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PRECIPITATION OF TUNGSTIC OXIDE

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This invention relates to a metallic body and to a method of producing the same. In its more specific aspect the invention is directed to a tungsten body of predetermined grain count, to tungsten particles of predetermined size and to an improvement in the method of preparing the same.

Heretofore in the process for producing a rare refractory metal body, as for example tungsten, it has been customary to obtain a tungstate, as for example potassium tungstate, from a tungsten containing ore. The tungstate generally in a substantially pure condition is added to an acid, such as hydrochloric acid, with which it reacts to produce tungstic oxide and potassium chloride according to the following equation:

$$K_2WO_4+2HCl \rightarrow H_2WO_4+2KCl$$

The hydrochloric acid employed was approximately 35% HCl by weight. To this hydrochloric acid the potassium tungstate solution is slowly and continually added until the solution is slightly acid. This batch of material is continually stirred throughout the addition step and also stirred for a limited period of time thereafter in order that complete reaction may take place between the tungstate and the hydrochloric acid. At the end of the reaction and when the solution is just slightly acid, the liquid containing potassium chloride in solution and the tungstic oxide compound as a sludge is decanted leaving the wet sludge or tungstic oxide H_2WO_4 compound behind. The tungstic oxide is then subjected to a water washing operation. At this stage the tungstic oxide compound is subjected to a drying operation carried out at an elevated temperature of about 100 to 120° C. This condition is maintained until all of the excess moisture is evaporated therefrom.

The dried tungstic oxide H_2WO_4, which at this period is in the form of relatively large lumps, is ground until the particle size thereof is of such dimensions as to pass an 80 mesh sieve. These relatively small tungstic oxide particles are placed in nickel boats. The boats containing the dried H_2WO_4 are placed and maintained in the ordinary hydrogen furnace operating at a relatively high temperature until all of the oxide has been reduced to its metallic form. I have found that the individual particles of about 10% of a batch of metal particles so produced have diameters below 1 micron and about ½ or less of a micron and that the individual particles of another 10% of said batch have diameters above 14 microns and about 15 or more microns. The remaining 80% of the particles of this batch range in size between about 1 and 14 microns.

Thereafter this batch of tungsten particles is subjected to the usual pressing and sintering operation in order that the same may be transformed into the ordinary tungsten bar which may be later mechanically treated in order that the same may be employed as the filament in incandescent lamps or the like. This sintered bar has a grain count of about four to five thousand per square mm.

Prior to the time of my invention it has been recognized that the grain size is an important consideration in an incandescent filament when the aforesaid material is employed for the production of an incandescent filament.

In order that a sintered metallic bar having a predetermined grain count may be obtained I make use of something which heretofore has never been appreciated by those in the prior art.

Prior to the time that I made my invention it was not appreciated by those in the art that the grain count and the grain size was closely dependent upon the acidity of the hydrochloric acid at the time of tungstate addition and at the time that the addition was terminated. As far as I am aware, I am the first in this art to have discovered that the size of the grains in sintered tungsten bars may be predetermined and controlled by controlling the acidity of the precipitant, HCl, and it is with this particular discovery that my invention is specifically concerned.

In the course of my experimentations with this problem, I have found that I may provide a batch of tungsten metallic particles of predetermined sizes. By following out my process as hereinafter described, it is possible to obtain a batch of tungsten particles having less than one-half of one per cent of the quantity thereof comprised of individual particles whose diameter is one-half or less of a micron, and less than one-half of one percent of the quantity thereof comprised of individual metal particles whose diameter is 14 or more microns. Because of the nature of my invention, it is possible to obtain a batch of metallic particles of any particular small range of sizes so that the bulk and at least about 95–98% thereof by number shall be within the desired limited range. All of these results may be realized by following the crux of my invention—acid control during precipitation.

An object of my invention is to provide a process for producing a batch of tungsten particles with the individual particles thereof being of predetermined size.

Another object of my invention is to provide an improved step in the manufacture of incandescent lamps.

A still further object of my invention is the improved step of employing a batch of tungsten particles whose sizes are of such magnitude and within a certain range to provide a tungsten body which will have improved incandescent filament characteristics.

According to my invention I may obtain a batch of any desired size of metal particles whose sizes are substantially all less than one micron, for example. For this purpose I employ concentrated hydrochloric acid 36% HCl by weight. One example of the method which may be followed for for this purpose when it is desired to treat about 1 kilogram of 2N potassium tungstate solution is as follows:

About 5000 grams of concentrated hydrochloric acid 36% of HCl is placed in a container and maintained at a temperature of about 80° C. The potassium tungstate solution is conducted to said container. The feed of said tungstate may be regulated so that there is but a very small quantity thereof and in a dispersed condition in the form of a fine mist passing through a tube of appreciable diameter.

Close to the tungstate feed end of the tube there is projected against said moving stream a stream of concentrated hydrochloric acid 36% HCl, also in the form of a mist with the quantity of hydrochloric acid solution admitted being ten times that of the admitted tungstate by weight. This mass of hydrochloric acid and the tungstate together with the reaction products thereof travel into the hydrochloric acid in the container in which the entire mass is agitated in any manner.

After the 1 kilogram of potassium tungstate is subjected to concentrated hydrochloric acid 36% HCl whose weight is about 15,000 grams and after this mass is agitated in all of the hydrochloric acid now in the container, the sludge in said container is separated from the liquor by a decantation process. The amounts and concentrations of the hydrochloric acid in the container and that added to the tungstate feed should be so regulated that the acidity of the liquor after complete precipitation shall be no less than approximately 33% HCl. This sludge which is essentially H_2WO_4 is subjected to water washing and the H_2WO_4 is dried by being elevated to a temperature of about 100–120° C.

This dried mass may be in the form of large lumps and is ground to reduce the size thereof so that it may pass an 80 mesh sieve. At this stage the ground mass is subjected to the usual elevated and reducing atmosphere to convert the H_2WO_4 to pure tungsten metal. This usually consists in maintaining the temperature at 600–850° C. and passing through the furnace 100 cu. ft. hydrogen per hour. The rate of stoking of the tungsten is about 700 grams per hour. The batch of metal particles so obtained has about 95–98% of the individual particles thereof no greater than 1 micron in diameter.

Similarly I may obtain a batch of tungsten particles with not over 10% of the quantity of the individual particles thereof by number having a diameter less than about 6 microns. For this purpose I follow the novel method outlined above and employ hydrochloric acid whose acidity is 5 per cent HCl at the initial precipitating step, during and at the end of the precipitation.

Thus it is readily apparent that I may obtain a batch of tungsten particles containing whatever per cent of certain sized particles that I desire merely by controlling the acidity of the precipitant, which in the present case happens to be hydrochloric acid.

I have further found that by maintaining the following acidity concentrations at the time of, during and after precipitation that I may obtain a batch of particles of predetermined individual particle size according to the below table:

Oxide No.	HCl percent by weight	Approximate particle size
		Microns
1	36	½
2	25	1
3	15	3
4	8	6
5	5	8
6	3	12

A further specific aspect of my invention is the application of acid control during precipitation in the course of incandescent filament manufacture.

Instead of beginning with a concentrated hydrochloric acid solution containing 36% HCl and adding potassium tungstate thereto until the solution is just slightly acid, I prefer to carry out the precipitation step with a different range of acid concentrations. One range that I have found suitable is beginning with a hydrochloric acid solution containing 25–26% HCl, stirring and adding a 2N potassium tungstate solution thereto until the concentration of HCl is about 7–8 per cent. This step is carried out with constant agitation, slow addition of the tungstate and maintaining the temperature of the solution at about 80° C.

By following this method I have found that the size of substantially all of the individual metal particles prepared in the usual manner from H_2WO_4 precipitate thus produced is between about 1 and 8 microns and that there is no appreciable percentage, and less than 5% of individual particles by number, that measure less than 1 micron or greater than 8 microns. A batch of individual metal particles so produced may in the usual manner be pressed, sintered and subjected to other normal operations for the preparation of incandescent filaments that may be employed in an incandescent lamp. The grain count of the sintered bar is between 16,000 and 20,000 per square mm. which may without the understanding of my invention be regarded as high, but which I have found to be a factor in the production of a superior filament.

The invention is susceptible to modifications and the scope thereof is to be limited only by the prior art.

What is claimed:

1. A method of preparing a batch of tungsten particles comprising treating a soluble alkali metal tungstate compound with hydrochloric acid whose HCl content is no greater than about 26% and during said treatment maintaining said HCl acid content between about 26% and 7%.

2. A step in the method of manufacturing a tungsten filament comprising to about 25–26% HCl solution adding a 2N solution of a water soluble alkali metal tungstate until the concentration of the HCl is about 7–8% and removing the precipitate therefrom.

3. A step in the method for manufacturing a

tungsten filament comprising to about 25–26% HCl solution adding a 2N solution of potassium tungstate until the concentration of the HCl is about 7–8% and removing the precipitate therefrom.

4. A step in the method of manufacturing tungsten comprising to about 25–26% HCl solution, adding a 2N solution of potassium tungstate until the concentration of the HCl is about 7 to 8%, agitating the admixture formed and maintaining the temperature thereof at about 80° C.

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