

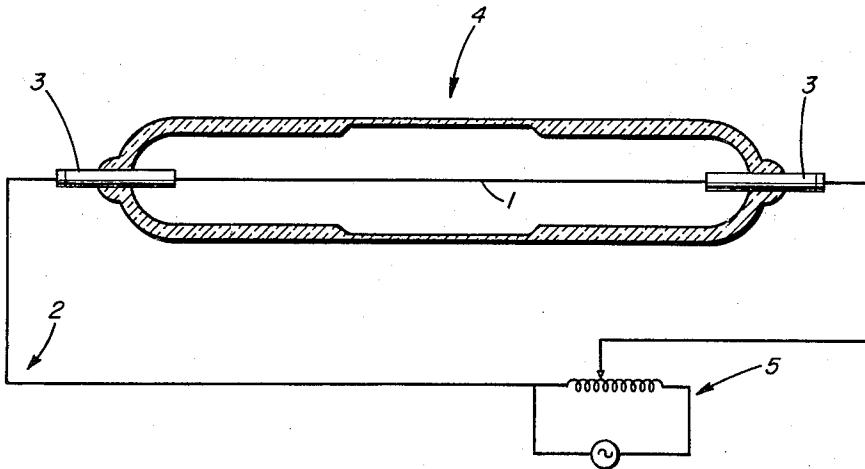
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METHOD FOR GROWING SINGLE CRYSTALS

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METHOD FOR GROWING SINGLE CRYSTALS

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention pertains to a novel method for growing single crystals from polycrystalline substances and more particularly to a novel solid-state method for growing large single crystals.

There are several known methods for growing single crystals from a polycrystalline base material. One such method entails initially growing (Bridgman Technique) or artificially providing solid seed crystals upon which large quantities of remaining liquid melt can solidify with an orientation similar to the initially grown or seeded crystal. This method presents many problems among which there can be mentioned; the difficulty in maintaining proper composition control in multi-component materials or alloys of homogeneous chemical compositions and the difficulty in finding a melt container that will not be dissolved by reactive elements with the great chemical affinity (e.g. Ti, Zr, certain rare earths, etc.) thereby contaminating the grown crystal.

Another method is the "strain-anneal" method which involves introducing a mechanical strain into the material which is followed by heating to a temperature near the melting point to provide both the energy gradient and the atomic mobility necessary to grow large single crystals. This method, however, cannot be used on brittle elements or materials (e.g., silicon, most intermetallic compounds, etc.) since they fracture when strained.

Accordingly, it is an object of this invention to provide a novel method for growing single crystals from polycrystalline substances.

It is another object of this invention to provide a solid-state method for growing large single crystals.

It is a further object of this invention to form single crystals from polycrystalline substances that are too brittle to be strained and too composition sensitive and/or reactive to be melted.

These and other objects will become more readily apparent from the following detailed description of the invention wherein the figure depicts a preferred apparatus for performing the method of the invention.

The objects of this invention are accomplished by heating and cooling the polycrystalline substance in an inert atmosphere in rapidly repeating cycles until a single crystal is formed. The method of this invention must be performed in an inert atmosphere (argon, helium, krypton, neon, under vacuum, etc.) since the presence of air or other reactive substances interferes with single crystal growth.

The material is heated to any temperature below its melting point; it is immediately cooled upon reaching the desired temperature and the heating and cooling is repeated in rapid cycles until a single crystal is formed.

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The minimum temperature to which the substance is initially heated is not critical since the process is operable at any temperature below the materials melting point but for practical purposes, the temperature of the heating should be at least 400° C. (assuming the material does not melt at 400° C.). The temperature to which the material is subsequently cooled is also not critical but it is to be understood that the process proceeds more rapidly with a wider gradient between the heating and cooling temperature, with a temperature gradient of at least 250° C. giving especially good results.

The important feature in this invention is the cyclic heating and cooling since heating at a constant temperature will not produce single crystal growth. There should be at a minimum about one cycle per minute with at least 8 cycles per minute being preferred. The more cycles per minute the faster the single crystal growth with the maximum number of cycles per minute being limited by the properties of the material, e.g. the maximum rate at which the material can be heated and cooled to the desired temperatures.

The optimum conditions of single crystal growth are dependent upon many factors such as thermal conductivity, relationship between crystal structure transition and recrystallization temperature, purity of the specimen, etc., but these optimum conditions can readily be determined by simple experimentation. It has been found that for many materials an initial heating to between about 750° and 1000° C., and a cooling to about 500° C. at at least 8 cycles per minute, with 12 cycles per minute being preferred, gives especially good results.

The method of this invention may be performed in a device such as the one illustrated in the figure. The polycrystalline substance 1 is placed in an electric circuit 2 by placing it between mounts 3 in a vacuum chamber 4 (cooling of the mounts 3 increases the rate of single crystal growth). The chamber is evacuated to a vacuum of lower than about 10⁻⁶ mm. and the specimen is heated and cooled in rapidly repeating cycles until a single crystal is formed by varying the current in circuit 2 by means of an autotransformer 5.

The progress in the change from a polycrystalline substance to a single crystal may be monitored by X-ray diffraction (Laue method using white radiation).

Although the method of this invention has been particularly described in regard to heating and cooling by electrical means, it should be understood that this method can be practiced with any other means that can effect heating and cooling in rapid cycles as for example, high frequency induction heating and cooling, electron bombardment, radiation, etc.

The method of this invention is operable on any polycrystalline metal, e.g., iron, copper, nickel, cobalt, titanium, tungsten, molybdenum, rhenium, etc.; single phase metallic alloy, e.g., TiNi (Nitinol), NiAl, Fe-Al, Zr₂Co, Cu-Ni, Fe-Ni tungsten borides, etc.; and semi-metal e.g., silicon, germanium, tellurium, etc. The invention is particularly applicable to brittle polycrystalline substances on which the "strain-anneal" methods are not practical as for example Ti₂Ni, Si, Ti₅Si₃, etc.

The following example illustrates a specific embodiment of the invention but its scope is not to be limited thereby.

EXAMPLE

The method of this invention was applied to several materials using the device shown in the figure. The materials and the conditions under which they were treated are shown below.

CRYSTAL GROWTH DATA (BASED UPON X-RAY DIFFRACTION MONITORING)

Specimen	Initial Specimen Condition	Chamber Pressure (mm.)	Specimen Heating Range (° C.)	Variable Temperature Cycles (~12/min.)	Remarks
TiNi-----	0.020" dia. wire, cold drawn and annealed at 800° C.	<10 ⁻⁶	500 to 900-----	~35,000	Single crystal entire length of specimen.
Fe-----	0.009" dia. annealed wire-----	<10 ⁻⁶	500 to 865-----	~33,500	Initiation of single crystal growth.
Cu-----	0.010" dia. annealed wire-----	<10 ⁻⁶	500 to 750-----	~17,000	Polycrystalline tendency prevails.
Cu-----	do-----	<10 ⁻⁶	500 to 750-----	~34,000	Initiation of single crystal growth.
Cu-----	do-----	<10 ⁻⁶	500 to 750-----	~50,500	Approaching single crystal alignment.
Ni-----	0.020" dia. wire-----	<10 ⁻⁶	500 to 1,000-----	~220	Single crystal.

The method of this invention provides a simple means of consistently growing high quality, composition controlled single crystals. It eliminates the necessity for applying a plastic pre-strain in the solid-state, thus enabling growth of single crystals from highly brittle materials. This method is especially valuable for growing single crystals from polycrystalline substances that are both too brittle to be subjected to the strain-anneal method and too composition sensitive and/or reactive to be subjected to the "melt" method.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood, that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A method for growing a single crystal from a polycrystalline substance selected from the group consisting of metals, single phase metallic alloys and semi-metals which comprises:

- heating the substance to a temperature that is below its melting point in an inert atmosphere,
- cooling the substance, and
- repeating (a) and (b) at least once per minute.

2. A method for growing a single crystal from a polycrystalline substance selected from the group consisting of metals, single phase metallic alloys and semi-metals which comprises:

- heating the substance to a temperature that is below its melting point in an inert atmosphere,
- cooling the substance to a temperature that is at least 250° C. lower than the temperature of (a), and
- repeating (a) and (b) at least once per minute.

3. The method of claim 2 wherein (a) and (b) is repeated at least 8 times per minute.

4. The method of claim 3 wherein said heating and cooling of (a) and (b) is effected by passing an electric current through said substance.

5. The method for growing a single crystal from a polycrystalline substance selected from the group consisting of metals, single phase metallic alloys and semi-metals which comprises:

- heating said substance to a temperature below its

melting point in an inert atmosphere, said temperature being at least 400° C. for substances that melt above 400° C.,

- immediately cooling said substance when it reaches the temperature of (a) to a temperature that is at least 250° C. lower than the temperature of (a), and
- repeating (a) and (b) at least 8 times per minute.

6. A method for growing a single crystal from a polycrystalline substance selected from the group consisting of metals, single phase metallic alloys and semi-metals which comprises:

- heating the substance to a temperature below its melting point in an inert atmosphere, said temperature being between about 750° and 1000° C. for substances that melt above 750° C.,
- cooling said substance to a temperature of about 500° C., and
- repeating (a) and (b) at least 8 times per minute.

7. A method for growing single crystals of TiNi which comprises:

- heating the TiNi to a temperature of about 900° C. in an inert atmosphere,
- cooling the TiNi to about 500° C., and
- repeating (a) and (b) at least 8 times per minute.

8. The method of claim 7 wherein (a) and (b) is repeated about 12 times per minute.

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