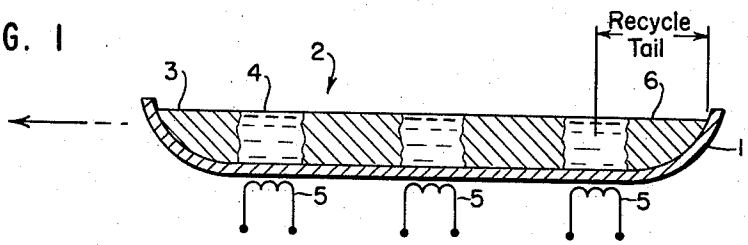
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ZONE REFINING METHODS AND APPARATUS

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FIG. 1



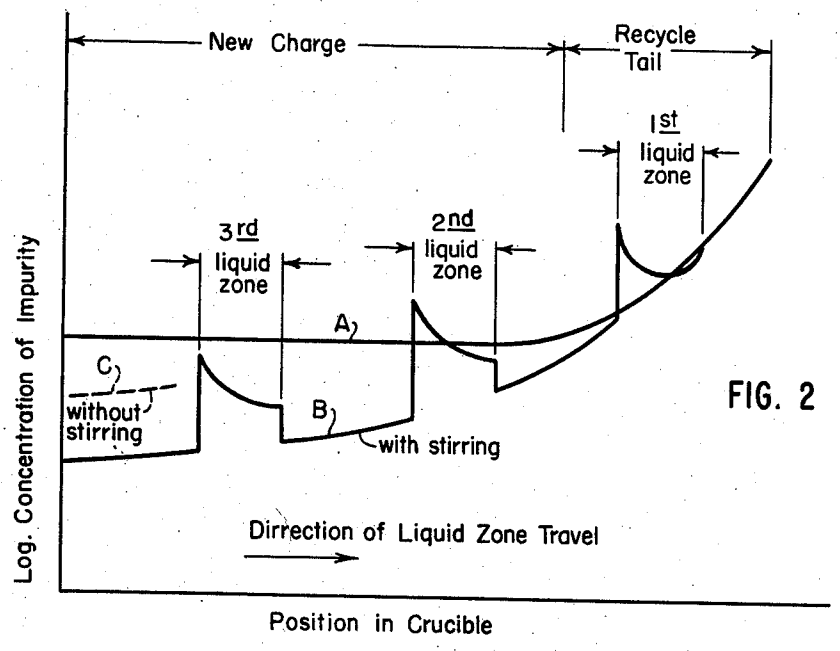
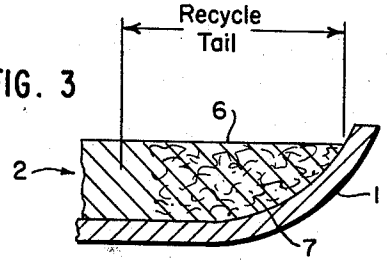


FIG. 2

FIG. 3



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FIG. 4

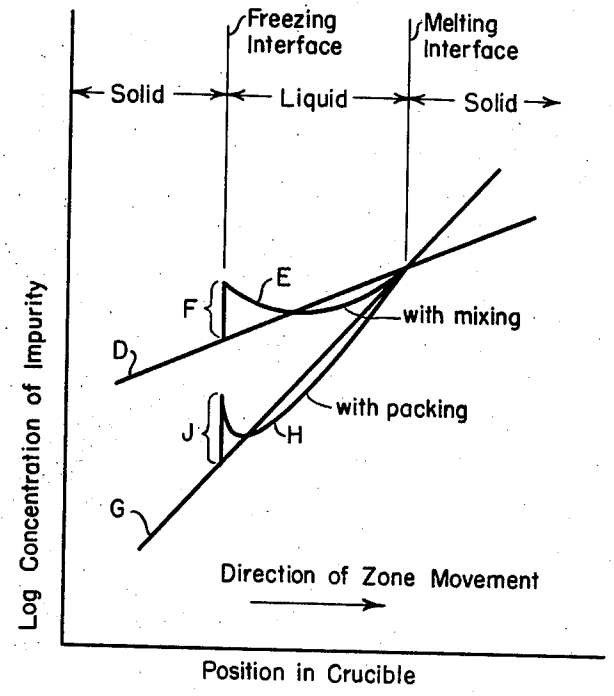
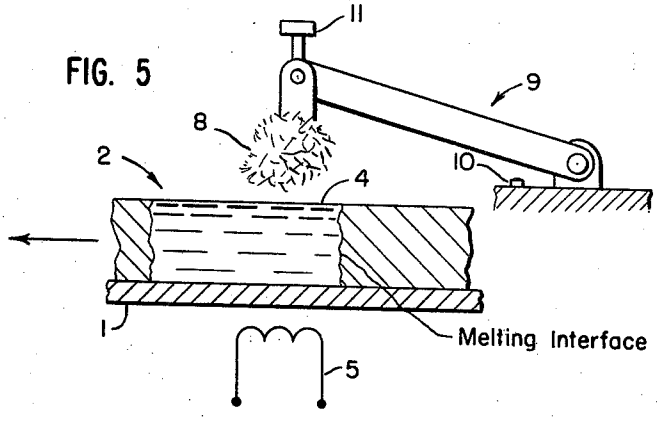


FIG. 5



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ZONE REFINING METHODS AND APPARATUS

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5 Claims. (Cl. 23—301)

My invention relates to zone refining, and in particular to improved methods and apparatus for increasing the concentration gradient attainable by zone refining.

While zone refining has been traditionally used as a means of preparing exceptionally pure material for use in semi-conductors, it is increasingly gaining recognition as a unit process of wide application in the refining art generally. Basically, the zone refining process depends on the differential solubility of an impurity in the liquid and solid phases of a material to be purified. In the process, a charge of material is moved relative to one or more heated zones in such a manner that liquified zones traverse the material. At the trailing interface in such a moving liquid zone, freeing takes place with rejection of the impurity into the liquid phase, because of the aforesaid difference in solubility. Thus, the liquid zones increase in concentration of impurity as they traverse a charge, and when the charge is again solidified, a concentration gradient in the impurity exists from one end to the other.

The most complete purification attainable by selective solubility between a liquid and a solid phase in a single step-batch process requires the attainment of substantial equilibrium. Since the rejection of the impurity occurs at the freezing interface, in the absence of convection or stirring, a relatively high concentration of impurity exists in the liquid phase immediately adjacent the freezing interface. Obviously, this highly concentrated region increases the amount of impurity that is obtained in the solid phase above that expected if equilibrium with the bulk concentration of the liquid could be attained. Accordingly, it has been generally assumed in the zone refining art that stirring of the liquid zone was highly beneficial, since such stirring would promote approaching equilibrium.

However, I have found that, while the above generalization is true for batch refining, it is only partly true for continuous refining or for zone refining operations in which the impurity-rich tail of a batch is recycled from batch to batch. More specifically, I have found that a higher concentration gradient in regions of the batch that are very rich in impurities can be attained by decreasing stirring or convective mixing in the liquid zones in those regions.

This phenomenon may also be viewed as effectively shortening the length of the liquid zone, which shortening is otherwise limited by engineering considerations such as heat flow and zone cross-sectional dimensions.

Accordingly, it is the primary object of my invention to provide a simple and inexpensive means for preventing mixing in the liquid zone in certain regions of a charge of material undergoing zone refining.

It is a further object of my invention to provide an improved process of zone refining in which impurities may be concentrated in a relatively small portion of the charge.

Other objects and further advantages of my invention will become apparent to those skilled in the art as the description proceeds.

Briefly described, my invention comprises the provision of a packing composed of permeable material which is incorporated in the batch being refined in the region of maximum impurity concentration. As applied to continuous zone refining, my invention may be practiced by moving the packing relative to the solid charge together with the moving liquid zone, the packing in this

case being limited to that portion of the liquid zone ahead of its concentration minimum. This provides maximum utilization by limiting the packing effect to the vicinity of the melting interface and avoiding its effect where it is not wanted near the freezing interface.

However, my invention also includes the intermediate application where the packing is stationary with respect to the solid zones and their retaining crucible or boat. Practical construction of such an arrangement is much more simple. While this practical compromise introduces packing near the freezing interface where it is undesirable as well as near the melting interface where desired, the net effect is advantageous. This is particularly so in that part of a zoning machine where the tail zones are not very hard pressed to transfer impurities, a situation common to all multiple-zone, constant cross-section, continuous or batch zone refiners. Also, a compromise is particularly advantageous for composition systems with near-unity segregation coefficients where a larger number of zone passes is more convenient than excessively long equipment to get the desired purity level.

My invention will best be understood by reference to the accompanying drawings, in which:

FIG. 1 is a schematic diagram, partly in cross-section, of typical apparatus for zone refining;

FIG. 2 is a graph showning certain relationships between concentrations of impurities as a function of position in a zone refining crucible;

FIG. 3 is a fragmentary cross-sectional view of a zone refining crucible and contents incorporating a first embodiment of my invention;

FIG. 4 is another graph of concentration of impurity as a function of position in a zone refining crucible, comparing the results of zone refining in accordance with my invention with the results attained by prior processes; and

FIG. 5 is a diagrammatic sketch, partly in cross-section, illustrating zone refining methods and apparatus in accordance with a second embodiment of my invention.

Referring now to FIG. 1, I have shown a typical zone refining crucible 1, containing a charge 2. The ambient temperature is assumed to be such that charge 2 is normally solid, as indicated at 3, but has liquid zones 4 created by a plurality of conventional induction heating coils 5. Conventional means, not shown, but indicated schematically by the dotted line at the left or front end of the crucible, are provided to move the crucible in the direction of the arrow with respect to the heated coils, so that the liquid zones traverse the charge 2 from left to right as seen in FIG. 1.

As indicated schematically in FIG. 1, the rear portion 6 of the charge 2 comprises a so-called "recycle tail." As is known in the art, it is conventional in the zone refining art to cut off the impurity-rich tail piece of each new charge and to recycle this tail portion by placing it in the rear of the crucible with the next charge. Thus, the recycle tail 6 would normally be of a much higher impurity concentration than the remainder of the charge.

As will appear, my invention is applicable to zone refining of any material which is capable of cyclic melting and freezing without decomposition. Accordingly, no specific material need be referred to in order to fully understand my invention. However, for purposes of illustration, if the refined material 2 were silicon, the crucible 1 would be conventionally made of quartz; if the charge were germanium, the crucible would preferably be made of graphite or carbon in some other form, but it might also be made of quartz or even porcelain. Other materials which can be refined by zoning, such as metals, ores, crystalline organic compounds, or the like, and suitable crucibles for containing them, will readily occur to those skilled in the art.

Referring now to FIG. 2, curve A shows the concen-

tration of a charge in a refining crucible such as crucible 1 in FIG. 1 before the refining process has begun. As indicated in FIG. 2, the concentration of impurity in the new charge is uniform, while the impurity concentration of the recycle tail portion is higher and has a steep gradient. In practice, in the case of germanium, for example, in this state the recycle tail will essentially be a solid block cut off from the previous charge, and the new charge would be a mixture of scraps, chips, or other particles of solid germanium of random sizes. However, after one pass through a heating coil, the whole charge will be fused into a relatively solid bar.

Curve B shows typical concentration gradients in the charge after three liquid zones have traversed from left to right in FIG. 2 to the extent indicated. It is assumed that stirring has been provided in the liquid zone, either by mechanical means such as a paddle or propeller dipping into the zone, or simply by convection currents. It will be seen that the entire charge has now acquired a gradient, with the solid portions toward the entering end being purified compared with the new charge, and increased concentrations of impurities in the liquid zones due to impurity picked up at the trailing or freezing interface of each liquid zone.

Dotted curve C shows the initial portion of a similar process carried out without stirring, or with little convective mixing occurring, and it is apparent that much less purification will take place at the entering end of the charge under these conditions. However, note the first liquid zone in FIG. 1, which has reached the recycle tail section. Here, more of the zone's work is done in re-establishing the concentration gradient lost during, or rather shortly after, melting. Only a minute portion of the freezing interface's capacity is devoted to a net mass transfer of impurity to displace the concentration curve. The reason for this is that the gradient in the recycle tail is quite steep and with the logarithmic concentration scale a displacement of a given amount of impurity makes a much smaller percentage change. Thus, liquefication of the zone with mixing results in a mixture of high impurity material with low impurity material, which is the reverse of the desired process and which requires substantial work to undo. This effect is not pronounced in the main portion of the charge, because the concentration gradient is much flatter in the new charge and the effect of mixing over the length of the liquid zone is less compared to the segregation coefficient (the ratio of the solubility of the impurity in the solid to its solubility in the liquid). This is brought about by mixing due to "washing" of the freezing interface by the less rich material of the bulk of the liquid zone.

Therefore, in accordance with my invention, I desire not only to avoid stirring in the tail region of the charge, but to provide means for positively preventing convection mixing in the liquid zone in this region. Referring now to FIG. 3, I have shown a simple and effective means of attaining this objective. As shown in FIG. 3, fibrous packing material 7 has been incorporated in the recycle tail portion 6. This material may be quartz or other siliceous fibers, for example, where the temperature of the melted charge or solubility of the fibers in the melt would not prevent its use; in the case of germanium refining, it would preferably be carbon wool, well known to the art and readily available, or it could be any other suitable fibrous or otherwise permeable material. The main criterion for the section of the material is a relatively high impedance to convection, but a relatively small cross-sectional area to avoid impeding the processes of diffusion which are essential to the zone refining process. Ideally, the packing would consist of extremely fine, inert fibers, as of quartz, platinum, or other suitable inert material, aligned longitudinally with the direction of zone travel and approximately equally spaced in a cross-section of the zone. However, it is not necessary to proceed to this degree of refinement since fibrous packing as indicated in FIG. 3 is much easier to incorporate and is nearly equally effective. Moreover, fibrous material is essentially self-supporting, and once the charge has been melted to embed the material in the charge, it is rigidly held in place during the traverse of the liquid zone by being frozen into the solid ahead of or behind the zone, or both. For this purpose, the length of the fibrous packing should preferably somewhat exceed the length of the liquid zone.

Naturally, the fibrous material and the size of the individual fibers must meet the practical requirement of lack of reactivity; they must be incapable of contaminating the system; and they must have sufficient physical strength and life to undergo the many cyclic liquefactions of the recycle tail portion of a zone refining charge. Where possible, it is also desirable to select a fibrous material that is wet by the charge, since this avoids the problem of the large forces that would be exerted upon the packing by the surface tension of the charge if the packing was not wet. This would be particularly true if the pore size, or the distance between the fibers, was small.

Obviously, other porous or spongy media other than fibers could meet the requirements of offering resistance to convective currents while permitting continuous diffusion in the liquid away from the freezing interface, and such media can obviously be employed without departing from the scope of my invention.

While I have illustrated the packing in FIG. 3 as being concentrated in the recycle tail, it should be noted that it may be desirable in some instances to embed it in a graduated fashion throughout a larger region, to progressively damp convection as it becomes more desirable and effective to do so.

Referring now to FIG. 4, I have illustrated the improvement in concentration gradient attainable by packing the liquid zone. In FIG. 4, line D indicates an effective concentration gradient attainable in a given process when convective mixing is allowed to occur. It will be seen that the concentration of an impurity in a liquid zone passing through the charge in this case shown by curve E, rises to a maximum at the freezing interface with a characteristic separation F at the interface from the concentration of the solid. This characteristic separation F is determined by the effective segregation coefficient, and is made slightly greater by the mixing.

Line G in FIG. 4 illustrates the improvement in concentration gradient attainable with packing. Here, the liquid concentration curve H approaches the freezing interface concentration more abruptly because there is no mixing action to "wash" the interface. Moreover, the characteristic separation J between the liquid concentration and the solid concentration at the freezing interface may be slightly smaller since the interface is not near equilibrium with the liquid zone as a whole. However, the average concentration of the liquid at the freezing interface can be much lower since this liquid has not been mixed with the more concentrated material in the region of the melting interface. Thus, the gradient that can be supported in this case is much higher, and the portion of the recycle tail containing the bulk of the impurity can either be shorter, or more highly concentrated, or both.

FIG. 5 shows a modification of my invention which is adapted for continuous zone refining, in which it is desired to move the packing with the liquid zone, at least during a selected portion of the refining process. The crucible and contents and the conventional heating coil 5 are indicated by the same reference numerals employed in FIG. 1. The fibrous material is now in the form of a wad or pad 8 which is attached to any conventional means such as the lever assembly 9 diagrammatically shown. As conventionally indicated, this lever assembly could be simply held up by a manual knob 11 until the crucible was in position and the liquid zone had been estab-

lished, and then allowed to drop down into the liquid zone, being supported by any conventional means such as a stop 10, or even by the bottom of crucible 1. Preferably, the packing in this case would be shorter than the liquid zone and would be located nearest the melting interface. This embodiment has the advantage of preventing mixing with the highly concentrated material near the melting interface, without interfering with convection and the attainment of equilibrium at the zoning or freezing interface. In this manner, the packing effectively shortens the liquid zone, much more than it would be practical to do by concentrating the heating coils and probably more than it would be thermally possible to do by this means. The packing in this case could be fibers, as indicated in FIG. 5, or it could be spherical or granular packing, cellular material with relatively small connecting passages, a solid with passages through or around it, or, as a further specific example, it could be desirably made in some instances in the form of a bundle of fine tubing aligned with the direction of movement of the zone.

In carrying out my invention in accordance with the modification shown in FIG. 5, the packing would only be introduced into the liquid zone when this zone had reached that region of high concentration gradient and relatively steep concentration in which packing is effective, as explained in detail in connection with the embodiment shown in FIG. 3.

While I have described various embodiments of my invention in detail, many changes and modifications will become apparent to those skilled in the art after reading my description, and such changes can obviously be made without departing from the scope of my invention. Accordingly, I do not wish to be limited to the details shown, but only by the scope of the followings claims.

Having thus described my invention, what I claim is:

1. In a continuous zone refining process wherein a charge of fusible material is moved at a predetermined rate relative to a heating device to cause a liquid zone to traverse the charge, the step of inserting a mass of fibrous material in the liquid zone of the material being refined to prevent mixing of liquids from the extremes of the zone, the fibrous material being insoluble in the liquid zone, chemically non-reactive with the charge material, non-sublimable at the maximum temperature of the liquid zone and having a melting temperature higher than the maximum temperature of the liquid zone.

2. The process for continuous zone refining of material selected from the group consisting of silicon and germanium which includes the steps of moving a charge of the material relative to a heating device to cause a liquid zone to traverse the charge; and packing said liquid zone of the material being refined with fibrous material selected from the group consisting of quartz, platinum and carbon to prevent mixing of liquid at one end of the zone with liquid at the other end of the zone.

3. A process for continuous zone refining of materials selected from the group consisting of silicon and germanium which includes the step of inserting a fibrous mass of material selected from the group consisting of quartz, platinum and carbon in a liquid zone of the material being refined to prevent mixing of liquids from the extremes of the zone to maintain a desired impurity concentration.

4. Apparatus for continuous zone refining comprising, in combination, heating means, a crucible chargeable with material to be refined and movable with respect to said heating means to cause a liquid zone to traverse said crucible, and a mass of fibrous material positioned in said crucible adjacent said heating means to prevent mixing in the liquid zone, said fibrous material being non-reactive with the material to be refined and having a melting temperature higher than the maximum temperature of the liquid zone.

5. Apparatus for continuous zone refining of material selected from the group consisting of silicon and germanium comprising: heating means; a crucible chargeable with the material to be refined and movable with respect to said heating means to cause a liquid zone to traverse said crucible; and packing means comprising a fibrous mass of material selected from the group consisting of quartz, platinum and carbon positioned in said crucible adjacent said heating means to inhibit mixing in the liquid zone.

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