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2,475,810

PREPARATION OF SILICON MATERIAL

Filed Jan. 5, 1944

2 Sheets-Sheet 1

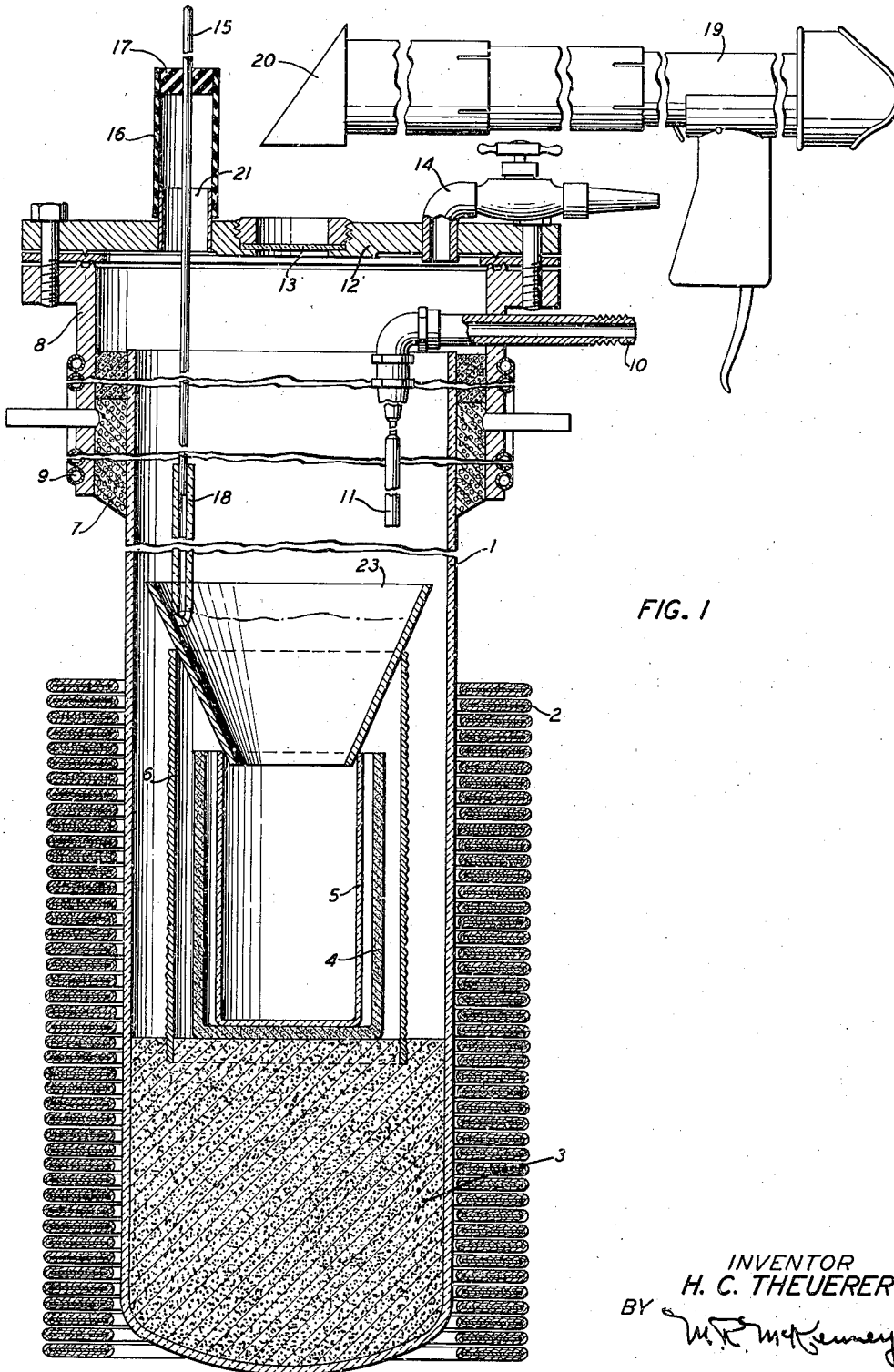


FIG. 1

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FIG. 2

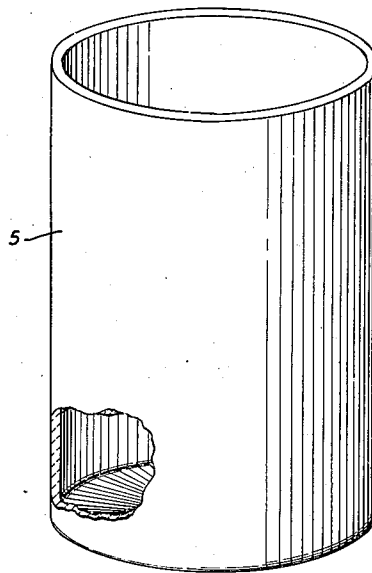


FIG. 3

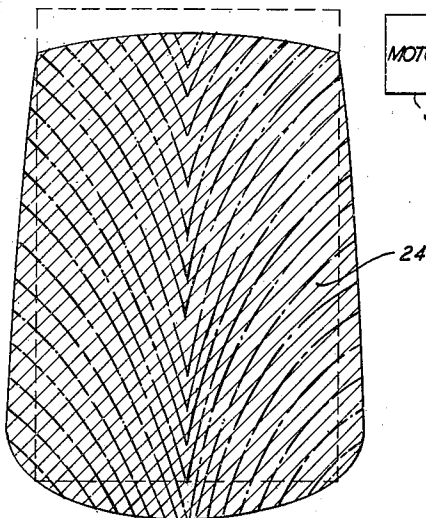
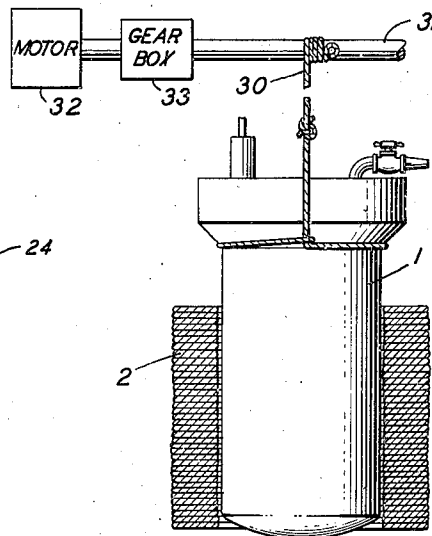


FIG. 4



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PREPARATION OF SILICON MATERIAL

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9 Claims. (Cl. 49—79)

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This invention relates to means and methods for the preparation of solid materials and particularly for the preparation of silicon ingots or castings.

An object of the invention is to effect a large increase in the size of solid bodies of fusible materials, such as silicon, when obtained by metallurgical methods.

Another object is to obtain these solid bodies of increased sizes and at the same time to retain certain desirable physical and electrical characteristics.

Another object is a method of forming ingots of fusible materials, such as silicon in which disposition is made of the forces of expansion and contraction which tend to impair the physical characteristics of the resulting material.

Other objects are to effect economies in the use of time and materials and to realize other improvements and advantages in the preparation of silicon ingots.

In the use of ultra-high frequencies involving wave lengths of only a few centimeters in the radio and allied signaling arts, it has been found that best results are obtainable with translators of the solid-contact type including rectifying elements of some solid material such as crystalline silicon. At the present time this material is prepared by fusing silicon powder of high purity and casting the melt in ingots. The method and apparatus now available for this purpose impose severe limitations on the amount of material that can be obtained from a single ingot. One reason for the limited yield from these prior methods is the difficulty of increasing the size of the melt and maintaining at the same time the definite physical structure of the material which is known to be essential to good electrical performance. Due to the peculiar density characteristic of silicon in the neighborhood of the solidification temperature the mass undergoes both expansion and contraction during the process of casting the ingot. Also as the silicon mass hardens it adheres to the walls of the crucible containing the melt, and the forces set up as a result of the changing volume prevent the hardening mass from assuming the desired physical structure and in fact often produce fissures and internal ruptures which impair the electrical properties of the resulting material.

In accordance with the present invention, these difficulties are overcome and it is possible to obtain ingots which are much larger in volume and which have the internal physical structure that is essential to the desired electrical performance

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when the material is used for electrical translators. More specifically, these results are realized by a method in which the silicon ingot is cast in a crucible of such material and of such design that the crucible itself is capable of disposing of the forces of expansion and contraction to prevent them from reacting adversely on the physical structure of the silicon melt. The crucible is made of silica which has a melting point substantially higher than that of silicon and which is also capable of assuming a state of partial plasticity when subjected to the proper heat treatment at the temperatures to which the silicon melt is raised in the fusion process. Furthermore, the crucible is designed with walls which are quite thin, permitting them to expand, without rupture, during that part of the process in which the temperature of the melt is approaching the solidification point. As the temperature approaches this point the silicon mass undergoes expansion, and the forces thus created, particularly in large melts, would react on the internal structure of the mass were it not for the yielding capability of the partially plastic crucible. The resulting expansion of the crucible relieves these forces and permits the internal structure of the cooling melt to assume the requisite physical characteristics.

Another feature of the invention is the method of casting ingots in which the adhesive forces between the surface of the ingot and the surface of the crucible containing it are prevented from reacting unfavorably on the physical characteristics of the resulting material of the ingot. This desirable end is achieved by controlling the heating cycle in such a manner that the internal walls of the crucible, particularly when the crucible is of vitreous silica, undergo a physical change which greatly weakens the bond between the ingot and the crucible. More specifically, the heat treatment to which the crucible is subjected before the melt passes below the temperature of solidification causes a substantial devitrification of the internal wall of the crucible. When thereafter the temperature of the melt falls below the temperature of solidification, the volume of the melt contracts, and the embrittled condition of the inner crucible walls permit the easy severance of the contracting melt, thus preventing the forces of contraction from setting up strains within the body of the cooling melt.

Another feature of the invention is the method of forming an ingot of silicon in which the crucible containing the molten mass of silicon is withdrawn at a definite rate from the coil which sup-

plies the heating energy. The effect of this procedure is to initiate solidification of the molten mass at the upper boundary surface, to cause the cooling to follow a temperature gradient which proceeds longitudinally or downwardly through the mass, and to exclude the presence of a transverse temperature gradient which might otherwise cause the mass to cool first around its exterior walls. The advantage of this method is the attainment of a crystalline structure which is uniform and is free from internal stresses and ruptures which impair the electrical characteristics.

These and other features of the invention, including the apparatus by which the foregoing methods are practiced, will be discussed more fully in the following detailed specification.

In the drawings accompanying the specification:

Fig. 1 is a cross-sectional view of an electric furnace and the accompanying apparatus for casting ingots of silicon;

Fig. 2 is a perspective view of the crucible;

Fig. 3 is a vertical section of one of the silicon ingots; and

Fig. 4 illustrates the mechanism for withdrawing the furnace from the heating coil.

The methods heretofore used for the production of silicon for use in microwave rectifiers have been slow and expensive because of the severe limitation upon the permissible size of the ingot. Generally speaking, it has not been possible to increase the size of the ingot much beyond 65 grams. If larger melts were attempted an impairment of the physical structure of the ingot usually resulted in the form of internal cracks and ruptures.

The method of the present invention, however, makes it possible to increase the size of the ingot severalfold. In fact, it is possible to cast an ingot weighing as much as 320 grams which is entirely free of cracks and other impairments and has the desired internal structure. This greatly increased ingot size is attained by the unique casting method which will be described hereinafter. Before discussing the method in detail, however, it should be explained that the electrical properties of the resulting silicon material are known to depend in large measure on the crystalline structure of the material and that this structure depends upon the heat treatment and other factors attending the casting of the ingot. It is believed that an approach to the ideal material would be realized in an ingot which was cast and solidified in such a manner that the solidification of the melt begins at the top and proceeds uniformly in a plane front toward the bottom, the solidification taking place under conditions such that no undue forces are imposed upon the internal structure. In such a case the crystal grains would assume a parallel disposition extending from top to bottom in the ingot and lying perpendicular to the plane along which the cooling front progresses.

The method of the present invention very closely approximates the ideal above mentioned; it is capable of producing material having the desired grain structure and other properties essential for good electrical rectification. Referring for the moment to Fig. 3, which shows a vertical cross-section of an ingot of silicon produced by the present method, it will be seen that the columnar grain structure follows in large measure the ideal pattern. The fan-like growth of the crystals is the result of the temperature

gradient, which is such that the cooling front proceeds from top to bottom along a surface which is more or less parabolic rather than plane as it would be in the ideal case. While this crystalline structure is important, another condition which is also very important to the ultimate performance is the freedom of the ingot from all cracks and other imperfections and from unnatural strains and stresses which tend to occur in material prepared by the ordinary methods.

The apparatus by which the method is performed is illustrated in Figs. 1 and 2. Essentially this apparatus comprises an electric induction furnace, including a silica tube 1 and a high frequency heating coil 2 surrounding the lower portion of the tube. The bottom end of the furnace tube 1 may be filled with some inert substance 3 such as aluminum oxide grain. This filler 3 serves as a bed for supporting a cylindrical graphite shield 4 within which the crucible 5 is disposed. The crucible 5 is a cylindrical cup of vitreous silica, and the walls and bottom are purposely made very thin to permit them to deform under the expanding influence of the ingot during the cooling process. The purpose of the graphite shield 4 is to develop heat by induction from the high frequency field set up by the coil 2 and to transfer this heat by conduction and radiation to the crucible 5 and to the contents thereof.

Surrounding the shield 4 and substantially concentric therewith is a second shield 6 which rests on the bed 3 and is preferably made of aluminum oxide. The purpose of the shield 6 is to retain and control the heat developed by the graphite shield 4.

The upper end of furnace tube 1 is sealed into the head 8 by a suitable cementing material 7. The head 8 is surrounded by a coiled pipe 9 through which water is circulated for cooling purposes. Also a gas inlet 10 enters the head 8 and terminates in a silica tube 11 in the interior of the furnace.

The top of the furnace head 8 is sealed by a cap 12 which is bolted thereto with gaskets of lead or other suitable material. The cap 12 contains a glass window 13, through which the interior of the furnace may be observed, and a gas outlet pipe 14. A stirring rod 15 extends through the head 12 and into the interior of the furnace. The rod 15, which is made of metal, is supported by a rubber seal 17 which fits into the upper end of a flexible rubber sleeve 16. The lower end of the flexible sleeve 16 fits over the end of the metal tube 21, which in turn is secured in an opening in the head 12. Within the furnace the metal rod 15 terminates in a section of silica tubing 18.

Any suitable optical pyrometer 19 is provided for observing the interior of the furnace while the heat is on. This instrument includes a cathedral prism 20, which receives light from the surface of the melt through the window 13, a series of filters which pass only monochromatic light, and a lamp having a calibrated filament. The lamp is connected to a milliammeter and a variable source of potential, not shown in the drawing. The brightness of the light coming from the surface of the melt is compared with the light from the calibrated filament, and in this manner it is possible to determine the temperature of the molten silicon within the furnace.

Since the silicon ingot is usually prepared from powdered silicon having a substantial volume before being melted, a hopper 23 is provided for

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holding the excess volume of the charge until it is melted. The small end of the hopper 23 enters the open end of the crucible 5, permitting the excess material to pass down into the crucible as it melts. To facilitate the movement of the powder from the hopper into the crucible the stirring rod 15 is manipulated from the exterior of the furnace while the melting operation is taking place, the flexibility of the rubber sleeve 16 being sufficient for this purpose.

The fusion process will now be described. With the cover plate 12 removed and the furnace tube 1 lowered into the heating coil 2, the silica crucible 5 and shields 4 and 6 are placed in position on the bed 3 of aluminum oxide grain. Next a measured charge of silicon having a high degree of chemical purity and preferably in the form of a powder is applied to the crucible 5 through the hopper 23, the excess of the charge remaining in the hopper after the crucible is full. The lid 12 is now replaced and bolted into position to seal the upper end of the furnace tube.

It is desirable to exercise a close control over the character of the atmosphere within the furnace during the heat. To this end the air within the furnace is first exhausted through the outlet pipe 14, following which an atmosphere of some inert gas, such as helium, is introduced through the pipe 10 and is maintained at a sufficient pressure within the furnace to insure an orderly fusion of the charge.

Alternating current of high frequency is applied to the heating coil 2 to develop about 5 kilowatts of power for an interval of about five minutes. During this time the temperature of the charge within the furnace is raised to a point in the neighborhood of 900° C. Next the power is increased sufficiently to raise the temperature to 1600° C., where it is held for a period of twenty minutes. During the temperature change from 900° to 1600° C., the silicon powder fuses and assumes a molten state, the melting point being at or possibly a little above 1400° C. As the powder is melting in the crucible 5 the operator manipulates the stirring rod 15 to facilitate the discharge of the excess powder from the hopper 23 down into the crucible.

The next step is to reduce the power applied to the heating coil until the temperature of the melt and the crucible containing it assumes a value between 1450° and 1550° C. The temperature is maintained at this point for a period of an hour. During this time the thin walls of the vitreous silica crucible 5 become sufficiently plastic to permit the crucible to undergo a substantial amount of deformation without rupture. Also during this heating interval a certain amount of devitrification of the silica takes place particularly in the surfaces of the crucible, including the surfaces which are adjacent the molten charge of silicon. These changes are very important for reasons which will be explained hereinafter.

The next step in the process is to effect the solidification of the melt in such a manner as to carefully control the character of the internal structure of the final ingot. This step is accomplished by holding the heating power constant and raising the furnace tube 1 up out of the heating coil 2 at a predetermined rate, such as an eighth of an inch per minute. The mechanism for raising the furnace is illustrated in Fig. 4. The furnace 1 is suspended in position in the heating coil 2 by a cord 30 which is secured to a shaft 31. The shaft 31 is driven by a motor 75

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32 through a gear reduction mechanism 33. As soon as the uppermost layer of the molten charge in the crucible passes out of the influence of the heating field its temperature drops, and this upper layer solidifies and seals the charge within the crucible. It should be noted at this point that the changes of temperature which have taken place during the previous steps of the process have been accompanied by changes of volume of the molten charge which correspond to the coefficient of expansion of the material. As long as the molten charge has a free surface these volume changes take place within the crucible without the exertion of any appreciable force against the walls thereof. As soon, however, as the upper layer of the metal has solidified, any positive volume changes occurring thereafter manifest themselves by the application of corresponding forces to the crucible.

As succeeding layers of the molten charge pass out of the heating field, their temperature falls below the melting point, and these layers in turn solidify. During the decline of the temperature from a point substantially above the solidification temperature of the molten silicon to the final cooling values the charge, because of the peculiar density characteristic of silicon, undergoes first a density and volume change in one direction and later a density and volume change in the opposite direction. More specifically, the volume of the silicon melt increases substantially during the time the declining temperature is approaching the solidification point and thereafter decreases in response to a continuing fall in the temperature. Therefore, as each of the progressive layers passes through this falling temperature range, it first expands and then contracts in volume. Since each expanding layer is confined by the solidified material above, it creates forces of expansion which are applied directly to the walls of the silica crucible. The crucible, however, is in a state of partial plasticity at this time and is capable of yielding sufficiently to prevent these forces from reacting and setting up stresses within the body of the solidifying material. Thus the progressively cooling layers of the melt 24 (Fig. 3) are permitted to assume their natural internal crystalline structure free from the influence of the external forces. In this figure the expansion that takes place in the melt relative to the original volume is illustrated by the solid and broken lines. The broken line shows the original interior boundaries of the crucible before deformation, and the solid line shows the boundary of the melt after it has expanded and deformed the plastic crucible.

In the manner above explained, the forces of expansion which occur during the first part of the cooling cycle are relieved by the ready deformation of the crucible and prevented from reacting unfavorably on the internal structure of the resulting ingot. It will now be explained how the present process prevents the forces of contraction from affecting the structure of the ingot. The adhesive properties of silicon are such that a bond of substantial strength is made between the external surface of the ingot and the interior surface of the crucible. Unless, therefore, some provision is otherwise made the contraction of the ingot, after it has solidified and is decreasing in temperature, sets up internal forces which affect the physical structure of the final material. This detrimental effect, however, is prevented by weakening the bonds between the solidifying ingot and the walls of the crucible. As above ex-

plained, this step in the process is effected by applying the heat for a substantial time while the temperature is above the point of solidification and above the range in which the silicon melt undergoes contraction in response to decreasing temperature. The result of this prolonged application of heat to the walls of the crucible is to devitrify and embrittle the silica of the crucible to a substantial depth so that the solidifying ingot can readily sever itself from the walls of the crucible when it subsequently undergoes contraction in response to the decline in temperature.

To recapitulate, the prolonged heat treatment just prior to solidification serves to devitrify and embrittle the outer surfaces of the silica crucible and to render the inner material of the walls and bottom partially plastic. Although sufficiently plastic to yield to the expanding melt, the crucible retains enough strength and rigidity to confine the melt in substantially its original shape until it solidifies.

After the furnace tube 1 is fully withdrawn from the heating coil 2 and is permitted to cool to room temperature, the lid is taken off and the crucible and ingot removed from the interior. The cast ingot is then removed from the crucible, the latter being broken into parts if necessary to facilitate the removal.

Throughout the cooling process the full intensity of the heating coil is applied to those portions of the mass which still remain within its influence. Thus, the cooling of each receding layer occurs with substantial uniformity throughout the entire cross-section of the mass. In other words, the cooling gradient proceeds substantially in a single direction from the top of the mass toward the bottom, and there is practically no gradient in a transverse direction through the mass. The advantage of this heat control is a final material which is free from internal stresses or other influences which react adversely upon the electrical characteristics thereof.

The resulting ingot, illustrated in Fig. 3, is a body of crystalline silicon having a well defined internal structure free from cracks, ruptures and internal stresses, and having a highly symmetrical columnar grain structure. The ingot 24 is also divided into zones with respect to the electrical properties of the material. The upper portion, which is first to solidify, develops a positive thermal electromotive force. That is to say, if a metallic point is placed in contact with an element taken from the upper zone, the combination is highly asymmetrical, and the direction of current flow is from the silicon element to the metallic point. This upper zone of the ingot is known as the positive or P zone. The lower portion of the ingot, which is last to cool, develops a negative thermal electromotive force and is known as the negative or N zone of the ingot. Translators made of material made from this zone conduct in the opposite direction. Between the P and the N zones is a thin separating layer known as the barrier layer.

If desirable additional steps in the process may be introduced to facilitate the separation of the cooling melt from the surfaces of the crucible. A first precaution that may be taken is to preheat the crucible at 1600° C., for about fifteen minutes prior to the introduction of the charge. This preheating operation augments the devitrification of the walls of the crucible. A second step is to coat the inner surface of the crucible with a hydrolyzed solution of ethyl silicate. This solution leaves a thin coating of silicic acid on the

inner walls of the crucible, which when heated to 1000° C. dehydrates to silica.

If desirable the graphite shield 5 may be protected by coating the inner surface thereof with beryllium oxide. This coating protects the shield in the event the crucible ruptures during the fusion of the silicon.

Any of the well-known methods may be used for cutting the ingot into units of suitable size and dimensions for use in electrical translating devices.

It will be understood that numerous variations may be made in the process above described without deviating from the invention. The values of power, temperature, and time given above have been found to give good results, but it will be obvious that these may be varied within reasonable limits.

What is claimed is:

1. The method which comprises fusing a quantity of silicon in a crucible, applying heat until the crucible assumes a state of partial plasticity, lowering the temperature of the melt toward the point of solidification resulting in an expansion of the volume thereof, and dissipating the forces caused by the expanding melt by a corresponding expansion of the walls of the plastic crucible.

2. The method which comprises fusing a quantity of silicon in a crucible, applying heat until the crucible assumes a state of plasticity, changing the temperature of the silicon melt over that part of the temperature scale in which the volume of the melt increases with the temperature change, and relieving the internal structure of the melt of the forces resulting from the expanding volume by dissipating said forces in a corresponding expansion of the plastic crucible.

3. The method of preparing an ingot of a fusible material which has the property of increasing in volume in response to a decrease in temperature, said method comprising applying heat to fuse a charge of said material in a crucible, and to plasticize the walls of said crucible until they are capable of yielding to the forces of expansion caused by the increasing volume of said charge.

4. The method of preparing an ingot of a fusible material which has the property of increasing in volume in response to a decrease in temperature, said method comprising applying heat to fuse a charge of said material in a crucible, and to plasticize the walls of said crucible until they are capable of yielding to the forces of expansion caused by the increasing volume of said charge, and reducing the temperature of said fused charge until it solidifies.

5. The method of preparing a silicon ingot which comprises applying heat to a quantity of silicon in a crucible which becomes partially plastic at temperatures in the neighborhood of the solidification point of the silicon to fuse the silicon and partially plasticize the crucible, lowering the temperature of the upper layer of the melt to effect solidification of said upper layer and to seal the molten interior, effecting a reduction of the temperature of the remainder of said melt and a corresponding increase in the volume thereof, and dissipating the forces of expansion incident to the increasing volume of the melt by a corresponding increase in the volume of the crucible to relieve the interior structure of the melt from said forces of expansion.

6. The method of forming in a crucible an ingot of a fusible material which has the property of adhering upon solidification to the material of which the crucible is formed and which has the

property of contracting in volume as the melt undergoes solidification, which comprises applying heat to said crucible and to a charge of the fusible material therein to raise said charge to a temperature above the melting point thereof, and to devitrify the inner walls of the crucible to permit the separation of the solidified ingot from said crucible.

7. The method of forming in a crucible an ingot of a fusible material which has the property of increasing in volume in response to decreasing temperatures in a certain range and decreasing in volume in response to decreasing temperatures in a lower range and which also has the property of adhering upon solidification to the material of which the crucible is formed, said method comprising applying heat to said crucible and to a charge of the fusible material therein to raise said charge to a temperature above the melting point thereof, maintaining said crucible at a temperature above said melting point until it becomes sufficiently plastic to yield to the expansion of said charge when undergoing a volume increase, and until the walls of said crucible become sufficiently devitrified to permit the free separation therefrom of the solidified charge when undergoing a volume decrease.

8. The method which comprises fusing a quantity of silicon in a crucible by the application of heat from an exterior source, and cooling the molten mass to form an ingot of crystalline silicon by withdrawing the crucible from the source of heat in such a manner and at such a rate that solidification is initiated at the free boundary of the mass and proceeds in a single direction toward the opposite boundary of the mass.

9. The method which comprises fusing a quantity of silicon in a crucible by applying heat thereto from a heating coil surrounding the crucible, and withdrawing the crucible from the coil in a given direction to initiate cooling of the molten mass at the free boundary thereof, to effect a cooling gradient which progresses from said boundary in a single direction toward the opposite boundary, and to form an ingot of silicon which is free from internal ruptures and stresses.

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