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PROCESS FOR THE PRODUCTION OF POWDERED METALS

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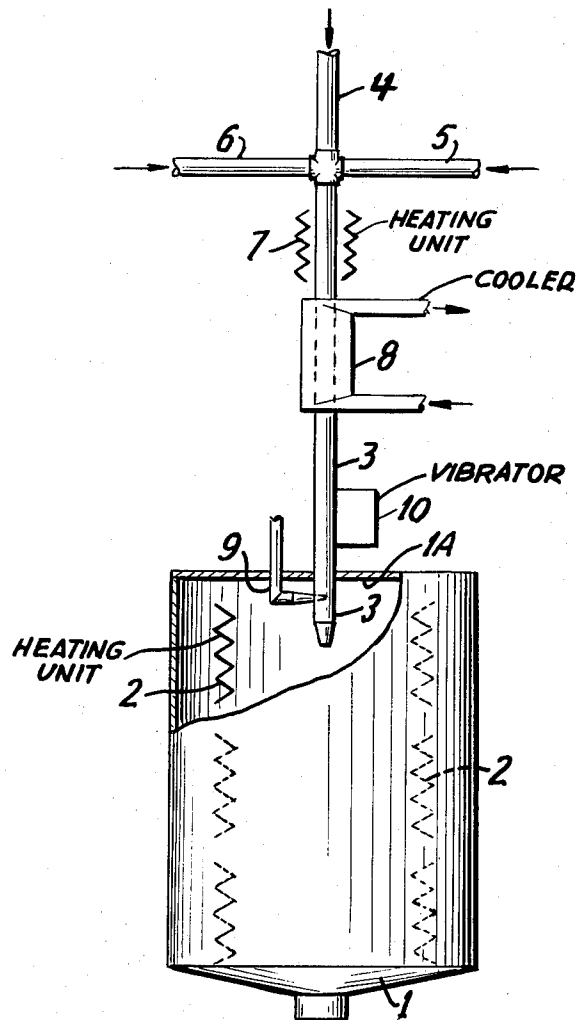


FIG. 1

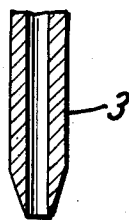


FIG. 2

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PROCESS FOR THE PRODUCTION OF POWDERED METALS

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9 Claims

ABSTRACT OF THE DISCLOSURE

An apparatus and process are provided for reducing metal halides to metal powder low in halide content, the process comprising providing a preheated substantially uniform mixture of reactants comprising a metal halide uniformly dispersed through hydrogen at a temperature above the reaction temperature for said reactants, and then immediately feeding the preheated mixture into a reaction chamber, whereby the reaction to metal powder is substantially spontaneously effected.

This invention relates to a process and apparatus for the production of metal powders by the reduction of metal halides and, in particular, to the production of such metal powders as tungsten, molybdenum, tantalum, niobium, rhenium, chromium and alloys thereof.

PRIOR ART AND THE PROBLEM CONFRONTING THE ART

It is known to produce tungsten powder by the hydrogen reduction of WO_3 by employing a batch operation in which powder WO_3 is placed in small boats following which the boats are heated to the desired reducing temperature in hydrogen. This process has its disadvantages in that the labor requirements are high and that large amounts of hydrogen gas are generally necessary.

As illustrative of one process disclosed in the literature, gaseous chlorides of heavy metals are reduced with a reducing agent, such as hydrogen gas. In this process, the two gases are fed through concentric tubes to a reaction chamber in such a manner that the gases are mixed together only when they reach the reaction furnace proper beyond the exit orifices or mouths of the tubes. However, this process is disadvantageous in that metal reduced out tends to form deposits at the tube orifices on the wall common to the concentric tubes. In an attempt to prevent the formation of such deposits, an additional concentric tube for supplying inert gas to the reaction chamber was proposed inserted between the tube for the metal chloride and the hydrogen tube. However, this expedient did not provide satisfactory mixing of the reaction components, the mixing being even further adversely affected, and, moreover, incomplete reduction resulted wherein the powder produced had a high chloride content. In addition, the metal tended to partially reduce out in the form of metal foil on the reactor walls which appeared as broken pieces (glittering fragments) in the powder produced which adversely affect the quality of the powder.

It was difficult with the foregoing process to measure the temperature of the gas mixture resulting from the flow through the concentric tubes prior to the entry of the mixture into the reactor. Generally speaking, the measurement was usually limited to measuring the temperature of the gas components before entry into the chamber. Because of this, it is very difficult to maintain an accurate control of the temperature of the mixture, which temperature control is an important parameter for obtaining and controlling the desired grain or particle size.

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Another known process comprises applying metal coatings to objects such as tungsten or molybdenum coatings. In this process, the gaseous reactants are mixed in a single tube with the conditions of reduction chosen to occur at the surface of the object to be coated. For example, the gas mixture is maintained at below the reaction temperature while the object is heated, e.g. inductively heated, to a temperature above the reaction temperature of the mixture to effect reduction at the surface of the object. As is quite apparent, the object here is not to form metal powder but to reduce out a metallic coat on the surface of objects.

In U.S. Pat. No. 3,450,525, a method is disclosed for producing metal powders in which metal halides are gasified in a pre-heating furnace and then mixed with hydrogen at a temperature below the reaction temperature of the mixture, following which the gas mixture is directed into a reaction chamber where heat is supplied at the walls thereof at substantially above the reaction temperature to avoid the formation of metal foil deposits on the walls. Because the reaction temperature is reached first within the reaction chamber by heat supplied by the walls, the process first proceeds relatively slowly and incompletely, which results in a relatively high content of residual halides in the metal powder produced and in the requirement of relatively large excess of hydrogen. An essential disadvantage of this process is that it is difficult to control the grain size of the resulting metal powder.

The present process differs in that metal powder of the desired grain size low in residual halide content can be produced by using less hydrogen than is normally employed in prior art processes.

OBJECTS OF THE INVENTION

It is thus the object of the invention to provide a process for the production of metal powder from metal halides, including oxyhalides.

Another object of the invention is to provide a process for producing metal powder from metal halides, such as chlorides of tungsten, molybdenum, tantalum, niobium, rhenium, chromium, and the like, by reduction with hydrogen with the following advantages: (1) control of grain size of the resulting metal powder; (2) use of lower amounts of hydrogen; (3) inhibition of metal foil formation on reactor walls, in feed lines and at the nozzles; and (4) production of metal powder with a low residual halide content.

These and other objects will more clearly appear from the following disclosure and the appended drawing, wherein:

FIG. 1 is a schematic representation of one apparatus embodiment for carrying out the invention; and

FIG. 2 is a fragment in cross section of a mixing tube.

SUMMARY OF THE INVENTION

Stating it broadly, a process is provided for reducing metal halides to metal powder low in residual halide content comprising, providing a preheated substantially unreacted mixture of reactants comprising a metal halide uniformly dispersed through hydrogen preheated to a temperature at least above the reaction temperature for said mixed reactants, and then immediately feeding the preheated mixture into the reaction chamber, whereby the reaction to metal powder is substantially spontaneously effected.

For example, in the case of the chlorides of tungsten, molybdenum, tantalum, rhenium, chromium, and the like metals, the reduction process is carried out in the presence of hydrogen in such a manner that the chlorides, in preferably the gaseous state, are mixed with hydrogen in one or several ducts at a first temperature above the reaction temperature before the mixture is fed into the

reactor, the preheated mixture being thereafter directed at a predetermined or controlled velocity into the reactor which is preferably, though not necessarily, heated to a second temperature above the first temperature. The resulting metal powder is then separated from the gas. The desired grain size of the powder product is determined by controlling one or more variables of the gas mixture, such as the temperature, the velocity of the gaseous reactants, the ratio of the reactants, etc. The apparatus employed for carrying out the process preferably utilizes a metal mixing tube which extends into the reactor, the apparatus being provided with means for adjusting the ratio of the mixture, the velocity of the mixture, the temperature thereof, and means for preventing the formation of metal foil deposits at the orifice or mouth of the tube extending into the reactor.

DESCRIPTION OF THE DRAWING

The schematic depicted in FIG. 1 shows a reactor 1 provided with a plurality of electric heating elements 2, the heating elements being divided in groups (known in the art) so that the thermal energy is supplied in a series of zones. A metal mixing duct 3 is provided which opens into the reactor, the mixing tube extending sufficiently inwardly from reactor end wall 1A in order to avoid reaction between the halide gas and the reduction gas at the end wall.

The metal duct preferably is mounted coaxially with the longitudinal axis of the reactor. However, the reactor may also be provided with several mixing ducts for the supply of mixed gas. In such cases, the ducts are preferably introduced into the reactor near or about the line of symmetry or longitudinal axis of the reactor and in parallel with said axis.

The reaction components in the gaseous state and possibly another gas (e.g. an inert gas) are supplied to the mixing tube through feed lines. The drawing shows a line 4 for the supply of metal halides in preferably the gaseous phase, a second line 5 being provided for supplying reduction gas (e.g. hydrogen), and a third line 6 for supplying, when desired, an inert gas, or a halogen in gaseous state or some other gas. A plurality of heating elements are shown at 7 for possibly supplying heat to the gas. These elements are arranged around the mixing tube in heat transfer relationship therewith in the conventional manner. Means 8 are provided for cooling the gas mixture to the desired first temperature where this is found necessary. At 9, is shown a thermocouple for measuring the temperature of the gas mixture before it enters the reactor. The thermocouple is mounted immediately before the place of entry as it has been found to be a suitable point for temperature measurement. Vibratory means 10 are provided for vibrating the mixing tube, the means being preferably attached immediately before the point of entry of the mixing tube into the reactor. By subjecting the mixing tube to vibration, it is possible to inhibit metal reduced out from depositing on the orifice of the mixing tube in the reactor. The shape of the orifice of the mixing tube in the reactor is shown in FIG. 2, where the annulus of the tube is pointed or tapered so as to provide a sharp edge, to further avoid adhesion of the metal reduced out.

DETAIL ASPECTS OF THE INVENTION

According to one embodiment of the invention, the halide gas and the reduction gas are mixed in one or several tubes prior to being fed into the reactor at a temperature exceeding the reaction temperature of the gas mixture. It is to be understood that the conditions for a reaction already prevail within the mixing tube, and that the reaction is beginning to commerce here. However, it is not desirable that the reaction proceed to any great extent within the mixing tube. The primary objective is to effect a highly homogeneous mixture and, secondly, to produce a mixture in which the reactants

are at a predetermined ratio, temperature and velocity such that a powder of a desired grain size is obtained. It is, therefore, important that the gas velocity should be selected relative to the length of the mixing tube so that there is sufficient time for only a slight reaction to begin within the mixing tube prior to the entry of the gas into the reactor. In a sense, the reaction incubates in the mixing tube just before it enters the reaction zone in the reaction chamber. Subsequent to the entry thereof into the reactor, the gas mixture satisfies all conditions required for a continued reaction, which takes place very rapidly and completely in the reactor which preferably, though not necessarily, is maintained at a higher temperature than the temperature in the mixing tube.

The metal powder obtained according to conventional processes in which substantial excess of hydrogen is employed usually is much too fine-grained, and, in most cases, falls within the grain size range from about 0.01 to 0.05 micron with the density between about 0.15 and 0.35 g./cm.³. The range which is of interest in commerce, however, lies between 0.05 and 10 microns, and the densities of interest are from 0.8 to 4 g./cm.³. In the present invention, by controlling the variables, powder may be obtained which falls within the aforementioned desired ranges. The ratio of mixture of reduction gas and halide gas affects the grain size in that an increase in the reduction gas content results in decreasing grain size. In accordance with the invention, a small grain size can be achieved with a relatively small excess of reduction gas which, in the case of hydrogen, usually does not exceed twice the stoichiometric amount required for the reaction. This is advantageous in that provides an economic process.

The temperature affects the grain size such that with increasing temperature of the mixing gas, a decrease in grain size is obtained. The grain size in the powder may be decreased more substantially by adding a halogen (e.g. chlorine) in the gaseous state to the gas mixture. This is because an indirect temperature increase results by the reaction of the halogen gas with excess hydrogen.

Inversely, larger grains in the powder are obtained by decreasing the temperature of the gas mixture. Normally, the hydrogen gas and the metal halide (e.g. chloride) gases are heated or cooled in advance to a temperature within the desired temperature range. Around the mixing tube may then be supplied extra heating or cooling means for slightly adjusting the temperature of the mixing gas to the desired range prior to the entry thereof into the reactor. Another method of rapidly adjusting the temperature of the mixing gas is by dilution with an inert gas, such as nitrogen gas or hydrogen chloride. Such a dilution of the mixing gas results in a powder of a greater grain size.

The reaction in the reactor, as already mentioned, proceeds efficiently to completion, whereby the produced powder has a very low chlorine content, in many cases below 0.5%. A further advantage is the highly improved quality of the powder, due to the absence of inhomogeneity in the form of flakes or glittering foils. It is generally desirable to raise the temperature in the lower reactor part by an additional supply of heat in order to assure completeness of the reaction.

According to the invention, it is also possible to co-reduce chlorides, for example, tungsten chloride and rhenium chloride, and thereby produce a metal powder in which substantially every grain is homogeneous from a compositional viewpoint.

The apparatus for carrying out the process comprises substantially a mixing tube extending into a reaction chamber. There may be a plurality of mixing tubes, but, irrespective of their number, they preferably are oriented along the line of symmetry or longitudinal axis of the reactor or spaced uniformly around said line as they enter the reactor chamber. The mixing tubes, further-

more, preferably open within the reactor some distance inside from its inner wall. The mixing tubes preferably are made of a metal. If the temperature of the gas mixture can be maintained below 600° C., tubes of nickel or Inconel (15% Cr. 6 to 7% Fe and the balance nickel) may be used without giving rise to aggravated corrosion problems which usually contaminated the powder to an appreciable degree. Previously, tubes of glass or quartz have been used, but such tubes had a very short life and, moreover, they contaminated the metal powder when they broke into pieces.

Tubes made of metal are advantageous also in other respects. They can be subjected to vibrations, so that possible incrustations on the tube can easily be removed by shaking. This can be effected very simply by placing a vibrator on the mixing tube immediately before its entry into the reactor. As stated hereinbefore, in order to prevent metal reduced out from adhering on the tube mouth in the reactor, the tube mouth preferably is pointed so as to form a sharp edge. It is also easy to supply or remove heat through the metal tube, which facilitates controlling the temperature of the gas mixture.

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

Example 1

Utilizing an apparatus of the type shown in FIG. 1, a flow of 22 kg. WCl_6 per hour was mixed with a flow of 96 litres of H_2 per minute (referred to room temperature) in a nickel tube opening into the reactor heated to 1000° C. The WCl_6 gas had a temperature of 400° C., and the H_2 gas of 525° C. This resulted in a mixture which immediately prior to its entry into the furnace had a temperature of about 440° C., since a certain amount of heat transfer between the mixing tube and the ambient environment had thereby taken place. The gas velocity was 25 m./sec. The tungsten powder produced had a residual chlorine content of about 0.26% by weight and a grain size of about 0.2 micron determined by means of an electron microscope. The density of the powder was 1.32 g./cm.³. The powder did not contain glittering metal fragments and was uniform, the inside of the mixing tube being free of metal coatings.

Example 2

A flow of 22 kg. WCl_6 per hour was mixed as in Example 1 with a flow of 70 litres of H_2 per minute (referred to room temperature) in a nickel tube into the reactor. The upper portion of the reactor was heated to 800° C., the central portion to 900° C., and the lower portion to 1000° C. The WCl_6 gas had a temperature of 400° C., and the H_2 gas a temperature of 150° C. This resulted in a mixture which immediately prior to its entry into the furnace had a temperature of about 320° C. A certain amount of heat transfer between the mixing tube and the ambient environment had already taken place. The gas velocity was about 16 m./sec. The tungsten powder produced had a residual chlorine content of about 0.8% by weight and a grain size of 2.1 microns determined by means an electron microscope. The density was 3.2 g./cm.³. The powder did not contain glittering fragments and was uniform. The inside of the mixing tube was free of metal coatings.

Example 3

Utilizing an apparatus of the type shown in FIG. 1, a flow of 13 kg. WCl_6 per hour and 3.0 kg. Cl_2 per hour was mixed with a flow of nitrogen gas of 96 litres/min. (referred to room temperature) in a nickel tube opening into the reactor heated to 1110° C. The mixture of WCl_6 and Cl_2 had a temperature of about 400° C. Subsequent to the admixing of the hydrogen gas, the temperature of the gas mixture was 415° C. immediately prior to the entry into the furnace. The gas velocity was 60 m./sec. The tungsten powder produced had a residual chlorine content of about 0.5% and a grain size of about 0.05 micron determined by

means of an electron microscope. The powder did not contain glittering fragments and was uniform. The inside of the mixing tube was free of metal coatings.

While the examples set forth hereinabove are directed to the reaction of tungsten hexachloride with hydrogen, the reaction of other halides may be carried out similar to Examples 1, 2 and 3.

Examples of the halide reactions which may be carried out similar to Examples 1, 2 and 3 are:

- (A) $WI_6 + 3H_2 \rightarrow W + 6HI$
- (B) $2NbCl_5 + 5H_2 \rightarrow 2Nb + 10HCl$
- (C) $2CrCl_3 + 3H_2 \rightarrow 2Cr + 6HCl$
- (D) $MoI_6 + 3H_2 \rightarrow Mo + 6HI$
- (E) $2TaCl_5 + 5H_2 \rightarrow 2Ta + 10HCl$
- (F) $CoI_2 + 2H_2 \rightarrow Co + 2HI$

The amount of hydrogen which may be employed in carrying out the reaction need not exceed two times the stoichiometric amount. As stated hereinbefore, the grain size can be controlled according to the amount of hydrogen used, that is, the greater the amount of hydrogen, the smaller the grain size. Similarly, the higher the mixing temperature of the unreacted ingredients, the smaller the ultimate grain size. The addition of a halogen to the gas mixture also results in a decrease in grain size. Larger grains may be produced by inversely controlling one or more of the foregoing variables, that is, by lowering the temperature, or lowering the ratio of hydrogen to the halide, etc., or by adding an inert gas or HCl.

Although the temperature of the reactor in each of the examples is higher than the mixing temperature of the reactants, the reactor temperature need not be higher so long as the reaction goes to completion therein and so long as the temperature of the substantially unreacted premixed ingredients fed to the reactor is above the reaction temperature. Generally speaking, the temperature in the reactor is usually higher than the temperature of the unreacted gas mixture fed to it. The temperature in the reactor may range up to about 1600° C. and, for example, from about 700° C. or 800° C. to 1600° C.

The minimum reaction temperature of a particular mixture of metal halide and hydrogen can be determined by tests. For example, tests have shown that heating WCl_6 in a quartz tube furnace under a low hydrogen flow indicated that the minimum reaction temperature in this system ranged from about 300° C. to 330° C.

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

What is claimed is:

1. A process for reducing metal halides to metal powder low in halide content which comprises, providing a preheated substantially unreacted mixture of reactants comprising a metal halide uniformly dispersed through hydrogen incubated at a temperature above the reaction temperature for said reactants, and then immediately feeding said preheated mixture into a reaction chamber, whereby said reaction to metal powder is substantially spontaneously effected in said reaction chamber.
2. The process of claim 1, wherein the metal halides are selected from the group consisting of halides of W, Mo, Ta, Nb, Re, Cr and mixtures thereof.
3. The process of claim 2, wherein the metal halide is tungsten hexachloride.
4. The process of claim 3, wherein the temperature of the preheated tungsten hexachloride prior to feeding into the reaction chamber is over about 300–330° C.

5. The process of claim 1, wherein the grain size of the ultimate metal powder is determined by controlling at least one of the parameters: ratio of the reactants, velocity of the reactant mixture, the temperature of the mixture, and the amount of gaseous diluent selected from the group consisting of inert gases and a halogen added to the reactant mixture; such that for increased amounts of hydrogen or increased velocity, or increased temperature of the mixture, a finer grain size is obtained, and where at least one of the foregoing parameters is decreased, a larger grain size is obtained; and such that when an inert gas is added to the mixture, a larger grain size is obtained, and when a halogen is added to the mixture, a finer grain size is obtained.

6. The process of claim 5, wherein a halogen gas is diluted with the reactant mixture to produce a finer grain size.

7. The process of claim 6, wherein the halogen gas is chlorine.

8. The process of claim 5, wherein an inert gas selected from the group consisting of nitrogen and HCl is added

to the gas mixture to increase the grain size of the ultimate metal powder.

9. The process of claim 1, wherein the temperature in the reaction chamber is higher than the temperature of the unreacted mixture.

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