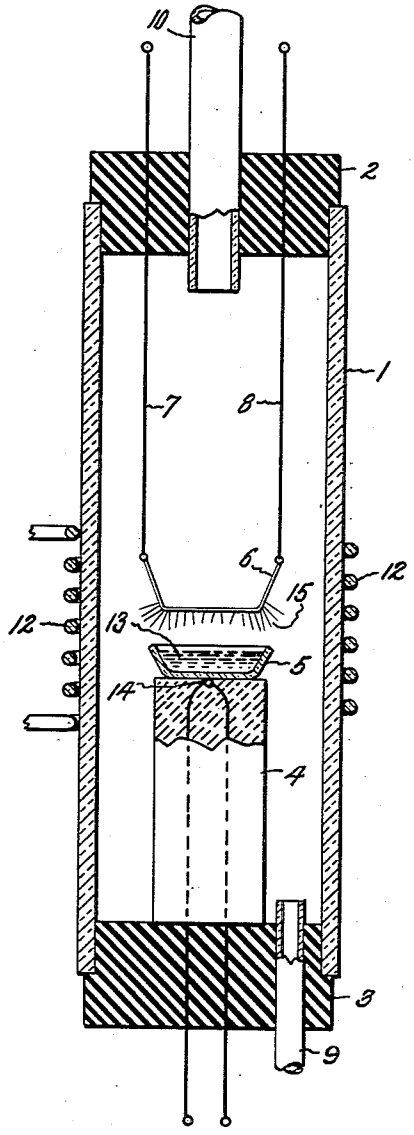
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METHOD AND APPARATUS FOR THE PRODUCTION OF SINGLE CRYSTALS

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METHOD AND APPARATUS FOR THE PRODUCTION OF SINGLE CRYSTALS

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The present invention relates to high strength single crystals and more particularly to a process and apparatus whereby such crystals may be prepared.

Previously known crystalline materials have never exhibited values for mechanical properties such as tensile strength, elastic limit, etc. as high as they theoretically should. Usually the actual strength of crystalline materials is of the order of several degrees of magnitude less than their theoretical maximum strength. It has been postulated that this difference is primarily caused by the presence of structural imperfections in the crystal lattice such as dislocations. It has been found that rod-like single crystals may be grown to have near-theoretical values of their mechanical properties. Because of their high strength, these crystals are useful as strain gauge elements, springs, and the like.

As disclosed in one of the present inventors' copending application Serial No. 523,359, filed July 20, 1955, and assigned to the assignee of the present application, near perfect single crystals of elements such as, for example, copper, silver, gold, iron, nickel, cobalt, and platinum may be grown by vapor deposition upon a substrate maintained at a temperature between about 430° C. and 960° C. As disclosed, the metal vapor from which these crystals are grown is provided by the decomposition of a volatile compound of the metal to be deposited.

Because of the known mechanical and electrical properties of conventional metallic tungsten, high strength near-perfect rod-like single crystals of tungsten would have many useful and unique applications as will be readily appreciated by those skilled in the metallurgical and electrical arts. All previous attempts, however, to grow such crystals from tungsten have failed.

We have discovered that high strength, near perfect, rod-like single crystals of tungsten may be grown at or near atmospheric pressure by the vapor deposition of tungsten upon a suitable substrate which is maintained at a temperature of the order of 2000° C. The phrase "at or near atmospheric pressure" or "substantially atmospheric pressure" is intended to cover a pressure range extending from a major fraction of one atmosphere to about one and one-half atmospheres.

It is a principal object of our invention to provide a method whereby high strength, near perfect, rod-like single crystals of tungsten may be grown. A yet further object of our invention is the provision of apparatus whereby such high strength single crystals of tungsten may be produced. Other and specifically different objects and novel features of our invention will become apparent from the detailed disclosure which follows.

In the following disclosure, reference will be made to the accompanying drawing in which a sectional semi-schematic representation of apparatus is illustrated which may be employed in practicing our invention.

In practicing our invention, a chemical compound of tungsten capable of being reduced by hydrogen is held in a flowing stream of hydrogen at a temperature slightly above its melting point. The substrate upon which the

high-strength single crystals of tungsten are to be grown is positioned adjacent to the molten tungsten salt and is maintained at a temperature of the order of 2000° C. High strength, near perfect, rod-like tungsten single crystals nucleate and grow on the heated substrate.

Our invention may be better described with reference to the accompanying drawing in which is shown, as an example, apparatus which may be used in the practice of our invention. A tubular enclosure 1 which is preferably constructed from a transparent material such as high temperature resistant glass or quartz is provided at each end with closure elements 2 and 3 to form a substantially closed reaction chamber. Closure elements 2 and 3 effectively exclude atmospheric air from the interior of tubular element 1 as will be more fully disclosed later. While tubular element 1 has been disclosed as being preferably made of a transparent material, it will be appreciated that opaque materials such as metals, for example, may be employed in its place, if direct visual observation of the interior of the reaction chamber is not desired or deemed necessary, or transparent "window" portions may be provided in the side walls of an otherwise opaque tubular member 1, if deemed necessary.

The reaction chamber comprising tubular element 1 and closure elements 2 and 3 is preferably arranged in a vertical position and a support preferably of a refractory material such as fire brick or ceramic is arranged upon closure element 3 as shown. A heat resistant non-reactive container such as a porcelain boat 5 may be conveniently arranged upon support 4.

An element 6 adapted to provide a surface or substrate for deposition thereon is positioned adjacent the open top of boat 5. Element 6 may be supported or otherwise positioned in the operative relationship to boat 5 shown on the drawing by any suitable means. Means are provided whereby substrate element 6 may be supplied with heat. As shown in the figure, this may be conveniently accomplished by constructing element 6 from a material such as tungsten ribbon and supplying an electric current to flow therethrough by means of leads 7 and 8. By appropriate regulation of the current flowing through substrate element 6, its temperature may be regulated and maintained as desired. While substrate element 6 has been disclosed as being heated by means of an electric current passing therethrough, it is obvious that other and equally effective means for heating the substrate surface may be employed. For example, substrate element 6 could obxiously be provided with a separate electrical resistance heater in intimate contact therewith or equally well might be heated by electrical induction. Other specifically different but equally satisfactory heating means will readily occur to those skilled in the art.

A tubular conduit 9 extends through closure member 3 and provides a passageway through which a gas such as hydrogen may be introduced into the interior of the reaction chamber. A tubular conduit 10 extends through closure element 2 and provides a passageway through which gas may flow from the interior of the reaction chamber. As shown, the conduit 10 is preferably larger in cross-sectional area than conduit 9.

High strength, rod-like tungsten single crystals may be deposited or grown upon substrate 6 in the following manner. An appropriate quantity of a chemical compound of tungsten capable of being reduced in hydrogen such as tungstates of the alkali metals and alkaline earths is placed within the container 5. The apparatus is assembled as shown and atmospheric gas entrapped within the reaction chamber is flushed therefrom by means of hydrogen introduced through conduit 9. After the atmosphere has been swept from the chamber, hydrogen is permitted to continue to flow

through the chamber and to exit through conduit **10**. Preferably the linear rate of hydrogen flow is maintained at up to about 50 centimeters per minute, and preferably about 25 centimeters per minute.

The tungstate compound within container **5** is melted by any convenient means such as, for example, an electrical resistance heating element shown at **12** and maintained at a temperature slightly above its melting point. In the case of sodium tungstate, for example, the temperature should be maintained between about 700° C. and 750° C. The temperature of the molten material **13** may be determined and maintained by any convenient means such as, for example, a thermocouple having its hot junction **14** in heat exchange relationship with container **5**. An electric current is supplied to substrate element **6** by means of leads **7** and **8** and the temperature of substrate element **6** is determined and maintained at between 1800° C. and 2200° C. This may be accomplished in any convenient manner such as, for example, by determining the temperature of element **6** by means of an optical pyrometer and making suitable adjustments in the electric current supplied to leads **7** and **8**. After a period of time, near-perfect rod-like single crystals of tungsten **15** will nucleate upon substrate **6** and grow therefrom.

As a specific example of the operation of the previously described apparatus according to our invention, about 5 grams of sodium tungstate was placed in a porcelain boat **5** which was then placed upon support **14** and the several elements comprising the reaction chamber assembled around support **14** as illustrated in the drawing. The interior of the reaction chamber was flushed with hydrogen introduced through conduit **9** and the linear rate of hydrogen flow was adjusted to about 40 cm. per minute. The hydrogen was permitted to freely escape the interior of the reaction chamber by means of conduit **10** so that the pressure within the reaction chamber remained substantially equal to atmospheric pressure.

The temperature of boat **5** and the sodium tungstate contained therewithin was then raised by means of heater **12** to about 725° C. thereby melting the sodium tungstate. The temperature of the tungsten substrate **6** was adjusted at about 2000° C. as determined by means of an optical pyrometer. A plurality of rod-like metallic structures grew from the surface of substrate **6** as shown at **15**. Upon examination these rod-like structures were each found to be single crystals of tungsten and to have near-theoretical mechanical properties.

From the foregoing, it will be apparent that we have invented an apparatus and a method whereby rod-like near-perfect single crystals of tungsten may be grown by deposition from the vapor phase.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A method for making high strength rod-like single crystals of tungsten comprising the steps of melting a tungstate of an element selected from the group consisting of alkali metal tungstates, alkaline earth tungstates and mixtures thereof in hydrogen at or near atmospheric pressure thereby producing an atmosphere comprised of hydrogen and tungsten-bearing vapor and passing said atmosphere over and around the surface of tungsten substrate maintained at a temperature between about 1800° and 2200° C. upon which high strength rod-like single crystals of tungsten are caused to be formed.

2. The method recited in claim 1 in which the tungstate consists essentially of sodium tungstate.

3. The method recited in claim 2 in which the molten sodium tungstate is maintained at a temperature of between 700° to 750° C.

4. The method recited in claim 3 in which the molten sodium tungstate is maintained at about 725° C.

5. The method recited in claim 4 in which the tungsten subtrate is maintained at about 2000° C.

6. The method recited in claim 2 in which the atmosphere is passed over and around the surface of the tungsten substrate at a linear flow rate of up to 50 cm. per minute.

7. The method recited in claim 6 in which the atmosphere flow rate is about 25 cm. per minute.

8. Apparatus for growing high strength, rod-like single crystals of tungsten comprising a reaction chamber, means for passing hydrogen into and through said reaction chamber, an open-top container within said reaction chamber, means for supplying heat to said open-top container, a tungsten substrate positioned adjacent said open-top of said open-top container and means for heating said tungsten substrate up to 2200° C.

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