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[54] **METHOD FOR PRODUCING REFRACTORY METAL POWDER**

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Related U.S. Application Data

[63] Continuation of Ser. No. 813,746, April 4, 1969, Pat. No. 3,701,649.

[52] **U.S. Cl.**..... **75/0.5 BB,** 75/84.4, 75/84.5

[51] **Int. Cl.. C22b 57/00,** C22b 49/00, C22b 51/00

[58] **Field of Search**..... 75/0.5 BC, 84.4, 75/84.5

[56] **References Cited**

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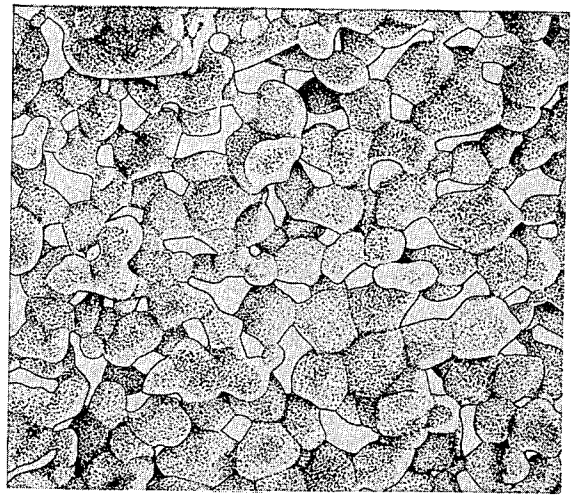
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[57] **ABSTRACT**

A method is provided for producing refractory metal powder from a refractory metal ferro-alloy containing a refractory metal selected from the group consisting of tungsten, molybdenum, niobium and tantalum and containing at least about 8 percent total of iron plus silicon, the silicon constituting at least one halidizable metal in addition to iron as an impurity. The alloy is crushed and then subjected to dissolution at a temperature of at least about 900° C with a gaseous hydrogen halide selected from the group HCl and HF for a time at least sufficient to effect substantial removal of said iron and said at least one other metal impurity as halide vapor, whereby to provide a finely divided refractory metal powder low in said impurities.

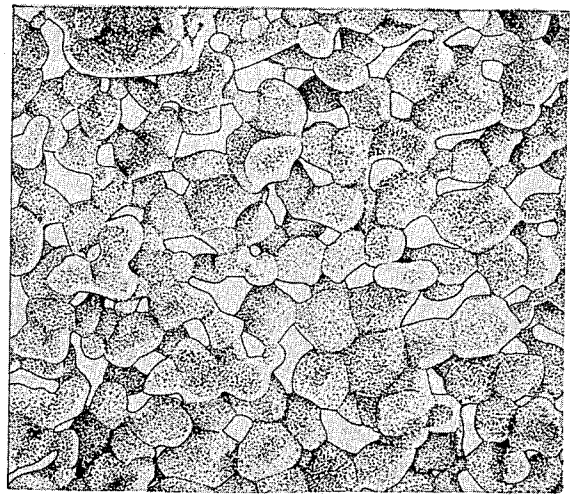
6 Claims, 2 Drawing Figures





X 3000

FIG. 1



X 10,000

FIG. 2

METHOD FOR PRODUCING REFRACTORY METAL POWDER

This application is a continuation-in-part of U.S. Pat. application Ser. No. 813,746, filed Apr. 4, 1969 now U.S. Pat. No. 3,701,649.

This invention relates to a method for producing refractory metal powder from refractory metal ferror-alloys, wherein an ingot of an alloy thereof is crushed and the crushed alloy then subjected to dissolution at an elevated temperature with a gaseous hydrogen halide, such as HCl or HF, to selectively remove impurities therefrom, such as iron, as a halide vapor and leave an enriched residue constituting said refractory metal powder.

RELATED CO-PENDING APPLICATION

In U.S. Pat. application Ser. No. 813,746, filed Apr. 4, 1969, a process is disclosed for producing tungsten metal powder from oxidic tungsten ore, wherein the ore is reduced and melted at an elevated temperature with a reducing agent, such as silicon, whereby to produce a tungsten-base alloy containing silicon, among other impurities, such as iron, manganese, and the like, which alloy is cast into an ingot. The ingot is then crushed, following which the crushed alloy is chlorinated at an elevated temperature to form tungsten chloride, amoung other metal chlorides, which is recovered by fractional distillation and thereafter reduced to tungsten metal. The purpose of fractional distillation is to separate the tungsten chloride from such impurities as halides of silicon, iron, manganese, etc. While the disclosure of the aforementioned application mentions in a general way that hydrochloric acid may be employed to selectively recover the tungsten from the alloy by dissolution, a method is not disclosed using hydrochloric acid for producing a finely divided refractory metal product substantially low in impurities and having utility and of meeting the high quanlity standards required in powder metallurgy.

BACKGROUND OF THE INVENTION

The use of tungsten powder is known for the production of wire and bar products. Tungsten powder is also used in the production of electrical contacts by mixing tungsten powder with a binder metal, e.g. silver, copper, etc., and forming a sintered product therefrom. Other uses include the production of molds for casting brass and the production of tungsten carbide for making cemented tungsten carbide products. All of these applications require as starting material a metal powder of fine particle size and fairly high purity.

A prevailing method for producing tungsten metal powder involves chemically leaching a tungsten ore to dissolve the tungsten metal value and then by various precipitation and redissolving steps remove impurities, isolate the oxide of tungsten in pure form and reduce the oxide to metal using hydrogen at an elevated reducing temperature.

This hydrometallurgical procedure tends to be complicated and varies according to different types of ores. Certain impurities commonly present in the ores may require extra precipitation steps, which further complicate the processing of the ores and which adversely affect the ultimate yield of the tungsten metal product. For example, the handling of leach liquors employed in the foregoing type of processes requires fairly large

pieces of equipment, considerable manipulation of solutions and the additional problem of disposing of large volumes of spent leach liquors which is costly and of avoiding pollution of the surrounding environment.

Several methods have been suggested for producing refractory metal powders, such as tungsten , molybdenum and the like, wherein the refractory metal is converted to a gaseous halide (e.g. fluorides or chlorides) and the halide then reduced at an elevated temperature with hydrogen. While such methods have advantageously provided stable metal powders of high purity and uniformity using continuous production techniques, such methods have been fraught with technical problems when applied industrically.

Attempts have been made to recover tungsten by first converting the ore to a tungsten alloy which thereafter was treated as discussed hereinbefore with hydrochloric acid to remove residual elements therefrom. While this process upgraded the tungsten product, generally the product contained residual elements above the desired limit. For example, in the case of silicon, the residual quantity in the final tungsten powder was as high as 2.9 percent by weight.

I have found that markedly improved results can be obtained by controlling the conditions of the hydrochloric acid treatment at a controlled elevated temperature, whereby to assure a refractory metal product low in residual impurities.

OBJECTS OF THE INVENTION

It is thus the object of the invention to provide a method for producing refractory metal powder low in impurities by the selective teaching of granulated refractory metal ferro-alloy with hydrochloric acid at a controlled elevated temperature.

Another object is to provide a method for producing tungsten metal powder by the selective leaching of a granulated tungsten-containing ferro-alloy with an acid selected from the group consisting of HC1 and HF, said leaching being conducted at an elevated temperature, whereby metal halide impurities, such as iron chloride, are removed as gases.

Other objects will more clearly appear when taken in conjunction with the following disclosure and the appended drawing, wherein:

FIG. 1 is a drawing reproduced from a photomicrograph of a crushed tungsten metal ferro-alloy enlarged 3,000 times; and

FIG. 2 is a similar representation of the inal tungsten metal product taken from a photomicrograph at 10,000 magnification.

STATEMENT OF THE INVENTION

Broadly stated, the invention is directed to a method for producing a refractory metal powder from a refractory metal ferro-alloy containing a metal from the group consisting of tungsten, molybdenum, niobium and tantalum, the alloy containing at least about 8 percent total by weight of iron plus silicon, and preferably at least about 10 percent, the silicon constituting at least one other halidizable metal impurity in addition to iron, the method comprising providing a refractory metal ferro-alloy crushed to a particle size of less than about 4 mm in size and then subjecting the crushed alloy to dissolution in the presence of a gaseous hydrogen halide selected from the group consisting of HC1 and HF at a temperature of at least about 900° C for a

time at least sufficient to effect substantial removal of the iron and said at least one other metal impurity (silicon and any other metal impurity that may be present) as a halide vapor, whereby to obtain a finely divided refractory metal powder low in said impurities.

It is preferred that the time of treatment be at least about 1 hour, e.g. range from about 1 to 4 hours, a more preferred time of treatment ranging from about 2 to 4 hours. The temperature may range from about 900° C to 1,200° C. It is also preferred that the average particle size of the alloy being treated be less than about 2 mm.

In the case of tungsten, it is possible to produce a powder of small particle size, for example, less than 20 microns, e.g. 1 to 10 microns, over a fairly narrow particle size range. Such a product is capable of being used for forming tungsten carbide employing conventional techniques for subsequent use in the production of cemented carbides. Other products may be produced from the powder where a relatively high quality tungsten powder is required.

The invention is particularly advantageous in that it provides a method which is simple, flexible and inexpensive, while also providing a high quality powder product. The method provided by the invention is applicable to the production of other refractory metals, such as niobium, molybdenum, tantalum, etc.

The starting material is an alloy containing the refractory metal to be produced, the material being a ferro-alloy type. For convenience, this alloy is referred to as a refractory metal ferro-alloy. A typical alloy is ferro-tungsten which can be obtained on the open market or it can be produced from an oxidic ore by reduction with a reducing agent, such as silicon, aluminum, carbon and the like. Generally, the ferro-alloy contains, in addition to the refractory metal, iron, silicon, manganese, etc., which are the impurities, among others, which are removed by the process of the invention. Where silicon is used as the reducing agent, it will be present in the alloy. Likewise, where aluminum is used as the reducing agent, it will similarly be present in the alloy as one of the impurities.

A method for producing a tungsten ferro-alloy is disclosed in U.S. Pat. application Ser. No. 813,746, filed Apr. 4, 1969. A typical oxidic tungsten ore is scheelite, wolframite or hubnerite. The reduction is carried out in an electric arc furnace comprising a graphite crucible and a graphite electrode. The furnace is heated to an operating temperature in the range of about 1,800° to 2,200° C by means of a slag, the ore mixed with a predetermined amount of a reducing agent, e.g. silicon, being added continuously into the molten slag. The reducing reaction is exothermic and enables a high rate of production. The charging of the ore mix is continued to the furnace until it is filled with a melt up to a desirable level, the slag being preferably tapped at suitable intervals. The metal reduced forms an ingot at the bottom of the furnace.

The ingot is crushed to a particle size less than 4 mm and preferably to a size not exceeding 2 mm. The crushed ingot is then treated at an elevated temperature with a hydrogen halide selective to the removal of impurities as gaseous halides, these impurities including at least iron and silicon and such other additional impurities as aluminum, manganese and the like, which may be present. A finished product is obtained comprising a refractory metal powder low in impurities and of a few microns in size as determined by the Fisher Sub Sieve Sizer device.

According to the invention, refractory metal ferro-alloys containing at least about 8 percent total of iron and silicon, preferably at least about 10 percent, are capable of being selectively leached with a hydrogen halide, such as hydrogen chloride, hydrogen fluoride and the like. In addition to iron and silicon, aluminum, manganese, tin and other impurities can be selectively removed from the alloy.

For consistent results, it is preferred that the process be controlled over the temperature range of 900° to 1,200° C and that the particle size of the crushed ingot not exceed 2 mm, although slightly larger sizes can be treated. Where the crushed alloy contains some SiO_2, it can be removed by pre-treatment with HF.

Where a ferro-alloy contains some carbon and it is carried over into the end product, it can be removed from the final metal powder by treatment with CO_2 at a temperature of about 900° C or higher. The carbon is selectively oxidized and removed as a gas without attacking the metal to any great extent. However, a final treatment with H_2 can be used to remove any trace of oxygen caused by the CO_2 treatment.

As illustrative of the various embodiments of the invention, the following examples are given:

EXAMPLE 1

A ferro-tungsten alloy of particle size less than 63 microns, treated in accordance with the invention, had the following analysis by weight: 12.3 percent Fe, 5.8 percent Si, 0.2 percent Mn, 0.16 percent Mo and the balance essentially tungsten. The alloy was treated with hydrogen chloride at 1,100° C for 4 hours. The resulting tungsten powder had a particle size of a few microns, about 1 to 7 microns, and was low in impurities as follows: 0.075 percent Fe, 0.14 percent Si, 0.002 percent Mn, 0.1 percent Mn and 0.14 percent oxygen. The analysis indicated that residual silicon was present as an oxide which could be further lowered by treatment with hydrogen fluoride.

EXAMPLE 2

The ferro-tungsten alloy having the same analysis as Example 1 but having a larger particle size not exceeding 2 mm was treated for 3 hours at 1,050°C to provide an end product having the following analysis by weight: 0.15 percent Fe, 0.6 percent Si, 0.1 percent Mn and the balance essentially tungsten.

As stated hereinfore, the temperature and time of treatment of the alloy should be such as to effect substantial removal of the impurities. The importance of controlling the conditions using HCl gas as the reagent will be apparent from the following example.

EXAMPLE 3

A ferro-tungsten alloy was crushed and sieved to provide a particle size in the range of 63 microns to 2 mm (2,000 microns). The analysis by weight was as follows: 22.2 percnet Fe, 0.8 percent Si, 0.25 percent Mn and the balance essentially tungsten. The alloy was treated at various times and temperatures as follows:

Table 1

Time hours	Temp. °C	Analysis after treatment % Fe	% Si	% Mn
0.5	800	9.4	0.34	0.097

Table 1-Continued

Time hours	Temp. °C	Analysis after treatment % Fe	% Si	% Mn
0.5	900	8.4	0.30	0.090
0.5	1100	5.6	0.22	0.050
2.0	800	8.6	0.30	0.090
2.0	900	0.88	0.06	0.014
2.0	1100	0.49	0.07	0.007
4.0	800	7.7	0.28	0.084
4.0	900	0.98	0.06	0.010
4.0	1100	0.58	0.07	0.007

Particle size has an influence on the efficiency of extraction of the impurities, particularly on the iron extraction Tests indicate that the particle size should be less than 4 mm and, more preferably, below 2 mm.

Thus, the same material as Example 3 was treated for 4 hours with HCl at a temperature of 900°C to provide a tungsten product having the following analysis by weight:

Table 2

Particle Size		% Fe	% Si	% Mn
< 63 microns		0.36	0.10	0.004
> 63 microns	<2 mm	0.98	0.06	0.010
> 2 mm	< 4 mm	1.46	0.08	0.017

As an additional example, a crushed tungsten alloy containing by weight 12.3 percent Fe, 5.8 percent Si, 0.20 percent Mn and the balance essentially tungsten and having an average particle size of aobut 63 microns was treated with HCl at 1,100°C for 4 hours to provide a tungsten metal powder containing 0.075 percent Fe, 0.14 percent Si and 0.002 percent Mn. The average particle size was 6.8 microns as determined by the Fisher Sub Sieve Sizer (FSSS).

As will be apparent from Table 1 above, iron is not removed sufficiently at 800°C and also that 0.5 hours is not long enough at any of the temperatures, thus indicating that the temperature should preferably be at least about 900° C and the time at least sufficient to remove the iron substantially to below 2 percent, desirably at least about 1 hour at 900° C. While the temperature may broadly range from about 900° to 1,200° C, 900° to 1,100° C appears preferable, while a temperature range of about 1,000° to 1,100° C appears most preferred, the times over the foregoing ranges ranging from about 1 to 4 hours, more preferably, from about 2 to 4 hours.

The yield of tungsten obtained is quite high, the amount of tungsten removed with the chlorides being about 0.1 percent. The yield is close to 100 percent.

Even though the particle size of the material being treated may range up to 4 mm, the particle size of the finished product is generally less than 20 microns, e.g. less than 10 microns, and usually range from 1 to 7 microns, e.g. less than 10 microns, and usually range from 1 to 7 microns. Referring to FIG. **1**, the particle size of the alloy particle there shown at 3,000 magnification is in the neighborhood of about 30 microns. After treatment with the process of the invention, the particle size of the product shown in FIG. **2** at 10,000 magnification falls within the range of 1 to 7 microns. As will be noted from FIG. **2**, the particle size of the end product is quite uniform in size. Tungsten carbide produced by carburizing this tungsten powder has provided cemented carbide compositions of excellent quality substantially pore-free, having a fine grain and having a uniform sturcture.

While the treatment with hydrogen halide removes iron, silicon, and manganese quite efficiently, other impurities which can be removed include tin, chromium, titanium, zirconium and aluminum, among others. The invention is applicable to ferro-alloys containing molybdenum, niobium and tantalum. Generally, niobium and tantalum are found together in ores and are recoverable together using the invention.

Ferro-alloys containing by weight the refractory metals W, Mo, Nb and Ta in amounts as low as 30 percent or 40 percent may be treated by the invention. Examples of ferro-alloys that can be treated are as follows:

Table 3

% W	% Fe	% Si
91	8	1
74	25	1
66	25	9
82	8	10
50	40	10

Table 4

% Refractory Metal	% Fe	% Si	% Mn	% Al
75 Mo	21.0	2	2	—
85 Mo	13.5	1	0.5	—
75 Nb+Ta	15.0	9	0.5	0.5
65 Nb+Ta	30.0	3.0	2.0	—
50 Nb+Ta	30.0	10.0	2.0	8.0
40 Mo	45.0	10.0	—	5.0

Additional illustrative examples of the invention are as follows:

EXAMPLE 4

A ferro-molybdenum alloy having the following composition, to wit: 25 percent Fe, 5 percent Si and the balance molybdenum is treated as follows: The alloy which is crushed to provide a particle size of between 45 to 65 microns is treated with gaseous HF at 1,000° C for 4 hours to remove substantially the iron and silicon present and provide molybdenum powder as the end product of average size falling within the range of 1 to 10 microns.

EXAMPLE 5

A ferro-niobium (Ta) alloy containing about 15 percent Fe, 9 percent Si, 0.5 percent Mn and 0.5 percent Al and the balance niobium combined with tantalum is crushed and sieved to provide an average particle size between 65 microns and 2 mm and the crushed alloy treated with HCl at 1,100°C for 4 hours to remove substantially the impurities present and provide a powder metal product of particle size within the range of about 1 to 10 microns.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are consid-

ered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. In a method of producing a refractory metal powder from a refractory metal ferro-alloy containing a refractory metal selected from the group consisting of W, Mo, Nb and Ta and containing at least about 8 percent total of iron plus silicon, said silicon constituting at least one other halidizable metal impurity in addition to iron, the improvement for substantially removing said iron and said at least one metal impurity and for providing a refractory metal product which comprises,

providing said refractory metal ferro-alloy having a particle size of less than about 4 mm,

and then subjecting said alloy to dissolution in the presence of a gaseous hydrogen halide selected from the group consisting of HCl and HF at a temperature of at least about 900° C for a time at least sufficient to effect substantial removal of said iron and said at least one metal impurity as halide vapor,

whereby a finely divided refractory metal powder of substantially reduced size is obtained low in said metal impurities.

2. The method of claim 1, wherein the particle size of the ferro-alloy is less than about 2 mm, wherein the temperature of dissolution ranges from about 900° to 1,200° C, and wherein the time of dissolution over said temperature is at least about 1 hour.

3. The method of claim 2, wherein the dissolution temperature ranges from about 1,000° to 1,100° C and the time of treatment from about 2 to 4 hours.

4. In a method of producing tungsten metal powder from a tungsten-containing ferro-alloy containing at least about 8 percent total of iron plus silicon, said silicon constituting at least one other halidizable metal impurity in addition to iron, and the balance of said alloy essentially tungsten, the improvement for substantially removing said iron and said at least one metal impurity which comprises,

providing said tungsten-containing ferro-alloy having a particle size of less than about 2 mm,

and then subjecting said alloy to dissolution in the presence of a gaseous hydrogen halide selected from the group consisting of HCl and HF at a temperature of at least about 900° C for a time at least sufficient to effect substantial removal of said iron and said at least one metal impurity as halide vapor,

and whereby a finely divided tungsten metal powder of substantially reduced size is obtained low in said metal impurities.

5. The method of claim 4, wherein the temperature of dissolution ranges from about 900° to 1,200° C, and wherein the time of dissolution is at least about 1 hour.

6. The method of claim 5, wherein the dissolution temperature ranges from about 1,000° to 1,100° C and the time of treatment ranges from about 2 to 4 hours.

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