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Kogut et al.

(54) ATTRITED TITANIUM POWDER

(76) Inventors: **Dariusz Kogut**, Tinley Park, IL (US); **Lance Jacobsen**, Minooka, IL (US); **William Ernst**, Frankfurt, IL (US); **Donn Armstrong**, Waukesha, WI (US)

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(60) Provisional application No. 60/814,362, filed on Jun. 16, 2006.

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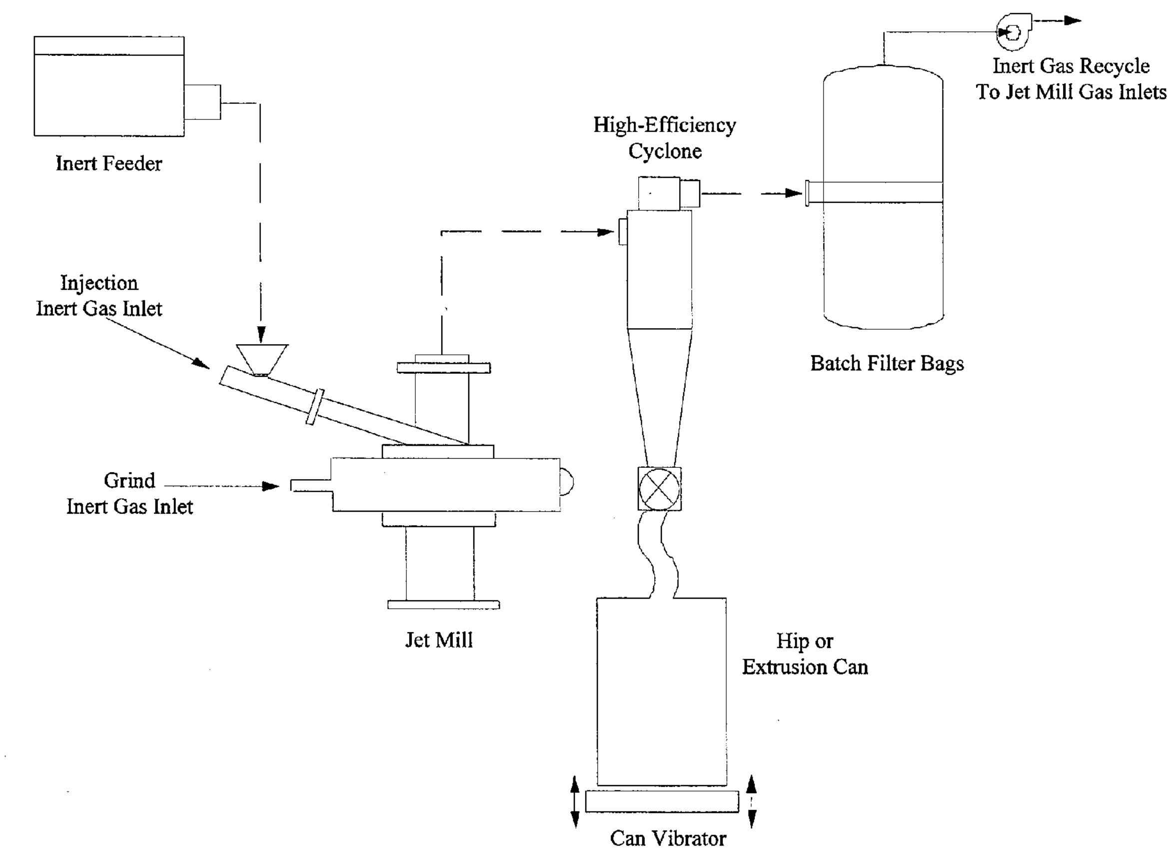
(57) **ABSTRACT**

A method of increasing the apparent density of agglomerated ligmental titanium or titanium alloy powder produced by the subsurface reduction of titanium tetrachloride vapor or a mixture of titanium tetrachloride and other halide vapors in a flowing stream of alkali or alkaline earth metal or mixtures thereof having a first apparent density after distillation is disclosed. The agglomerated ligmental titanium or titanium alloy powder is introduced into an attriting system wherein the agglomerated ligmental titanium or titanium alloy powder is attrited until the powder becomes more spherical than ligmental and the first apparent density is increased by a factor of from about 3 to about 8. Inert atmosphere may be used to prevent unwanted oxygen contamination.



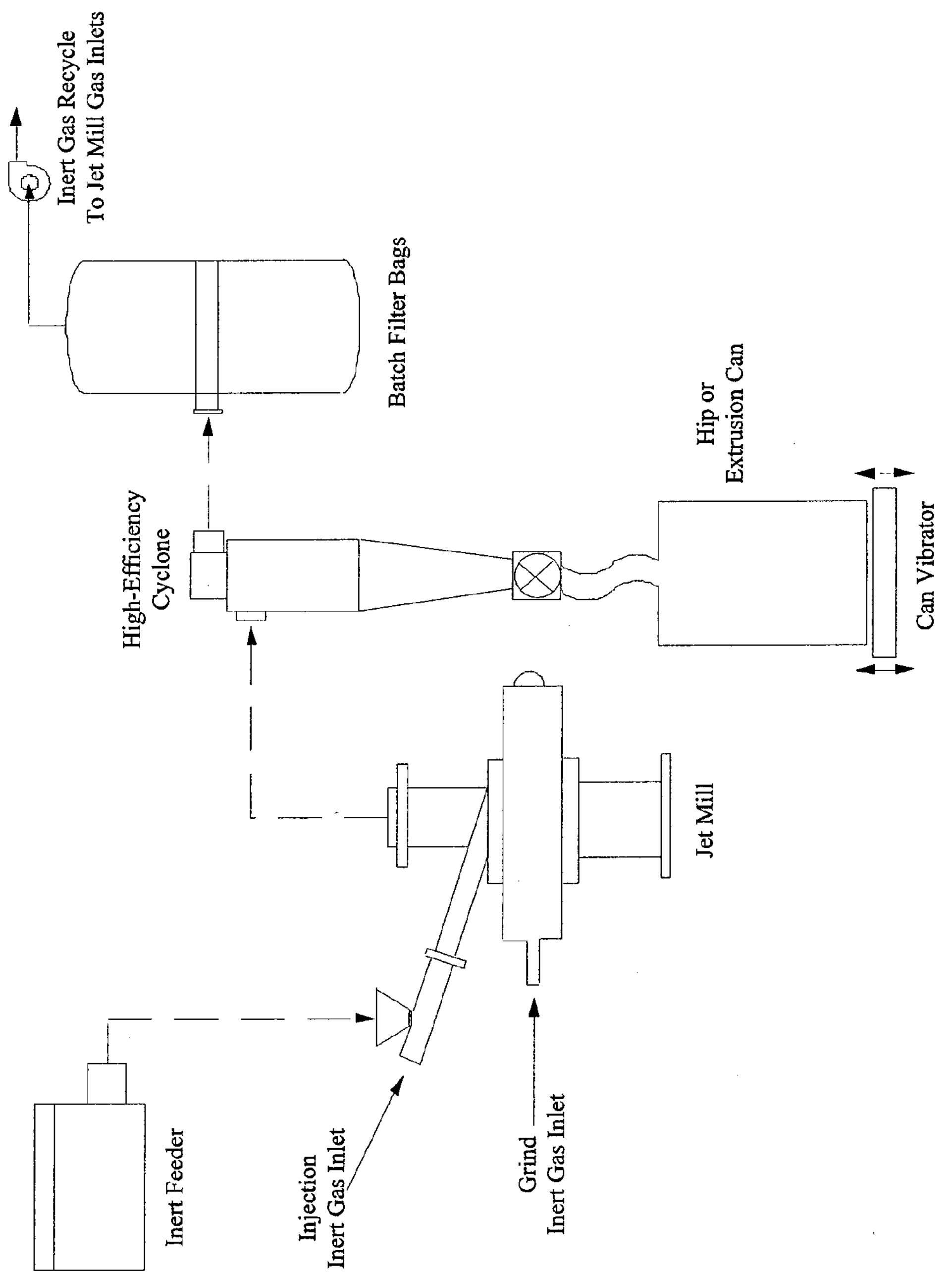

Inert Gas Recycle
To Jet Mill Gas Inlets
Batch Filter Bags
High-Efficiency
Cyclone
Hip or
Extrusion Can
Can Vibrator
Jet Mill
Inert Feeder
Injection
Inert Gas Inlet
Grind
Inert Gas Inlet

FIG. 1

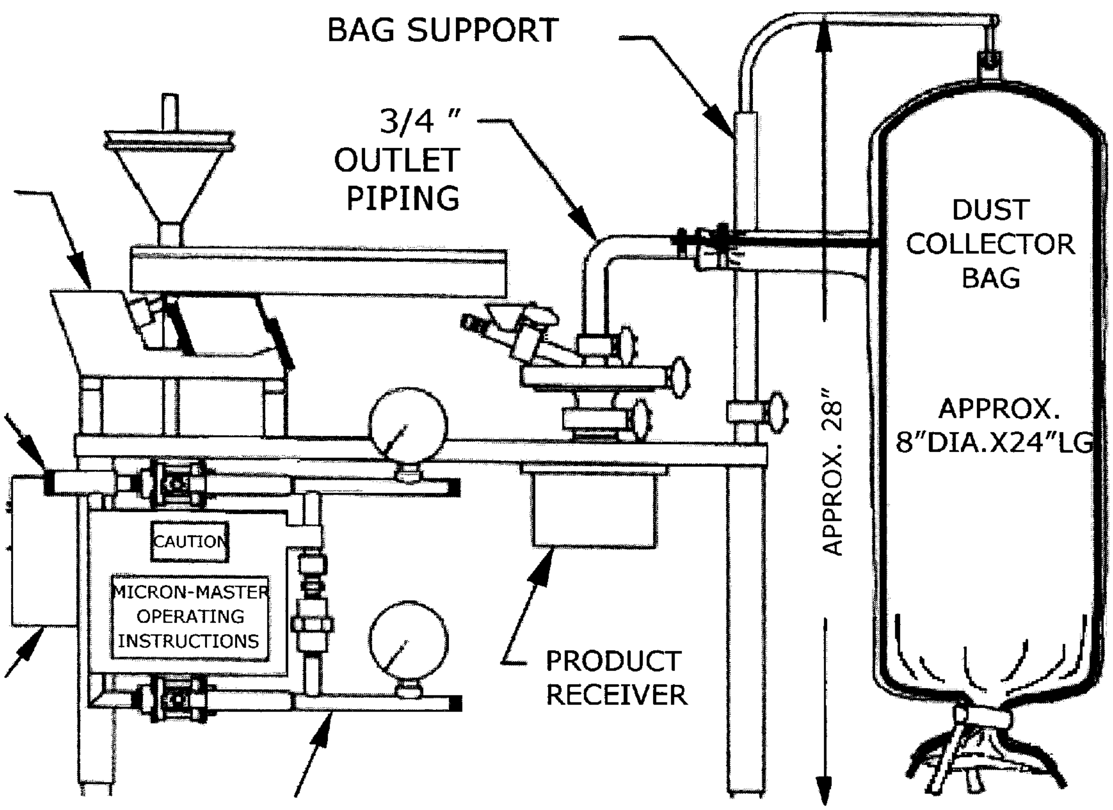

BAG SUPPORT
3/4 "
OUTLET
PIPING
DUST
COLLECTOR
BAG
APPROX.
8"DIA.X24"LG
APPROX. 28"
CAUTION
MICRON-MASTER
OPERATING
INSTRUCTIONS
PRODUCT
RECEIVER

FIG. 2

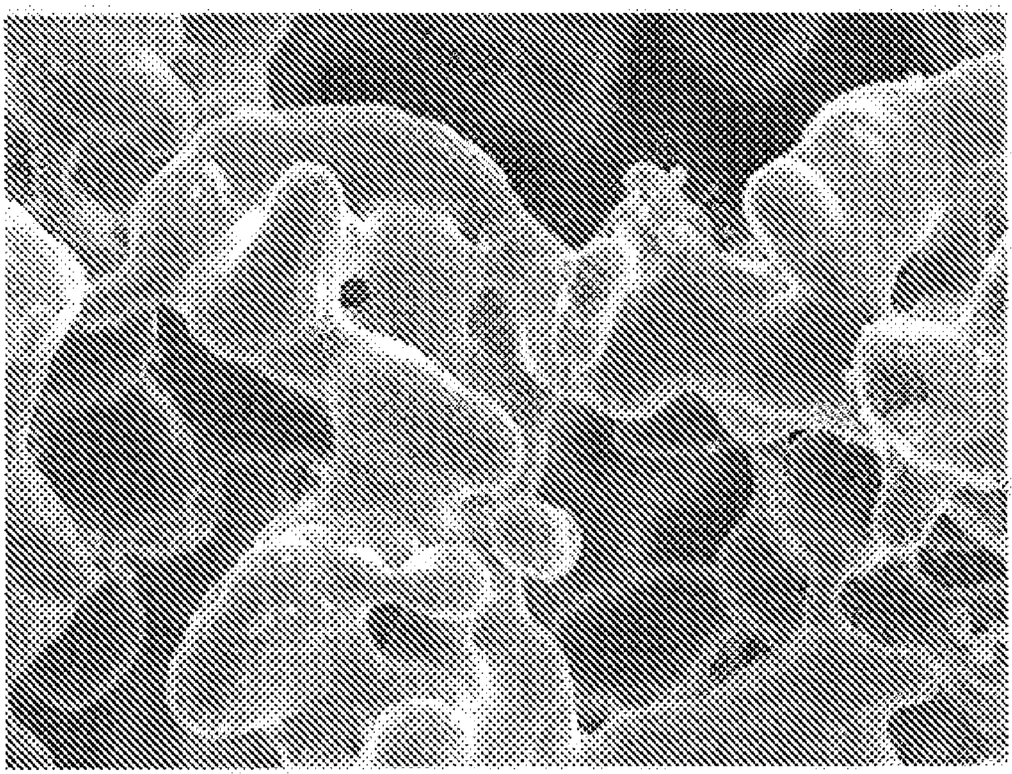


FIG. 3

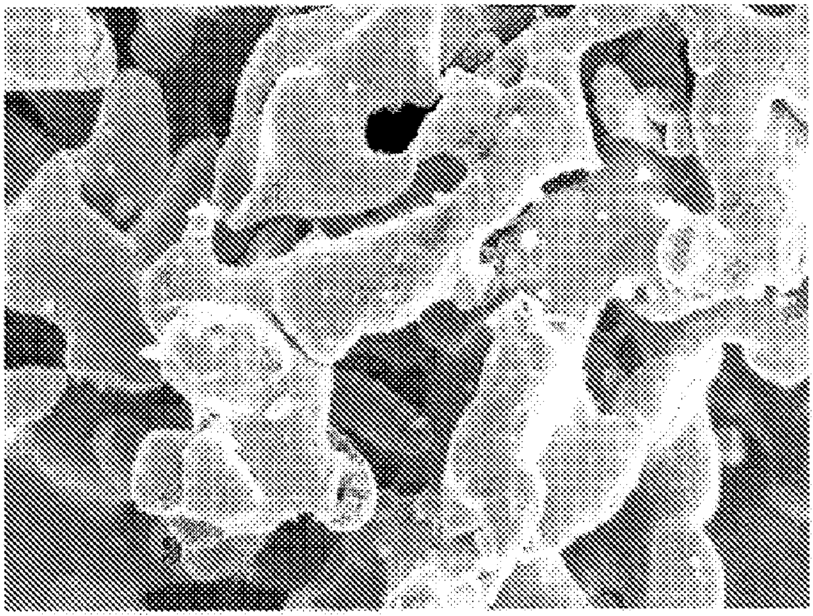


FIG. 4(a)

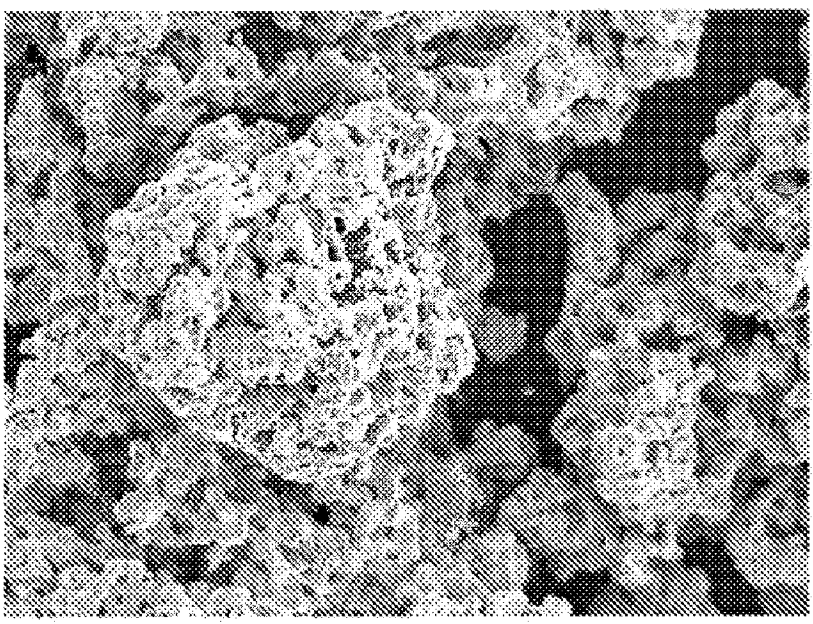


FIG. 4(b)

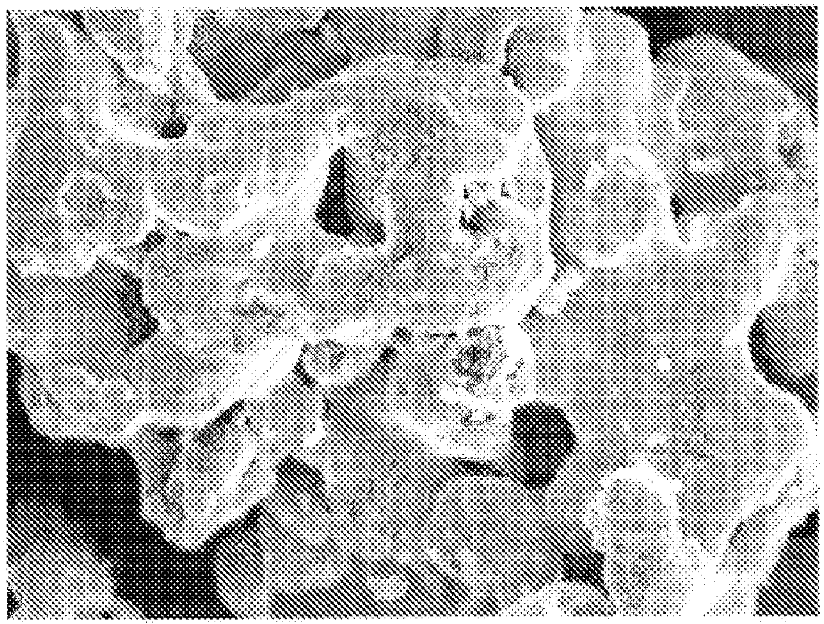


FIG. 5(a)

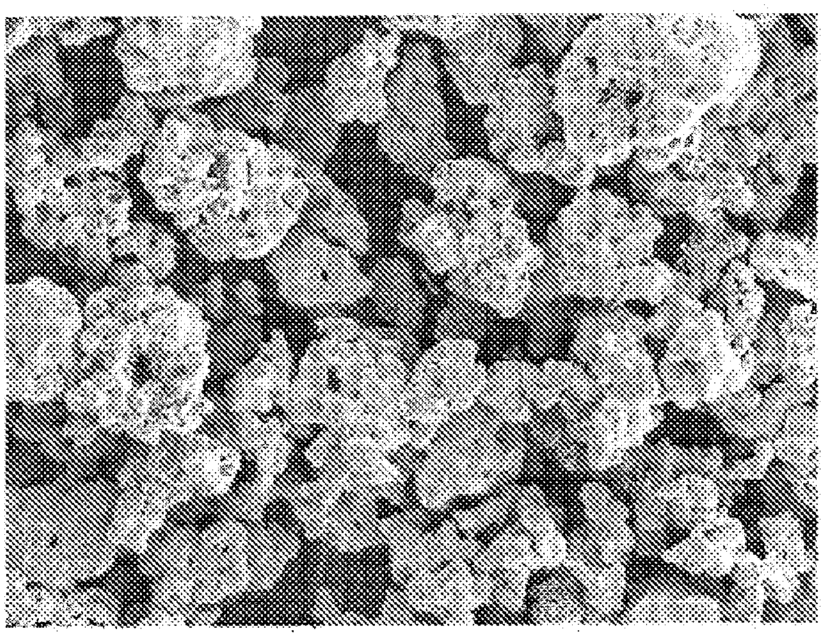


FIG. 5(b)

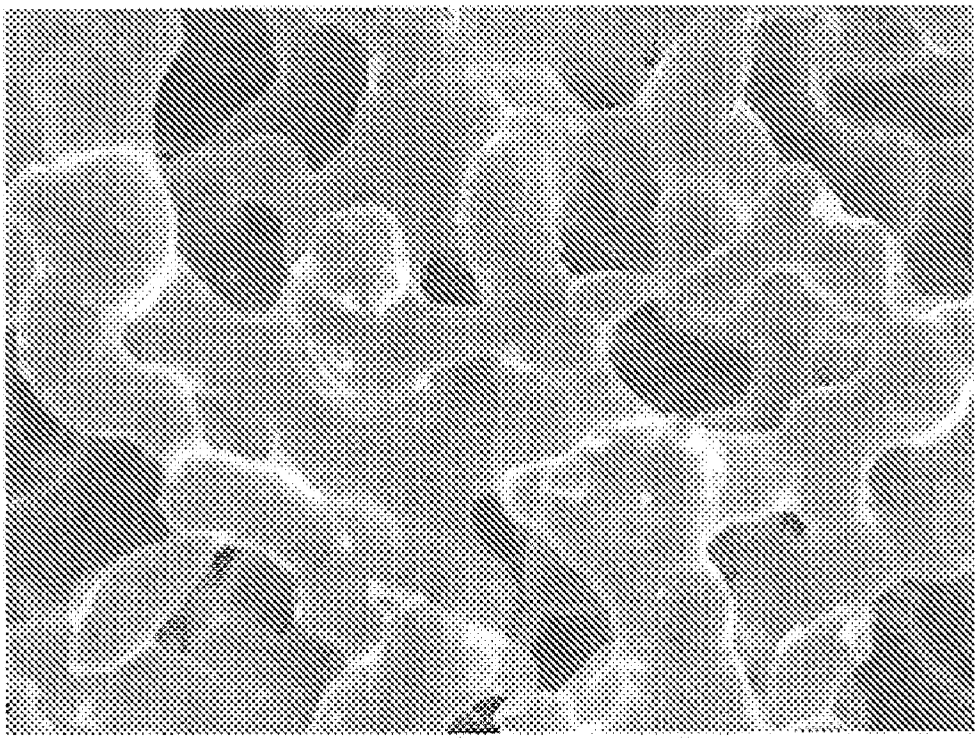


FIG. 6

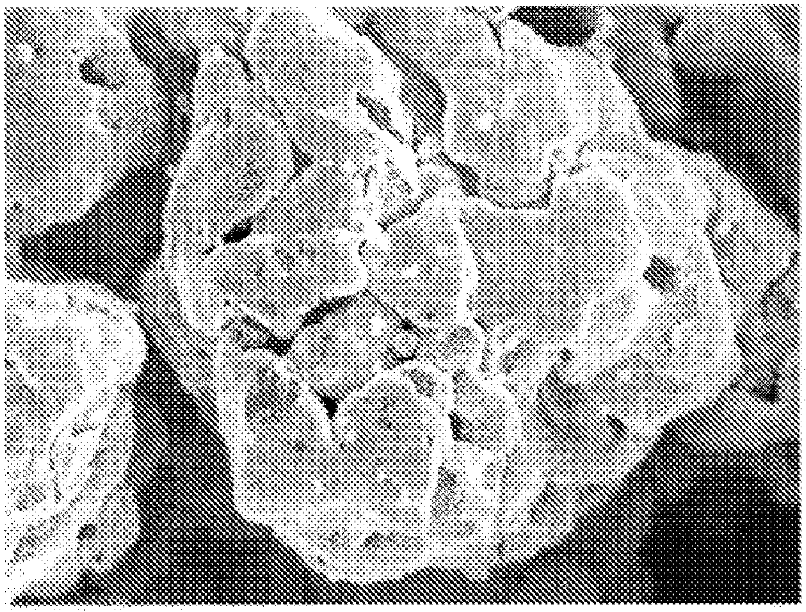


FIG. 7(a)

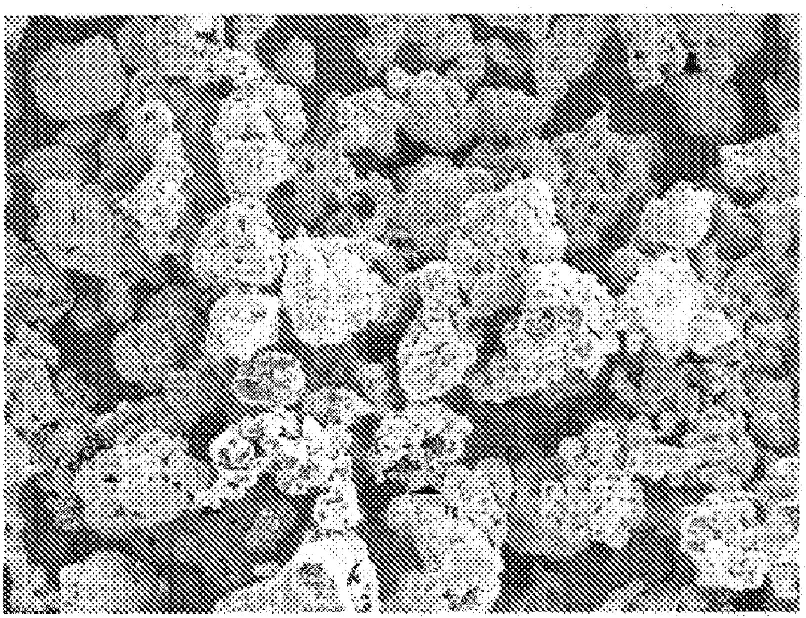


FIG. 7(b)

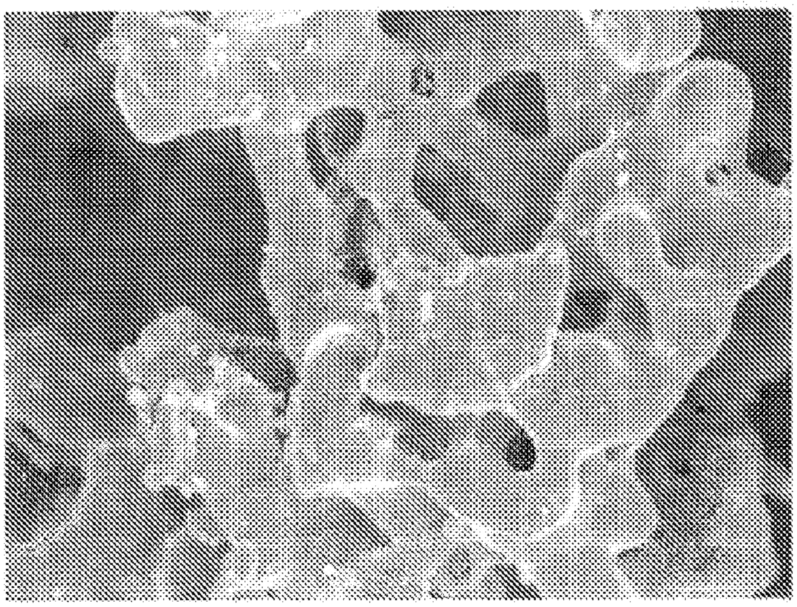


FIG. 8(a)

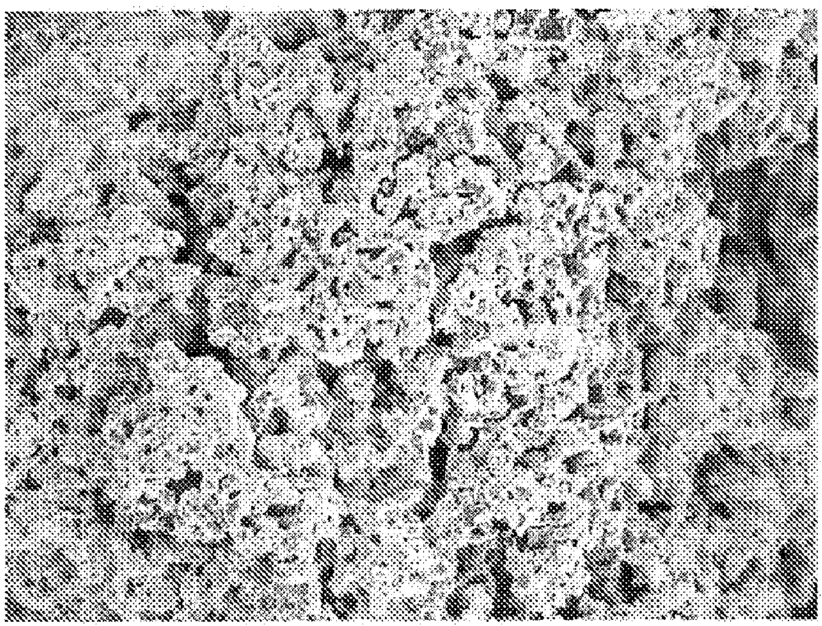


FIG. 8(b)

ATTRITED TITANIUM POWDER

RELATED APPLICATIONS

[0001] This application is a continuation of U.S. Ser. No. 11/820,107 filed Jun. 18, 2007, which claims priority to U.S. Provisional Application Ser. No. 60/814,362 filed Jun. 16, 2006, the entire disclosures of both applications are hereby expressly incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention relates to a process whereby titanium and titanium alloy powders produced by the Armstrong process are inertly attrited to increase the apparent density, tap density and packing fraction while maintaining the powder chemistry for further processing to obtain high quality consolidated material.

BACKGROUND OF THE INVENTION

[0003] The powder of the invention is produced by the Armstrong Process as previously disclosed in U.S. Pat. Nos. 5,779,761, 5,958,106 and 6,409,797, the entire disclosures of which are herein incorporated by reference.

[0004] Production of titanium powder by the Armstrong Process inherently produces agglomerated ligmental powder in which the average diameter of individual particles is less than five microns with a packing fraction in the range of from about 4% to about 11%. Tap density is defined as the mass of a material that, upon packing in a precisely specified manner, fills a container to a specified volume, divided by the container volume. Apparent density is defined as the weight per unit volume of a metal powder, in contrast to the weight per unit volume of the individual particles. Packing fraction percentage is the tap density divided by the theoretical density and multiplied by 100.

[0005] Many projected powder metallurgy uses of titanium and titanium alloy powders require a apparent density or packing fraction higher than the powder typically produced by the Armstrong Process. Increasing the apparent density or packing fraction of the powders produced by the Armstrong Process without significantly increasing oxygen concentration is important to future commercial success in the powder metallurgy field. Powder metallurgy processes include consolidation, molding and also several direct powder to mill shape processes such as powder extrusion and powder roll compaction.

SUMMARY OF THE INVENTION

[0006] Accordingly, a principal object of the present invention is to provide a titanium or titanium alloy powder having apparent densities and packing fractions greater than powder produced by the subsurface reduction of titanium tetrachloride vapor or mixtures of halide vapors in a flowing stream of alkali or alkaline earth metal or mixtures thereof.

[0007] Another object of the present invention is to provide powder with increased apparent density or packing fraction without significantly increasing the oxygen concentration or other contamination above as-produced powder.

[0008] Yet another objection of the present invention is to provide a method of increasing the apparent density of agglomerated ligmental titanium or titanium alloy powder produced by the subsurface reduction of titanium tetrachloride vapor or a mixture of titanium tetrachloride and other halide vapors in a flowing stream of alkali or alkaline earth metal or mixtures thereof having a first apparent density after distillation, comprising introducing the agglomerated ligmental titanium or titanium alloy powder into an attriting system, attriting the agglomerated ligmental titanium or titanium alloy powder until the powder becomes more spherical than ligmental and the first apparent density is increased by a factor of from about 3 to about 8.

[0009] Still another object of the present invention is to provide a method of increasing the apparent density of agglomerated ligmental titanium or titanium alloy powder produced by the subsurface reduction of titanium tetrachloride vapor or a mixture of titanium tetrachloride and other halide vapors in a flowing stream of sodium or alkaline earth metal or mixtures thereof having a first apparent density after distillation, comprising introducing the agglomerated ligmental titanium or titanium alloy powder into an attriting system, attriting the agglomerated ligmental titanium or titanium alloy powder in an inert atmosphere until the powder becomes more spherical than ligmental and the first apparent density is increased by a factor of from about 3 to about 8.

[0010] A final object of the present invention is to provide a method of increasing the apparent density of agglomerated ligmental titanium or titanium alloy powder produced by the subsurface reduction of titanium tetrachloride vapor or a mixture of titanium tetrachloride and other chloride vapors in a flowing stream of sodium or alkaline earth metal or mixtures thereof having a first apparent density after distillation, comprising introducing the agglomerated ligmental titanium or titanium alloy powder into an attriting system including a jet mill, attriting the agglomerated ligmental titanium or titanium alloy powder in an inert atmosphere in the jet mill until the powder becomes more spherical than ligmental and the first apparent density is increased by a factor of from about 3 to about 8.

[0011] The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWING

[0012] For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawing a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

[0013] FIG. **1** is a schematic of an attriting system for inertly attriting titanium and/or titanium alloy powder in a jet mill for subsequent consolidation and processing;

[0014] FIG. **2** is another schematic of an attriting system utilizing a jet mill;

[0015] FIG. **3** is an SEM of agglomerated ligmental titanium powder with an as produced apparent density of 0.27 g/cc;

[0016] FIGS. **4**(*a*) and **4**(*b*) are SEMs of agglomerated ligmental titanium powder after milling with an apparent density of 1.13 g/cc;

[0017] FIGS. **5**(*a*) and **5**(*b*) are SEMs of agglomerated ligmental titanium powder after milling with an apparent density of 0.82 g/cc;

[0018] FIG. **6** is an SEM of agglomerated ligmental titanium powder with an as produced apparent density of 0.26 g/cc;

[0019] FIGS. **7**(*a*)-(*b*) are SEMs of agglomerated ligmental titanium powder after milling with an apparent density of 1.12 g/cc; and

[0020] FIG. **8**(*a*)-(*b*) are SEMs of agglomerated ligmental titanium powder after milling with an apparent density of 0.68 g/cc.

DETAILED DESCRIPTION OF THE INVENTION

[0021] Referring to FIGS. **1** and **2**, an attriting system for titanium or titanium alloy powder is disclosed with powder being placed in an inert feeder containing an inert gas atmosphere. The powder is fed into a jet mill that uses an inert gas to provide the milling action where it is attrited by impact between powder particles. Attrited powder is carried out of the mill to a classifier by an inert gas stream. The classifier removes the desired, densified powder from the gas stream, and possibly, recycles the entrained fines to the jet mill. The densified powder may then pass directly to another process or container without ever making contact with oxygen that could increase the oxygen content of the powder. For example, the powder could be placed into an inerted container that could either be used directly in another process such as extrusion or roll compaction or be used to transport the powder to another process.

[0022] A variety of different mechanisms may be used to attritte powder such as but not limited to a ball mill, a jet mill, a high pressure water mill, a mechanco-fusion mill or a hammer mill all of which are included in the invention. A jet mill is illustrated in FIGS. **1** and **2** is preferred and should be inerted to prevent undesirable oxygen pick-up. Any noble gas or nitrogen may be used, with nitrogen being preferred. Although various ASTM grades of Ti or its alloys may be used in this invention, CP (grade 2) Ti and (grade 5) 6:4 alloy are the most commonly used.

[0023] The milling of the titanium powder was done on two different Micron-Master jet mills, which are manufactured by the Jet Pulverizer Company. The powder was fed into the mill through a rotating screw conveyor. From that conveyor, the powder flowed into the mill. The compressed nitrogen entered the mill through two nuzzles and the two streams met together in the main chamber of the mill, where the actual milling takes place, as seen in FIGS. **1** and **2**.

[0024] Three different batches of titanium powder were used to perform the attrition study. Batch R**20**.**13**, R**20**.**14**, and R**20**.**15** was milled on an 8 inch mill to develop the appropriate jet milling parameters for the desired apparent density. Those parameters were subsequently used to scale up to an 12" but a 24" jet mill or larger could be employed. Table 1 summarizes the results from an 8" mill test. Pre-sieving of the titanium powder was necessary in order to feed the powder into an 8" mill, which can be eliminated by using a larger mill.

TABLE 1

Parameters for an 8" mill

8" mill			
Sample ID	Sample Size lb	Feed rate lb/hr	Pressure psi
R20.13	5.1	50	93
R20.14	5.2	50	70
R20.15	4.0	50	40

[0025] The feed rates and pressures determined from jet milling the powder on an 8" mill were used to directly feed batch R**19**.**28**, R**19**.**29**, R**22**.**23**, and R**22**.**24** into a 12" mill. The parameters used for a 12" mill are shown in Table 2.

TABLE 2

Parameters for a 12" mill

12" mill			
Sample ID	Sample Size lb	Feed rate lb/hr	Pressure psi
R19.28	7.1	110	93
R19.29	12.5	110	30
R22.23	11.0	110	93
R22.24	10.8	110	30

[0026] The attrition study concentrated on improving the apparent density of the Armstrong Process powder while minimizing the subsequent oxygen pick up resulting from the jet milling process. The purpose for improving the powder density was to make Armstrong powder more amenable to standard powder metallurgy practices. Typically, densities greater than 20% are desired. Based on previous small scale milling experience with Armstrong powder, ITP selected an opposed jet mill as the means to accomplish the attrition. Summary of results for the attrition study is shown in Table 3.

TABLE 3

Results of the attrition study

	Density				Particle Size Analysis			Chemical Analysis		
	Apparent		Tap		Mean	d50	d90	O_2	N_2	H_2
Sample ID	g/cc	%	g/cc	%	um	um	um	%	%	%
R20.12	0.26	5.73	0.29	6.39	Raw powder (not milled)			0.234	0.021	0.0032
R20.13	1.05	23.13	1.39	30.53	133.5	63.43	327.1	0.297	0.039	0.0025

TABLE 3-continued

Results of the attrition study											
	Density				Particle Size Analysis			Chemical Analysis		
	Apparent		Tap		Mean	d50	d90	O_2	N_2	H_2
Sample ID	g/cc	%	g/cc	%	um	um	um	%	%	%
R20.14	0.95	20.93	1.25	27.62	139.1	60.88	383.9	0.361	0.05	0.0029
R20.15	0.68	14.98	0.90	19.77	222.4	162.5	525.2	0.295	0.057	0.003
R19.27	0.27	5.95	0.29	6.39	Raw powder (not milled)			0.175	0.003	0.0032
R19.28	1.13	24.89	1.49	32.85	91.26	46.06	176.6	0.275	0.009	0.0038
R19.29	0.82	18.06	1.08	23.84	187.8	102	386.2	0.238	0.01	0.0032
R22.21	0.26	5.73	0.30	6.61	Raw powder (not milled)			0.143	0.009	0.0018
R22.23	1.12	24.67	1.48	32.56	113.5	50.58	259	0.331	0.021	0.0045
R22.24	0.68	14.98	0.90	19.77	240.5	200.4	473.1	0.256	0.009	0.0038

[0027] Scotts biometric density meter was used to determine the attrited batch sample's apparent densities and all samples showed considerable improvement. The apparent densities ranged from approximately 6% for raw powder to 25% for milled powder. The particle size analysis was preformed using Coulter LS 230 and showed as expected a decrease in particle size as the apparent density increased across all samples. Inert gas fusion method was used to conduct the chemical analysis for oxygen, nitrogen, and hydrogen. The results showed an increase in oxygen level with dissimilar amounts for different samples. The large increase in oxygen could have resulted from not having a closed system during the milling process. Therefore, to optimize the milling process an inert feeding chamber and completing closed mill might minimize the oxygen increase. The hydrogen level was virtually unchanged during the milling process. Nitrogen level for the powder samples after attrition did increase to some extent, but not enough to cause any problems in further processing of the powder. Scanning Electron Microscope (SEM) was used to evaluate the influence of jet milling on titanium powder particles. SEM's of batch samples R**19** and R**22** are shown in FIGS. **3**, **4**(*a*)(*b*), **5**(*a*)-(*b*), **6**, **7**(*a*)-(*b*) and **8**(*a*)-(*b*). The SEM's showed agglomerated ligmental that as the apparent density increased, the particles became more spherical in shape, which improved the apparent and tap densities.

TABLE 4

JET PULVERIZER ATTRITION RESULTS							
4 inch mill	Feed rate (PPH)	Prssure (psi)	d50/d100 (MICRON)	PF (%)	O2	tap density (g/cc)	apparent density (g/cc)
R7U3.10A	25	65	223/2000	20	0.329	0.908	0.69008
R7U3.10B	8	120	25/1143	37	0.516	1.6798	1.276648
R7U3.10C	5	120	18.5/282	45	0.666	2.043	1.55268
R7U3.10E	20	110	45/2000		0.384		
R7U3.10D	STARTING POWDER			5	0.296	0.227	0.19976
4 inch mill	Feed rate (PPH)	Prssure (psi)	d50/d90 (MICRON)	PF (%)	O2	tap density (g/cc)	apparent density (g/cc)
R6U2.15B	STARTING POWDER				0.2		
R6U2.15B	20	110	39/92	25	0.37	1.135	0.8626
R12U3.3	STARTING POWDER				0.266		
R12U3.3	20	110	48/155	27	0.39	1.2258	0.931608
R7U3.10D	STARTING POWDER				0.3		
R7U3.10D	5	130	21/75	40	0.6	1.816	1.38016
8 inch mill	Feed rate (PPH)	Prssure (psi)	d50/d90 (MICRON)	PF (%)	O2	tap density (g/cc)	apparent density (g/cc)
R15U2.06, R15U2.07	STARTING POWDER				0.22		
R15U2.06, R15U2.07	8	100	17.52/28.71	42	0.487	1.9068	1.449168
R15U3.10, R15U3.11	STARTING POWDER				0.11		
R15U3.10, R15U3.11	7	110	20.65/33.08	41	0.395	1.8614	1.414664
R15U3.13	STARTING POWDER				0.19		
R15U3.13	8	110	17/27	45	0.496	2.043	1.55268

[0028] Table 4 shows additional results using 4 and 8 inch mills such as illustrated in FIGS. **1** and **2**. Here, the results showed that apparent densities increased from about 3 to about 8 times without significantly increasing the oxygen content of the agglomerated ligmental titanium powder produced by the Armstrong Process set forth in the incorporated patents and illustrated in the SEMs of FIGS. **3** and **6**. FIGS. **4**(*a*)-(*b*), **5**(*a*)-(*b*), **7**(*a*)-(*b*) and **8**(*a*)-(*b*) are SEMs of powder milled and reported in Tables 1-3. Table 4 reports results of powders like FIGS. **3** and **6** milled as previously described herein.

[0029] For certain powder metallurgy, tap densities between about 20% to about 30% are preferred, but as illustrated in Tables 1-4, packing fractions of as produced powders (inherently in the range of from about 4% to about 11%) may be increased to at least 45%, see particularly Table 4. The jet mills were operated at various feed rates in pounds per hour (lb./hr) and at various pressures in pounds per square inch (psi). Pressure as low as 30 psi (Table 1) or up to 130 psi (Table 4) have been used and feed rates from 5 to 110 lbs/hr. have been used (Tables 1 and 4). Pressures and feed rates affect the increase in apparent density, tap density and packing fraction.

[0030] While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

What is claimed is:

1. A method of increasing the apparent density of agglomerated ligmental titanium or titanium alloy powder produced by the subsurface reduction of titanium tetrachloride vapor or a mixture of titanium tetrachloride and other halide vapors in a flowing stream of alkali or alkaline earth metal or mixtures thereof having a first apparent density after distillation, comprising:

introducing the agglomerated ligmental titanium or titanium alloy powder into an attriting system,

attriting the agglomerated ligmental titanium or titanium alloy powder until the powder becomes more spherical than ligmental and the first apparent density is increased by a factor of from about 3 to about 8.

2. The method of claim **1**, wherein the attriting is performed in an inert atmosphere.

3. The method of claim **2**, wherein the inert atmosphere includes argon.

4. The method of claim **2**, wherein the inert atmosphere includes nitrogen.

5. The method of claim **1**, wherein the attriting system includes at least one of a ball mill, a jet mill, a high pressure water mill, a mechanco-fusion mill or a hammer mill.

6. The method of claim **1**, wherein the titanium or titanium alloy powder having a first apparent density has a first packing fraction in the range of from about 4% to about 11% and after attrition has a packing fraction in the range of from about 20% to about 45%.

7. The method of claim **6**, wherein the packing fraction after attrition is in the range of from about 20% to about 30%.

8. A titanium or titanium alloy powder made according to the method of claim **1**.

9. A titanium or titanium alloy powder made according to the method of claim **7**.

10. A method of increasing the apparent density of agglomerated ligmental titanium or titanium alloy powder produced by the subsurface reduction of titanium tetrachloride vapor or a mixture of titanium tetrachloride and other halide vapors in a flowing stream of sodium or alkaline earth metal or mixtures thereof having a first apparent density after distillation, comprising

introducing the agglomerated ligmental titanium or titanium alloy powder into an attriting system,

attriting the agglomerated ligmental titanium or titanium alloy powder in an inert atmosphere until the powder becomes more spherical than ligmental and the first apparent density is increased by a factor of from about 3 to about 8.

11. The method of claim **10**, wherein the inert atmosphere includes a noble gas and/or nitrogen.

12. The method of claim **10**, wherein the inert atmosphere is nitrogen.

13. The method of claim **10**, wherein the titanium alloy is substantially 6% Al and 4% V by weight with the balance titanium.

14. The method of claim **10**, wherein the attriting system includes at least one of a ball mill, a jet mill, a high pressure water mill, a mechanco-fusion mill or a hammer mill.

15. A titanium or titanium alloy powder made according to the method of claim **10**.

16. A titanium or titanium alloy powder made according to the method of claim **14**.

17. A titanium alloy made according to the method of claim **13**.

18. A method of increasing the apparent density of agglomerated ligmental titanium or titanium alloy powder produced by the subsurface reduction of titanium tetrachloride vapor or a mixture of titanium tetrachloride and other chloride vapors in a flowing stream of sodium or alkaline earth metal or mixtures thereof having a first apparent density after distillation, comprising

introducing the agglomerated ligmental titanium or titanium alloy powder into an attriting system including a jet mill,

attriting the agglomerated ligmental titanium or titanium alloy powder in an inert atmosphere in the jet mill until the powder becomes more spherical than ligmental and the first apparent density is increased by a factor of from about 3 to about 8.

19. The method of claim **18**, wherein the jet mill is operated at a pressure of at least 70 psi.

20. The method of claim **18**, wherein the jet mill is operated at a pressure of at least 90 psi.

* * * * *