April 12, 1960 W. G. PFANN 2,932,562

ZONE-MELTING WITH JOULE HEAT

Filed Dec. 27, 1956

FIG. 1

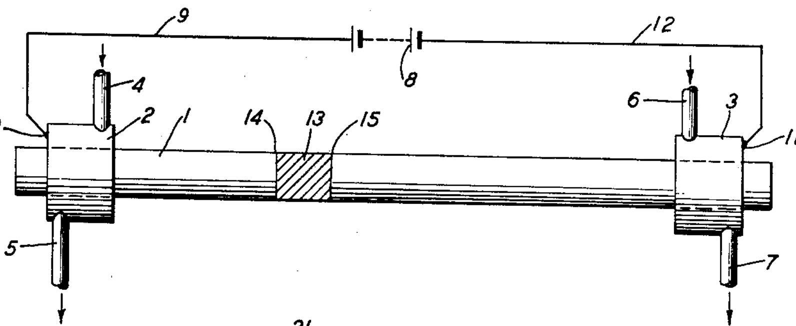


FIG. 2

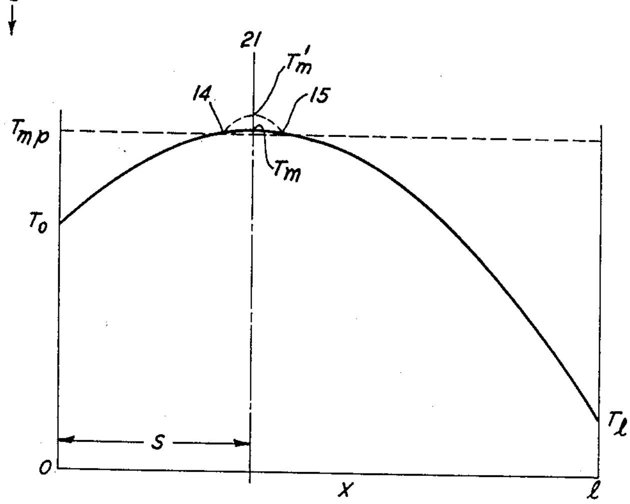


FIG. 3

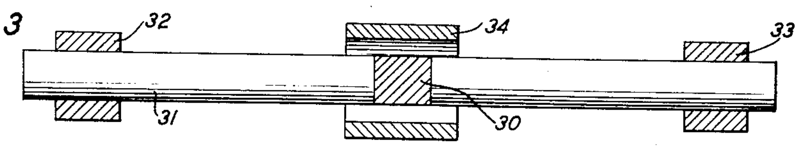
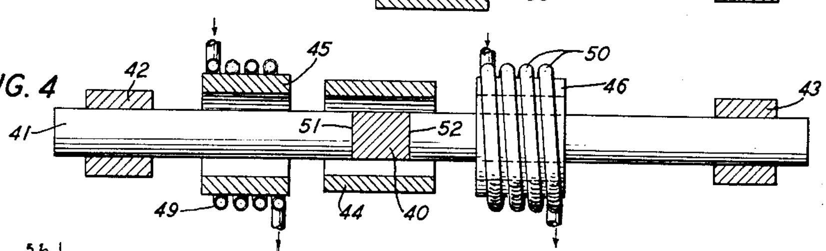
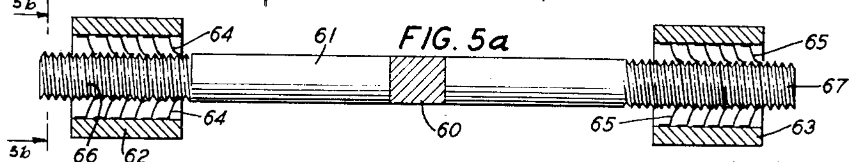


FIG. 4





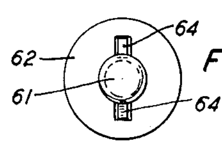


FIG. 5b

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ZONE-MELTING WITH JOULE HEAT

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11 Claims. (Cl. 75—10)

This invention relates to zone-melting methods in which molten zones are produced by Joule heat and are caused to progress without the use of moving heating means. The methods herein may be used in conjunction with any zone-melting apparatus and are particularly useful in the zone-refining of reactive metals when used in conjunction with any of the crucibleless zone-melting procedures known to the art.

Developed primarily as a method of refining and controlling impurity content in semiconductive materials, the basic zone-melting processes announced to the public in 1951 have found increasingly broad application in both industry and research. In addition to being used in the processing of a major portion of semiconductive materials such as germanium and silicon destined for use in semiconductor transducing devices such as rectifiers and transistors, the zone-melting principle now finds application to such diverse objectives as the purification of organic materials such as naphthalene and benzoic acid, metals such as tin, antimony, aluminum and iron, chemicals such as gallium trichloride, semiconductive materials of diamond-cubic and related crystal structures such as compounds of the group III–group V classes of the periodic table according to Mendelyeev and to some materials which are normally molten at or near room temperature, such as water and gallium.

Various crucibleless zone-melting techniques have been developed for use in the processing of certain reactive materials such as titanium, zirconium, iron and other materials of such purity level that crucible contamination at the elevated temperature necessary to produce a molten zone becomes a deterrent to the production of materials of desired impurity content. In certain of these processes a molten zone is produced through the entire cross-section of the ingot and is suspended between the two solid-liquid interfaces of the adjoining portions of the solid ingot, the remaining surface of the zone contacting only a protective atmosphere or being protected by an evacuated region. Such procedures include the floating zone technique of copending United States application, Serial No. 326,561, filed December 17, 1952, in which a moving molten zone is suspended between two interfaces chiefly by virtue of adhesive forces between the molten zone and the solid portions of the ingot and cohesive forces within the molten zone itself. Another such process is the suspension zone-melting technique of copending United States patent application Serial No. 516,221, filed June 17, 1955, in which a molten zone is held in position between two solid-liquid interfaces in a horizontal ingot by virtue of the reactive force resulting from the interaction of a magnetic field and a current flow.

Other zone-melting techniques designed to avoid crucible contamination make use of moving molten zones which do not penetrate the entire cross-section of the ingot being processed, the molten portion being retained primarily by adhesive forces. Such methods also include processes in which molten zones are passed along the top surface of the ingot such as described in United

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States Patent 2,739,088, issued March 20, 1956, the technique sometimes referred to as "cage-zone-melting" in which a molten zone extending through all but a plurality of fin-like projections of a vertical ingot is passed through the ingot and retained in position, partly by reason of adhesion of the molten material to the fin-like extremities described in Review of Scientific Instruments 26, 303 (1955), and a process in which a sector-shaped zone extending from the upper surface at least half-way through an ingot is caused to traverse the entire ingot in a spiral path by rotating the ingot during the progression of the zone.

In all of these crucibleless methods as heretofore used the difficulty of producing steep thermal gradients within materials under treatment limits the dimension of the molten region at right angles to the direction of traversal. For example, in the floating zone technique referred to above, especially where the material under treatment has the high thermal conductivity evidenced, for example, by most metallic materials, the use of external heating means results in a limitation on the diameter of an ingot which may be so processed. In these techniques, where the chief limitation in producing a stable zone is the length of the zone, rather than the cross-section, the limitation in molten cross-section resulting from the use of external heaters severely limits the quantity of product so produced.

By use of the internal heating means herein described the cross-sectional area of molten zones is made substantially independent of the thermal conductivity of the material under treatment. As applied to the floating-zone technique this results in the practicability of passing stable zones having volumes many times as great as those produced by exterior heating means such as the ring-type heaters now commonly used. Use of this process therefore, results in increased output for a similar investment in apparatus. In addition to this obvious application to crucible-free zone-melting which may for the first time make treatment of certain materials by this process commercially feasible, the elimination of external heaters and the accompanying simplification of apparatus makes the use of the processes herein described advantageous in the conventional zone-melting of many materials. Crucible zone-melting processes to which the techniques of this invention are applicable include those using bar-shaped solid-ingots as well as those using powder, composite bar and helical and other non-bar-shaped starting bodies.

In accordance with this invention a molten zone is created in an ingot of a non-insulating material by passing either an alternating or direct current through the ingot, the current being of such magnitude that the I^2R heat (Joule heat) is sufficient to raise the ingot to its melting point. The length of the molten zone so formed is restricted by use of heat sinks which may, for example, take the form of air-cooled or water-cooled clamps at the extremities of the ingot. Use of such heat sinks results in a double temperature gradient with the low ends at the extremities of the ingot and a high temperature region intermediate the extremities, the latter corresponding with the position of the molten zone. If, for example, the heat sinks are maintained at the same temperature the molten zone will be at a point mid-way between the cooled portions of the ingot. The zone so formed is caused to progress by varying the relative temperatures of the two heat sinks, zone travel being produced in a direction away from the cooler of the sinks. If it is desired to maintain the length of the molten zone constant during progression, the temperatures of the two sinks are programmed simultaneously, one being cooled and the temperature of the other being raised. Further control of molten zone position and length and improvement in heat efficiency may be effected by use of reflectors and sinks as will be described. Methods for compensating for thermal expansion and contraction during the process will also be discussed.

A chief advantage of the processes of this invention results from the generation of the heat required to produce and maintain the zone within the ingot itself, thereby avoiding the difficulties associated with the use of external heaters. As will be discussed in detail, in certain systems, such for example as the usual metallic system, a decrease in the value of electrical conductivity and/or thermal conductivity in the molten phase as compared with those values in the solid phase results in a further advantage in that a larger amount of heat is generated in the precise position in which it is desired, that is, within the molten zone. As will also be discussed the invention is, however, not to be limited to operation on such systems in which electrical and/or thermal conductivity decreases in the molten zone, but is effective for use in a broader range of systems, the limiting characteristics of which are set forth herein.

For convenience in describing the invention reference will be had to the following figures in which:

Fig. 1 is a schematic front elevation view of an ingot being zone-melted and zone-melting apparatus in accordance with the present invention;

Fig. 2 depicts graphically the temperature gradients in an ingot such as that of Fig. 1 during processing;

Fig. 3 is a schematic front elevation in section of an ingot undergoing zone-melting in accordance with the processes herein in which a moving reflector is used to effect further control over the movement and dimensions of the molten zone;

Fig. 4 is a schematic front elevation in section of an ingot undergoing the treatment of Fig. 3 but in which process moving heat absorbers are used in addition to the moving heat reflector;

Fig. *5a* is a schematic front elevation in section of an ingot undergoing zone-melting treatment on an apparatus designed to compensate for thermal expansion and contraction resulting during treatment; and

Fig. *5b* is an end view of the ingot and apparatus of Fig. *5a*.

Referring again to Fig. 1 ingot **1**, which in this instance is rod-shaped, and which may, for example, be iron or other material meeting the requirements set forth below, is held in clamps **2** and **3**. Means are provided for varying the temperatures of clamps **2** and **3** over a range below the melting point of the material of ingot **1**. In the apparatus depicted clamps **2** and **3** are hollow and are water-cooled, water passing in inlet **4** and out outlet **5** in clamp **2** and in inlet **6** and out outlet **7** in clamp **3**. The required temperature variation may result either from a variation in the flow rate of water or other coolant through clamps **2** and **3**, by a variation in the temperature of the coolant or by a combination of the two. An electrical current produced by battery or other electrical power source **8** is caused to flow successively through wire **9**, electrode contact **10**, clamp **2**, ingot **1**, clamp **3**, electrode contact **11** and wire **12**. The current thereby produced is such that the resultant Joule heat is sufficient to melt ingot **1**. Molten zone **13**, thereby produced, is prevented from expanding beyond solid-liquid interfaces **14** and **15** by virtue of the axial heat loss directed from interface **14** to cooling clamp **2** and from interface **15** to cooling clamp **3**. The depicted off-center position of molten zone **13** in respect to clamps **2** and **3** indicates that at this stage of the process clamp **3** is at a lower temperature than clamp **2**. If molten zone travel is desired from left to right, the temperatures of clamps **2** and **3** are monitored by simultaneously decreasing the temperature of clamp **2** and increasing the temperature of clamp **3**. A method of setting up a program by use of which moving molten zone **13** is maintained at a fixed length during traversal will be set forth.

Fig. 2 is an idealized curve of the temperature gradient in ingot **1** of Fig. 1 for the position of molten zone **13** indicated. The curve of temperature against distance between cooling clamps **2** and **3** is idealized in that radiation and heat losses other than those produced axially in the direction of cooling clamps **2** and **3** are neglected. The other assumption made is that the resistivity R of ingot **1** as a function of temperature T is constant. The general form of the curve is the same for the actual case in which there is radiation or other lateral heat loss. The variation in resistivity with temperature in many materials such as the usual metallic material is such as to favor control of a molten zone produced in accordance with this invention. This will also be discussed.

For the idealized case discussed, the general form of the temperature gradient curve is parabolic and follows the general equation:

$$T = T_m - \frac{Q}{2k}(x-s)^2 \qquad (1)$$

which is the algebraic equation for an inverted parabola centered at $x=s$ in which

T=temperature in degrees Kelvin
T_m=maximum temperature obtained in degrees Kelvin
Q=power per unit volume in watts per cubic centimeter
k=thermal conductivity in watts per centimeter squared per degree C. per centimeter
s=distance from a cool end of the ingot on the inside of a cooling clamp to the point of maximum temperature (T_m) in the direction of zone traversal in centimeters. *Note.*—The position of T_m generally corresponds with the center of the zone.
x=distance along the ingot measured from the left-hand cool end in centimeters.

For the position of zone **13** shown it is seen that the curve of T against x rises from a value of T_0 at the cool end of ingot **1** to T_{mp}, the melting point of ingot **1** at position **14** and continues to rise to T_m, the maximum temperature at position **21** corresponding with the center of zone **13**. From this peak value the curve then drops to the melting point at interface **15** which in this instance represents the leading solid interface of zone **13** in the direction of traversal and from there to the value T_1 representing the temperature of the ingot at the cool end just inside cooling clamp **3**. Since for the idealized case the only loss of heat is through ingot **1** into cooling blocks **2** and **3**, the position of zone **13** and its length for a given power input are determined solely by end temperatures T_0 and T_1. Equations may now be presented for required sink temperatures T_0 and T_1 in relation to zone position s.

$$T_o = T_m - \frac{Q}{2k}s^2 \qquad (2)$$

$$T_l = T_m - \frac{Q}{2k}(l-s)^2 \qquad (3)$$

in which l=length of ingot between clamps in centimeters from which the temperature drops are in the ratio

$$\frac{T_m - T_o}{T_m - T_l} = \frac{s^2}{(l-s)^2} \qquad (4)$$

Under ordinary circumstances, especially in crucibleless zone-melting, it is desirable to prevent contact of the molten zone with either of the end clamps. As an example, where it is desired that T_m be no closer to a clamp than about one-fifth the length of the ingot between the clamps, so that, for the case in which $s=0.2l$, it is seen that the extreme ratio of temperature differentials, that is, the ratio in the left-hand portion of Equation 4 is $(0.2)/(0.8)^2$ or 1/16.

The slopes of the parabolic curve of Fig. 2 are determined by the ratio $Q/2k$ in Equation 1. The greater this ratio the steeper the parabola and the less sensitive is the length of the molten zone as a function of temperature fluctuations due, for example, to random fluctuations in power input. In the zone-melting process it is generally desirable to operate with short molten zones of fixed length.

In Fig. 2 the solid line parabolic curve is drawn for the case of constant thermal conductivity and constant electrical conductivity in the solid and liquid phases of the material being processed. However, for the usual system both thermal and electrical conductivities differ from the solid to the molten phase. As an example, for most metal systems both thermal and electrical conductivities are of the order of half as great for the molten phase, resulting, in such systems, in a ratio $Q/2k$ in the molten phase which is about four times that for the solid. The dashed line parabolic curve 14—15 shown on Fig. 2 is illustrative of such a system in which the thermal and electrical conductivities are less in the molten than in the solid phase. The advantages of such a system when undergoing processing in accordance with this invention are apparent; a decrease in electrical conductivity in the molten phase results in an increase in the product of I^2R and a consequent increase in the amount of power generated in the molten zone, while the accompanying decrease in thermal conductivity results in somewhat lower axial heat flow from the position of T_m to the solid part of the ingot, thereby resulting in a steeper gradient at the interface and better control of zone length. That advantage may be taken of this decrease in thermal and electrical conductivities in the molten phase will be seen from the Illustrative Calculation 1 below.

Although it is apparent that an advantage is gained by use of a system in which electrical and/or thermal conductivity decreases in the molten zone, so as to result in an increase in the value of $Q/2k$, it is to be understood that this invention is not to be limited to the operation of the processes described and claimed herein to systems of this nature. However, although from a theoretical standpoint the processes herein operate effectively on any system no matter what the variation in $Q/2k$ in the molten phase, since increase in thermal and/or electrical conductivity can result in the ultimate in no worse than constant temperature across the zone from the trailing interface to the leading interface, from a practical standpoint it is found that a severe decrease in the value of $Q/2k$ in the molten phase results in an unstable zone, the length of which can be controlled only by the use of extremely short ingot lengths and extremely low sink temperatures. Although such short ingot length and low sink temperatures may be obtained effectively in virtually all non-insulating materials including germanium, silicon, and other semiconductive materials by use of species of the invention discussed, for example, in connection with Fig. 4, it has been found that for efficient operation in accordance with the apparatus of Fig. 1, effective control over zone length may be had only if any increase in thermal and/or electrical conductivity in the zone is such as to produce a value of $Q/2k$ which is no less than one-half that of the value of this ratio in the solid portion of the ingot.

Materials fulfilling this requirement include iron, molybdenum, titanium, zirconium, tungsten, rhenium, bismuth, and many others. Semiconductive materials such as germanium and silicon sometimes have

$$\frac{Q}{2k}$$

values in the molten phase which are lower than one-half that in the solid. Such materials may be processed on apparatus such as that of Figs. 3 and 4.

The following illustrative example relates to a metallic system undergoing processing in accordance with apparatus such as that depicted in Fig. 1.

Illustrative Calculation 1

In accordance with this calculation power input and variation in heat sink temperatures required to move a molten zone through an iron ingot are determined. It is desired to move the center of such a zone from $X=5$ centimeters to $X=20$ centimeters in an ingot 25 centimeters long and 1 square centimeter in cross-sectional area. The extreme values of T_0 and T_l are for the positions of the zone at $X=5$ and $X=20$ centimeters.

The thermal conductivity of solid iron is about 0.5 watt/centimeter²/° C./centimeter. The electrical resistivity in the solid phase, ρ_s, is about 1.3×10^{-4} ohm-centimeter at the melting point. The melting point of iron T_{mp} is 1540° C. In accordance with experiments that have been made it is assumed that a desirable value for T_m is 10° C. above the melting point so that T_m is 1550° C. It is here assumed that the thermal conductivities and electrical conductivities do not vary from solid to liquid phase so that $k_s=k_l$ and $\rho_s=\rho_l$. k is approximately equal to 0.5 so that $Q/2k=Q/1$ for which a value of 4 is assumed. Since $Q=I^2\rho$ watts per cubic centimeter, the required current, I, is calculated as follows:

$$I=\sqrt{Q/\rho}=176 \text{ amperes}$$

For a molten zone centered at $X=5=s$, the required sink temperatures from Equations 2 and 3 are:

$$T_o=T_m-\frac{Q}{2k}s^2=1550-4(5)^2=1450° \text{ C.}$$

and

$$T_l=T_m-\frac{Q}{2k}(l-s)^2=1550-4(20)^2=-50° \text{ C.}$$

Still assuming equal thermal and electrical conductivities in the liquid and solid phases, the zone-length, $2(x-s)$ is calculated from Equation 1 as follows:

$$T_{mp}=T_m-Q/2k(x-s)^2$$

$$(x-s)^2=T_m-\frac{T_{mp}-T_{mp}}{Q/2k}=\frac{1550-1540}{4}=2.5$$

and

$$\text{Zone length}=2(x-s)=3.1 \text{ centimeters}$$

The process has been discussed in terms of the idealized case in which thermal conductivity and electrical conductivity are constant throughout the ingot in both phases over the entire temperature range. In any practical system, both of these values vary. For design purposes variations both thermal and electrical conductivity in the solid phase may be ignored. The variation from the solid to the liquid phase, however, is significant and should be taken into account. For the usual metal system both the electrical and thermal conductivities are about twice as great in the solid phase as in the liquid. As a result the value

$$\frac{Q}{2k}$$

in the liquid for such systems here designated $Q'/2k'$, is about four times that in the solid. Still assuming no heat loss other than axially in the direction of the sinks, the form of the thermal conductivity curve in the liquid zone remains parabolic. However, since the value

$$\frac{Q'}{2k'}$$

is approximately four times as great as

$$\frac{Q}{2k}$$

the curve peaks more sharply in the molten zone resulting in a parabolic curve of the form of the dashed line on the plot of Fig. 2, peaking at T_m'. The resultant steeper temperature gradient on the molten side of both interfaces is very helpful in maintaining a short and constant zone-length.

The relationship between zone-length and temperature differential in the zone may be seen from the following calculation:

Illustrative Example 2

Assuming a temperature differential in the molten zone of 10° C., the zone-length, $2(x-s)$, may be calculated as follows:

$$(x-s)^2=\frac{T_m-T_{mp}}{Q'/2k'}=\frac{10}{(4)(4)}=0.62 \qquad (5)$$

$2(x-s)$=true zone-length$=2(0.79)=1.6$ centimeters

From Equation 5 it is seen that if the temperature differential in the molten zone were to vary from about 20 degrees to about 5 degrees, within which any controlled process may be expected to operate with facility, the total variation in zone-length would be from 2.2 centimeters to 1.1 centimeters.

A zone-length of 1.6 centimeters for iron is suitable for zone refining in a container, and for zone melting using the magnetic suspension method of Pfann and K. D. Hagelbarger, Journal of Applied Physics 27, pages 12–18 (1956). Generally, for the floating zone method a shorter zone, less than 1 centimeter long, is desirable. This may be obtained by reducing the temperature differential in the zone to about 3° C., which may be done, for example, by reducing the heating current.

Whereas variations in thermal and electrical conductivity in the case of a metallic system operate to the advantage of the process, lateral losses of heat such as that due to radiation tend to decrease the control gained by variation of temperature at the heat sinks. Since, however, radiation losses are governed by a plurality of conditions and since loss by such mechanism may, in large part, be controlled by and even used to the operator's advantage by use, for example, of the apparatus discussed in connection with Figs. 3 and 4, exact mathematical expressions for the effect of such lateral losses are not presented. In general, since radiation losses are greater for greater temperature gradient, it is seen that the effect of radiation is to decrease somewhat the slopes of the axial gradients or to flatten out the parabolic curve. Such deformation of the thermal gradient curve of Fig. 2 tends to increase the range of temperature variation at the heat sinks necessary to cause movement of the zone. Since the form of the temperature gradient curve remains approximately parabolic, however, a molten zone may still be formed and caused to progress in accordance with the stated principles.

Fig. 3 is illustrative of one type of apparatus in which radiation losses in the proximity of the zone are diminished. In this figure molten zone **30** is formed in ingot **31** by the Joule heat generated by a current which is passed axially through ingot **31** by means of a power source not shown. Heat sinks **32** and **33** may also act as end clamps and current electrodes as in Fig. 1. Motion of zone **30** may be produced in the direction of heat sinks **33** by increasing the temperature of that sink while decreasing the temperature of sink **32** as has been described. Radiation shield **34** is moved progressively along ingot **31** by means not shown so as to continually encompass molten zone **30**. Such a radiation shield may be made of quartz having a bright coating of platinum or other suitable heat resistant reflecting material on its inside surface.

In Fig. 4 control of the length of the molten zone is further aided by supplementing the moving heat reflector with moving heat sinks. Molten zone **40** is produced in ingot **41** by Joule heat generated by the passage of current axially through ingot **41** by reason of a power source and electrodes not shown, while positioning and zone-length are again controlled by varying the temperatures of heat sinks **42** and **43**. Radiation losses in the proximity of molten zone **40** are diminished by heat reflector **44** which may be ring-shaped and constructed

of quartz with an inner coating of bright platinum and is moved along the rod at the same rate as molten zone **40** by means not shown. Heat sinks **45** and **46** are also moved along the rod in the direction of zone travel and at the same rate on either side of heat reflector **44** and generally at fixed position relative thereto by means not shown. The heat sinks **45** and **46** depicted are cylindrical in shape, are constructed of a black body material such as graphite or a dull metal, may have fins on the inner surface and are water-cooled by means of coils **49** and **50**. Moving heat sinks **45** and **46** are shown spaced from reflector **44** to keep the heat flux from the zone through interfaces **51** and **52** substantially axial. By reducing the spacing between moving reflector **44** and moving heat sinks **45** and **46**, the temperature gradients at interfaces **51** and **52** are increased in slope so that somewhat closer control of zone-length is afforded. However, close spacing will result in a large component of heat flux in a direction normal to the axis of ingot **41** resulting in interfaces **51** and **52** which are concave in the direction of the molten material. Since such concavity results in a diminution of a maximum volume of a zone which may be suspended in any of the crucible-less zone-melting procedures, it is suggested that heat sinks **45** and **46** be spaced at such distance from reflector **44**; that the heat flux component in a direction normal to that of the axis of ingot **41** at the interface be small compared to the axial component.

A variation in the use of the apparatus of Fig. 4 depends primarily upon positioning and/or temperatures of heat sinks **45** and **46** for determining the size and location of molten-zone **40**, thereby decreasing effective ingot length and increasing control at the expense of somewhat complicating the apparatus. Control may be further enhanced by use of end blocks **42** and **43** as additional sinks as described above.

In the floating zone or magnetic suspension zone techniques described above, and in other forms of crucible-less zone-melting, especially where the molten zone penetrates the entire cross-section of the ingot, a clamping effect may exist where there is appreciable expansion or contraction as the solid rod heats or cools, respectively, during the period before or after a molten zone is established. Expansion, in particular, tends to buckle the ingot, because most materials are soft at temperatures near their melting point. Where the end product is advantageously single crystalline and where it is desired to avoid crystalline imperfections this desire may be frustrated by the expansion or contraction resulting when the molten zone is frozen in the final position of traversal. Even where crystalline imperfections are not serious, excessive change in volume may result in the instability of the zone otherwise stable by virtue of its dimensions. An arrangement which automatically allows an ingot to expand and contract, but which, when no expansive or contractive forces are present, exerts no force on the ingot, is shown in Figs. *5a* and *5b*.

In the apparatus of Figs. *5a* and *5b* molten zone **60** is produced in ingot **61** and caused to progress in the manner already described by reason of a programming of temperatures at fixed position heat sinks on either side of and separated from molten zone **60**. The zone is produced by Joule heat resulting from the passage of current through ingot **61**. The electrical path is completed by electrodes and a power source, neither of which is shown. Clamps **62** and **63** differ from those shown in the preceding figures in that contact with ingot **61** is through leaf springs **64** in clamp **62** and leaf springs **65** in clamp **63**. It should be noted that springs **64** and **65** are inclined in the same direction in relation to ingot **61**. Gripping of the ingot **61** by springs **64** and **65** is improved by serrations or screw threads **66** and **67**. On contraction of ingot **61** between clamps **62** and **63**, for example, due to freezing of zone **60** in its final position in the usual metal system, slippage of ingot **61** through clamp **62** is permitted by spring **64**. In the event of expansion by that portion of ingot **61** between clamps **62** and **63**, due, for example, to formation of zone **60** at its initial position in the usual metal system, slippage of the serrated or threaded portion of ingot **61** within clamp **63** is permitted by spring **65**. The result is a net movement of ingot **61** from left to right during each complete heating-cooling cycle. It is apparent that where a large number of molten zones are to be passed successively through an ingot such as **61** of Fig. *5a*, a sufficient portion of the ingot should be allowed to project past the end of clamp **62** to allow for this movement.

This invention has been discussed primarily in terms of moving a zone of constant length through a metallic material such as iron in a crucibleless process such as the "floating zone technique" to which reference is made above. This procedure may be modified in many ways in accordance with current zone-melting procedures so as to obtain desired segregation characteristics in the end product. For example, the temperatures of the heat sinks may be monitored in accordance with some program which will result in a predetermined variation in zone-length. Consequences which will follow are apparent by reference to existing practices. Use of such programming may, for example, result in a uniform distribution of an impurity added to the zone in its initial position by a process sometimes referred to as "starting charge only zone-melting," see United States Patent 2,739,088, issued March 20, 1956, or may result in a predetermined variation in segregation due to changing volume of the traversing zone also disclosed in that patent, or in sharp distribution changes in the final product as are produced by "rate-growing." If any of these procedures is to be carried out by one of the crucibleless techniques, it is of course necessary to maintain the maximum length of the zone within the range required for stability. Such limits have been reported in the literature relating to the concerned processes, see for example above cited article by Pfann and Hagelbarger.

Although the Joule heat method of producing and causing a molten zone to traverse an ingot appears to be of primary importance for use where crucible contamination is to be avoided by any of the techniques set forth above, it is likely that this method, due to its extreme simplicity, ready control over dimensions and rates attainable, and the inexpensive apparatus required may find use in conjunction with any of the zone-melting procedures in which the ingot is processed in a boat or other type of crucible. From a mechanical standpoint the elimination of closely fitted moving heaters and of the heat exchange problems resulting from the use of heaters exterior to the crucible is of practical value.

Although the accompanying figures all depict the ingot under treatment with its major dimensions disposed horizontally, it is apparent that the position of the ingot will have no fundamental effect on the Joule heat method of producing the zone. Consequences which do follow by virtue of a displacement of the major dimension from the horizontal are well known to those skilled in the art. Thus, crucibleless zone-melting such as by the floating zone technique is frequently carried out with the major axis of the ingot substantially normal to the horizontal, this position resulting in a stable zone of maximum volume. Suspension zone-melting in which the zone is maintained in position by virtue of a reactive force resulting from the interaction of a current and magnetic field is generally carried out on a substantially horizontal ingot.

Other variations which are applied to zone-melting may be utilized in conjunction with the Joule heat method herein without in any way affecting the principles of operation. Such variations include doping of the molten material, either at the initial position of the molten zone or during traversal by solid-liquid or gas phase doping and the perturbation method of obtaining sharp variations in minor ingredient distribution described in United States Patent 2,739,088.

The description of this invention has been restricted to a form of molten zone produced by Joule heating which is caused to move primarily or solely by virtue of temperature gradients produced through the use of heat sinks. Other methods of causing movement of such a molten zone formed through Joule heating may, however, be substituted for the temperature gradient method described. For example, sufficient current may be passed through an ingot to raise the temperature of the solid material to within a very few degrees of its melting point after which a molten zone may be produced by the use of auxiliary heating equipment such, for example, as a gas torch. In a system in which the resistivity increases upon melting as in the usual metallic system such a molten zone once formed will continue to exist by virtue of its increased resistance relative to the solid portion of the ingot and the accompanying increase in Joule heating resulting therefrom. Restriction of the cross-sectional area of such a molten zone adjacent an interface will result in the further increase in resistance in that portion of the zone with further accompanying increase in Joule heating. The net result of such an unequal distribution of Joule heating within the molten zone results in progression of that solid-liquid interface adjacent the restricted portion of the zone and regression of the other interface.

Such a restriction in cross-sectional area in a molten zone may be brought about by several alternate mechanisms. An extremely simple method is to incline the ingot from the horizontal, thereby the redistribution of the molten material under the influence of gravity resulting in restriction of the uppermost portion of the molten zone and expansion of the lowermost portion. Such an arrangement, therefore, results in movement of a molten zone through an ingot without the use of moving heating and/or cooling means and without the use of variable temperature heat sinks. Although such a method may result in some matter transport in the downward direction, this may be eliminated by operating at a critical tilt angle, see Transactions A.I.M.E., volume 197, page 1441, 1953.

Other methods of restricting the cross section of a molten zone at or adjacent a solid-liquid interface include moving magnetic poles so arranged as to depress the liquid over the desired area, and immersion of an inert, electrically insulating member in the molten zone at or near this interface so as to restrict the cross sectional area of conducting liquid in this position. In such a process the magnetic poles or immersed member, must be moved with the zone.

The well-known floating zone technique naturally lends itself to use of such a Joule heating method. In accordance with such a process a zone is retained in position in a vertically disposed ingot between two solid portions of the ingot. Under the influence of gravity, such a zone, retained in position solely by adhesive and cohesive forces, becomes enlarged in cross section near its lower interface and restricted near its upper. Passage of current through such a zone results in greater generation of heat near the top of the zone and consequent movement of the zone in the upward direction.

What is claimed is:

1. Method of zone-melting a non-insulating solid material comprising passing an electrical current through the material, the current being of such magnitude that the Joule heat generated thereby is sufficient to raise the material to its melting point, removing heat so generated from two fixed positions in the material by the use of heat sinks, the said heat sinks being in fixed positions relative to the said material, the temperatures of the sinks and mechanism of heat exchange such that there is between the sinks a molten region intermediate two solid regions, and causing at least one of the interfaces be-

tween the molten region and a solid region to progress by varying the amount of heat removed by at least one heat sink.

2. Method in accordance with claim 1 in which there is a thermally conductive path between the material and the heat sinks and in which the primary mechanism of heat exchange is conductive.

3. Method in accordance with claim 2 in which there is a simultaneous variation in the amount of heat removed by a heat sink at each of the two positions, the amount of heat removed being increased at one position and being decreased at the other position.

4. The method of claim 1 in which radiation losses in the vicinity of the molten region are reduced by use of a heat reflector.

5. The method of claim 4 in which additional cooling is produced in the solid regions adjacent the molten region by use of radiant heat absorbers.

6. The method of claim 4 in which the said material is a fusible semiconductive material.

7. The method of claim 3 in which the only solid material contacted by the said molten region is that of the said solid regions.

8. The method of claim 7 in which the value $Q/2k$ of the said material in the molten phase is at least as great as one-half of the value of $Q/2k$ of the said material in the solid phase, in which Q equals power per unit volume of material in watts per cubic centimeter and k equals thermal conductivity in watts per square centimeter per degree C. per centimeter.

9. The method of claim 7 in which the direction of progression of the said at least one interface is substantially vertical and in which the said molten region is retained in position primarily by reason of adhesive forces between the said molten region and the said solid regions and cohesive forces within the said molten region.

10. The method of claim 7 in which the direction of progression of the said at least one interface is substantially horizontal and in which the said molten region is retained in position primarily by reason of a reactive force resulting from the interaction of the said electrical current and a magnetic field a component of which is horizontal and normal to the direction of electrical current flow.

11. The method of claim 8 in which the said material is iron.

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