substantially uniform coherent tungsten metal matrix interlaced throughout with a connected network of interstitial pores of substantially uniform size and shape.

2. The porous tungsten metal shape of claim 1 having at least two-thirds of said pores within the porous shape of substantally equal volume.

References Cited

UNITED STATES PATENTS

3,050,386	8/1962	Von Dohren	75—222 X
3,141,769	7/1964	Saunders	75—222
3,175,903	3/1965	Herron	75—213 X

FOREIGN PATENTS

707,512	4/1954	Great Britain.
717,034	10/1954	Great Britain.

L. DEWAYNE RUTLEDGE, *Primary Examiner.*

BENJAMIN R. PADGETT, *Examiner.*

A. J. STEINER, *Assistant Examiner.*