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2,798,808

METHOD OF INTRODUCING ZIRCONIA INTO TUNGSTEN POWDER PRELIMINARY TO FORMING ELECTRODES

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Our invention relates to the consolidation of tungsten powder of a particular composition especially adapting it for use in the manufacture of welding electrodes.

The principal object of our invention, generally considered, is the manufacture of tungsten welding rods containing zirconium dioxide within the range between .1% and 1%, but preferably within the smaller range between .20% and .5%, whereby grain growth is inhibited and the presence of thorium dioxide, the customary doping agent, is avoided, thereby obviating the possibly undesirable radioactivity of thorium dioxide.

Another object of our invention is to introduce zirconium dioxide into tungstic oxide, as by the employment of any soluble salt of zirconium which will ignite to zirconium dioxide, firing the doped tungstic oxide in air at between 800° and 1000° C. and then reducing in hydrogen to metal powder.

A further object of our invention is to produce tungsten metal powder impregnated or doped with the desired proportion of zirconium dioxide, by blending such tungsten metal powder, produced from oxide doped with an excessive amount of zirconium dioxide, with undoped tungsten powder, in proportions required to produce a proportion of zirconium dioxide in the final product within the desired range between .1% and 1%.

Other objects and advantages of the invention will become apparent as the description proceeds.

There are certain uses of tungsten which require a fine grain structure. This necessitates some means of inhibiting grain growth during the various high temperature heat treatments used in the metallurgy of tungsten. This grain inhibiting action has generally been accomplished by the impregnation or "doping" of tungstic oxide with thorium dioxide, starting with a soluble salt, such as thorium nitrate, which changes to thorium dioxide on ignition. However, in the case of certain uses of tungsten, such as welding electrodes, the presence of thorium oxide may be undesirable because of its radioactive properties.

The patent which discloses and claims the production of drawn tungsten is that to W. D. Coolidge, No. 1,082,933, dated December 30, 1913. This patent discloses how tungstic oxide is "doped" or impregnated with thoria, starting with thorium nitrate in an amount which is equivalent to about 2% of thoria referred to tungsten. This patent discloses not only the production of tungsten metal powder but also the pressing, sintering, working and drawing of such metal tungsten, as is conventional in the "powder metallurgy process," by which we merely mean that in which the metal in powder form is consolidated to coherent metal, to filaments suitable for use in incandescent lamps.

The Hall et al. patent, No. 2,431,690, dated December 2, 1947, discloses an improvement over said Coolidge patent in the production of tungsten in dense coherent form at a lower temperature than that previously thought necessary, the metal powder which might be employed

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being such the production of which is disclosed in said Coolidge patent.

Neither of the above patents, however, contemplated the employment of zirconia in the proportions here contemplated, nor did either of them contemplate the blending of tungsten metal powder excessively doped, with undoped tungsten powder in order to accomplish the results desired.

In accordance with our invention, we produce by methods, conventional other than the doping of the metal powder and the blending operations, tungsten in a form such as welding rods containing zirconium dioxide in varying quantities, but within the range from .1% to 1% of zirconia. The maximum quantity of zirconia is limited only by its effects on the workability of the tungsten. We introduce the zirconium dioxide into the tungsten by "doping" tungstic oxide, WO_3 , with any soluble salt of zirconium which will ignite to the oxide. Examples are zirconium nitrate, zirconium acetate, zirconium tartrate and any other soluble zirconium organic acid salt.

The doped tungstic oxide is fired in air at from 800° C. to 1000° C. and then reduced to metal in hydrogen, pressed, sintered to coherent form and hot mechanically worked in accordance with conventional practice. Colin J. Smithells' book on "Tungsten," third edition, 1952, after on pages 132, 133, 134, 137, 139 and 143, disclosing the employment of thoria in the doping of tungsten, states on page 271:

"The addition of small quantities of either hafnium or zirconium oxides increases the difficulty of working tungsten bars far more than a corresponding amount of other oxides. This appears to be due to the reduction of the oxides and the formation of hafnium or zirconium-tungsten alloys. The difficulty can be avoided by sintering the bars in nitrogen or argon instead of hydrogen."

In our development work using zirconia, we ran into exactly the same condition which Smithells described. Tungsten ingots made up by doping the oxide so as to give 1% of zirconia, broke up at swaging. In order to make material which would run satisfactorily, using a hydrogen atmosphere for sintering (the use of a nitrogen or argon sintering atmosphere is not suitable for our purpose), we therefore tried out a different method, as follows, of introducing the zirconium oxide:

Instead of introducing zirconium dioxide directly into the tungsten metal powder in the ultimate percentage desired, we preferably reduce a portion of the tungstic oxide to metal without doping and mix therewith metal powder produced from oxide which has been doped with a zirconium compound, which will give zirconia on ignition, in a proportion sufficient to produce tungsten metal powder containing a greater-than-desired proportion of zirconia.

For example, to obtain tungsten metal having .4% of zirconia, we preferably blend four parts by weight of undoped tungsten metal powder with one part by weight of tungsten metal doped with 2% of zirconia. The mixture is then pressed, sintered to coherent form, and mechanically worked in accordance with conventional practice. A preferred blending range is from two to five parts of undoped tungsten powder to one part of overdoped tungsten powder. This material worked entirely satisfactorily and we were able to produce welding electrodes of .060", .093" and .125" diameters by this method.

Advantages obtained by the use of our invention are as follows:

1. The life of welding rods so produced is increased as compared to pure tungsten electrodes.
2. The metal of such rods is uniformly fine grained.

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3. Growth of the grain in the tungsten is inhibited, even at high temperatures, by the zirconium dioxide inclusion.

4. Zirconium dioxide has a melting point close to that of thorium dioxide, thus being very stable at high temperatures.

5. Such zirconia doped material can be used where radioactivity is undesirable.

It will, therefore, be seen that we have produced tungsten impregnated with zirconia as an ideal substitute for thoria, while avoiding the disadvantages of the latter, as well as the manufacturing difficulties noted by Smithells. While zirconia-doped tungsten may be satisfactorily produced without our blending method if the proportion of the zirconia is very small, say from .1% to .25%, yet such tungsten with a zirconia content as high as 1%, may be satisfactorily made by our improved blending method.

Although preferred embodiments have been disclosed, it will be understood that modifications may be made within the spirit and scope of the invention.

We claim:

1. The method of introducing zirconia into tungsten powder as a step prior to pressing to coherent form and sintering in a hydrogen atmosphere, comprising doping tungstic oxide with a soluble compound of zirconium which will form zirconium dioxide on heating and in a quantity sufficient to produce an excessive amount of zirconia over that desired, reducing said doped tungsten oxide to a tungsten metal powder containing zirconia, blending said zirconia-containing tungsten metal powder with a large proportion of zirconia-free tungsten metal powder in amounts so that said blend contains a proportion of zirconia of from 0.1% to 1% by weight of total tungsten metal powder.

2. The method of introducing zirconia into tungsten powder as a step prior to pressing to coherent form and

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sintering in a hydrogen atmosphere, comprising doping tungstic oxide with a soluble compound of zirconium which will form zirconium dioxide on heating and in a quantity sufficient to produce an excessive amount of zirconia over that desired, reducing said doped tungsten oxide to a tungsten metal powder containing zirconia, blending said zirconia-containing tungsten metal powder with a large proportion of zirconia-free tungsten metal powder in amounts so that said blend contains a proportion of zirconia of from 0.2% to 0.5% by weight of total tungsten metal powder.

3. The method of introducing zirconia into tungsten powder as a step prior to pressing to coherent form and sintering in a hydrogen atmosphere, comprising doping tungstic oxide with a soluble compound of zirconium which will form zirconium dioxide on heating and in a quantity sufficient to produce 2% of zirconia with respect to the tungsten, reducing said doped tungsten oxide to a tungsten metal powder containing zirconia, blending said zirconia-containing tungsten metal powder with a large proportion of zirconia-free tungsten metal powder in amounts so that said blend contains a proportion of zirconia of 0.4% by weight of total tungsten metal powder.

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