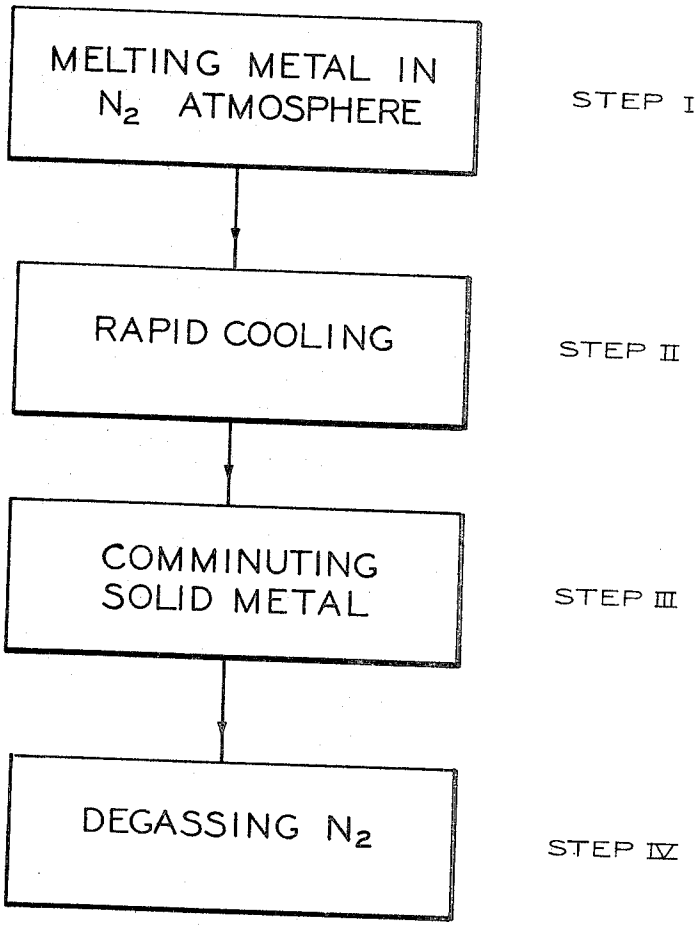
May 9, 1967 E. L. FOSTER, JR., ETAL 3,318,683

REFRACTORY METAL POWDERS

Filed July 27, 1964



INVENTORS
ELLIS L. FOSTER JR. &
WALTER J. HILDEBRAND
BY Gray, Mase & Dunson
ATTORNEYS

United States Patent Office

3,318,683

Patented May 9, 1967

3,318,683

REFRACTORY METAL POWDERS

Ellis L. Foster, Jr., Powell, and Walter J. Hildebrand, Columbus, Ohio, assignors, by mesne assignments, to Battelle Development Corporation, Columbus, Ohio, a corporation of Delaware

Filed July 27, 1964, Ser. No. 385,301
12 Claims. (Cl. 75—0.5)

This invention relates to a process for the preparation of metallic powders and, in particular, to preparing powders of the refractory metals, W (tungsten), Mo (molybdenum), and Re (rhenium) and their alloys. (The standard recognized chemical symbols of the refractory metals and their alloys will be used throughout in place of the fully spelled metals or alloys).

A common characteristic of these refractory metals and their alloys is that they do not form stable combinations with nitrogen at high temperatures (1000° C. or higher), but do have solubility for nitrogen that increases with temperatures over 1000° C. The particular metals mentioned (W, Mo and Re) and their alloys may exhibit considerable ductility at room temperature. Because of this ductility, it is difficult to prepare suitable feed for grinding mills.

The alloys of the refractory metals W, Mo, and Re included by this invention are listed below. This invention includes all the alloy combinations within the composition limits designated below.

All molybdenum alloys with:

W, all compositions	Pt, up to 10 w/o
Re, all compositions	Ir, up to 25 w/o
Os, up to 15 w/o *	Pd, up to 10 w/o
Rh, up to 10 w/o	

*w/o=weight percent

All tungsten alloys with:

Mo, all compositions	Pt, up to 10 w/o
Re, all compositions	Ir, up to 25 w/o
Os, up to 15 w/o *	Pd, up to 10 w/o
Rh, up to 10 w/o	

*w/o=weight percent

All rhenium alloys with:	Rh, up to 10 w/o
W, all compositions	Pt, up to 10 w/o
Mo, all compositions	Ir, up to 25 w/o
Os, up to 15 w/o *	Pd, up to 10 w/o

*w/o=weight percent

It has been very difficult and costly to prepare good quality powders from these particular metals and their alloys because they are not normally brittle. Not being brittle, they resist conventional crushing techniques to the extent that only after extensive energy application in recognized crushing techniques is it possible to render these metals and their alloys into powder forms suitable for use in compacted forms of various shapes.

For example, a technique employed to embrittle other ductile metals (U, Ti, Zr) is to expose these metals and their alloys to an atmosphere of hydrogen at an elevated temperature. The temperature employed is sufficient to heat the metals or their alloys but not sufficient to melt them. At the elevated temperature, some hydrogen diffuses into the metal and a chemical reaction occurs between the hydrogen gas and the solid metals to form hydrides. The resulting hydrides of these metals and their alloys are brittle. However, Mo, W, and Re and their alloys do not readily react with hydrogen to form hydrides.

Another process used to condition metals for subsequent crushing and powder preparation is the coreduction of metal oxides. However, by this technique the choice of alloys is limited as dictated by the thermochemical relationships of the reactants in the process. An undesirable collateral effect of these types of reactions is the high level of impurities that contaminate the reacted metals and very frequently the residual highly reactive surfaces produced. The active surfaces are desirable from sintering characteristics but poor from a contamination tendency.

The processes employed to date for preparing powdered alloys of W, Mo and Re are inadequate. This inadequacy is due to (1) the ductility of the metals and their alloys, (2) the high receptivity of contaminants by the metals, and (3) the associated high cost for recovery of the alloy content from the crushed contaminated powder.

To date, industries have clearly spelled out the need for powdered refractory metal alloys of very high purity. However, processes currently in vogue are unable to meet the rigid standards prescribed by industries for powdered high-purity, low-cost refractory metals and alloys. The subject invention does fulfill this need of industry, and meets all the prescribed rigid requisites.

An object of this invention, therefore, is to prepare a refractory metal or alloy powder which will exhibit the properties of the wrought refractory metal or alloy.

Another object is to develop a process for preparing a variety of metallic compositions using W, Mo, and Re.

Still another object is to develop a simple process for fabricating refractory metal powders.

Still another object is to develop a process to fabricate refractory metal powders at low cost.

Still another object of this invention is to prepare refactory metal and alloy powders of very high purity.

Another object is to effect a homogeneous distribution of an embrittling agent in the preparation process of obtaining high-quality powdered refractory metals and alloys.

Yet another object is to effect a rapid distribution of an embrittling agent in the process of obtaining high-quality refractory metals and alloys.

Another object is to efficiently remove the embrittling agent from the powdered refractory metal or alloy.

Other objects and advantages of the invention will be apparent from the following detailed description thereof.

The single figure is a simplified flow sheet of the steps involved in the process of this invention. Step I is the melting of the refractory metal or alloy under an atmosphere of nitrogen until equilibrium is established between the nitrogen in the gaseous atmosphere and the nitrogen dissolved in the liquid metal.

Step II is the very rapid cooling of the molten metal, once equilibrium is established between the nitrogen in the atmosphere above the metal and the nitrogen dissolved in the liquid metal.

Step III is the comminuting of the solid cooled metal to a desired size.

Step IV is the degassing of nitrogen from the comminuted metal at subatmospheric pressure and at a temperature below the sintering temperature of the comminuted metal.

Broadly, this invention consists of a process to prepare high-purity powdered refractory metals and alloys of same. In essence, the process comprises melting the refractory metal or alloy under an atmosphere of nitrogen or ammonia until an equilibrium is reached between the gaseous atmosphere and the gas entrapped or absorbed in the molten refractory metal or alloy. Then the molten metal or alloy is very rapidly cooled and solidified, entrapping excessive gas in the metal. Next, the solidified metal is crushed or ground to a desired degree by conventional techniques. The comminuted metal is subjected to subatmospheric pressure at an elevated temperature which is, however, below the sintering temperature of the metal powder to remove excess nitrogen gas

that may have been absorbed or entrapped in the metal when it was rapidly cooled and solidified. With the gas removed, the very pure powdered refractory metal or alloy is ready to be compacted and processed to any desired shape.

The particular refractory metals pertinent to this invention, W, Mo, Re, and their alloys, have been very difficult to prepare as powders of high purity. In this invention, the metals are melted in an electric arc furnace. Some of the standard recognized types of furnaces suitable for use in the process of this invention are (1) inert electrode arc furnace, (2) consumable electrode arc furnace, and (3) electrodeless arc furnace.

As the metal is melted in the arc furnace, it is subjected to an atmosphere of nitrogen or ammonia, or of nitrogen or ammonia in combination with an inert gas such as helium or argon. Either nitrogen or ammonia is continuously added to the system as the metal is melted. The liquid metal is mixed with the gas until a homogeneous mixture of gas and metal is created.

The solubility of helium or argon in the molten refractory metal is extremely small compared to that of nitrogen and for all practical purposes helium and argon are to be considered as insoluble in the molten refractory metal under the conditions prescribed in this invention. The principal function of the inert gas, huch as helium or argon, is to furnish gas ions over which the electric arc in the furnace can travel. The nitrogen gas is absored into the molten metal. The presence of the insoluble helium or argon permits the process to proceed more smoothly than if nitrogen were used alone in the furnace.

The ammonia, if used at the high temperature of the melted W, Mo, or Re metals, dissociates into nitrogen and hydrogen gases. The molten metal dissolves the nitrogen. The use of nitrogen is preferred to ammonia.

The gas pressure used over the molten metal must be at least 0.10 atmosphere nitrogen, if nitrogen is used alone. If nitrogen is in combination with hydrogen or argon or helium, then the nitrogen partial pressure must be at least 0.10 atmosphere. The solubility of nitrogen in the molten refractory is dependent on the nitrogen pressure and the temperature of the molten liquid metal.

Nitrogen or ammonia are continuously added to the system as the nitrogen is dissolved into the molten metal and the nitrogen pressure drops off. The nitrogen or ammonia is fed into the system at a rate sufficient to maintain a nitrogen pressure of at least 0.10 atmosphere. If any helium or argon is present, its partial pressure remains relatively constant because of its low solubility in the molten refractory metal compared to nitrogen.

The nitrogen-bearing gas is fed into the molten metal-gas system until sufficient nitrogen is dissolved in the molten refractory metal to embrittle it. The solubility limit of nitrogen in the molten refractory metal is a characteristic of the metal and the nitrogen pressure. The pressure used in the process is sufficient to dissolve sufficient nitrogen to embrittle the metal.

The liquid metal is effectively mixed with the gas to the extent that a homogeneous mixture of gas and metal is created. Once an equilibrium is established between the nitrogen in the liquid metal at a level sufficient to embrittle the metal, and the gas atmosphere above it, then the molten refractory metal is very rapidly cooled to room temperature with a water heat exchange system in the arc furnace. The rapid cooling period can range from less than one second to thirty minutes. The objective of the rapid cooling is to "freeze" or lock in nitrogen in the metal as it cools off rapidly.

As the temperature in the nitrogen gas-saturated metal drops rapidly, the solubility of the nitrogen in the molten metal decreases also. The net result is a tendency for the metal to reject the included nitrogen gas that is in excess of solubility limits in the refractory metal at the ultimate room temperature. Because the cooling process is so rapid, most of the nitrogen gas in excess of solubility limits in the metal or alloy does not escape because the metal or alloy "freezes" (solidifies) and retards the escape of the excess gas. The excess nitrogen gas entrapped in the frozen metal imposes structural stresses on the metal and effectively embrittles it.

It is believed that the net embrittlement of the solidified metal is a composite of the three influential factors assignable to the nitrogen gas. These factors are (1) solid solution hardening of the metal due to the supersaturated level of nitrogen in the metal; (2) formation of a brittle phase at the grain boundaries of the metal crystals; and (3) the effect of the pressure within the confines of the metal due to the pressure of the confined internal gas.

The homogeneously embrittled metal or alloy, under the internal stress of pressure-confined nitrogen, is in a condition which easily lends the metal to conventional crushing or grinding processes, such as by ball mills or rolling mills.

When the embrittled metal has been reduced in size to the desired level, residual amounts of nitrogen remain in the crushed metal. This residual nitrogen is removed from the metal particles by a vacuum heat treating process. The metal particles are heated and a vacuum or low atmospheric pressure (less than 0.10 atmosphere of nitrogen pressure) permits the residual nitrogen in the metal to escape and leave a very pure good-quality refractory metal powder. (The reference to metal throughout is intended to include the pure refractory metals, W, Mo, and Re and their alloys previously listed.)

The temperature at which vacuum heat treatment can be applied to any of the powder refractory metals to remove the residual nitrogen contained therein depends upon the sintering temperature of the particular metal powder. Each powdered metal has its own sintering temperature which can be determined by reference to technical handbooks or other well known sources.

The rate of nitrogen removal from the powdered metal increases rapidly as the temperature increases and the ambient gas pressure drops as the metal approaches its particular sintering temperature in the vacuum chamber. However, caution should be exercised so that the sintering temperature of any of the powder metals is not attained. If the sintering temperature is reached, the nitrogen affiliated with the powdered metal will be effectively removed in the vacuum chamber, but the residual nitrogen-free metal would probably be a solid sintered mass of metal. A temperature of about 200° C. below the sintering temperature of the particular refractory metal powder is more than adequate to drive off the residual nitrogen of the metal while under a pressure of less than 0.10 atmosphere of nitrogen. (The vacuum chamber need not be any particular type or kind but any of a number of standard recognized chambers on which heat and vacuum can be applied.)

The embrittling qualities developed by this process are very superior to those of other techniques, e.g., coreduction processes.

A commercial alloy bar stock of tungsten–26 w/o (weight percent) rhenium was treated with hydrogen to form a hydride. Also prepared was an alloy of tungsten–26 w/o rhenium from sintered elemental W and Re which was arc-melted and nitrogen treated by the process of this invention. As a standard of reference, a sample alloy of the tungsten–26 w/o Re was arc-melted from the sintered elemental W and Re but untreated in nitrogen. The results of a grinding test of each of these three materials was as follows:

W–Re 26 w/o	Wt. percent Material Ground	Time to Grind
Hydrogen treated	20	1 hour.
Nitrogen treated	20	3 minutes.
Untreated	None	1 hour.

By practicing this invention for preparing refractory metal powders, several specific advantages will accrue to the practitioner. They are:

(1) A refractory metal or alloy that can be powdered.
(2) A refractory metal or alloy that can be very rapidly grund to minimize impurity pickup.
(3) a refractory metal or alloy powder with a very high starting purity.
(4) A refractory metal or alloy powder whose nitrogen contamination can be removed by relatively simple treatment.
(5) A relatively inexpensive process for making pre-alloyed powder.

Other advantages that can be realized by practicing this invention, reside in the process employed itself, such as

(1) The use of an electric arc furnace for rapid heating
(2) the ability to rapidly extinguish the heat source
(3) the use of a water-cooled crucible for rapid cooling
(4) the active state of the nitrogen as ionized in the arc
(5) the use of inert gas such as helium or argon to stabilize arc plasma
(6) the ability to remove gaseous contaminaiton inside the furnace, and
(7) the variation of gas pressures that are possible.

Example 1

A 25-gram alloy of tungsten–26 weight percent rhenium is melted in an arc furnace (see flow sheet) at 3400° C. and produces a "button" type casting. This casting is then subjected to a pressure of 1 atmosphere which is composed of four parts nitrogen and 1 part helium. The casting is melted an additional four times. The button is turned over between each melt to insure homogeniety of the nitrogen throughout the button. The absorbed nitrogen is replenished after each melt to maintain the 4:1 ratio. Each melt consists of a 30-second exposure to the nitrogen atmosphere at the melting temperature and is then cooled rapidly for 30 seconds before another melting cycle occurs.

After the last melting-rapid cooling cycle, the tungsten–26 weight percent rhenium alloy is finely crushed in a ball mill. The finely crushed alloy is then subjected to a vacuum heat treatment at 1300° C. to remove the nitrogen confined in the powdered alloy. The remaining powder is free of contamination and suitable for any metallic use.

Example 2

A 50-gram alloy of Mo and 25 weight percent W is melted in an arc furnace at 2800° C. under an atmosphere of nitrogen where the nitrogen pressure is maintained at 1 atmosphere by continuous metering of nitrogen into the system as the nitrogen is dissolved in the molten metal. The nitrogen is added until 20 p.p.m. of it are dissolved in the metal.

The metal is chilled very rapidly to room temperature in 1 minute to freeze the nitrogen in the metal. The solidified metal is removed from the furnace and ground to a powder in a laboratory ball mill to about 100 mesh.

The nitrogen was removed from the powdered metal in a vacuum oven at 1100° C.

Example 3

A 40-gram alloy of Re–10 w/o W is melted in an electric arc furnace at 3200° C. in an atmosphere of ammonia whose pressure is maintained at 2 atmospheres. When gas equilibrium is established at a level where 15 p.p.m. of nitrogen are dissolved in the molten metal, the metal is rapidly cooled to room temperature in about two minutes.

The solid metal is ground to a powder in a ball mill and the residual nitrogen in the powdered metal is removed in a vacuum oven at a temperature of 1200° C. under vacuum. The powdered nitrogen free metal is then ready for use in a very pure state.

Example 4

A 40-gram sample of Mo–10 w/o Os is melted at 2700° C. in an electric arc furnace under an atmosphere of argon and nitrogen in which the nitrogen:argon ratio is 4:1. As the nitrogen is dissolved in the metal alloy, additional nitrogen is metered into the system to maintain the 4:1 ratio in an overall atmospheric pressure of 1 atmosphere. When the equivalent of 10 p.p.m. of nitrogen is dissolved in the refractory alloy, the alloy is quickly cooled to room temperature in a period of about 10 minutes. The metal is ground and degassed of nitrogen in a vacuum oven at a temperature of 1100° C.

Example 5

A 30-gram alloy of W–8 w/o Rh is melted at 3400° C. in an electric arc furnace under an atmosphere of nitrogen and helium at a pressure of 1 atmosphere and a constant nitrogen:helium ratio of 9:1. When a level of 5 p.p.m. of nitrogen is dissolved in the alloy, the metal is rapidly chilled to room temperature in 5 minutes, then ground to a powder. The powder is degassed of nitrogen in a vacuum oven at a pressure of less than 0.10 atmosphere and at 1300° C.

Example 6

A 25-gram sample of Re–4 w/o Pt alloy is melted at 3200° C. in an arc furnace under an atmosphere of nitrogen at a constant pressure of 0.50 atmosphere until 5 p.p.m. of nitrogen are dissolved in the molten refractory alloy. The alloy is cooled to room temperature in about 30 minutes. The alloy is ground to a powder and degassed of nitrogen at a temperature of 1200° C. in a vacuum oven.

Example 7

A 30-gram sample of Re–15 w/o Ir is melted in an electric arc furnace at a temperature of 3200° C. under an atmosphere of nitrogen at a pressure of 0.10 atmosphere. The nitrogen pressure is maintained until there is indicated that about 5 p.p.m. of nitrogen are dissolved in the molten alloy. The alloy is then cooled to room temperature in about 30 seconds and then ground to a powder. The dissolved nitrogen remaining in the powder after grinding is removed in a vacuum oven at a temperature of 1200° C.

Example 8

A 30-gram alloy of Mo–8 w/o Pd is melted at 2700° C. in an electric arc furnace under an atmosphere of nitrogen at a pressure of 1.5 atmospheres. When 12 p.p.m. of nitrogen are dissolved in the alloy, it is cooled to room temperature in 15 minutes then ground to a powder.

The powder is degassified of nitrogen in a vacuum oven at 1200° C.

Example 9

A 40-gram alloy of W–2 w/o Pt is melted at 3300° C. in an electric arc furnace under a blanket of nitrogen at a pressure of 5 atmospheres. The nitrogen pressure is maintained on the molten metal until 20 p.p.m. of nitrogen are dissolved in the molten metal. The alloy is then cooled to room temperature in 1 minute. Next it is ground to a powder and then degassified of residual nitrogen in a vacuum oven at 1300° C.

Example 10

A 25-gram alloy of Re–5 w/o Os is melted in an electric arc furnace at 3100° C. under a blanket of nitrogen at a pressure of 0.75 atmosphere until 16 p.p.m. of nitrogen are dissolved in the molten alloy. The alloy is then rapidly cooled to room temperature in about 3 minutes. The cooled alloy is ground to a powder easily and then the residual nitrogen in the powder is removed in a vacuum furnace in an atmosphere of helium at a pressume of 0.05 atmosphere at a temperature of 1200° C.

Example 11

A 30-gram alloy of W–6 w/o Pd is melted in an electric arc furnace at a temperature of 3400° C. under an atmosphere of nitrogen and argon in a ratio of 4:1 and a pressure of 2 atmospheres. The nitrogen is continuously metered into the system as it is dissolved in the molten alloy to maintain the designated gas ratio and pressure. When 18 p.p.m. of nitrogen are dissolved in the liquid metal, it is quickly cooled to room temperature in 2 minutes. The solid metal is then easily ground to a powder and then degassified of residual nitrogen in a vacuum furnace under a vacuum at a temperature of 1300° C.

Example 12

A 25-gram alloy of W–2 w/o Pt is melted in an arc furnace at a temperature of 3300° C. in an atmosphere of nitrogen at a pressure of 1 atmosphere. When 20 p.p.m. of nitrogen are dissolved in the molten alloy, the alloy is very rapidly cooled to room temperature in 30 seconds. The embrittled alloy is then easily ground to a powder. The powder is next degassed of residual nitrogen in a vacuum oven at a temperature of 1300° C.

Example 13

A 25-gram alloy of Mo–5 w/o Rh was melted at a temperature of 2700° C. in an atmosphere of nitrogen at a pressure of 1 atmosphere and held at that temperature and nitrogen pressure until 6 p.p.m. of nitrogen were dissolved in the alloy. The alloy was cooled to room temperature in 20 minutes then ground and finally degassified of nitrogen at a temperature of 1100° C. in a vacuum furnace.

Example 14

Samples of 50 grams each of pure W, Mo, and Re are processed to their respective powders under the following conditions:

	W	Mo	Re
Melting Furance	Electric Arc (E.A.).	E.A.	E.A.
Melting Temperature	3,300° C.	2,700° C.	3,200° C.
Blanket Atmosphere	Nitrogen.	Nitrogen.	Nitrogen.
Nitrogen Pressure Atmosphere	1.0.	1.0.	1.0.
Nitrogen Dissolved (p.p.m.)	12.	16.	18.
Cooling Period	3 minutes.	2 minutes.	1 minute.
Powdered by	Grinding.	Grinding.	Grinding.
Nitrogen Degassifying Temperature	1,300° C.	1,100° C.	1,200° C.
Nitrogen Degassifying Pressure	Vacuum.	Vacuum.	Vacuum.

The critical and most distinctive feature of this invention is the addition of nitrogen into the molten phase of the metal to effect a rapid homogeneous distribution of the gas in the molten metal followed by very rapid cooling of the gas-saturated metal to effect nonequilibrium retention of the gas at lower temperatures. The rejection of nitrogen at the low temperature causes effective embrittlement of the refractory metal or alloy.

The preferred method of this invention is to add nitrogen as a gas during electric-arc-furnace melting of the refractory metal so as to blanket the molten metal. Under these conditions a rapid distribution of nitrogen is effected in the liquid metal. In addition, the nitrogen in the arc ionizes. This enhances the chemical activity of the gas which promotes the rapid attainment of nitrogen equilibrium between the liquid metal and the ambient atmosphere above. The preferred ambient nitrogen gas pressure is one atmosphere. The nitrogen pressure is maintained for a time period sufficient to permit the solution of 20 p.p.m. (parts per million) of nitrogen in the molten metal. The molten metal is next rapidly cooled to room temperature in one minute using a water-cooling

heat exchange device which is an incorporated feature in the arc furnace. The solidified nitrogen impregnated, embrittled metal is next ground by a conventional method (e.g., ball mill, rod mill, etc.).

The nitrogen contaminated powdered metal is degassed of nitrogen under a vacuum in a vacuum oven at a temperature of at least 200° C. or more below the recognized sintering temperature of the powdered metal.

The foregoing description herein is for purposes of illustration only, and it is therefore intended that this invention be limited only by the appended claims or their equivalents.

What is claimed is:

1. A process for preparing homogeneous powdered high-purity refractory metal alloys selected from the group of refractory alloys consisting of

Mo-W	Mo-Pd	W-Pd
Mo-Re	W-Re	Re-Os
Mo-Os	W-Os	Re-Rh
Mo-Rh	W-Rh	Re-Pt
Mo-Pt	W-Pt	Re-Ir
Mo-Ir	W-Ir	Re-Pd

and comprising the steps of:

(a) melting the said refractory metal alloy in a gaseous atmosphere selected from the group of gases consisting of nitrogen and ammonia,

(b) rapidly cooling the said refractory metal alloy in the said gaseous atmosphere,

(c) comminuting the said rapidly cooled refractory metal alloy, and

(d) removing the nitrogen-gas atmosphere contained therein.

2. The process of claim 1 wherein the said refractory metal alloys are selected from the group of binary refractory alloys whose alloying compositions include all compositions within the ranges of

Mo-W, all compositions	W-Rh (up to 10 w/o)
Mo-Re, all compositions	W-Pt (up to 10 w/o)
Mo-Os, up to 15 w/o	W-Ir (up to 25 w/o)
Mo-Rh, up to 10 w/o	W-Pd (up to 10 w/o)
Mo-Pt, up to 10 w/o	Re-Os (up to 15 w/o)
Mo-Ir, up to 25 w/o	Re-Rh (up to 10 w/o)
Mo-Pd, up to 10 w/o	Re-Pt (up to 10 w/o)
W-Re, all compositions	Re-Ir (up to 25 w/o)
W-Os, up to 15 w/o	Re-Pd (up to 10 w/o)

3. The process of claim 1 wherein the said molten refractory metal alloy is cooled to room temperature in a period of one second to thirty minutes.

4. The process of claim 1 wherein the nitrogen gas is removed from the powdered refractory metal alloy under subatmosphere pressure.

5. The process of claim 1 wherein the nitrogen gas is removed from the refractory metal alloy powder at a temperature less than the sintering temperature of the said powdered alloy.

6. The process of claim 1 wherein the nitrogen gas is removed from the powdered refractory metal alloy at a temperature of at least 200° C. less than the sintering temperature of the said refractory metal alloy.

7. The process of claim 5 wherein the nitrogen gas in the said powdered refractory metal alloy is removed from the said alloy leaving a residual of nitrogen gas of less than 20 p.p.m. in the said alloy.

8. The process of claim 1 wherein the gaseous atmosphere exerts a pressure of at least 0.10 atmosphere of nitrogen on the molten refractory alloy.

9. The process of claim 1 wherein the refractory alloy is melted in an electric arc furnace.

10. The process of claim 1 wherein the said gaseous atmosphere is introduced into the arc melting furnace as the refractory metal alloy is being melted.

11. The process of claim 1 wherein an inert gas selected from the group consisting of helium and argon is introduced into the atmosphere above the melted refractory alloy along with the gas selected from the group consisting of nitrogen and ammonia.

12. The process of claim 1 wherein the molten refractory alloy is subjected to the gaseous atmosphere for a period of time sufficient to permit at least 5 p.p.m. of nitrogen gas to be distributed into the said molten refractory alloy.

References Cited by the Examiner

UNITED STATES PATENTS

2,107,279	2/1938	Balke et al.	75—84
2,875,034	2/1959	Ham	75—10

OTHER REFERENCES

Case, S. L.: Summary report on "A Metallurgical Study of Molybdenum" to Office of Naval Research, Navy Department, Oct. 15, 1954, p. 41.

DAVID L. RECK, *Primary Examiner.*

W. W. STALLARD, *Assistant Examiner.*

Dedication

3,318,683.—*Ellis L. Foster, Jr.*, Powell, and *Walter J. Hildebrand*, Columbus, Ohio. REFRACTORY METAL POWDERS, Patent dated May 9, 1967. Dedication filed Sept. 11, 1975, by the assignee, *The Battelle Development Corporation.*

Hereby dedicates to the People of the United States the entire remaining term of said patent.

[*Official Gazette November 11, 1975.*]