

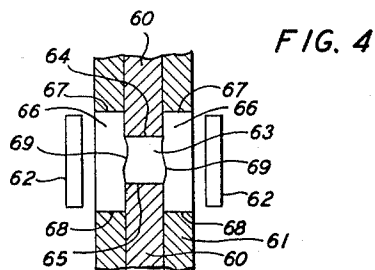
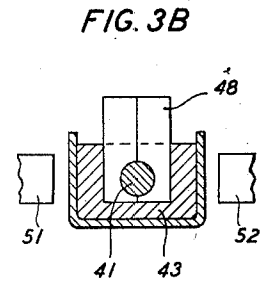
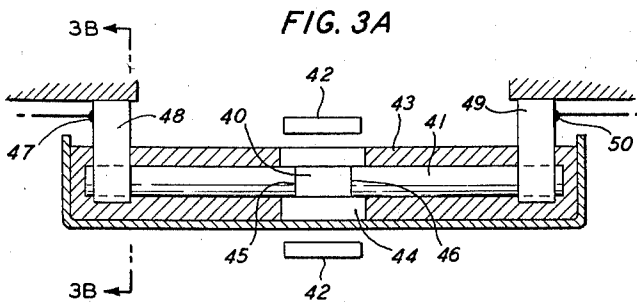
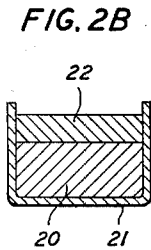
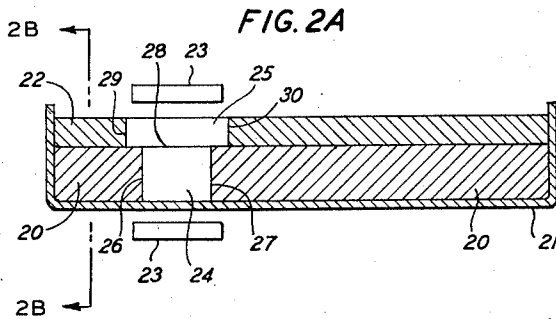
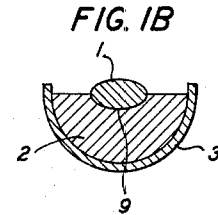
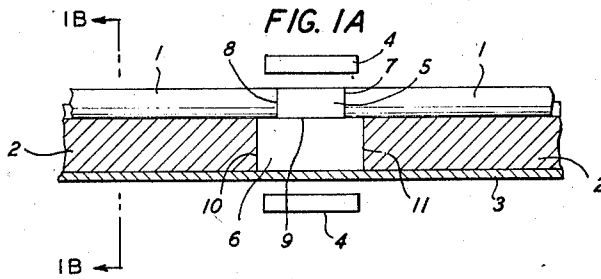
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2,875,108

ZONE-MELTING PROCESS

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2,875,108

ZONE-MELTING PROCESS

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Application June 25, 1957, Serial No. 667,757

12 Claims. (Cl. 148—1)

This invention relates to a process for crystallizing, refining and otherwise processing fusible materials by zone-melting.

In the zone-melting procedures of this invention, molten zones traversing material under treatment are contacted during traversal by a second substantially immiscible body of liquid material which may merely serve the mechanical function of physically supporting the molten zone or may contribute the further redistribution mechanism resulting from a liquid-liquid exchange between zone material and contacting liquid. Other advantages realized by use of such contacting liquid bodies are described.

Since their introduction in 1951 the zone-melting procedures have found increasing application in the processing of an ever-broadening group of materials. These procedures are of special importance in the semiconductor field and it is most likely that the material used in any semiconductor transducing device other than those using counter electrodes has at least once undergone a zone-melting processing step whether for refining, obtaining uniform segregation of significant impurity, creation of a desired gradient of such impurity, production of one or more p-n junctions, or for the purpose of attaining the best available crystallinity. The process is well known also in the treatment of other materials and is applicable to virtually anything which may be caused to undergo a phase transformation from the solid to the liquid and back to the solid without deleteriously affecting the material involved.

In common, however, with other processes of such broad application, special problems have arisen in certain isolated instances generally due to the special characteristics of the particular materials being treated. One of the best known of these difficulties occurs in the treatment of extremely pure high melting materials which are reactive either with atmospheric gases or with the usual crucible materials. Probably the best known instance of such difficulty arises in the processing of high purity silicon intended for use in crystal rectifiers, transistors, solar batteries and other such transducing devices. In the processing of this material, it is found that the use of the more conventional zone-melting apparatus in which there is intimate contact between the molten silicon zones and the crucible material results in contamination from the crucible itself of such magnitude as may often result in an end product several orders of magnitude less pure than may be realized theoretically.

Considerable attention has been directed to this problem resulting in crucible materials and conditions which reduce such contamination. A somewhat different approach directed to the same problem has resulted in the development of zone-melting processes in which the molten zone is kept out of contact with solid crucible materials during processing. Such processes include the floating zone method now finding commercial application in the processing of silicon, titanium, and other reactive

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materials and, also, the magnetic suspension process of my copending application Serial No. 516,221, filed June 17, 1955. Such processes although avoiding crucible contamination to a great extent, impose certain special conditions on the process, particularly in limiting the volume and dimensions of molten zones which may be kept mechanically stable during treatment. For this reason, the search for non-contaminating crucible materials continues.

A species of this invention, in defining a process in which a molten zone is supported over its entire length by a second body of liquid which is immiscible with the material of the zone itself and thereby avoids any solid-liquid interfaces other than those within the material being treated, opens up a whole new field of inquiry in the search for new non-contaminating liquid crucible materials. A class of liquid crucible materials suitable for the practice of this species of the invention is described herein as are the requisite characteristics of other crucible materials which may be found suitable in specific processing applications. Other species of this invention include the provision of a protective blanket of liquid to prevent interaction of zone materials and atmospheric elements during processing, addition of a liquid-liquid extraction mechanism to the basic zone-melting processes; a species, the use of which results in an increase in the maximum volume of a zone which may be maintained stable in the magnetic suspension zone-melting process; and also a species which similarly increases the utility of the floating zone-melting process.

In essence, the processes of this invention achieve the above results by the passage of contiguous molten zones through contiguous solid materials so chosen that the major components of the two solid materials are substantially immiscible in the liquid phase. Additional material requirements necessary for the practice of each of the species of this invention are set forth. For convenience, the processes of this invention are referred to herein as "two-liquid zone-melting."

The invention can be better understood by reference to the accompanying drawings in which:

Figs. 1A and 1B are schematic front elevation and end views respectively, both in section, of a two-liquid zone-melting process in which the only solid material contacted by a molten zone in the material being treated is that of the material itself;

Figs. 2A and 2B are schematic front elevation and end views respectively, both in section, of a two-liquid zone-melting process in which the molten zone of the material undergoing processing is blanketed by the liquid material of the adjacent zone;

Figs. 3A and 3B are schematic front elevation and end views respectively, both in section, of an electromagnetic zone suspension method utilizing the two-liquid zone-melting principle; and

Fig. 4 is a schematic front elevational view, in section, of a portion of a body undergoing processing by a floating zone method also utilizing the two-liquid principle of this invention.

Referring again to Figs. 1A and 1B, charge 1 of solid fusible material which in accordance with known zone-melting procedure may be a solid body, two or more such bodies, or may be in granular or in other convenient physical form is embedded in solid containing medium 2 which is in turn supported by crucible wall 3. Heater 4 which may be a ring-shaped heater containing resistance windings or which may be an induction furnace or any other type of furnace commonly used for this purpose is moved relative to charge 1 and supporting medium 2 and is maintained at such temperature as to result in molten zone 5 within charge 1 and

molten zone 6 within supporting medium 2. In the instance depicted, supporting medium 2 has a substantially lower melting point than does charge 1 thereby resulting in a molten zone 6 which is substantially longer in the direction of zone traversal than is contiguous zone 5. There are three interfaces of interest in the process depicted, solid-liquid interfaces 7 and 8 within the charge 1 and liquid-liquid interface 9 between molten zone 5 and molten zone 6, the latter of interest where liquid-liquid extraction occurs. Additionally, solid-liquid interfaces 10 and 11 within medium 2 are present and may play a part in resegregating impurities which are redistributed by liquid-liquid extraction across liquid-liquid interface 9.

For the process shown in Figs. 1A and 1B, charge 1 has been embedded in supporting medium 2 to a depth such that the relative densities of the two materials in the liquid phase result in a zone 5 which is on substantially the same level with that of the solid part of the charge 1. It is helpful but not necessary that a charge be so embedded before initiating zone traversal since one or two zone passes will automatically result in embedment of charge 1 to the proper depth in supporting medium 2. Once the charge has been so embedded the molten material of zone 5 rests on the surface of the molten material of zone 6 as shown, being retained in position primarily through interphasal forces between the solid and liquid portions of the charge and by surface tension. As is shown in Fig. 1B, the processed charge 1 generally assumes an approximately elliptical cross-section whose dimensions will vary in accordance with the relative densities of the charge and supporting medium materials and also in accordance with the relative surface tensions of the same two materials.

General requirements of the material of medium 2 are that it be substantially immiscible in the liquid phase with the liquid phase of the material undergoing treatment and also that it be a stable liquid well above the melting point of the material undergoing treatment. Where an objective in the use of the two-liquid zone-melting procedure is to avoid liquid-solid contact between the molten zone of the material undergoing treatment and solid material other than that of the charge itself, it is a requirement that the medium have a melting point at least as low as that of the material undergoing treatment. Where such solid-liquid contact is to be avoided, the use of a medium having a melting point below that of the material undergoing treatment results in a medium zone longer than that of the material undergoing treatment, assuming a medium liquid phase thermal conductivity which is not overwhelmingly less than that of the material undergoing treatment, as depicted in Figs. 1A and 1B, thereby obviating contact between the molten zone of the charge and the solid material of the supporting medium in the vicinity of the solid-liquid interface in the charge. It is also preferred that the density of such a medium material in the liquid phase be greater than that of the liquid phase of the charge and required that it not be appreciably less than that of the charge.

Although material 2 is referred to as the supporting medium for the purpose of the description of this figure, this material may serve other functions. For example, where the material of the charge undergoes a substantial change in volume when undergoing a phase transformation from the liquid to the solid, the use of such a liquid-supporting medium may result in a more perfect crystal of processed charge material than occurs where a relatively inflexible solid crucible material furnishes the only support.

Although it is a requirement of the processes herein that the major components of the charge and second material be substantially immiscible in the liquid phase, redistribution of minor ingredients may nevertheless result across the liquid-liquid interface 9 separating the

molten zones of the two materials. In a zone-refining process in which two or more zones are passed through the contiguous materials, such liquid-liquid extraction may be further aided by a redistribution at the trailing interface of zone 6.

In Figs. 2A and 2B, there is depicted a two-liquid zone-melting process in which a charge material 20 supported by solid crucible wall 21 is blanketed by a second material 22. Heaters 23 which may be of any suitable type result in molten zone 24 within the charge material 20 and molten zone 25 within the second material 22. Solid-liquid interfaces 26 and 27 within charge 20 perform the usual functions associated with zone-melting. In addition, further redistribution of any minor ingredients within charge material 20 may be effected by a redistribution across liquid-liquid interface 28. Where such redistribution takes place by the liquid-liquid extraction mechanism, any material removed may be further redistributed within medium 22 by virtue of liquid-solid redistribution across solid-liquid interfaces 29 and 30 within medium 22. Possible objectives served include such liquid-liquid extraction and consequent improvement in efficiency of removal of undesirable minor ingredients from charge 20, and also include blanketing of molten material of zone 24 from atmospheric elements by the molten material of zone 25 while retaining the flexibility generally realized only by the use of a protective gas so as to remove the likelihood of crystalline strains otherwise resulting from the use of a relatively inflexible solid cover.

The general requirements of the material of medium 22 of the embodiment of Figs. 2A and 2B are the same as that of supporting medium of Figs. 1A and 1B except that in this instance the second material is preferably of a somewhat lower density than is that of the charge material in the liquid phase, although the retaining influence due to interfacial forces at interfaces 26 and 27, surface tension at interface 28 and support given zone 25 by solid portions of material 20 permit the use of a second material of slightly greater or the same density as that of the charge material.

Further stabilization of a liquid zone in a charge undergoing processing by the electromagnetic suspension zone-melting process of my copending application Serial No. 516,221, filed June 17, 1955 is achieved by use of the two-liquid zone-melting process of Figs. 3A and 3B. In these figures, a molten zone 40 has been produced and is being caused to traverse charge material 41 under the influence of moving heater 42. Charge 41 is completely embedded in second material or medium 43 which must generally meet the requirements of the media of the embodiments of Figs. 1A and 1B and also 2A and 2B and the additional requirement that the densities of the charge and second materials be about the same. In operation, heater 42 also has the effect of producing an enveloping molten zone 44 which is in intimate contact with the entire surface of zone 40 with the exception of those parts of the zone contacting the solid material of the charge at interfaces 45 and 46. In addition to any one or more of the functions served by the media zones of the previous two embodiments, the buoyancy provided by the molten material of enveloping zone 44 helps to stabilize zone 40 within charge 41.

As in the electromagnetic suspension process of my copending application to which reference is made above, some stabilization is afforded the molten zone 40 by means of the reactive force resulting from the interaction of a current flow through the zone and a magnetic field imposed at right angles to the zone on a horizontal plane of such direction as to result in a reactive force in a vertical direction so as to oppose any net force seeking to displace the zone. However, whereas in the usual instance in my copending application the current and magnetic field components are generally of such magnitude as to oppose displacement due to gravi-

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tational force dependent almost solely on the mass of the molten material of the zone, use of the two-liquid zone-melting processes of these figures results in an effective decrease in such mass due to the buoyancy of the molten material of enveloping zone 44.

For a totally immersed molten zone 40, and ignoring the stabilizing influence of the interfacial forces at interfaces 45 and 46, the requisite current magnetic field product may be obtained from the following equation:

$$JH=10^4(\rho_A-\rho_B)$$

in which

J =current density in amperes per square centimeter

H =magnetic field intensity in oersteds

ρ_A and ρ_B denote densities of liquid charge material and medium material, respectively, in grams per cubic centimeter

It is not a requirement of this embodiment that medium material 43 be of a density less than that of the zone material 40. Following the principles taught in my copending application, the direction of current and magnetic field components are chosen so as to result in a net reactive force of a direction and magnitude such as to compensate for the displacing force due to the difference in densities of the two materials.

In the apparatus depicted in Figs. 3A and 3B current from a source not shown flows through, respectively, contact 47, clamp 48, charge 41, including zone 40, clamp 49 and contact 50. A horizontal magnetic field occupying the same position relative to charge 41 as moving heater 42 is produced across zone 40 on a substantially horizontal plane by magnetic poles 51 and 52 of opposite polarity.

In accordance with Fig. 4 the length, and therefore the cross-section, of a zone which may be supported in a floating zone process is increased by application of the two-liquid zone-melting principles. In this figure there is depicted charge 60 within second material or medium 61. Heater 62 which moves relative to charge 60 and medium 61 is of such temperature as to result in molten zone 63 having liquid-solid interfaces 64 and 65 between the molten zone 63 and the material of charge 60 and annular molten zone 66 within second material 61 having solid-liquid interfaces 67 and 68. Liquid-liquid interchange may take place across liquid-liquid interface 69. The general requirements for a suitable medium material in this embodiment are the same as those for the other embodiments shown with a density preference such that the densities of the two materials in the liquid phase be about the same. However, use of any medium having a density greater than that of the atmosphere and not over twice that of the liquid of the charge results in an effective decrease in the force displacing the liquid charge material, thereby permitting suspension of larger zones.

In the practice of the processes of this invention in the treatment of semiconductive materials such as silicon, certain of the halide salts are found to be useful. Such materials include magnesium fluoride having a melting point of 1396° C., a boiling point of 2239° C. and a density of about 3 grams per cubic centimeter, tin chloride having a melting point of 246° C., a boiling point of 623° C. and a density of 3.34 grams per cubic centimeter and a wide range of materials having intermediate melting and boiling points. Physical properties of the halide salts are set forth in many standard texts such as that of the Handbook of Chemistry and Physics and are sufficiently diversified to enable selection of a material suitable for a wide range of processing operations in accordance with this invention. Unlike many solid crucible materials the liquid medium materials used herein may be purified to a very high degree by any of several well-known liquid refining procedures, such for example, as zone-refining.

For two-liquid zone-melting of metals, often another

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metal will be suitable as the medium. About 100 pairs of metals which are immiscible when liquid are listed in Table 2 of a paper by N. F. Mott, Philosophical Magazine, volume 2, No. 14, page 259, February 1957. Lead, for example, is a suitable medium for silicon in certain of the variations of the two-liquid zone-melting method.

The following examples illustrate the use of the two-liquid zone-melting processes of Figs. 1 through 4.

Example 1

With reference to the process of Figs. 1A and 1B, a rod of silicon $\frac{3}{8}$ inch in diameter is embedded in a charge of calcium fluoride (CaF_2) in a graphite boat of semicircular cross-section of a length of 12 inches and a radius of 0.5 inch. The rod, the calcium fluoride and the boat are heated by an induction coil having several turns of water-cooled copper tubing operated at a frequency of 5 megacycles, the coil being outside a quartz tube containing the boat. The coil is moved axially along the quartz tube at the rate of $\frac{1}{16}$ inch per minute, thereby producing two moving zones as depicted in the figures.

Example 2

A germanium ingot having a cross-section of 1 square inch is placed in a graphite boat of a length of 12 inches and a semicircular cross-section of a radius of 0.5 inch, and a layer of sodium fluoride of a depth of $\frac{1}{4}$ inch is placed within the boat on the upper surface of the germanium ingot. An induction coil operated at 450 kilocycles is moved along the charge at $\frac{1}{16}$ inch per minute and the sodium fluoride so as to result in two moving zones such as depicted in Figs. 2A and 2B.

Example 3

With reference to the process of Figs. 3A and 3B, a cylindrical rod of aluminum having a cross-sectional area of 1 square centimeter is embedded in a charge of sodium iodide and is placed in the apparatus shown in Fig. 3A. A current of 10 amperes is passed through the rod from left to right and a magnetic field having an intensity of 1000 oersteds is impressed across the rod at right angles to the current flow with the north pole in front of the zone and the south pole behind the zone so as to result in an upward reactive force. Two moving immiscible liquid zones are produced as shown in the figures by a Nichrome wire resistance heated coil moving at $\frac{1}{64}$ inch per minute.

Example 4

A cylindrical rod of aluminum having a diameter of 1 centimeter is embedded in a charge of sodium iodide within a fused silica container having a cylindrical cross-section and of an inside diameter of 3 centimeters. The embedded rod is disposed vertically and contiguous zones, one centimeter long in the aluminum and three centimeters long in the sodium iodide, are passed through the rod and charge at $\frac{1}{64}$ inch per minute in an upward direction by means of a moving Nichrome wire resistance heater. The transparency of the molten sodium iodide permits visual observation of the molten zone in the aluminum rod.

Although each of the embodiments depicted herein assumes a medium melting point somewhat lower than that of the molten material of the charge, and although such relationship is generally preferred, it is not a requirement of every species herein that such relationship obtain. It is useful in some embodiments to select a medium melting point or thermal conditions such that only a portion of the molten zone in the charge is contacted by liquid material of the medium zone so that, for example, solid support may be furnished at a melting interface while still permitting liquid-liquid extraction between the charge zone and the medium zone.

Although the processes herein have been described in terms of only a small representative grouping of zone-melting operations, the processes herein are suitable for use in any zone-melting process whether the objective be

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the formation of a complex configuration of p-n junctions within a semiconductive material or merely the preparation of a crystal with a minimum of crystalline imperfections. These processes are, of course, not limited to their operation upon semiconductive materials but are useful in the processing of the entire range of materials which may be treated by zone-melting.

What is claimed is:

1. A process comprising causing a molten zone to simultaneously traverse at least a portion of each of two adjacent solid fusible materials thereby producing a liquid-liquid interface between at least a portion of each of the two molten regions, the composition of the adjacent materials being such that the major components of each are immiscible in the liquid state.

2. A process in accordance with claim 1 in which a minor ingredient within one of the two adjacent materials has a liquid-liquid segregation coefficient between the two said molten zones which differs from unity.

3. A process for treating a first fusible material comprising contacting said first fusible material with a second fusible material and causing a molten zone to simultaneously traverse the said first and second fusible materials such that there is during a substantial portion of the traversal a liquid-liquid interface between the two said molten zones, the said first and second fusible materials being such that the major component of each is immiscible with the other.

4. The process of claim 3 in which the direction of molten zone traversal is substantially horizontal, in which the said second fusible material in the molten phase has a density at least as great as that of the said first fusible material in the molten phase and in which a liquid-liquid interface exists at a lower surface of the first fusible material.

5. The process of claim 4 in which a minor ingredient contained in at least one of the said materials is miscible with an ingredient in the other of the said materials.

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6. The process of claim 5 in which the said ingredient of the other of the said materials is the major component of the other of the said materials.

7. The process in accordance with claim 3 in which the direction of molten zone traversal is substantially horizontal, in which the liquid phase density of the said first material is at least as great as the liquid phase density of the said second material and in which a liquid-liquid interface exists at an upper surface of the first fusible material.

8. The process of claim 7 in which there is contained in one of said materials an ingredient which is miscible with an ingredient in the other of the said materials.

9. The process in accordance with claim 8 in which the said ingredient of the other of the said materials is the major component of the other of the said materials.

10. A process in which a molten zone is caused to traverse a first fusible solid material and in which a second molten zone is simultaneously caused to traverse a solid portion of second fusible material in such manner that the entire surface of the said first molten zone is contacted by the said second fusible material and by solid material of the said first material, the composition of the said first and second fusible materials being such that the major components of each are immiscible in the liquid state.

11. The process in accordance with claim 10 in which the direction of molten zone traversal in the said first material is substantially horizontal and in which an electrical current is passed through the said first molten zone, and a magnetic field is impressed across the said first molten zone, the said electrical current and magnetic field being such that there are on a horizontal plane normal components of electrical current and magnetic field such as to result in a reactive force opposing the net displacing force operating on the said first molten zone.

12. The process in accordance with claim 10 in which molten zone traversal is substantially vertical.

No references cited.