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PROCESS FOR FORMING POROUS TUNGSTEN
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The present invention relates to a process for forming porous tungsten for use as a high temperature porous material.

Many applications in the aerospace field require a material which has both the ability to withstand high temperatures and also requires a high degree of porosity. For example, rocket nozzle throat inserts where it is desired to cool the throat insert by permeating a cooling liquid through the material. Other applications are found in ion motor components, thrust vector control probes, fuel cells and related component parts. Although tungsten has the ability to withstand high temperatures it is difficult to form in a porous form. Commercially available tungsten powder when sintered forms a dense non-porous structure and is unsuitable for the above applications due to the preponderance of small particles of the tungsten powder. Even the relatively large particles are found to be primarily an agglomerate of small particles which break down when sintered rather than desired large strong single grain structures.

It is an object of the present invention therefore to provide a process for forming large single grains of tungsten which may be sintered to form a porous tungsten material.

Other objects and advantages of the present invention will become apparent with reference to the present description.

It is known that the addition of small amounts of nickel to tungsten metal powder will produce a sintered tungsten structure having high density at low sintering temperatures. Many of the variables involved in this process such as: the method of adding nickel, the nickel content, the sintering time and the sintering temperature have been investigated and published. Sintered compacts formed in this manner are brittle and fracture along the grain boundaries. This is believed due to the formation of a brittle nickel tungsten intermetallic compound at the grain boundaries. Therefore when these compacts are broken or crushed, they break down into particles equal in size to the grains in the sintered compact. This is particularly true for compacts which have been heat treated at high temperatures and long times to cause large grain growth.

The process for obtaining the coarse tungsten powder and forming it into porous tungsten components is:

- (1) Blending or mixing the nickel and tungsten powders.
- (2) Compact and sinter the nickel-tungsten material in a manner to provide a grain size in the sintered compact equal to the desired particle size of tungsten powder.
- (3) Crushing or grinding the sintered compact to produce tungsten powder of the desired particle size.
- (4) Removing the nickel from the tungsten powder by preferential solution by a solvent material.
- (5) Compacting and sintering the powders produced by steps 1-4 to the desired density.

As will later be discussed, step 4 may be eliminated to achieve certain desired effects.

A minimum nickel content of .05 weight percent to tungsten powder is necessary to achieve desired tungsten grain growth during sintering. Higher nickel content can be used, but the larger concentrations of nickel are more difficult to remove subsequent to sintering and grinding. Nickel concentrations greater than 3% inhibit grain

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growth. The permissible nickel content is therefore from .05 to 3% by weight with a preferred range from .05 to 1% by weight. The nickel can be added in a number of well known mixing techniques:

- (1) Metal powder addition and blending.
- (2) Blending tungsten powder with nickel chloride dissolved in water and subsequently heating in a hydrogen atmosphere to dissociate the NiCl and drive off the chlorine gas.
- (3) Blending tungsten oxide powder with an aqueous solution of nickel nitrate and simultaneously reducing tungsten oxide and nickel nitrate by heating in a hydrogen atmosphere.

Other methods of uniformly blending small amounts of a metal addition may be used.

The powder mixed in the above manner is then compacted into a briquette having size and shape suitable for subsequent crushing and grinding. The compact or briquette can be pressed at pressures ranging from 5000 p.s.i. to 2000 p.s.i. The compacting pressure is not, however, critical and a minimum pressure should be selected which will provide adequate handling strength in the compact.

The sintering time and temperature for the compact should be selected to obtain a grain size equal to the desired ultimate particle size of the tungsten powder. The specific time and temperature variables are dependent on each other; on the desired grain size; on the nickel content; and size of the starting tungsten particles. An illustrative example is as follows: For an initial commercially available tungsten powder having a maximum particle size of .044 mm. to which .2% by weight of nickel has been uniformly blended, sintering at a temperature of 3200° F. for 3 hours produces an approximate tungsten particle size of .130 mm. or has caused a particle size growth of approximately 3 times. Those skilled in the art can adjust sintering time and temperature to best achieve in the most economical manner a desired grain size by empirical determination.

After sintering, the compact is crushed using a jaw crusher and/or impact grinding equipment such as a high speed hammer mill. As previously mentioned the sintering material is brittle and will readily break down by impact type crushing operations into a single grain particle.

The diffusion of tungsten into the nickel phase during sintering is much more rapid than the diffusion of the nickel into the tungsten phase; so that essentially all of the nickel content of the particles is contained on the surface of the particles. This characteristic permits the nickel content to be readily removed by selectively dissolving it in a nitric acid solution or other suitable solvent. The leaching process should be continued until essentially pure tungsten powders are obtained.

The tungsten powders obtained from the above process are then compacted into the desired shape of an end article by hydrostatically pressing in suitably formed dies. Water and/or organic binders may be added to achieve the necessary compact strength for handling depending on particle size and distribution of the tungsten powders. The compacting pressure is preferably in the range of 10,000 to 20,000 p.s.i.

The final form compacts are then sintered in a final sintering operation. In the final sintering step the time and temperature of sintering will be primarily established by the required strength of the end article and porosity is to a lesser extent affected. I have found an economical compromise by way of illustration is to sinter at 3800° F. for 3 hours and this will provide adequate strength while maintaining desired permeability. Standard sintering processes are contemplated for the final step although

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it is pointed out that in general higher temperatures may be used because of the initial large tungsten particle grain size leading to additional strength in the end article.

For certain special purposes the leaching or nickel removal step of my process may be dispensed with entirely or accomplished after the final sintering step. For example in a fuel cell where it is desired to use a nickel surface as a catalyst for a fuel element, the nickel may be retained in the final article by eliminating the leaching step.

Further since the final sintered article has a high degree of porosity most of the nickel can be removed by leaching subsequent to final sintering with nitric acid or other suitable solvent.

I claim:

1. A process for forming a porous tungsten article comprising the steps of: forming a uniformly blended powder mixture consisting of .05% to 3% by weight of nickel and the balance substantially all tungsten; compacting said powdered mixture to form a briquette; sintering said briquette to induce growth of the tungsten particles within said briquette to a predetermined size substantially greater than the tungsten particle size within said powder mixture; breaking said briquette at the grain boundaries to form a loose powder of large grain size tungsten particles; compacting said large grain size tungsten powder into a briquette of final article shape; sintering said briquette of final article shape to form a sintered porous article.

2. A process for forming a porous tungsten article comprising the steps of: forming a uniformly blended powder mixture consisting of .05% to 3% by weight of nickel and the balance substantially all tungsten; compacting said powdered mixture to form a briquette; sintering said briquette to induce growth of the tungsten particles within said briquette to a predetermined size substantially greater than the tungsten particle size within said powder mixture; breaking said briquette at the grain

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boundaries to form a loose powder of large grain size tungsten coated with nickel; selectively dissolving said nickel coating from said large grain size powder with a nickel solvent solution to provide substantially pure large grain size tungsten powder; compacting said large grain size tungsten powder into a briquette of final article shape; sintering said briquette of final article shape to form a sintered porous tungsten article.

3. A process for forming a porous tungsten article comprising the steps of: forming a uniformly blended powder mixture consisting of .05% to 3% by weight of nickel and the balance substantially all tungsten; compacting said powdered mixture to form a briquette; sintering said briquette to induce growth of the tungsten particles within said briquette to a predetermined size substantially greater than the tungsten particle size within said powder mixture; breaking said briquette at the grain boundaries to form a loose powder of large grain size nickel coated tungsten particles; compacting said large grain size tungsten powder into a briquette of final article shape; sintering said briquette of final article shape to form a sintered porous article; immersing said sintered porous article in a nickel solvent solution to selectively dissolve a portion of the nickel coating.

References Cited by the Examiner

UNITED STATES PATENTS

2,227,445	1/41	Driggs et al.	29—182
2,227,446	1/41	Driggs et al.	29—182
2,620,555	12/52	Lenz	29—182

FOREIGN PATENTS

699,916	11/53	Great Britain.
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