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VAPOR DEPOSITION OF SINGLE CRYSTALS

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Fig. 1.

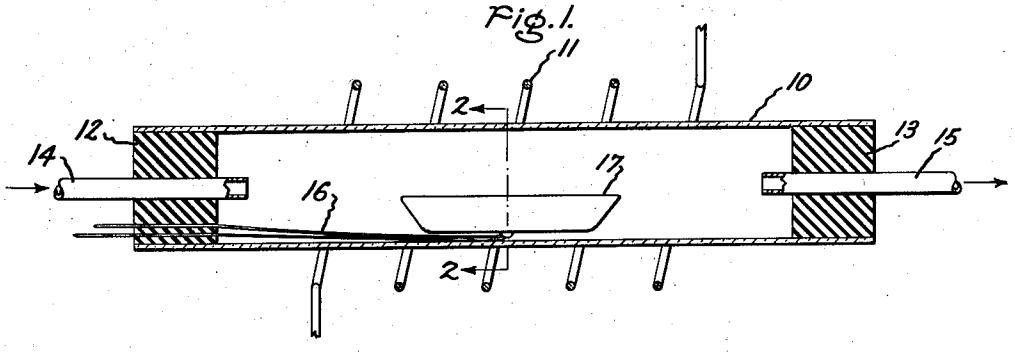
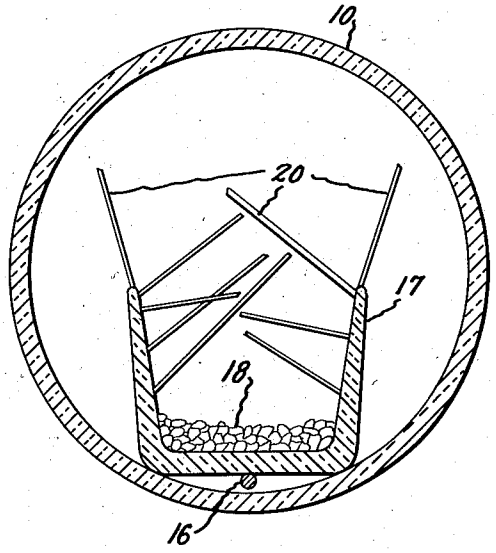


Fig. 2.



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VAPOR DEPOSITION OF SINGLE CRYSTALS

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12 Claims. (Cl. 148—1.6)

The present invention relates to high strength crystals and more particularly to a process whereby such crystals may be grown at or about atmospheric pressure, and is a continuation-in-part of my co-pending application Serial No. 471,075, entitled "Single Crystals," filed November 24, 1954, now abandoned.

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.

I have discovered that near-perfect single crystals may be grown at or near atmospheric pressure during the hydrogen reduction of a volatile metal compound, such as halide, and also under the same pressure conditions by the thermal decomposition of a volatile compound, such as a metal halide. 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 therefore a principal object of my invention to provide a process whereby rod-like high strength single crystals may be grown by deposition from the vapor phase at or near atmospheric pressure.

A further object of my invention is the provision of a process whereby rod-like high strength single metal crystals may be grown by vapor phase deposition of the metal resulting from the decomposition of a volatile metal compound.

Other and different objects of my invention will become apparent from the following disclosure which will be more readily understood when read with reference to the accompanying drawing, in which Fig. 1 is a semi-schematic elevational view, partly in vertical section, of an embodiment of apparatus useful in the practice of my invention, and Fig. 2 is a sectional view taken along plane 2—2 of Fig. 1 showing details thereof in greater detail.

In practicing my invention, a volatile metal compound is subjected to heat adjacent a suitable substrate, such as, for example, glass, porcelain or the like. The metal compound is vaporized, substantially simultaneously decomposed and the metal deposited from the vapor phase upon the substrate to form high strength rod-like single crystals. The rate at which the metal deposits upon the substrate is functionally related to the temperature of the substrate.

I have found that a conventional horizontal tube furnace to be a convenient source of heat. The volatile

compound may be conveniently placed in an open top porcelain boat or the like and inserted in the tube furnace. This apparatus is schematically illustrated in Fig. 1 of the drawing in which the tube furnace is conventionally composed of a hard glass or ceramic tube **10** and an electrical resistance heating element **11**. As is well known, such furnaces are usually provided with a thermal insulating jacket protecting the heating element, but for clarity of illustration this has been omitted in the drawing. Tube **10** is provided with end closures **12** and **13** of any suitable material which may be provided with tubular members **14** and **15** extending therethrough to permit the passage of a gas through the tube furnace if desired, as indicated by the arrows. Additionally, either closure member may be provided with an opening or openings through which a temperature-sensing means such as a thermocouple **16** may be inserted, as shown. In the practice of my invention with the apparatus shown, a quantity of the volatile metal compound to be treated is placed in a suitable container such as a porcelain boat **17** and the container positioned in the hot zone of the tube furnace as shown. The temperature-sensing means **16** is placed in contact with the container and the end closures inserted in the ends of the tube **10**. The furnace is heated by energizing the heating element **11** and the temperature of the container **17** is measured by means of a thermocouple and regulated by controlling the power supplied to the heating element **11**. If the crystal growth is to be accompanied by the vapor phase reduction of a volatile metal compound, a reducing atmosphere at substantially atmospheric pressure is provided. I have found that hydrogen passed through the tube furnace by means of tubular members **14** and **15** provides such an atmosphere and it may be conveniently disposed of by burning at the output end. As the temperature of the boat is increased, the volatile metal compound contained therein begins to vaporize and elemental metal is deposited in the form of rod-like high strength single crystals upon surfaces of the boat **17** which are exposed to the metal vapor. This is illustrated in greater detail in Fig. 2, in which a cross-section of boat **17** is shown resting within the tube **10** with thermocouple **16** in contact with boat **17**. The volatile metal compound is shown as a particulate mass at **18**, however, it will be appreciated that at the higher temperatures employable with some of the compounds to be disclosed, a liquid phase may be formed, depending upon the particular material being treated. The high strength rod-like single crystals of metal **20** are deposited as shown upon the surfaces of the boat, usually but not exclusively on the inner side surfaces of the boat. In the event that a volatile metal compound is to be thermally decomposed, a reducing atmosphere is not necessary and the crystal growth as illustrated in Fig. 2 may be accomplished in air, provided the material does not oxidize or otherwise react with the atmosphere at the temperature employed for decomposition. If such a reaction would take place, a neutral protective atmosphere may be provided. In any event, volatile products of either thermal decomposition or reduction are permitted to leave the reaction zone. The reaction involving the hydrogen reduction of a volatile metal compound, such as, for example, a metal halide, may be characterized by the equation

$$MeX + \tfrac{1}{2}H_2 \xrightarrow{\Delta} HX + Me$$

and the thermal decomposition of a volatile compound, such as, for example, a metal halide, by the equation

$$MeX \xrightarrow{\Delta} Me + \tfrac{1}{2}X_2$$

More specifically, the following table lists examples of metals from which rod-like high strength single crystals have been grown according to my invention.

Metal	Optimum Temperature, ° C.	Reaction
Copper	620	$CuI+\frac{1}{2}H_2 \rightarrow Cu+HI$
Silver	800	$AgCl+\frac{1}{2}H_2 \rightarrow Ag+HCl$
Iron	730	$FeCl_2+H_2 \rightarrow Fe+2HCl$
Iron	760	$FeBr_2+H_2 \rightarrow Fe+2HBr$
Nickel	740	$NiBr_2+H_2 \rightarrow Ni+2HBr$
Cobalt	650	$CoBr_2+H_2 \rightarrow Co+2HBr$
Platinum	800	$PtCl_4 \xrightarrow{(Air)} Pt+2Cl_2$
Gold	550	$AuCl_x \xrightarrow{(Air)} Au+Cl_2$

From the foregoing, it may be seen that the first six reactions involve the reduction of a volatile metal halide, while the last two examples illustrate thermal decomposition of volatile metal halides.

It will be noted here that the single crystals of gold listed in the foregoing table were formed during the thermal decomposition of a commercially obtained sample of "gold chloride" for which no analysis is available, but which probably consisted of a mixture of auric chloride ($AuCl_2$) and aurous chloride (AuCl). In view of the fact that the reaction temperature employed is well above the decomposition temperatures of both gold chlorides, the exact composition of the salt is believed immaterial and therefore the reaction equation has not been balanced. In this respect it should be here noted that extremely pure metal salts are not necessary in the practice of my invention. I have found that reagent grade salts are entirely satisfactory.

The temperatures given for the several reactions is about that at which optimum single crystal growth occurs. Actually, high strength copper single crystals, for example, may be grown over the range of about 430° C. to 800° C. Similarly, the temperatures listed for the latter five examples represent values which permit about optimum growth, but which may be varied by about ±100 to 200° C. before, on the lower side, crystal growth is slowed to an impractical rate or, on the higher side, before imperfections are introduced by too rapid growth. The rate at which the reducing atmosphere is passed over the growth sites of the crystals may be varied over a substantial range. For example, hydrogen flow rates of the order of from about 10 centimeters per minute to about 100 centimeters per minute have been successfully employed in the practice of my invention.

The crystals prepared according to my invention were removed from the furnace and tested by bending. The crystals supported elastic strains up to 1.5%, a load condition requiring an elastic limit far in excess of that realizable by conventional imperfect metals. For example, annealed single crystals, conventionally prepared from such materials and similarly tested, seldom support elastic strains as high as 0.01%.

From the foregoing, it will be apparent that I have provided a method for producing near-perfect high strength rod-like single crystals of metals comprising the ferromagnetic group, i. e. iron, cobalt and nickel, group I(B) of the periodic table, i. e., copper, silver and gold, and platinum by the decomposition of volatile metal compounds of these metals to permit their deposition from the vapor phase.

In view of the known characteristics of the halogen compounds and particularly metal halides, it is contemplated that my invention may be applied to other halides of these metals as well as to halides of other metals, provided the compounds are volatile. Further, my invention may be applied to other volatile metal compounds which may be either reduced or thermally decomposed in the manner disclosed.

From the foregoing, it is apparent that I have provided a novel, useful process for producing near-perfect high strength crystals. In the foregoing description of my invention, the several embodiments thereof have been cited as exemplary and I intend in the appended claims to cover all changes and modifications which do not constitute departures from the spirit and scope of the invention.

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

1. A method for producing high strength rod-like metallic single crystals comprising the steps of providing a metal vapor by the decomposition of a volatile metal compound at substantially atmospheric pressure and depositing the metal upon a suitable substrate at a rate less than that at which imperfections are introduced thereby forming a rod-like single crystal of said metal which is capable of supporting elastic strains as high as 1.5 percent.

2. The method recited in claim 1 in which the volatile metal compound is a halide of a metal selected from the group consisting of the ferromagnetic group, group I(B) of the periodic table and platinum.

3. The method recited in claim 2 in which the decomposition is accomplished by reducing the metal halide vapor.

4. The method recited in claim 3 in which the metal halide is copper iodide and the rate of deposition is controlled by maintaining the substrate at a temperature between about 430° C. and 800° C.

5. The method recited in claim 3 in which the metal halide is silver chloride and rate of deposition is controlled by maintaining the substrate at a temperature between about 650° C. and 900° C.

6. The method recited in claim 3 in which the metal halide is iron chloride and the rate of deposition is controlled by maintaining the substrate at a temperature between about 600° C. and 900° C.

7. The method recited in claim 3 in which the metal halide is iron bromide and the rate of deposition is controlled by maintaining the substrate at a temperature between about 560° C. and 960° C.

8. The method recited in claim 3 in which the metal halide is nickel bromide and the rate of deposition is controlled by maintaining the substrate at a temperature between about 540° C. and 940° C.

9. The method recited in claim 3 in which the metal halide is cobalt bromide and the rate of deposition is controlled by maintaining the substrate at a temperature between about 450° C. and 850° C.

10. The method recited in claim 2 in which the decomposition of the metal halide is accomplished by heating.

11. The method recited in claim 2 in which the metal halide is platinum tetrachloride and the rate of deposition is controlled by maintaining the substrate at a temperature between about 650° C. to 900° C.

12. The method recited in claim 2 in which the metal halide is gold chloride and the rate of decomposition is controlled by maintaining the substate at a temperature between about 350° C. to 750° C.

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