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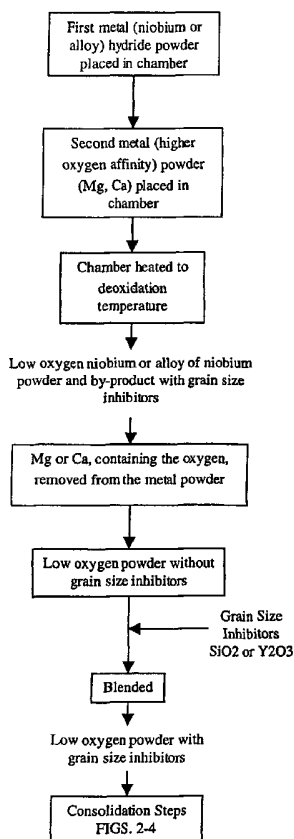
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(54) Title: STABILIZED GRAIN SIZE REFRACTORY METAL POWDER METALLURGY MILL PRODUCTS



(57) Abstract: A powder metal (P/M) mill product and the method of fabrication such product made out of low oxygen (<400 ppm) refractory metal, or alloys thereof, using oxide additive (such as MgO, SiO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>) for co-fabrication to achieve refractory metal grain size stabilization as required in high temperature applications. One such product is a sheet with small grain size containing oxide particles as grain size stabilizers. The product has good mechanical properties, low oxygen content in refractory metal fiber derivatives of the powder within the mill product and if is available as large pieces of sheet (lateral dimensions). The metal powder is consolidated to a sheet bar by different methods, which may weigh 50 pounds or more.

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STABILIZED GRAIN SIZE REFRACTORY  
METAL POWDER METALLURGY MILL PRODUCTS

BACKGROUND OF THE INVENTION

The invention relates generally to metal mill products (and fabricated parts) made from powders of refractory metals including the elemental metals and their alloys and, more particularly to the use of oxide  
5 dopants for grain size stabilization in mill products and fabricated parts to be subjected to high temperature application usage and/or high temperature fabrication processes.

Users of refractory metals have had a long-standing interest in replacing tantalum with niobium. One driving force for such replacement of  
10 tantalum is price as well as the limited availability of tantalum. Many mill products involve high temperature exposure in fabrication and/or use. The high temperatures can cause grain growth. In various applications large grains, as a consequence of such grain growth, are detrimental to the performance of the material. This has been a limitation of niobium  
15 substitution for tantalum. Other limitations include lesser strength and hardness as-fabricated niobium and its alloys.

Currently, areas of interest include furnace parts, sintering trays and deep drawn cups as used for manufacturing synthetic diamonds. These products require material with small grain size. Furnace parts  
20 particularly require the material to have slow grain growth during service in order to prevent premature deterioration of the mechanical properties.

Currently tantalum material with stabilized grain size, due to alloying additions or other artifacts, is used for wire or sheet. In one embodiment or state of interaction,  $\text{SiO}_2$  is used as a grain stabilizer. The disadvantage of  
25 such a manufacturing method (resistance-sintering) for grain size stabilized tantalum powder metallurgy (P/M) material is that it

is limited to a lot size of 30 pounds for tantalum and approximately 15 pounds for niobium. It is desirable to make lot sizes of up to 1000 pounds of tantalum and 500 pounds of niobium respectively.

Current manufacturing methods for large P/M sheet sizes/strip length are not capable of providing large pieces of sheet or long coils of sheet with the same low level of oxygen content and good mechanical properties

It is an object of this invention to provide a powder metallurgy (P/M) route to fabrication of refractory metals in large lots with low oxygen content and to provide resultant mill products with low oxygen content.

It is a further object of this invention to provide a P/M source for mill products and eventual mill products with a finer grain and a decreased grain growth than are achieved with ingot source materials.

These objects are applicable to refractory metals generally and more particularly to niobium and its alloys.

The objects set forth above as well as further and other objects and advantages of the present invention are achieved by the invention as described hereinbelow

## SUMMARY OF THE INVENTION

The invention relates to a process for making a metal mill product from a refractory metal powder comprising (a) providing a low oxygen refractory metal powder; (b) adding to the powder a grain growth inhibitor to the low oxygen refractory metal powder before consolidating the powder, (c) consolidating the powder by either hot isostatic pressing, extrusion or another thermomechanical working process; and (d) subjecting the consolidated powder to subsequent thermomechanical processing, and thereby forming the mill product. The invention also relates to products made from such a process.

Grain growth inhibitors are added to niobium powder by blending inhibitors such as  $\text{SiO}_2$  and  $\text{Y}_2\text{O}_3$  prior to consolidation or as a residue of a de-oxidation process where magnesium is added to capture the oxygen

from the niobium powder and form magnesium oxide during the de-oxidation process.

The powder is consolidated either by hot isostatic pressing (HIPing), extrusion or other thermomechanical working. Such methods of consolidation are capable of providing suitable P/M sheet bars with a weight of up to several hundred pounds, e.g., five hundred pounds, one thousand pounds or more. Subsequent thermomechanical processing of the P/M sheet bar is applied similarly to then P/M derived refractory metals as to metals from ingot sources.

The present invention inhibits grain growth in niobium P/M sheets during high temperature exposure. A low oxygen niobium powder (< about 400 ppm, preferably < about 200 ppm) is needed as a starting material. Powders with a higher content in oxygen cannot be consolidated to full density and/or will not yield good mechanical properties.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a flow chart showing a process of the present invention to create stabilized grain size powder; and

Figs. 2-4 are flow charts showing examples of consolidating steps to create products made of stabilized grain size powder.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The invention relates to a process for making a metal mill product from a refractory metal powder comprising (a) providing a low oxygen refractory metal powder; (b) adding to the powder a grain growth inhibitor to the low oxygen refractory metal powder before consolidating the powder, (c) consolidating the powder by either hot isostatic pressing, extrusion or another thermomechanical working process; and (d) subjecting the consolidated powder to subsequent thermomechanical processing, and thereby forming the mill product. The invention also relates to products made from such a process.

The low oxygen niobium powder can be any powder, which when used in accordance to the invention, enables user to meet an object of the invention. The metal powders with stabilized grain size of the present

invention are preferably produced via the following procedure as discussed in U.S. Patent 6,261,337, incorporated herein in its entirety. Niobium alloys can also be used.

5 In other embodiments, instead of using niobium powders, powders made from a refractory metal selected from hafnium, molybdenum, niobium, rhenium, tantalum, tungsten, vanadium, and zirconium metals can be used. Also, alloys of these metals can also be used.

10 As illustrated in Fig. 1, low oxygen niobium and grain growth inhibitor powders (for example  $\text{SiO}_2$  or  $\text{Y}_2\text{O}_3$ ) are blended to form low oxygen powder with grain size inhibitors. Figs. 2-4 illustrate the consolidation steps with the master blend. The physical processes of blending and consolidating achieve a uniform distribution of grain growth inhibiting particles in the powder metal sheet bars. The powders are made by the process described in US 6,261,337 and as described  
15 herein.

These powders are blended to produce the desired alloy composition. The powders are then sealed in an evacuated can, heated to a desired temperature, and extruded such that the extrusion ratio is at least 8:1. This is done to completely consolidate the niobium powders and the  
20 included inhibitors. The can may be removed either just before or just after the rolling operation.

The above process can afford advantages of more stable grain size in the final material, more uniform material properties (such as ultimate tensile strength and hardness), lower manufacturing costs, better control  
25 of fiber size, and greater flexibility for alloy modifications and control of properties.

Niobium sheets produced from powder blends of niobium and grain inhibitors, for example silicon, were tested for grain growth, ultimate tensile strength, and hardness. The test results are presented in Table 1  
30 below.

Table 1

Silicon (ppm)	1065°C @90 min (ASTM)	1150°C @180 min (ASTM)	1300°C @180 min (ASTM)	Ultimate Tensile Strength (KSI)	Hardness (VICKERS)
0	9.5	9.5	7.5	49.3	114
150	9.5	9.0	8.0	50.3	117
300	9.5	9.5	8.5	49.5	125
Nb I/M	5.5	<1	<1	32	72

P/M sheet with grain growth inhibitors, preferably silicon, of 0, 150, and 300 ppm were thermomechanical processed to a thickness of 0.015 inches and annealed at 1065°C for 90 minutes to produce grain sizes of approximately ASTM 9.5. Niobium sheet produced from ingot metallurgy (I/M) a grain size of approximately ASTM 5.5 under the same anneal heat treat conditions. The P/M and I/M test samples were subjected to additional annealing heat treatments at 1150°C for 180 minutes and 1300 °C for 180 minutes. The P/M test samples yielded grain sizes greater than ASTM 7.0 compared to I/M test samples that yielded grain sizes coarser than ASTM 1.

Additionally, the higher P/M Ultimate Tensile Strength of 49.3 KSI, 50.3 KSI, and 49.5 KSI and hardness of 114 VHN, 117 VHN, and 125 VHN are significant improvements over typical I/M material of Ultimate Tensile Strength of 32 KSI and hardness of 72 VHN. The fine grain sizes and improved tensile strength and hardness after heat treatment of the P/M material is a significant advantage, compared to I/M material, in applications where large amounts of deformation are required during fabrication, such as deep drawn diamond cups, or capacitor cans.

Alternatively, the blended powders may be isostatically pressed into a bar prior to canning and extrusion, as illustrated in Fig. 2. The advan-

tage of this method would be to put a higher weight into the compact prior to extrusion to aid in consolidation and increase yield per extrusion.

Now returning to Fig. 1, niobium hydride powder is placed into a vacuum chamber, which also contains a metal having a higher affinity for oxygen, such as calcium or magnesium, preferably the latter. Preferably, the starting hydride powder has oxygen content less than about 1000 ppm. The chamber is heated to the dehydration temperature to remove the hydrogen, then heated to the deoxidation temperature to produce a powder of niobium or alloy of niobium having a target reduced oxygen content of less than about 400 ppm preferably below 200 ppm and more preferably below 100 ppm. The magnesium, containing the oxygen, is then removed from the metal powder by evaporation and subsequently by selective chemical leaching or dissolution of the powder.

For example, a niobium powder with less than 400 ppm oxygen can be produced by the deoxidization of niobium hydride under partial pressure of argon. Niobium hydride powder would be blended with 0.3 wt.-% magnesium and placed in a vacuum furnace retort, which is evacuated, and backfilled with argon. The pressure in the furnace would be set at about 100 microns with Argon flowing and the vacuum pump running.

The furnace temperature would be ramped to about 650°C in approximately 50°C increments, held until temperature equalized, then ramped up to 950°C in approximately 50°C increments. When the temperature equalized at 950°C it would be held for about two hours. After such hold, the furnace is shut down. Once the furnace cools its powder content is removed from the retort.

The magnesium, containing the oxygen, would then be removed from the metal powder by acid leaching to produce the resulting niobium powder having an oxygen content of less than 300 ppm.

As described above, in the process for producing formed powder metal products of niobium, the metal hydride powder is deoxidized to an oxygen content of less than about 400 ppm. The powder is consolidated to



form a niobium or alloy product, having an oxygen content below about about 400 ppm, or below about 300 ppm or below about 200 ppm or below about 100 ppm, but for many powder metallurgy purposes between about 100 ppm and 150 ppm. According to the present invention, a  
5 formed refractory metal product (niobium product), having a stabilized grain size, may be produced from metal hydride powder, as treated as described above, by any known powder metallurgy techniques.

Exemplary of these powder metallurgy techniques used for forming the products are the following, in which the steps are listed in order of  
10 performance. Any of the following single techniques or sequences of techniques may be utilized in the present invention: cold isostatic pressing, sintering, encapsulating, hot isostatic pressing and thermomechanical processing; cold isostatic pressing, sintering, hot isostatic pressing thermomechanical processing; cold isostatic pressing, encapsulating, hot  
15 isostatic pressing and thermomechanical processing; cold isostatic pressing, encapsulating and hot isostatic pressing; encapsulating and hot isostatic pressing; cold isostatic pressing, sintering, encapsulating, extruding and thermomechanical processing; cold isostatic pressing, sintering, extruding, and thermomechanical processing; cold isostatic  
20 pressing, sintering, and extruding; cold isostatic pressing, encapsulating, extruding and thermomechanical processing; cold isostatic pressing, encapsulating and extruding; encapsulating and extruding; mechanical pressing, sintering and extruding; cold isostatic pressing, sintering, encapsulating, forging and thermomechanical processing;  
25 cold isostatic pressing, encapsulating, forging and thermomechanical processing; cold isostatic pressing, encapsulating and forging; cold isostatic pressing, sintering, and forging; cold isostatic pressing, sintering and rolling; encapsulating and forging; encapsulating and rolling. cold isostatic pressing, sintering and thermomechanical processing;  
30 mechanical pressing and sintering; and mechanical pressing, sintering, repressing and resintering; other combinations of consolidating, heating and deforming may also be utilized.

The production of a formed niobium product having a stabilized grain size can be achieved by cold isostatic pressing of various kinds of known niobium powders to form a compact, followed by a hot isostatic pressing (HIPing) step to densify the compact and then thermomechanical processing of the powder compact for further densification and completion of the bonding, as illustrated in Fig. 3. Preferably, niobium powder with grain size inhibitors would be cold isostatically pressed at 60,000 pounds/sq. in. and room temperature, into a compact with rectangular or, preferably, round cross section, then hermetically encapsulated and hot isostatically pressed (HPed) at 40,000 lbs./sq. in. and 1300°C for four hours. The HPed compact would be unencapsulated and converted to sheet or foil by thermomechanical processing steps.

A similar process, as illustrated in Fig. 4, of just cold isostatic pressing, sintering and thermomechanical processing using niobium powder having an oxygen content of less than 300 ppm can be conducted by cold isostatically pressing at 60,000 lbs./sq. in. into a bar shape preform. This preform would be sintered at 1500°C for two hours in a vacuum of less than about 0.001 Torr to yield a preform having a density of about 95% theoretical density (Th) and less than 400 ppm oxygen. The sintered preform would be converted into sheet and foil by thermomechanical processing steps.

Production of a formed niobium sheet or foil having a stable grain size by hot extrusion and thermomechanical processing can be made, using niobium powder having an oxygen content of less than 400 ppm as the starting powder. This powder can be hermetically encapsulated then extruded through a rectangular or, preferably, round die at 1000°C to produce an extruded product having oxygen content of less than 400 ppm. The extruded product can be converted to sheet or foil by the thermomechanical processing.

Niobium sheet or foil with oxygen content of less than 400 ppm can be produced by cold isostatic pressing, hot extrusion and thermomechanical processing. This compact made by cold isostatically pressing could

be hermetically encapsulated then extruded at 1000°C to produce an extruded product with an oxygen content of about 300 ppm which can be converted into sheet and foil by thermomechanical processing steps.

5        Niobium products having stable grain size can be prepared by mechanical pressing, sintering, repressing and resintering.

      Niobium powder blend having oxygen content of less than 400 ppm can be utilized as the starting powder. It is placed in a die and mechanically pressed, using uniaxial pressure. The pressed tablet should be then sintered at 1500°C for two hours in a vacuum evacuated to less than  
10       about 0.001 Torr. The sintered tablet would then be repressed and resintered at 1500°C for two hours in a vacuum evacuated to less than about 0.001 Torr.

      The resintered tablet will have oxygen content of less than about 400 ppm and be suitable for thermomechanical processing to produce a  
15       formed niobium product.

      In one embodiment, a copper or steel container is filled with niobium powder, evacuated, hermetically sealed, and extruded through a die to give a 10:1 extrusion ratio. The copper container is removed by acid treatment and the extruded bar is thermo-mechanically processed into a  
20       sheet form flat. In another embodiment, a steel container is filled with the niobium powder, evacuated, hermetically sealed and HIPed. The steel container is removed by machining and the HIPed piece is thermo mechanically processed into a sheet form flat.

      Anneals may be used to improve workability of the material in  
25       between two deformation steps or to adjust grain size and texture through recrystallization although a final anneal may not be necessary. When the powder is canned during the consolidation (usually to protect it from the environment at high temperature), the can will bond to the niobium.

      In another embodiment, the process provides P/M sheets of large  
30       size (>100 pounds) having good mechanical properties and small stable grain size, capable of a higher yield than conventional P/M processes for sheet manufacture, typically 50 pounds or less. Low oxygen niobium

powder of less than 400 ppm, preferably less than 150 ppm, of non-spherical particles and sizing less than 250 microns FAPD (Fisher Average Particle Diameter), is provided per processes described herein. Powders with a higher content in oxygen cannot be consolidated to full density and/or will not yield good mechanical properties. The powder is consolidated to full density either by HIPing (hot isostatic pressing) or by extrusion. Both methods of consolidation are capable of providing suitable P/M sheet bars with a weight of up to several hundred pounds.

Thermomechanical processing of the P/M sheet bar is similar to standard processes.

Numerous variations and modifications may obviously be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention herein described are illustrative only and are not intended to limit the scope of the invention.

WHAT IS CLAIMED IS:

1. A process for making a metal mill product from a refractory metal powder comprising:
  - (a) providing a low oxygen refractory metal powder;
  - 5 (b) adding to the powder a grain growth inhibitor to the low oxygen refractory metal powder before consolidating the powder;
  - (c) consolidating the powder by either hot isostatic pressing; extrusion or another thermomechanical working process; and
  - (d) subjecting the consolidated powder to subsequent
  - 10 thermomechanical processing, and thereby forming the mill product.
2. The process of Claim 1, wherein the refractory metal is niobium or a niobium alloy.
3. The process of Claim 1, wherein the refractory metal is selected from the group consisting of hafnium, molybdenum, rhenium,
- 15 tantalum, tungsten, vanadium, and zirconium metals, alloys of the foregoing metals, and combinations thereof.
4. The process of Claim 1, wherein prior to consolidating the powder, the grain growth inhibitor is added to the powder by (i) blending an inhibitor component with the powder or (ii) a residue of a de-oxidation
- 20 process.
5. The process of Claim 4, wherein the residue is a residue formed in a de-oxidation process, wherein magnesium is added to capture the oxygen from the niobium powder and magnesium oxide forms during the de-oxidation process.
- 25 6. The process of Claim 4, wherein the inhibitor component is selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Y}_2\text{O}_3$ , and mixtures thereof.
7. The process of Claim 1, wherein the low oxygen niobium powder has an oxygen content that is less than about 400 ppm.
8. The process of Claim 1, wherein the low oxygen niobium
- 30 powder has an oxygen content that is less than about 300 ppm.
9. The process of Claim 1, wherein the low oxygen niobium powder has an oxygen content that is less than about 200 ppm.

10. The process of Claim 1, wherein the low oxygen niobium powder has an oxygen content ranging from about 100 ppm to about 150 ppm.
11. The process of Claim 1, wherein the low oxygen niobium powder has an oxygen content that is less than about 100 ppm.
12. The process of Claim 1, wherein the mill product is a sheet containing oxide particles.
13. The process of Claim 1, wherein the mill product is a foil.
14. The process of Claim 1, wherein the mill product is a sheet weighing at least 100 pounds.
15. A mill product comprising a stabilized grain size made from a process comprising:
- (a) providing a low oxygen refractory metal powder;
  - (b) adding to the powder, before consolidating the powder, a grain growth inhibitor to the low oxygen refractory metal powder,
  - (c) consolidating the powder by either hot isostatic pressing, extrusion or another thermomechanical working process; and
  - (d) subjecting the consolidated powder to subsequent thermomechanical processing, and thereby forming the mill product.
16. The process of Claim 15, wherein the refractory metal is niobium or a niobium alloy.
17. The mill product of Claim 15, wherein the refractory metal is selected from the group consisting of hafnium, molybdenum, rhenium, tantalum, tungsten, vanadium, and zirconium metals, alloys of the foregoing metals, and combinations thereof.
18. The mill product of Claim 15, wherein prior to consolidating the powder, the grain growth inhibitor is added to the powder by blending an inhibitor component or (ii) a residue of a de-oxidation process.
19. The mill product of Claim 15, wherein the residue is a residue formed in a de-oxidation process, wherein magnesium is added to capture the oxygen from the niobium powder and magnesium oxide forms during the de-oxidation process.

20. The mill product of Claim 18, wherein the inhibitor component is selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Y}_2\text{O}_3$ , and mixtures thereof.

21. The mill product of Claim 15, wherein the low oxygen  
5 niobium powder has an oxygen content that is less than about 400 ppm.

22. The mill product of Claim 15, wherein the low oxygen niobium powder has an oxygen content that is less than about 300 ppm.

23. The mill product of Claim 15, wherein the mill product is a sheet or a foil.

10 24. A process for making a metal mill product from a niobium powder comprising:

(a) providing a low oxygen niobium powder having an oxygen content that is less than about 400 ppm;

(b) adding to the powder a grain growth inhibitor to the low  
15 oxygen niobium powder before consolidating the powder by blending an inhibitor component or (ii) a residue of a de-oxidation process, wherein the residue is a residue formed in a de-oxidation process, wherein magnesium is added to capture the oxygen from the niobium powder and magnesium oxide forms during the de-oxidation process,

20 (c) consolidating the powder by either hot isostatic pressing, extrusion or another thermomechanical working process; and

(d) subjecting the consolidated powder to subsequent thermomechanical processing, and thereby forming the mill product.

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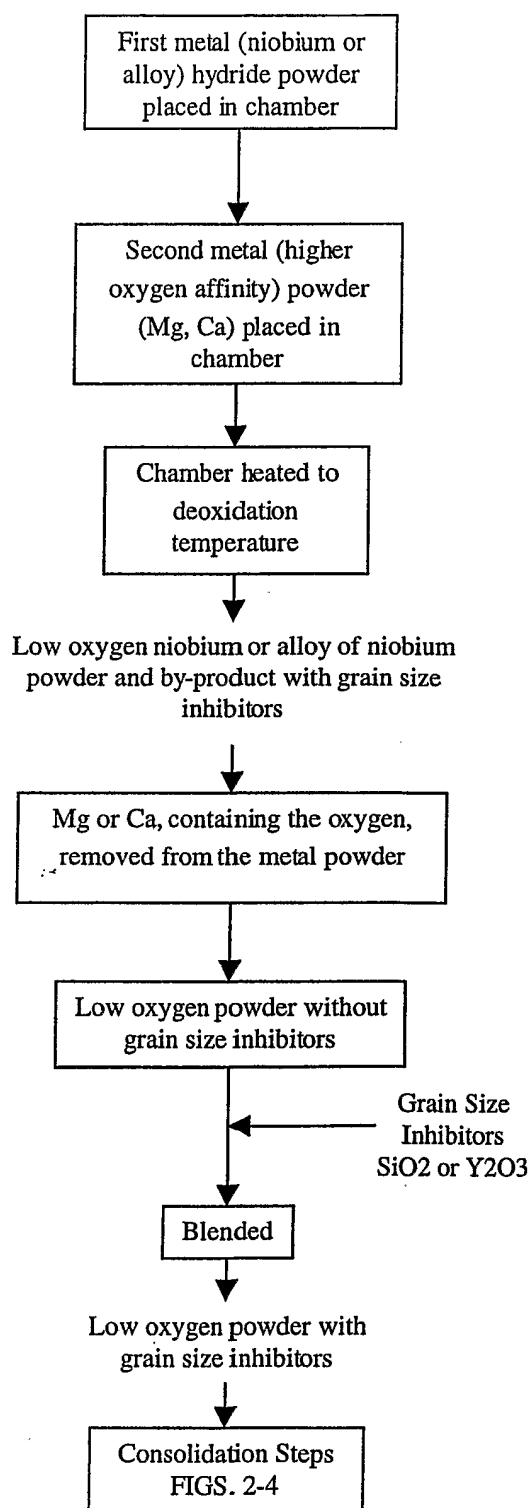


FIG. 1



Low oxygen powder with  
grain size inhibitors

FIG 1

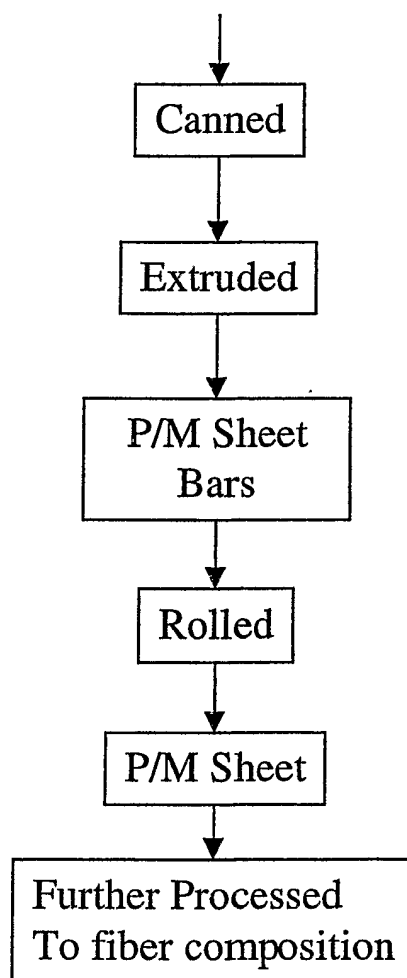


FIG. 2

Low oxygen powder with  
grain size inhibitors

FIG 1

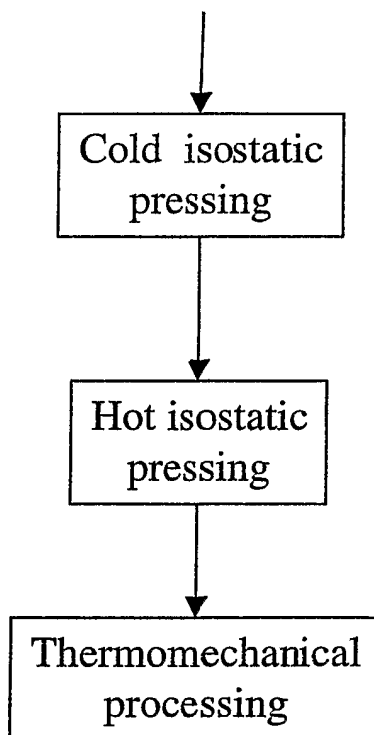


FIG. 3

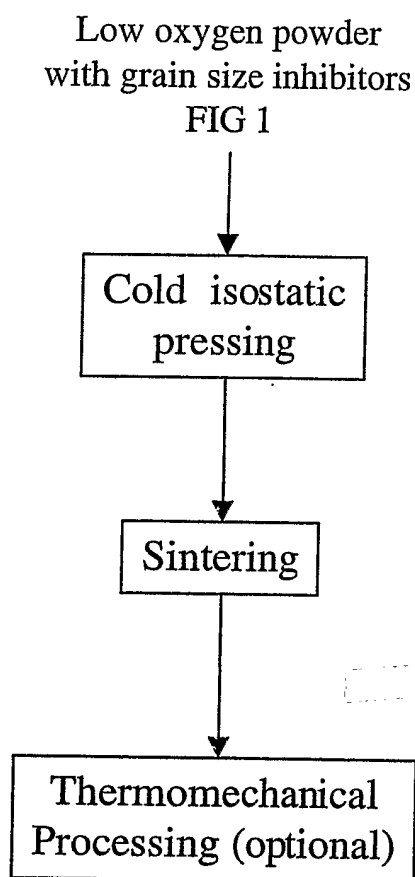


FIG. 4