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DEHYDROGENATING TITANIUM METAL POWDER

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This invention relates to the preparation of finely divided titanium metal powder, and more particularly to dehydrogenating such powder.

It is known that titanium readily absorbs hydrogen and when hydrogenated it becomes extremely brittle. It has been proposed to employ this characteristic in the preparation of powder from more or less massive pieces of titanium metal by first hydrogenating to embrittle, then grinding while in the embrittled condition and then dehydrogenating to produce a pure fine metal powder. Hydrogenation presents no problem; the metal is simply heated in a hydrogen atmosphere and the hydrogen is rapidly absorbed. After grinding however, the dehydrogenation of the powder, which may be extremely fine, is not so readily accomplished. The hydrogenation reaction, which presumably forms titanium hydride, is reversible depending on super imposed gas pressure, and heating in vacuo above about 400° C. will release the hydrogen previously absorbed. Heating fine powder, while evacuating the container in which the powder is placed, results, however, in a rapid generation of hydrogen gas when the temperature at which the titanium hydride decomposes has been reached. This generation of gas may reach almost explosive violence, blowing the fine powder around in its container, associated pipe lines and the vacuum pumping equipment.

It is therefore the object of this invention to provide an improved method for dehydrogenating titanium metal powder. This and other objects of the invention will be apparent from the following complete description thereof.

This invention in its broadest aspects contemplates a process in which hydrogen-containing titanium metal powder is heated in an enclosed container, while evacuating said container, until the temperature of the powder is slightly below that at which hydrogen is evolved, for instance, about 400° C. At this temperature the vacuum pump is either shut off, or its effect on the gas pressure controlled, so that the gas pressure in the container is not reduced below about 500 mm. of mercury absolute. Heating is continued under these conditions until the powder reaches a temperature between 650° and 750° C. at which temperature the powder becomes slightly sintered into a soft but coherent cake. After the powder has become sintered, heat is applied at a lower rate so that the temperature of the sinter is maintained between 400° C. and 750° C. and the container is evacuated at high speed to remove the hydrogen as it is evolved. When the pressure in the container can be maintained at a value of a few microns by the vacuum pump it is evident that no more hydrogen is being evolved and the powder is substantially completely dehydrogenated. After cooling and removal from the container, the soft semi-sintered mass of titanium powder is readily broken up by a light grinding or disintegration and will be restored to substantially the same fineness as before dehydrogenation.

The first part of the heating operation is conducted under as low a pressure (high vacuum) as possible in order

to prevent contamination of the powder by formation of oxides and nitrides. Titanium hydride apparently decomposes at about 450° C. under pressures of the order of 1 mm. or less of mercury absolute, breaking down into metal and hydrogen gas which is evolved in considerable volume with appreciable violence if the container is in a state of high evacuation at this stage. Therefore when the powder has reached a temperature of about 400° C., which is slightly below the decomposition temperature, the vacuum pump is either disconnected or throttled so that an appreciable pressure of hydrogen, at least 500 mm. mercury absolute, is allowed to build up in the container. This hydrogen pressure depresses the dissociation reaction and prevents violent evolution of gas and blowing around of the fine powder while its temperature is being raised.

If desired the vacuum pump may be shut off completely and the hydrogen pressure allowed to build up in the container to impede dissociation of the titanium hydride to a greater degree. This is not particularly advantageous however and involves design and construction of apparatus which will withstand such pressures as well as being vacuum tight. A pressure of 500 mm. of mercury absolute will prevent too rapid evolution of gas and pressures above this and up to atmospheric pressure will provide proper and convenient gas evolution control. In addition, since the initial and final steps in the process require evacuation of the container in which the powder is heated, control of the pressure at this stage may readily be accomplished by keeping a valve in the vacuum pipe line only slightly open to provide the partial evacuation required to maintain a suitable pressure of hydrogen above the powder. Heating is then continued, meanwhile maintaining the hydrogen pressure in the container, until the powder has formed a soft semi-sintered cake. This will occur at a temperature generally between 650° C. and 750° C. and the optimum temperature within this range will depend on

(1) The particle size of the powder.
(2) The purity of the powder.
(3) The time at sintering temperature.

In the case of titanium powder of, for instance, minus 100 mesh and of moderate purity as indicated by a Brinell hardness number of about 200, a temperature in the higher portion of the general range, that is, between about 725° and 750°, will form a satisfactory semi-sinter with no free powder and yet soft enough to be readily disintegrated to its previous particle size after dehydrogenation. For powders of greater purity, for instance, as indicated by a 160 Brinell hardness number of minus 100 mesh size, a temperature of about 700° C. will produce a suitable semi-sinter. For finer particles, for instance, minus 200 mesh, the sintering temperature should be within the lower portion of the range given, that is, between 650° and 700° C.

The time at high temperature is not important except for the finest and purest powders. These should not be held for long times at temperatures substantially above their incipient sintering temperatures to avoid formation of hard sinters which cannot be readily disintegrated. In such cases the powder may be brought up to the desired temperature, for example, 700° C., for an hour to form the required soft semi-sintered cake and then the temperature lowered somewhat for example to 650° C. while the hydrogen is being evolved and withdrawn by vacuum which may take up to 6 or 8 hours. The temperature during the hydrogen removal period should however exceed 450° C. and best results are obtained when the temperature during this period is maintained as high as possible without over-sintering the powder; this will most

often be about the temperature reached during the sinter formation step.

The following example illustrates an embodiment of this invention.

Example 1

Titanium metal fragments were hydrogenated until brittle and then ground in a rod mill to the following fineness.

20%	−100	+200 mesh
40%	−200	+325 mesh
40%	−325	mesh

A charge of the ground powder was placed in a stainless steel closed container connected through a valve to a vacuum pump. The container was placed in an electric furnace and heat applied and the container evacuated. The pressure in the container was reduced to 10μ. When the temperature of the powder reached 400° C., the valve in the vacuum line was closed. When the powder reached 450° C., the pressure in the container started to rise rapidly indicating evolution of hydrogen. The vacuum line valve was then opened slightly so as to maintain a pressure in the container of about 550 mm. of mercury absolute while the powder has heated further to a temperature of 725° C., forming a soft sinter cake. Upon reaching a temperature of 725° the heat supply was cut down so that this temperature was maintained but not exceeded. The vacuum line valve was then fully opened slowly and the full capacity of the vacuum pump applied to the container. After six hours at 725° C. the pressure in the container had reached 1 micron indicating that no further evolution of hydrogen was taking place. The heat supply and vacuum pump were shut off, and after cooling, the container was opened. The powder was in the form of a soft coherent cake and no powder had separated or been blown away from the main mass. A light grind in a rod mill reduced the cake to fineness comparable to that of the original hydrogenated powder. The hydrogen content of the dehydrogenated powder was .008% and the Brinell hardness number was 170 indicating good purity.

The process of this invention results in efficient and rapid dehydrogenation of titanium powder without affecting its quality. When the heating and evacuating steps are carried out as described, the soft semi-sintered cake formed will retain all the powder in a coherent mass during evolution of hydrogen. Under these conditions the gas may be withdrawn from the powder at a rapid rate without displacement of the powder in its container or loss in vacuum lines and other parts of the apparatus. At the same time, the semi-sintering operation does not apparently appreciably affect the ultimate size of the individual particles, and after cooling the cake may be readily broken up by a light grinding action, and it is significant that the resulting fineness of the product will be substantially the same as before dehydrogenation.

I claim:

1. A method for dehydrogenating previously hydrogenated titanium metal powder which comprises (*a*) heating said powder in an enclosed container until said powder has attained a temperature of about 400° C. meanwhile evacuating said container, (*b*) continuing to heat said powder in said container under an atmosphere of hydrogen evolved from said powder at a pressure of not less than 500 mm. of mercury absolute until the temperature of said powder has reached between 650° C. and 750° C. and said powder forms a soft semi-sintered cake, and (*c*) continuing to heat said soft semi-sintered cake in said container to maintain a temperature thereof between about 450° C. and about 750° C. meanwhile evacuating said container until the hydrogen is substantially completely removed from said powder.

2. A method for dehydrogenating previously hydrogenated titanium metal powder which comprises (*a*) heating said powder in an enclosed container until said powder has attained a temperature slightly below the decomposition temperature of titanium hydride meanwhile evacuating said container, (*b*) continuing to heat said powder in said container meanwhile partially evacuating said container to maintain a hydrogen gas pressure therein of not less than 500 mm. of mercury absolute and up to atmospheric pressure until the temperature of said powder has reached between 650° C. and 750° C. and said powder has formed a soft semi-sintered cake and (*c*) continuing to heat said soft semi-sintered cake in said container to maintain a temperature thereof between about 450° C. and about 750° C. meanwhile evacuating said container until the hydrogen is substantially completely removed from said powder.

3. A method for dehydrogenating previously hydrogenated titanium metal powder which comprises (*a*) heating said powder in an enclosed container until said powder has attained a temperature slightly below the decomposition temperature of titanium hydride meanwhile evacuating said container, (*b*) continuing to heat said powder in said container meanwhile partially evacuating said container to maintain a hydrogen gas pressure therein of not less than 500 mm. of mercury absolute until the temperature of said powder has reached between 650° C. and 750° C. and said powder has formed a soft semi-sintered cake and (*c*) continuing to heat said soft semi-sintered cake in said container to maintain a temperature thereof about that reached in step (*b*) meanwhile evacuating said container until the hydrogen is substantially completely removed from said powder.

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