(54) Title: PROCESS FOR THE PRODUCTION OF MEDIUM AND HIGH PURITY SILICON FROM METALLURGICAL GRADE SILICON
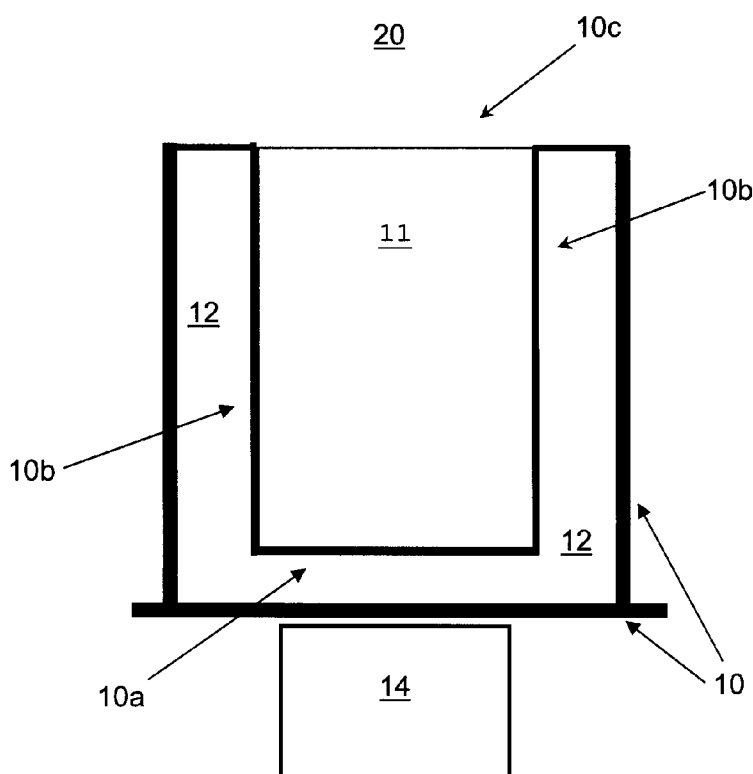
FIG.1A

(57) **Abstract:** A process for purifying low-purity metallurgical grade silicon, containing at least one contaminant and obtaining a higher-purity solid polycrystalline silicon is provided. The process includes containing a melt of low-purity metallurgical grade silicon in a mould having insulated bottom and side walls, and an open top; solidifying the melt by unidirectional solidification from the open top towards the bottom wall while electromagnetically stirring the melt; controlling a rate of the unidirectional solidification; stopping the unidirectional solidification when the melt has partially solidified to produce an ingot having an exterior shell including the higher-purity solid polycrystalline silicon and a center including an impurity-enriched liquid silicon; and creating an opening in the exterior shell of the ingot to outflow the impurity-enriched liquid silicon and leave the exterior shell which has the higher-purity solid polycrystalline silicon.

NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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PROCESS FOR THE PRODUCTION OF MEDIUM AND HIGH PURITY SILICON FROM METALLURGICAL GRADE SILICON

5   **FIELD OF THE INVENTION**

This invention relates generally to the production of silicon metal, more particularly it concerns a process of purification by crystallization that produces medium and/or high purity silicon metal for use in photovoltaic applications.

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BACKGROUND OF THE INVENTION

There are many and varied applications of silicon (Si), each application with its own particular specifications.

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Most of the world production of metallurgical grade silicon goes to the steel and automotive industries, where it is used as a crucial alloy component. Metallurgical grade silicon is a silicon of low purity. Typically, metallurgical grade silicon that is about 98% pure silicon is produced via the reaction between carbon (coal, charcoal, 20   pet coke) and silica (SiO_2) at a temperature around 1700 °C in a process known as carbothermal reduction.

A small portion of the metallurgical grade Si is diverted to the semiconductor industry for use in the production of Si wafers, etc. However, the semiconductor industry 25   requires silicon of ultra-high purity, e.g. electronic grade silicon (EG-Si) having approximately a 99.9999999% purity (9N). Metallurgical grade silicon must be purified to produce this electronic grade. However, the purification process is elaborate resulting in the higher cost of electronic grade silicon.

30   The photovoltaic (PV) industry requires silicon of a relatively high degree of purity for the production of photovoltaic cells, i.e. solar cells. The purity requirements of silicon for best performance in solar cell applications are:

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boron (B) < 3 ppmw,

phosphorus (P) < 10 ppmw,

total metallic impurities < 300 ppmw and preferably < 150 ppmw.

5   Although the degree of silicon purity required by the photovoltaic industry is less than that of the semiconductor industry, an intermediate grade of silicon, i.e. solar grade (SoG-Si) silicon, with the necessary low boron and low phosphorus content is not readily commercially available. One current alternative is to use expensive ultra-high purity electronic grade silicon; this yields solar cells with efficiencies close to the

10 theoretical limit but at a prohibitive price. Another alternative is to use less expensive "scrap" or off-specification supply of electronic grade silicon from the semiconductor industry. However, improvements in silicon chip productivity have resulted in a decrease in the "scrap" supply of electronic grade silicon available to the PV industry. Moreover, parallel growth of the semiconductor and photovoltaic industries has also

15 contributed to the general short supply of electronic grade silicon.

Several methods of purifying low-grade silicon, i.e. raw silicon or metallurgical grade silicon, are known in the art.

20 In US 2005/0074388 it is mentioned that:

"For electronic and photovoltaic applications that require high degrees of purity, the method of producing finished products such as photoelectric cells or solar panels comprises a step to produce pure silicon from a basic material that is a silicon

25 *essentially with a low content of boron and phosphorus.*

For a long time, declassified products derived from the production of electronic silicon have formed the main source of photovoltaic quality silicon, but this source is insufficient to supply the increasing market demand so that other silicon sources are

30 *necessary such as metallurgical silicon produced by carbothermal reduction of silica in a submerged electric arc furnace, for which the quality may be improved using various secondary metallurgy refining treatments, for example, refining with chlorine*

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described in patent EP 0.720.967 (Pechiney Electrometallurgie). Thus, a silicon is produced satisfying specifications for example such as the following (% by weight):

Iron < 0.30%;

Calcium < 0.10%;

5   *Aluminium < 0.30%;*

Boron 20 to 50 ppm;

Phosphorus 20 to 100 ppm.

The phosphorus content is very dependent on the reduction agents used. With

10   *charcoal, it is easy to obtain silicon with a phosphorus content of about 50 ppm; this type of silicon is used particularly for making silicones. With fossil reduction agents, a silicon with a phosphorus content of less than 25 ppm can be produced, for which the main application is manufacturing of aluminium-silicon alloys. However, the purity level of these two grades is still very different from the purity level required for*

15   *electronic and photovoltaic applications.*

Segregated solidification has been known for a long time, and can lower the contents of many impurity elements in silicon. However, this technique is not efficient in achieving the required boron and phosphorus purity levels, starting from the two

20   *grades mentioned above.*

Thus, under the pressure of the increasing market demand, a large research effort was undertaken to make a silicon with a low boron and phosphorus content starting from metallurgical silicon, particularly using purification of silicon molten under

25   *plasma. These plasma treatment techniques were designed on a laboratory scale and it is difficult to transpose them to industrial scale as a result of technical difficulties encountered in making larger tools."*

Also known in the art is US 4,094,731, which discloses a process for producing

30   crystalline silicon having an iron concentration less than about one-twentieth of the iron concentration of the mother liquor. Iron-contaminated silicon is introduced into a mould and the mould walls are maintained at a temperature sufficient to cause

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silicon crystalline growth. The mother liquor is agitated with a carbon rod stirrer or by bubbling a gas to wash the exposed surfaces of the growing silicon crystals and to prevent the freezing of the top surface of the mother liquor. A hollow crystalline silicon ingot is formed and both the inner zone centrally of the crystalline ingot and

5   the outer zone adjacent to the mould wall are removed leaving an inner zone having an iron concentration less than one-twentieth of the iron concentration of the original mother liquor. However, neither boron nor phosphorous is removed by this process.

Over the past years a lot of effort has been put into the development of a process for

10   making solar grade silicon at a competitive cost and on a large-scale. However, there is still a need for a process for the production of solar grade silicon on a large-scale basis.

SUMMARY OF THE INVENTION

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An object of the present invention is to provide a process for purifying silicon metal that satisfies the above-mentioned need.

It is also an object of the present invention to provide a process for the production of

20   solar grade silicon directly from metallurgical grade silicon. The specification requirements for silicon are determined by the photovoltaic application and in turn by the photovoltaic cells; the specification requirements for a silicon necessary to obtain the best performances are boron < 3 ppmw, phosphorus < 10 ppmw, total metallic impurities < 300 ppmw and preferably <150 ppmw.

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Accordingly, the present invention provides a process for purifying low-purity metallurgical grade silicon, containing at least one of the following contaminants Al, As, Ba, Bi, Ca, Cd, Fe, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Sn, Sr, Ti, V, Zn, Zr, O, C and B, and obtaining a higher-purity solid polycrystalline

30   silicon. The process includes the steps of:

      (a)   containing a melt of low-purity metallurgical grade silicon in a mould, the mould having an insulated bottom wall, insulated side walls, and an open top;

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(b)   solidifying the melt by unidirectional solidification from the open top towards the insulated bottom wall of the mould while electromagnetically stirring the melt;

(c)   controlling a rate of the unidirectional solidification;

(d)   stopping the unidirectional solidification when the melt has partially solidified to produce an ingot having an exterior shell comprising the higher-purity solid polycrystalline silicon and a center comprising an impurity-enriched liquid silicon; and

(e)   creating an opening in the exterior shell of the ingot to outflow the impurity-enriched liquid silicon and leave the exterior shell comprising said higher-purity solid polycrystalline silicon thereby obtaining the higher-purity solid polycrystalline silicon.

Preferably, the insulated bottom wall and the insulated side walls are heated to minimize a formation of a skin of silicon on the insulated bottom wall and the insulated side walls of the mould.

The rate of unidirectional solidification may be controlled by an insulation of the insulated bottom wall and the insulated side walls. The rate of unidirectional solidification may also be controlled by controlling a rate of heat extraction from the melt at the open top of the mould. Preferably, the controlling a rate of heat extraction may include placing a cooling medium (for example, water or air) in contact with a free surface of the melt at the open top of the mould.

The rate of unidirectional solidification may be adjusted in combination with the stirring power of the electromagnetic stirrer so as to wash the solidification interface and prevent impurity rich liquid to be trapped by dendrite formation and obtain a polycrystalline unidirectional solidification. Preferably, the rate of unidirectional solidification is between 1×10^{-4} m/s and 5×10^{-6} m/s.

Stopping of the unidirectional solidification is preferably done when 40 to 80% of the melt has solidified.

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Creating an opening in the exterior shell of the ingot includes piercing the exterior shell of the ingot. The piercing may be done by mechanical means or thermal lance. Creating an opening in the exterior shell of the ingot may be accomplished through a

5   tap opening in the mould.

The process may further include an additional step before step (e) of removing the ingot from the mould.

10   Additionally, the process may include a step (f) of melting the higher-purity solid polycrystalline silicon and repeating steps (b) to (e).

In accordance with the process, a top portion of the higher-purity solid polycrystalline silicon may contain approximately at least 90% less metal contaminants Al, As, Ba,

15   Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sc, Sn, Sr, Ti, V, Zn, Zr than the low-purity metallurgical grade silicon. The higher-purity solid polycrystalline silicon may contain approximately at least 45% less phosphorus and approximately at least 10% less boron than the low-purity metallurgical grade silicon. The impurity-enriched liquid silicon contains less than 60 ppmw of carbon and less

20   than 20 ppmw of oxygen and is a low carbon and low oxygen grade of silicon.

The objects, advantages and other features of the present invention will become more apparent and be better understood upon reading of the following non-restrictive description of the invention, given with reference to the accompanying drawings.

25   **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1A is a cross-sectional view of a mould containing a melt of low-purity silicon, according to one embodiment of the invention.

FIG. 1B is a cross-sectional view of the mould of FIG. 1A, showing partial

30   solidification of the melt with a solid silicon exterior shell and a liquid silicon center,

according to one embodiment of the invention.

FIG. 2 is a schematic representation of a cross-sectional view of the mould and ingot of FIG. 1B, showing removal of the ingot from the mould, according to one
5   embodiment of the invention.

FIG. 3 is a schematic representation of a cross-sectional view of the mould and ingot of FIG. 1B, showing removal of the ingot from the mould and the creation of an opening in the exterior shell of the ingot, according to one embodiment of the
10   invention.

FIG. 4 is a schematic representation of dendritic growth during solidification of a liquid. [PRIOR ART]

15   FIG. 5 is a graphical representation of the Scheil equation. [PRIOR ART]

FIG. 6 is a cross-sectional view of a mould containing a melt and of an electromagnetic stirrer used to stir the melt.

20   FIG. 7 is a graphical representation of the location within an ingot of samples analyzed for a solidification trial without electromagnetic stirring.

FIGs. 8A to 8H are graphical representations for various elements of the elemental distribution as a function of the location in the ingot as depicted in FIG. 7.
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FIG. 9 is a graphical representation of the location within an ingot of samples analyzed for a solidification trial with electromagnetic stirring.

FIG. 10A to 10H are graphical representations for various elements of the elemental
30   distribution as a function of the location in the ingot as depicted in FIG. 9.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

While the invention will be described in conjunction with example embodiments, it will be understood that it is not intended to limit the scope of the invention to such

5 embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents. The following description is to be read with reference to FIGs. 1A to 10H.

GENERAL DESCRIPTION OF THE INVENTION

10 As mentioned, the present invention relates to a process of purification by crystallization that produces medium and/or high purity silicon metal for use in photovoltaic applications.

More specifically, in accordance with one aspect of the invention, there is provided a

15 process for purifying low-purity metallurgical grade silicon, containing at least one of the following contaminants Al, As, Ba, Bi, Ca, Cd, Fe, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Sn, Sr, Ti, V, Zn, Zr, and B, and obtaining a higher-purity solid polycrystalline silicon.

20 The basic steps of this process are discussed more fully hereinafter with particular reference to FIGs. 1 to 3, and FIG. 6.

(a) Containing a melt of low-purity metallurgical grade silicon in a mould

25 Low-purity liquid metallurgical grade silicon is produced by carbothermal reduction of quartz in an electric arc furnace. The liquid silicon (the melt) 11 may be transferred into ladles from where it may be then outpoured into a mould 10 having an insulated bottom wall 10a, insulated side walls 10b, and an open top 10c. The mould 10 may have a rectangular, cylindrical, inverted-bell shape, or any other shape known to a

30 person skilled in the art. It may also have a tap 24 provided thereon (see FIG. 1B).

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(b) Solidifying the melt by unidirectional solidification from the open top towards the insulated bottom wall of the mould while electromagnetically stirring the melt

In order to obtain a unidirectional solidification, the side walls 10b and bottom wall 10a of the mould are insulated with an appropriate insulation, for example silica sand or some appropriate refractory lining, while the top 10c of the mould is open to allow the exposed surface of the melt to emit heat (see FIGs. 1A and 1B). Accordingly, the solidification of the ingot along the side walls 10b and the bottom wall 10a should be negligible compared to that along the top 10c. Heating of the insulation is recommended in order to minimize the thickness of a silicon skin that may solidify and form on the walls of the mould 10.

To ensure a continuous washing of the solidification interface and to dilute the concentration of impurity elements that accumulate at the solidification front, the silicon melt is stirred electromagnetically. The electromagnetic stirring may be provided by any appropriate electromagnetic stirrer 14. FIGs. 1A, 1B, 2, 3, and 6 show a mould with an electromagnetic stirrer placed underneath the mould. Electromagnetic stirring, unlike conventional mechanical stirring, is a non-contact stirring, i.e. no part of the actual stirrer comes into contact with the molten metal.

(c) Controlling a rate of the unidirectional solidification

In order to minimize the quantity of impurity rich liquid silicon trapped by dendrite formation, the rate of unidirectional solidification must be controlled. Preferably, the rate of unidirectional solidification is less than 1×10^{-4} m/s or even more preferably comprised between 1×10^{-4} m/s and 5×10^{-6} m/s.

The rate of unidirectional solidification may be controlled by controlling the rate of heat extraction from the open top 10c of the mould 10. It should be noted that the term "heat extraction" is understood to include heat removal and simple heat emission. This may be accomplished with the type of insulation used for the bottom

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and side walls as well as by placing the free surface of the melt at the open top of the mould in contact with a cooling medium 20, such as air or water. For example, the solidification can be slowed by using a light insulation or accelerated by using a water shower to cool the exposed free surface of the melt.

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(d) Stopping the unidirectional solidification when the melt has partially solidified

When 40 to 80% of the melt has solidified, the unidirectional solidification is stopped

10   thus obtaining an ingot 19 having an exterior shell made of higher-purity solid polycrystalline silicon 18 and a center made of an impurity-enriched liquid silicon 16. Stopping the unidirectional solidification simply implies not allowing the melt to completely solidify and proceeding to the next step.

15   **(e) Obtaining the higher-purity solid polycrystalline silicon**

Once 40 to 80% of the melt has solidified, a crack or an opening 22 is created in the exterior shell of the ingot 19 to outflow the impurity-enriched liquid silicon 16 from the center and leave behind the exterior shell of higher-purity solid polycrystalline silicon

20   18.

The liquid silicon 16 may be extracted from the center of the ingot 19 by piercing the exterior shell of the ingot 19, for example by mechanical means or thermal lance, to create an opening 22 in the exterior shell of the ingot 19 through which the liquid

25   silicon may be extracted.

The actual extraction of the liquid silicon 16 from the ingot 19 may be done by tapping the ingot through a tap 24 found in the mould 10 (see FIG. 1B), either in the bottom wall 10a of the mould 10 or a side wall 10b. For example, a thermal lance

30   may be used to create an opening in the exterior shell of the ingot through the tap 24 in the mould 10 to outpour the liquid silicon 16.

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The process may further include an additional step before step (e) of removing the ingot 19 from the mould 10 (see FIG. 2), for example by lifting the ingot 19 out of the mould 10 using an appropriate suspension mechanism 26 (see FIG. 3). For example, in this way, while the ingot 19 is suspended in mid-air, the bottom portion of the ingot

5   19 is caused to crack, by piercing or quenching, to draw off the liquid silicon 16.

A top portion of the higher-purity solid polycrystalline silicon thus obtained may contain approximately at least 90% less of contaminants Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sc, Sn, Sr, Ti, V, Zn, Zr than the

10   silicon starting material.

The higher-purity solid polycrystalline silicon may contain approximately at least 45% less phosphorus and approximately at least 10% less boron than the metallurgical grade silicon starting material.

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Advantageously, the impurity-enriched liquid silicon may contain less than 60 ppmw of carbon and less than 20 ppmw of oxygen and thus may provide a low carbon and low oxygen grade of silicon.

20   Of course, the entire process – from step (a) to (e) – may be repeated using the higher purity solid polycrystalline silicon, a so-called medium purity silicon, as starting material to thereby obtain a final silicon material of an even higher purity, a so-called high purity silicon. In this way, solar grade silicon may be obtained from metallurgical grade silicon.

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DETAILED DESCRIPTION OF THE INVENTION

1. DIRECTIONAL SOLIDIFICATION

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1.1 Dendritic Solidification

Directional solidification is a common method of purification. Metallurgical grade silicon contains a significant level of impurities which favours structural supercooling
5   during solidification. When there is a presence of supercooling during solidification of a liquid metal, the type of solidification is dendritic, as shown in FIG. 4. Dendritic solidification is a very inefficient directional solidification – a certain quantity of impurity-rich liquid (L) is trapped during solidification by the dendritic arms.

10   With no electromagnetic agitation of the melt during solidification of the melt, 50% of the initial liquid is trapped by the dendritic arms. This gives us a purification efficiency of:

$$[El]_{solid} = (1 - R) \cdot k_{th} \cdot [El]_{liquid} + R \cdot [El]_{liquid} = k_{eff} \cdot [El]_{liquid}$$

$$k_{eff} = (1 - R) \cdot k_{th} + R$$

15   where

$[El]_{solid}$: concentration of the solute in the solid metal;

$[El]_{liquid}$: concentration of the solute in the liquid metal;

R: fraction of the impure melt trapped in the solid metal during crystallization;

k_{th}: segregation coefficient determined by Czochralski crystallization of silicon;

20   k_{eff}: segregation coefficient determined by our new process.

A sampling of the solidified melt of metallurgical grade silicon, taken from the surface of the ingot, yields the following information:

$$\frac{0.17\% Fe}{0.35\% Fe} = (1 - R) \cdot 0.0000064 + R$$

25

thus, $R = 0.49 \approx 0.50$

The constant R is valid for all elements for this particular technique.

Some examples:

$$[Fe]_{solid} = (1 - 0.50) \cdot 0.0000064 \cdot [Fe]_{liquid} + 0.50 \cdot [Fe]_{liquid} = 0.50 \cdot [Fe]_{liquid}$$

$$[P]_{solid} = (1 - 0.50) \cdot 0.35 \cdot [P]_{liquid} + 0.50 \cdot [P]_{liquid} = 0.68 \cdot [P]_{liquid}$$

$$[B]_{solid} = (1 - 0.50) \cdot 0.80 \cdot [B]_{liquid} + 0.50 \cdot [B]_{liquid} = 0.90 \cdot [B]_{liquid}$$

Table 1

Element	k_{eff}
Al	0.50
Ca	0.50
Co	0.50
Cr	0.50
Cu	0.50
Fe	0.50
Mg	0.50
Mn	0.50
Mo	0.50
Ni	0.50
P	0.68
Ti	0.50
V	0.50
Zr	0.50
B	0.90

A purification efficiency of approximately 50% is obtained for a majority of the elements (except boron and phosphorus). In fact, about 30% of the phosphorus and 10% of boron can be removed by our technique of large mould segregation by directional solidification without electromagnetic stirring.

The partition (segregation) coefficient (k_{eff}) stays the same during solidification however the composition of the liquid at equilibrium with the solid increases in solute content. The Scheil equation describes well this phenomenon.

1.2 The Scheil Equation

The composition of the solid at the solidification interface is, according to the Scheil equation (diffusion and convection in the liquid, no diffusion in the solid):

$$C_s = k \cdot C_o \cdot (1 - f_s)^{k-1}$$

14

where

C_s: Concentration of the solute in the solid;

C_o: Initial concentration of the solute in the liquid;

k: Segregation coefficient;

f_s: Solid fraction.

Therefore, if the solidification is stopped at a specific moment and an analysis of the solid on average is carried out, the average concentration of the solute in the solid portion is:

$$\overline{C_S} = \frac{1}{f_s} \int_0^{f_s} k \cdot C_o \cdot (1-x)^{k-1} \cdot dx$$

$$\overline{C_S} = C_o \cdot \frac{1-(1-f_s)^k}{f_s}$$

A graphical representation of the above equation is given in FIG. 5.

It is worth noting that depending on the solid fraction, the average efficiency of the purification is affected. The first solid formed is the most pure. When the solidification is stopped and a global chemical analysis of the solid is performed, the efficiency is slightly lower because of the increase in the concentration of the liquid in solute. This explains well the experimental results observed after complete solidification of a silicon ingot (but only the layer solidified from the upper surface of the ingot).

It is noted that when solidification is carried out without agitation of the liquid (melt), the lower part of the ingot is typically richer in impurities than the upper part. An explanation for this could possibly be found in the difference in densities between the (cooler) impurity-rich liquid and that of the center of the ingot: the composition of the liquid is not homogeneous.

When the melt is only partially solidified, the liquid may be separated from the solid by creating an opening or a crack in the shell for example by piercing the shell of the

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ingot (for example: by thermal lance, mechanical piercing, or other). The opening or crack may be obtained by solidifying the silicon in a mould provided with a closable outlet in the bottom portion. Once the liquid has solidified to the required degree, the outlet is opened and the shell pierced to draw off the liquid. As shown in the embodiments of FIGs 1 to 3, the opening or crack can also be obtained by lifting up the shell from the mould with an appropriate suspension system. While the shell is in suspension in the air, the bottom portion is caused to crack by piercing or quenching to draw off the liquid. The ingot could also be completely solidified so as to then remove the portions that are of interest chemically. The mould may have a rectangular or cylindrical shape. It could also have the shape of upside down bell or any other shape known to a person skilled in the art. (See FIGs. 1 to 3)

The final silicon solid contains fewer impurities (i.e. is depleted of impurities) while the liquid at the center of the ingot is enriched in impurities.

Example:

We want to obtain the concentration of iron in the solid and in the liquid upon solidification of 70% of the silicon melt (time of solidification: 4.5 hours). The quantity of liquid silicon is 5.0 mt and the composition of the liquid silicon includes 0.35% Fe.

$$k_{sol}^{Fe} = f\left(k_{eff}^{Fe}, f_s\right)$$

$k_{sol}^{Fe} = 0.65$, obtained from FIG. 5.

By taking into account the mass distribution we obtain:

$$k_{liq}^{Fe} = \frac{1 - k_{sol}^{Fe} \cdot f_s}{1 - f_s} = \frac{1 - 0.65 \cdot 0.70}{1 - 0.70}$$

$k_{liq}^{Fe} = 1.82$

Therefore, after treatment, we obtain:

$\Rightarrow$ 3.5 mt of solid silicon at 0.23 %Fe

$\Rightarrow$ 1.5 mt of liquid silicon at 0.64 %Fe

1.3 Minimizing dendritic formation

During solidification, the dendrites trap impurity-rich liquid coming from a diffusion layer at the solid/liquid interface.

5

To minimize the presence of dendrites, a planar solidification front may be promoted. A certain quantity of solute may be trapped with planar solidification, but this quantity is far less than that trapped during dendritic solidification. A planar directional solidification may be promoted by allowing heat to escape from a single surface of 10   the ingot.

In addition, to homogenize the impurity-rich liquid and break down the diffusion layer at the solid/liquid interface, the liquid should preferably be agitated, stirred.

15   **2. POLYCRYSTALLINE DIRECTIONAL SOLIDIFICATION WITH AGITATION**

In order to obtain a substantially polycrystalline unidirectional solidification, the walls of the mould may be insulated (as shown in FIGs. 1 to 3) while the top may be open to allow heat to be emitted therefrom (the solidification of the melt can be slowed by 20   a light insulation or accelerated by a water shower). Accordingly, the solidification along the walls and the bottom should be negligible compared to that along the top of the ingot (heating of the insulation is recommended in order to minimize the thickness of the silicon skin solidified on the walls of the mould).

25   The present invention involves the use of an electromagnetic stirrer. Electromagnetic stirrers are known for stirring molten metal. For example, they are used to stir aluminum as it melts in a furnace. The electromagnetic stirrer utilizes the principle of a linear motor and differs from the conventional mechanical and decompression types as it is a non-contact stirrer in which no part touches the 30   molten metal (see FIG. 6).

As shown in FIG. 6, a coil installed at the bottom of the mould generates a moving magnetic field (H) when a 3-phase AC voltage is applied to this coil (inductor). Electric power force is generated in the molten metal due to the action of the magnetic field (magnetic flux) and causes induction current (I) to flow. This current

5   then acts with the magnetic field of the inductor to induce electromagnetic force (F) in the molten metal. As this thrust moves in the direction of the moving magnetic field, the molten metal also moves. In other words, a stirring action is applied. Furthermore, as this thrust has components in the horizontal direction and in the vertical direction, the molten metal flows diagonally upwards resulting in a uniform

10   temperature and chemical composition in both the top and bottom layers of the molten metal.

2.3 Preliminary calculations

15   The speed of the solidification interface is fixed by the rate of heat loss. For a surface without insulation (the upper portion of the ingot) the thickness of the solid silicon and the rate of solidification in ambient air are (from experiment):

$$E = 134 \frac{mm}{\sqrt{hr}} \cdot \sqrt{t}$$

$$v = \frac{dE}{dt} = 67 \frac{mm}{\sqrt{hr}} \cdot \frac{1}{\sqrt{t}}$$

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where E is the thickess of the top solid layer of the ingot, v is the rate of solidification at the interface, and t is the total time of solidification.

2.4 Experiments

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2.4.1 Experiment # 1: Agitation-free solidification (control experiment)

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2.4.1.1 Ingot sample

A control experiment was carried out: unidirectional solidification in an insulated mould without electromagnetic stirring of the melt during solidification.

A sample was taken from the center of the ingot, according to the diagram shown in FIG. 7, and analyzed the results are given hereinbelow in Table 2. A graphical representation of the elemental impurity distribution in the ingot as a function of position in the ingot of several of the elements is shown in FIGs. 8A to 8H.

Table 2.

	Liq.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Al	0.3028	0.1689	0.1641	0.1290	0.1397	0.1476	0.1295	0.3336	0.5828	0.1969	0.2420	0.4253	0.5233	0.4394	0.2552	0.2826	0.2858	0.4562	1.6030
As	0.0050	0.0030	0.0029	0.0025	0.0024	0.0029	0.0028	0.0038	0.0044	0.0037	0.0046	0.0078	0.0097	0.0084	0.0047	0.0044	0.0053	0.0174	0.0299
Ba	0.0011	0.0005	0.0005	0.0003	0.0005	0.0005	0.0003	0.0031	0.0084	0.0005	0.0006	0.0010	0.0012	0.0011	0.0006	0.0012	0.0013	0.0023	0.0089
Bi	0.0002	0.0003	0.0002	0.0002	0.0002	0.0001	0.0002	0.0003	0.0004	0.0003	0.0004	0.0006	0.0009	0.0009	0.0005	0.0004	0.0005	0.0016	0.0025
Ca	0.0742	0.0313	0.0321	0.0211	0.0317	0.0299	0.0187	0.2393	0.6633	0.0258	0.0314	0.0550	0.0672	0.0572	0.0334	0.0893	0.0882	0.1806	0.4187
Cd	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Co	0.0006	0.0006	0.0006	0.0005	0.0005	0.0005	0.0005	0.0006	0.0008	0.0006	0.0007	0.0012	0.0012	0.0010	0.0008	0.0007	0.0008	0.0021	0.0032
Cr	0.0037	0.0025	0.0022	0.0023	0.0018	0.0020	0.0020	0.0026	0.0030	0.0027	0.0034	0.0057	0.0070	0.0059	0.0035	0.0033	0.0040	0.0131	0.0209
Cu	0.0043	0.0027	0.0025	0.0020	0.0021	0.0023	0.0021	0.0031	0.0034	0.0032	0.0040	0.0071	0.0088	0.0074	0.0042	0.0038	0.0046	0.0165	0.0278
Fe	1.3665	0.8744	0.8224	0.6788	0.6707	0.7498	0.6853	0.9783	1.0696	1.0273	1.2536	2.1771	2.7017	2.2976	1.3181	1.2426	1.5025	5.1867	8.5841
La	0.0033	0.0021	0.0020	0.0017	0.0017	0.0019	0.0017	0.0026	0.0034	0.0025	0.0029	0.0050	0.0061	0.0052	0.0038	0.0030	0.0036	0.0123	0.0190
Mg	0.0010	0.0005	0.0005	0.0004	0.0004	0.0005	0.0004	0.0012	0.0026	0.0007	0.0008	0.0014	0.0015	0.0014	0.0008	0.0009	0.0012	0.0063	0.0170
Mn	0.0238	0.0174	0.0141	0.0117	0.0116	0.0136	0.0118	0.0168	0.0197	0.0181	0.0232	0.0386	0.0483	0.0405	0.0236	0.0226	0.0264	0.0930	0.1550
Mo	0.0012	0.0015	0.0020	0.0005	0.0009	0.0015	0.0013	0.0010	0.0019	0.0010	0.0010	0.0013	0.0012	0.0012	0.0011	0.0010	0.0005	0.0022	0.0029
Na	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0097	0.0915
Ni	0.0024	0.0015	0.0015	0.0015	0.0012	0.0013	0.0012	0.0016	0.0019	0.0018	0.0022	0.0037	0.0046	0.0038	0.0023	0.0021	0.0025	0.0093	0.0145
P	0.0047	0.0034	0.0039	0.0038	0.0033	0.0032	0.0032	0.0039	0.0045	0.0049	0.0061	0.0082	0.0084	0.0078	0.0053	0.0046	0.0047	0.0077	0.0121
Pb	0.0007	0.0004	0.0003	0.0005	0.0006	0.0002	0.0004	0.0004	0.0006	0.0004	0.0002	0.0005	0.0005	0.0004	0.0004	0.0003	0.0005	0.0009	0.0014
Sb	0.0028	0.0018	0.0015	0.0012	0.0014	0.0014	0.0013	0.0029	0.0042	0.0021	0.0023	0.0042	0.0050	0.0043	0.0027	0.0024	0.0029	0.0064	0.0148
Sc	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001	0.0002	0.0002	0.0002	0.0001	0.0001	0.0002	0.0005	0.0009
Sn	0.0006	0.0001	0.0005	0.0008	0.0002	0.0001	0.0006	0.0003	0.0007	0.0004	0.0005	0.0001	0.0006	0.0009	0.0004	0.0001	0.0005	0.0008	0.0004
Sr	0.0008	0.0003	0.0003	0.0002	0.0003	0.0003	0.0002	0.0027	0.0078	0.0002	0.0003	0.0006	0.0007	0.0006	0.0003	0.0009	0.0010	0.0020	0.0049
Ti	0.0893	0.0554	0.0536	0.0432	0.0433	0.0482	0.0440	0.0627	0.0695	0.0663	0.0811	0.1435	0.1762	0.1493	0.0848	0.0797	0.0997	0.3386	0.5625
V	0.0018	0.0011	0.0011	0.0009	0.0009	0.0010	0.0009	0.0013	0.0015	0.0013	0.0016	0.0028	0.0035	0.0029	0.0017	0.0016	0.0020	0.0078	0.0126
Zn	0.0006	0.0004	0.0004	0.0003	0.0003	0.0003	0.0003	0.0008	0.0005	0.0005	0.0004	0.0008	0.0010	0.0009	0.0005	0.0005	0.0006	0.0016	0.0031
Zr	0.0177	0.0112	0.0108	0.0089	0.0088	0.0098	0.0090	0.0125	0.0136	0.0133	0.0162	0.0279	0.0341	0.0289	0.0168	0.0159	0.0197	0.0648	0.0987
B	0.0039	0.0036	0.0036	0.0036	0.0036	0.0035	0.0036	0.0038	0.0041	0.0042	0.0045	0.0048	0.0050	0.0047	0.0044	0.0045	0.0044	0.0031	0.0024

20

2.4.1.2 Results of Analysis

A sampling of the silicon at surface of the ingot yields the following information:

$$k_{eff} = (1 - R) \cdot k_{th} + R$$

$$\frac{0.68\% Fe}{1.37\% Fe} = (1 - R) \cdot 0.0000064 + R$$

so, $R = 0.50$

The purification efficiency should be:

$$[Fe]_{solid} = (1 - 0.50) \cdot 0.0000064 \cdot [Fe]_{liquid} + 0.50 \cdot [Fe]_{liquid} = 0.50 \cdot [Fe]_{liquid}$$

$$[P]_{solid} = (1 - 0.50) \cdot 0.35 \cdot [P]_{liquid} + 0.50 \cdot [P]_{liquid} = 0.68 \cdot [P]_{liquid}$$

$$[B]_{solid} = (1 - 0.50) \cdot 0.80 \cdot [B]_{liquid} + 0.50 \cdot [B]_{liquid} = 0.90 \cdot [B]_{liquid}$$

Table 3

Element	Theory k_{eff}	Experimental k_{eff}
Al	0.50	0.46
Ca	0.50	0.43
Co	0.50	0.43
Cr	0.50	0.71
Cu	0.50	0.49
Fe	0.50	0.49
Mg	0.50	0.49
Mn	0.50	0.49
Mo	0.50	0.75
Ni	0.50	0.50
P	0.68	0.70
Ti	0.50	0.48
V	0.50	0.50
Zr	0.50	0.50
B	0.90	0.92

Experimental results show that about 50% of most of the elements may be removed from the upper part of the silicon ingot. This type of solidification may also remove about 30% of phosphorus and about 10% of boron from the upper part of the silicon ingot.

5

As seen in the graphs of FIGs. 8A to 8H, the more cool impurity-rich liquid silicon which is more dense accumulates at the bottom of the liquid found at the center of the ingot where it may be trapped by dendrite formation at the bottom of the ingot.

10   **2.4.2 Experiment # 2: Solidification with electromagnetic agitation**

An experiment was carried out: unidirectional solidification in an insulated mould with electromagnetic stirring of the melt during solidification.

15   **2.4.2.1 Ingot sample**

A sample was taken from the center of the ingot, according to the diagram shown in FIG. 9, and analyzed the results are given hereinbelow in Table 4. A graphical representation of the elemental impurity distribution in the ingot as a function of
20   position in the ingot of several of the elements is shown in FIGs. 10A to 10H.

Table 4

	Liq.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Al	0.1184	0.0849	0.0185	0.0011	0.0007	0.0070	0.0194	0.0202	0.0366	0.0613	0.0942	0.1592	0.2481	0.4626	0.7623	0.7187	0.2259	0.0132	0.0011	0.0124	0.0357
As	0.0011	0.0006	0.0003	0.0006	0.0006	0.0001	0.0005	0.0007	0.0003	0.0011	0.0011	0.0020	0.0027	0.0047	0.0077	0.0068	0.0027	0.0003	0.0002	0.0003	0.0006
Ba	0.0001	0.0009	0.0004	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0003	0.0003	0.0002	0.0002	0.0002	0.0002	0.0003
Bi	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0002	0.0002	0.0001	0.0003	0.0003	0.0004	0.0007	0.0008	0.0004	0.0000	0.0000	0.0001	0.0001
Ca	0.0072	0.0557	0.0150	0.0013	0.0008	0.0009	0.0012	0.0031	0.0015	0.0028	0.0031	0.0041	0.0057	0.0100	0.0154	0.0144	0.0054	0.0012	0.0006	0.0078	0.0104
Cd	0.0001	0.0001	0.0000	0.0000	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000	0.0000	0.0001
Co	0.0005	0.0008	0.0007	0.0006	0.0007	0.0006	0.0007	0.0007	0.0007	0.0008	0.0008	0.0009	0.0010	0.0013	0.0018	0.0017	0.0010	0.0006	0.0006	0.0006	0.0007
Cr	0.0014	0.0004	0.0001	0.0002	0.0001	0.0002	0.0004	0.0005	0.0006	0.0010	0.0014	0.0025	0.0032	0.0058	0.0091	0.0087	0.0030	0.0003	0.0001	0.0002	0.0006
Cu	0.0017	0.0018	0.0014	0.0015	0.0014	0.0015	0.0017	0.0017	0.0019	0.0023	0.0028	0.0042	0.0052	0.0084	0.0131	0.0125	0.0048	0.0016	0.0014	0.0014	0.0018
Fe	0.3053	0.0834	0.0051	0.0099	0.0038	0.0269	0.0704	0.0805	0.1141	0.1874	0.2817	0.5029	0.6844	1.2379	2.0215	1.9060	0.6252	0.0421	0.0079	0.0192	0.1057
La	0.0007	0.0008	0.0004	0.0004	0.0004	0.0005	0.0006	0.0006	0.0007	0.0008	0.0010	0.0016	0.0020	0.0031	0.0047	0.0044	0.0018	0.0005	0.0004	0.0005	0.0007
Mg	0.0004	0.0006	0.0001	0.0000	0.0000	0.0000	0.0001	0.0001	0.0001	0.0002	0.0003	0.0005	0.0007	0.0014	0.0023	0.0022	0.0007	0.0001	0.0000	0.0001	0.0004
Mn	0.0083	0.0038	0.0013	0.0021	0.0013	0.0019	0.0028	0.0048	0.0040	0.0061	0.0091	0.0149	0.0203	0.0366	0.0602	0.0566	0.0194	0.0029	0.0019	0.0019	0.0041
Mo	0.0001	0.0018	0.0009	0.0011	0.0004	0.0004	0.0010	0.0004	0.0008	0.0009	0.0010	0.0016	0.0017	0.0018	0.0033	0.0025	0.0012	0.0003	0.0001	0.0001	0.0001
Na	0.0000	0.0009	0.0009	0.0013	0.0009	0.0011	0.0009	0.0010	0.0008	0.0009	0.0008	0.0008	0.0007	0.0005	0.0007	0.0005	0.0008	0.0011	0.0010	0.0024	0.0017
Ni	0.0021	0.0004	0.0000	0.0001	0.0001	0.0002	0.0004	0.0004	0.0007	0.0011	0.0019	0.0033	0.0047	0.0088	0.0142	0.0135	0.0042	0.0002	0.0001	0.0001	0.0005
P	0.0023	0.0012	0.0007	0.0009	0.0011	0.0011	0.0020	0.0013	0.0017	0.0024	0.0038	0.0043	0.0059	0.0072	0.0113	0.0103	0.0047	0.0020	0.0012	0.0008	0.0012
Pb	0.0001	0.0000	0.0000	0.0001	0.0001	0.0000	0.0001	0.0002	0.0001	0.0000	0.0001	0.0001	0.0003	0.0001	0.0006	0.0005	0.0000	0.0001	0.0001	0.0001	0.0001
Sb	0.0008	0.0006	0.0003	0.0003	0.0002	0.0002	0.0003	0.0004	0.0005	0.0008	0.0010	0.0017	0.0020	0.0039	0.0059	0.0054	0.0020	0.0003	0.0001	0.0001	0.0005
Sc	0.0001	0.0005	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0005	0.0005	0.0005	0.0005	0.0006	0.0006	0.0008	0.0008	0.0006	0.0004	0.0004	0.0004	0.0005
Sn	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Sr	0.0000	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0001
Ti	0.0409	0.0083	0.0004	0.0003	0.0003	0.0033	0.0093	0.0086	0.0172	0.0252	0.0378	0.0695	0.0956	0.1726	0.2838	0.2686	0.0849	0.0047	0.0003	0.0020	0.0119
V	0.0026	0.0006	0.0000	0.0000	0.0000	0.0002	0.0006	0.0006	0.0010	0.0016	0.0024	0.0044	0.0058	0.0106	0.0171	0.0164	0.0053	0.0003	0.0000	0.0001	0.0007
Zn	0.0007	0.0004	0.0001	0.0004	0.0002	0.0002	0.0003	0.0004	0.0005	0.0006	0.0008	0.0012	0.0017	0.0030	0.0049	0.0046	0.0016	0.0003	0.0001	0.0002	0.0003
Zr	0.0061	0.0013	0.0001	0.0000	0.0000	0.0005	0.0015	0.0014	0.0024	0.0039	0.0058	0.0105	0.0141	0.0251	0.0399	0.0379	0.0127	0.0007	0.0000	0.0003	0.0021
B	0.0057	0.0048	0.0043	0.0045	0.0044	0.0048	0.0053	0.0052	0.0058	0.0063	0.0067	0.0071	0.0078	0.0089	0.0104	0.0098	0.0077	0.0056	0.0046	0.0043	0.0045

2.4.2.2 Results of Analysis

Electromagnetic agitation had a large effect on the distribution of impurities in the silicon ingot. The agitation prevented the separation of impurities towards the bottom of the silicon ingot. Moreover, there was a large increase in the segregation of impurities (the surface layer is much more pure).

A sampling of the silicon at surface of the ingot yields the following information:

$$k_{eff} = (1 - R) \cdot k_{th} + R$$

$$\frac{0.0051\%Fe}{0.305\%Fe} = (1 - R) \cdot 0.0000064 + R$$

so, $R = 0.017 \approx 0.02$

In theory, the efficiency of the purification is:

$$[Fe]_{solid} = (1 - 0.02) \cdot 0.0000064 \cdot [Fe]_{liquid} + 0.02 \cdot [Fe]_{liquid} = 0.02 \cdot [Fe]_{liquid}$$

$$[P]_{solid} = (1 - 0.02) \cdot 0.35 \cdot [P]_{liquid} + 0.02 \cdot [P]_{liquid} = 0.36 \cdot [P]_{liquid}$$

$$[B]_{solid} = (1 - 0.02) \cdot 0.80 \cdot [B]_{liquid} + 0.02 \cdot [B]_{liquid} = 0.80 \cdot [B]_{liquid}$$

Table 5

Element	Theory k_{eff}	Experimental k_{eff}
Al	0.02	0.01
Ca	0.02	0.18
Co	0.02	- - -
Cr	0.02	0.07
Cu	0.02	- - -
Fe	0.02	0.02
Mg	0.02	- - -
Mn	0.02	0.16
Mo	0.02	- - -
Ni	0.02	0.05
P	0.36	0.39
Ti	0.02	0.01
V	0.02	- - -
Zr	0.02	- - -
B	0.80	0.79

24

These results show that we can expect to obtain a very pure layer (approximately 30 cm thick at the top surface of the ingot) upon partial solidification of the silicon melt. This should correspond to a solidification time of approximately 4.5 hours with air-cooling at the open top of the ingot.

5

The experiments conducted showed that the ingot obtained with agitation of the melt during solidification of the melt developed a lot more cracks than the ingot obtained without agitation of the melt during solidification of the melt. Each crack can lead to a
10   small amount of contamination caused by an intrusion of impure metal into the "purified" zone. However, this cracking should be lessened by not solidifying completely the melt.

A more homogeneous liquid is obtained with electromagnetic agitation (i.e.,
15   electromagnetic stirring) of the melt during solidification of the melt.

According to the results obtained, this procedure may be capable of removing more than 50% of phosphorus and makes the method very interesting for the production of Solar Grade silicon from Metallurgic Grade silicon.
20

The solidification speed may range between 10^{-6} m/s and 10^{-4} m/s. High solidification speeds may be achieved with this method as compared with other crystallization methods. This provides a cost effective solution for mass production of high-purity silicon.
25

The outer layer (first skin of silicon) of the ingot freezes rapidly, relieving the heat in excess. Then the temperature of the liquid silicon drops to approximately 1410°C. At this moment, we obtain the minimum solubility values for carbon and oxygen.

30   Analytical results of the liquid center of the ingot confirm a carbon content of less than 60 ppmw and an oxygen content of less than 20 ppmw. Analysis done by an external laboratory confirmed a carbon content of less than 20 ppmw and an oxygen

25

content of less than 20 ppmw. Advantageously, we have now a new process that produces a grade of silicon with low-carbon and low-oxygen content.

CLAIMS

1. A process for purifying low-purity metallurgical grade silicon, containing at least one of the following contaminants Al, As, Ba, Bi, Ca, Cd, Fe, Co, Cr, Cu, Fe, La, Mg,
5   Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Sn, Sr, Ti, V, Zn, Zr, and B, and obtaining a higher-purity solid polycrystalline silicon, said process comprising the steps of:

(a)   containing a melt of low-purity metallurgical grade silicon in a mould, said mould having an insulated bottom wall, insulated side walls, and an open top;

10   (b)   solidifying the melt by unidirectional solidification from said open top towards said insulated bottom wall of said mould while electromagnetically stirring the melt;

(c)   controlling a rate of said unidirectional solidification;

(d)   stopping said unidirectional solidification when the melt has partially
15   solidified to produce an ingot having an exterior shell comprising said higher-purity solid polycrystalline silicon and a center comprising an impurity-enriched liquid silicon; and

(e)   creating an opening in said exterior shell of said ingot to outflow said impurity-enriched liquid silicon and leave the exterior shell comprising
20   said higher-purity solid polycrystalline silicon thereby obtaining said higher-purity solid polycrystalline silicon.

2. A process according to claim 1, wherein said insulated bottom wall and said insulated side walls are heated to minimize a formation of a skin of silicon on said
25   insulated bottom wall and said insulated side walls of said mould.

3. A process according to claim 1, wherein said rate of unidirectional solidification is controlled by an insulation of said insulated bottom wall and said insulated side walls.

30   4. A process according to claim 1, wherein said rate of unidirectional solidification is controlled by controlling a rate of heat extraction from the melt at said open top of said mould.

5. A process according to claim 4, wherein said controlling a rate of heat extraction comprises placing a cooling medium in contact with a free surface of the melt at said open top of said mould.

5

6. A process according to claim 5, wherein said cooling medium is water or air.

7. A process according to claim 1, wherein said rate of unidirectional solidification is determined so as to minimize dendrite formation.

10

8. A process according to claim 7, wherein said rate of unidirectional solidification is less than 1×10^{-4} m/s.

9. A process according to claim 7, wherein said rate of unidirectional solidification is

15   comprised between 1×10^{-4} m/s and 5×10^{-6} m/s.

10. A process according to claim 1, wherein said stopping the unidirectional solidification is done when 40 to 80% of the melt has solidified.

20   11. A process according to claim 1, wherein said creating an opening in said exterior shell of said ingot of step (e) comprises piercing said exterior shell of said ingot by mechanical means or thermal lance.

12. A process according to claim 1, wherein said creating an opening in said exterior

25   shell of said ingot of step (e) is accomplished through a tap opening in said mould.

13. A process according to claim 1, wherein said process further comprises an additional step before step (e) of removing said ingot from said mould.

30   14. A process according to claim 1, wherein said process further comprises an additional step (f) of melting said higher-purity solid polycrystalline silicon and repeating steps (b) to (e).

28

15. A process according to claim 1, wherein a top portion of said higher-purity solid polycrystalline silicon contains at least 90% less metal contaminants Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sc, Sn, Sr, Ti, V, Zn, and Zr than the low-purity metallurgical grade silicon.

16. A process according to claim 1, wherein said higher-purity solid polycrystalline silicon contains approximately at least 45% less phosphorus and approximately at least 10% less boron than the low-purity metallurgical grade silicon.

17. A process according to claim 1, wherein said impurity-enriched liquid silicon contains less than 60 ppm of carbon and less than 20 ppm of oxygen and is a low carbon and low oxygen grade of silicon.
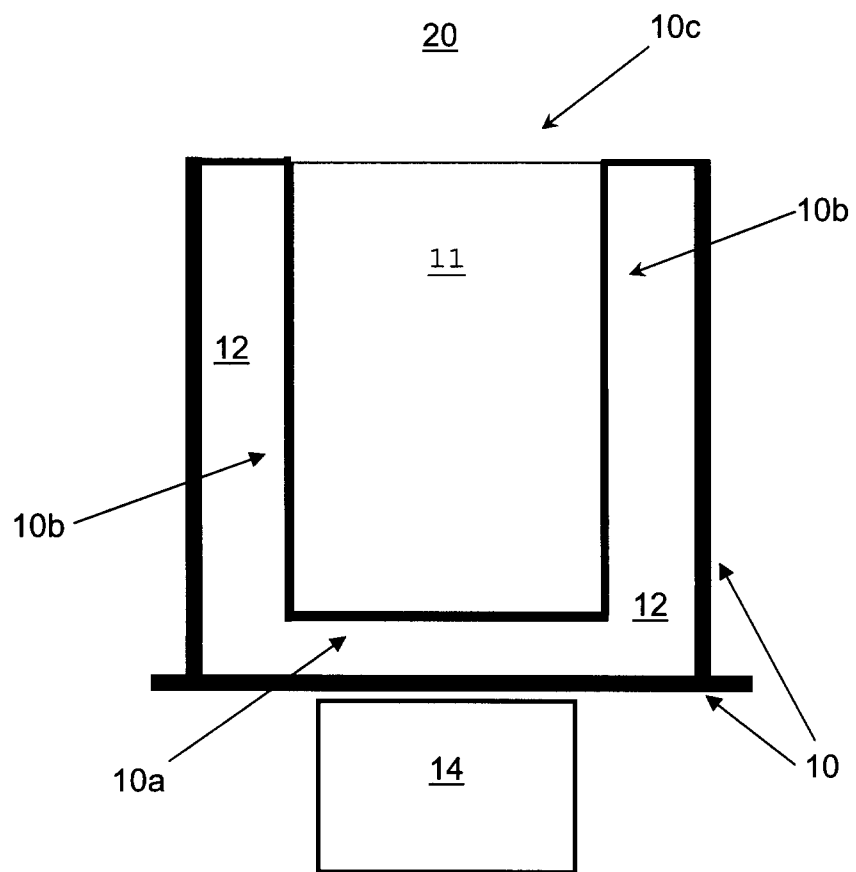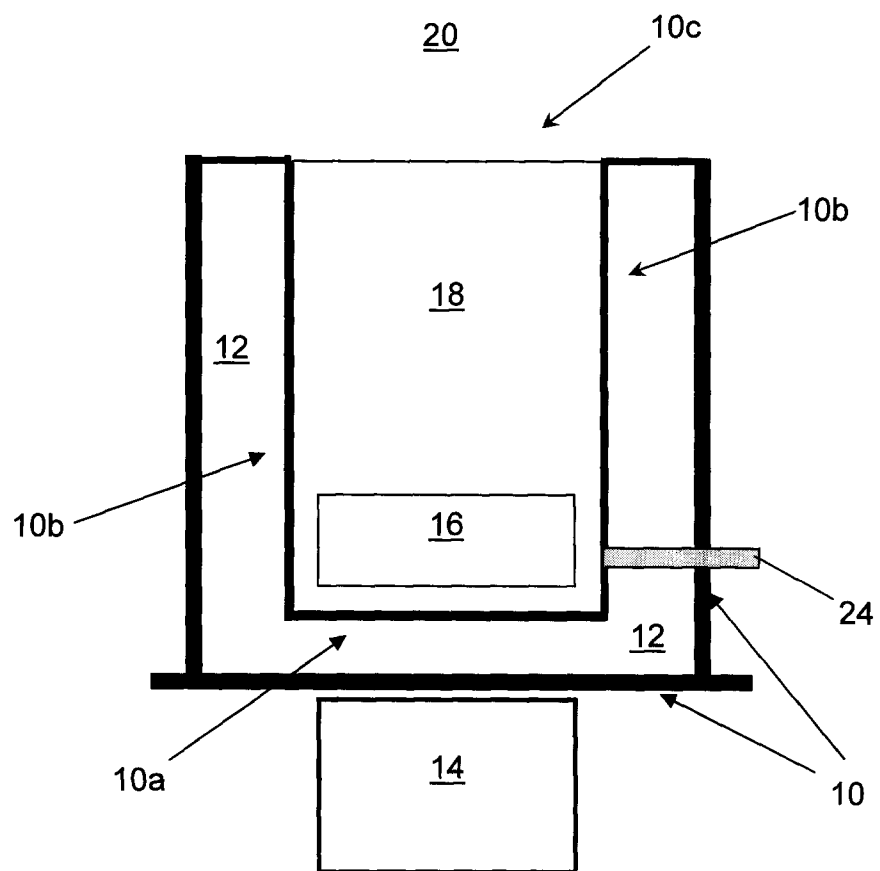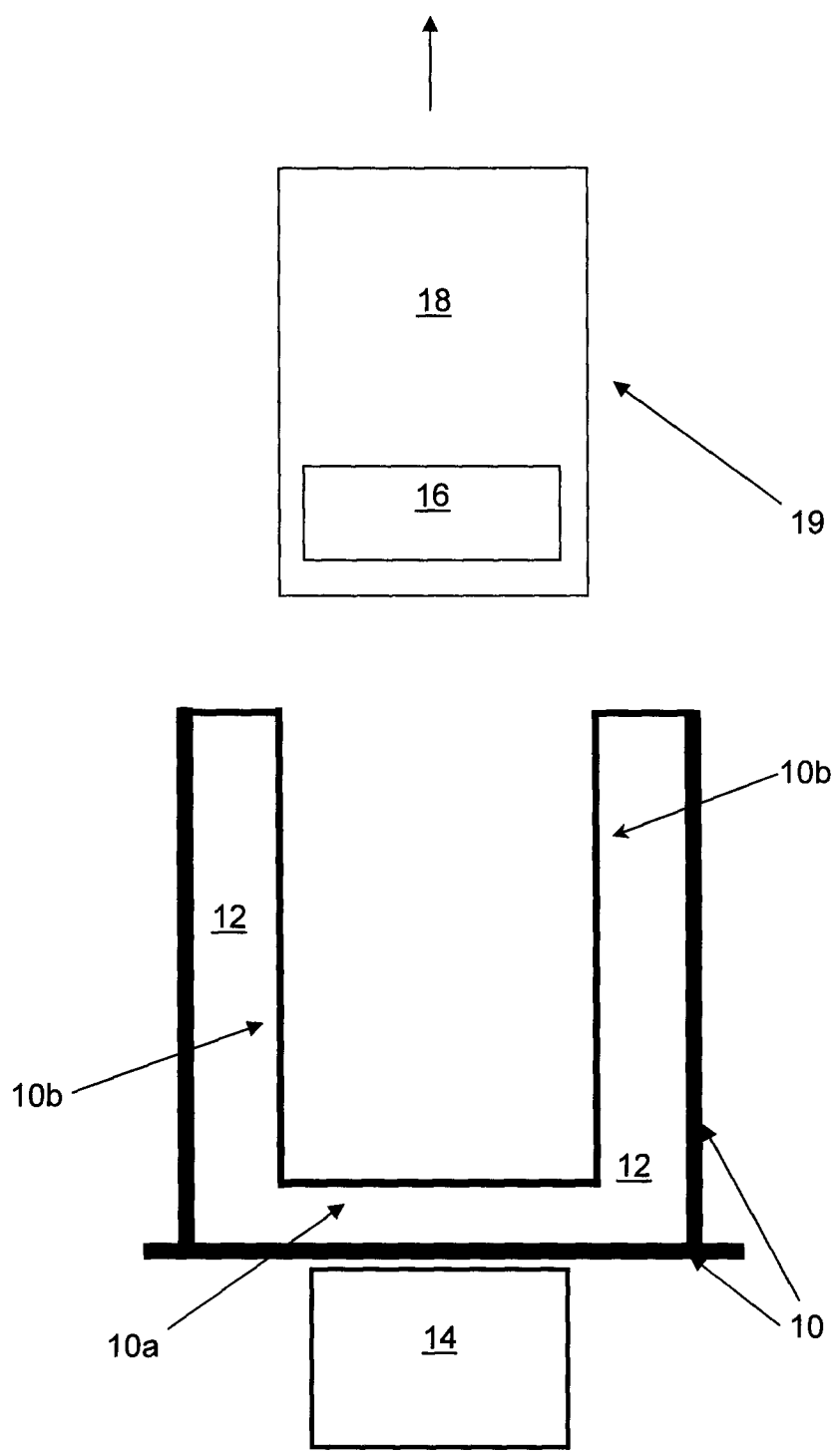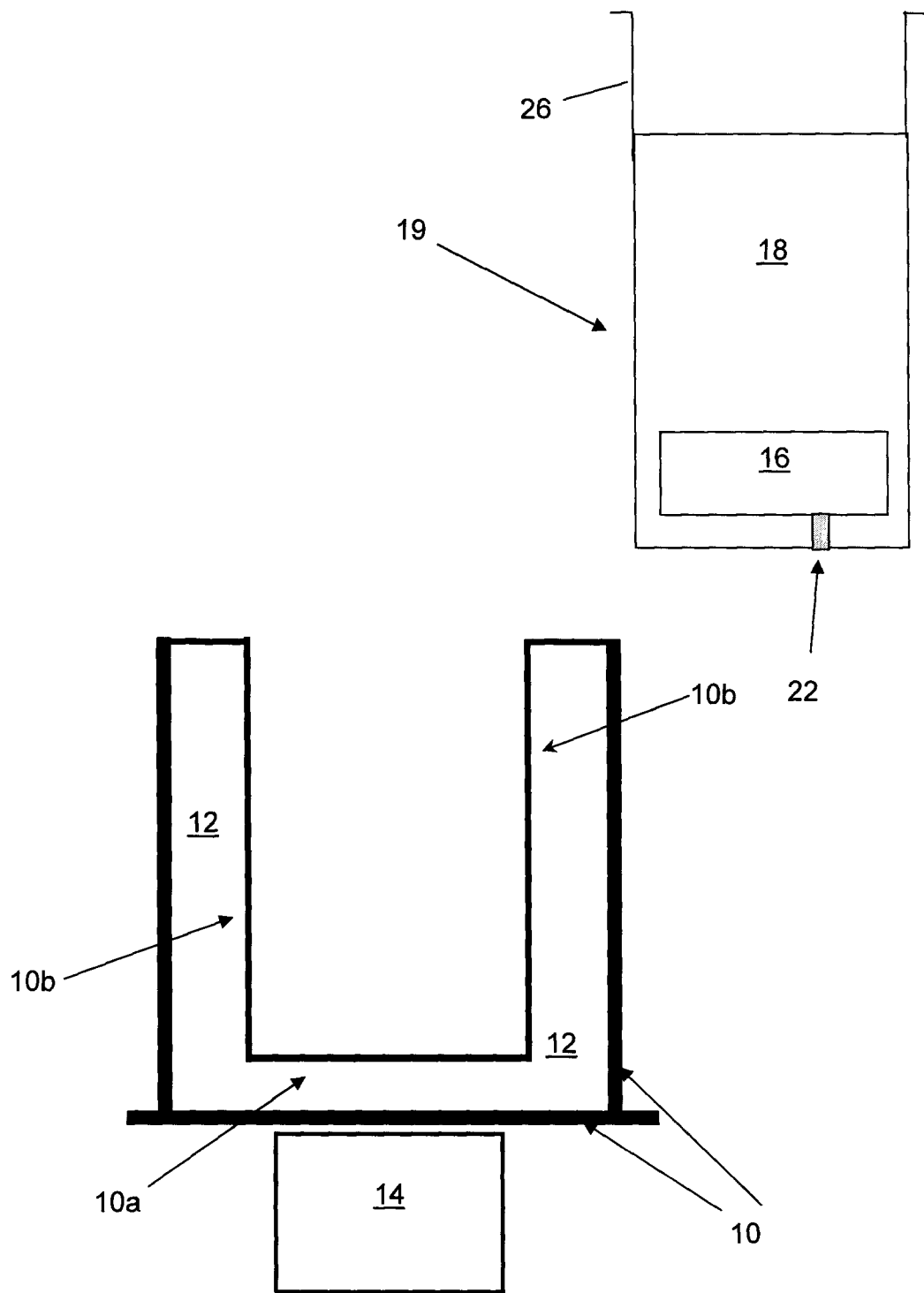
FIG.1A

FIG.1B

FIG. 2

FIG. 3
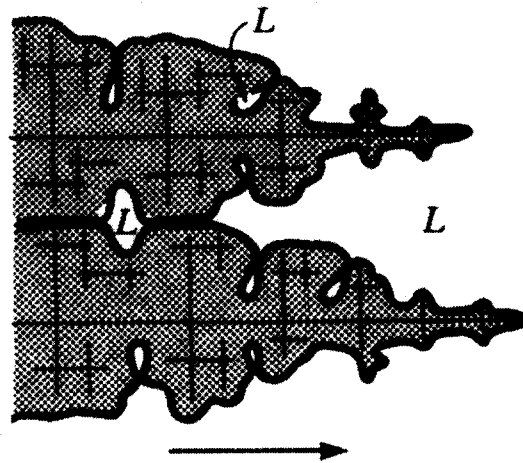
FIG. 4
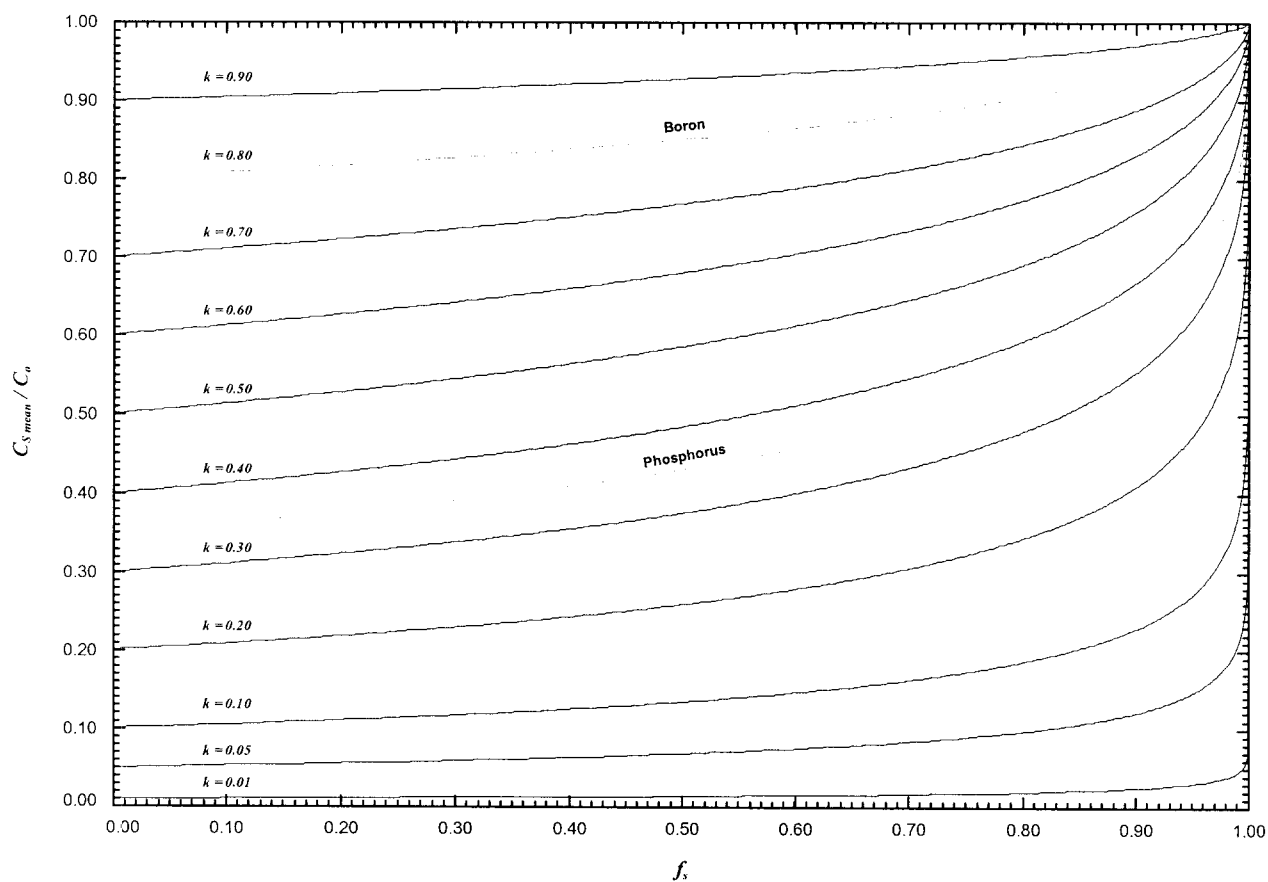
FIG. 5
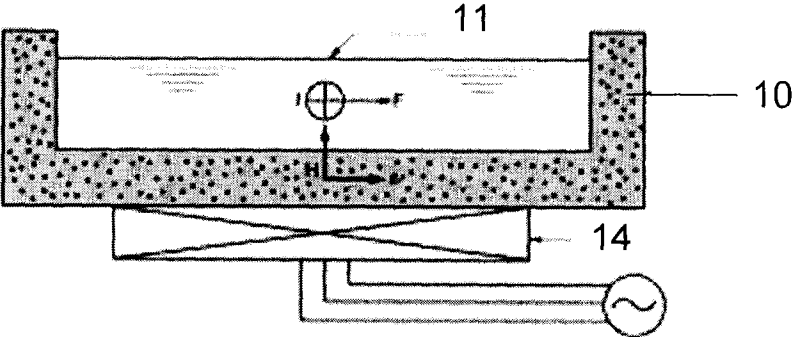
FIG. 6
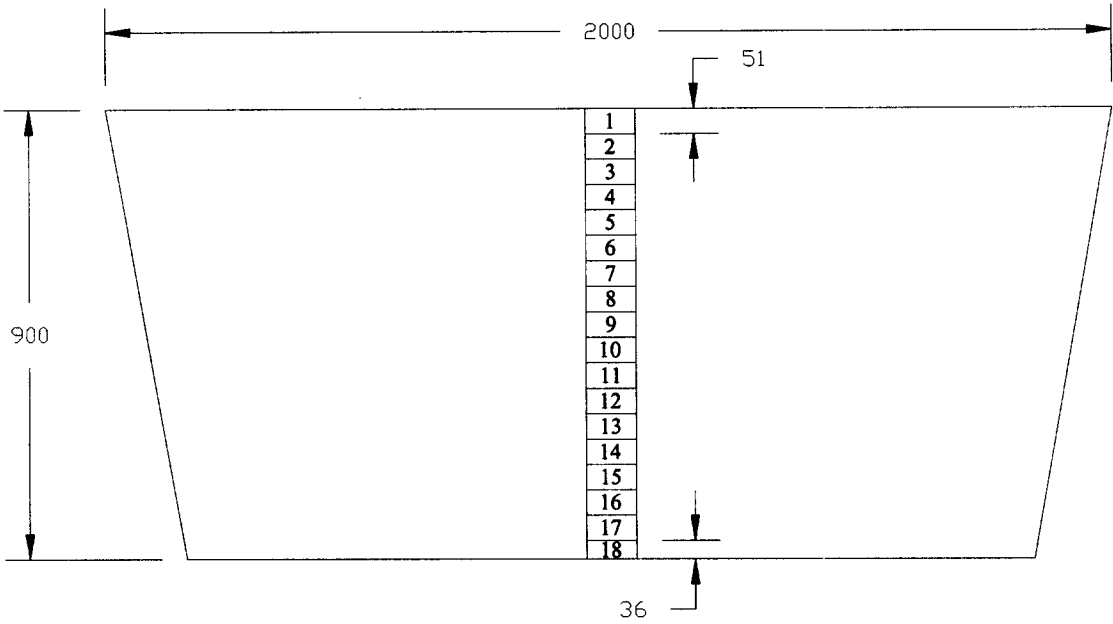
FIG. 7

Aluminum distribution
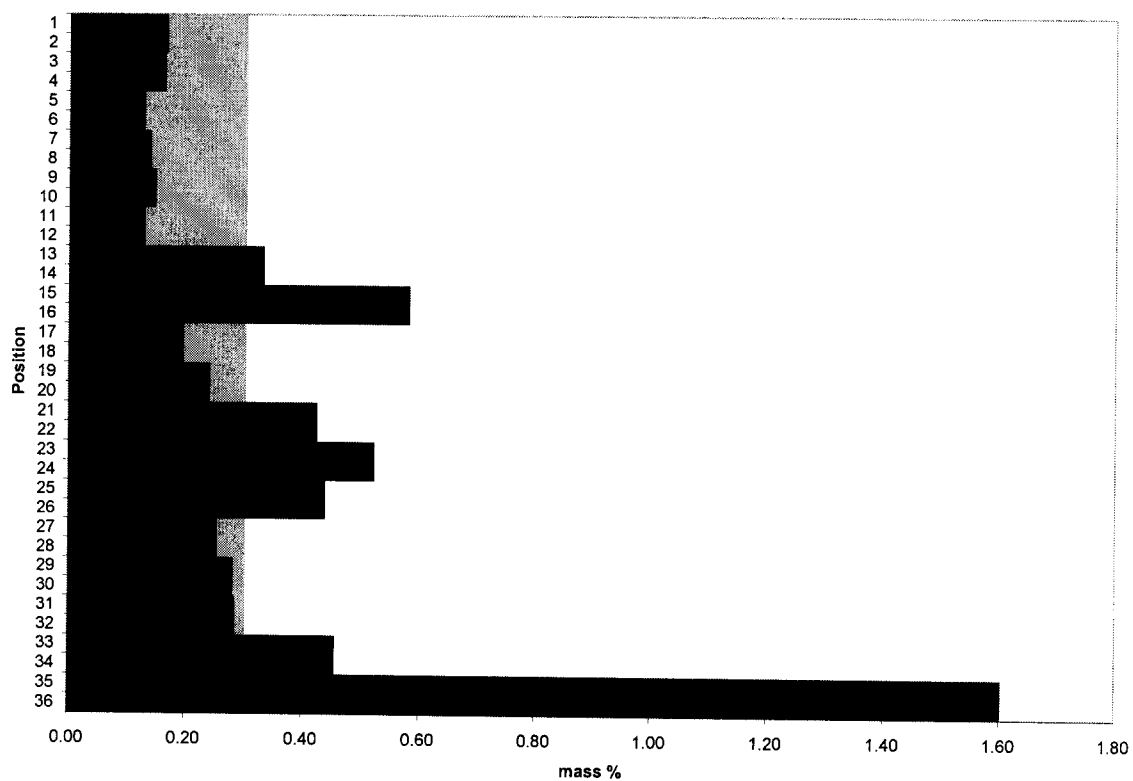
FIG. 8A

Calcium distribution
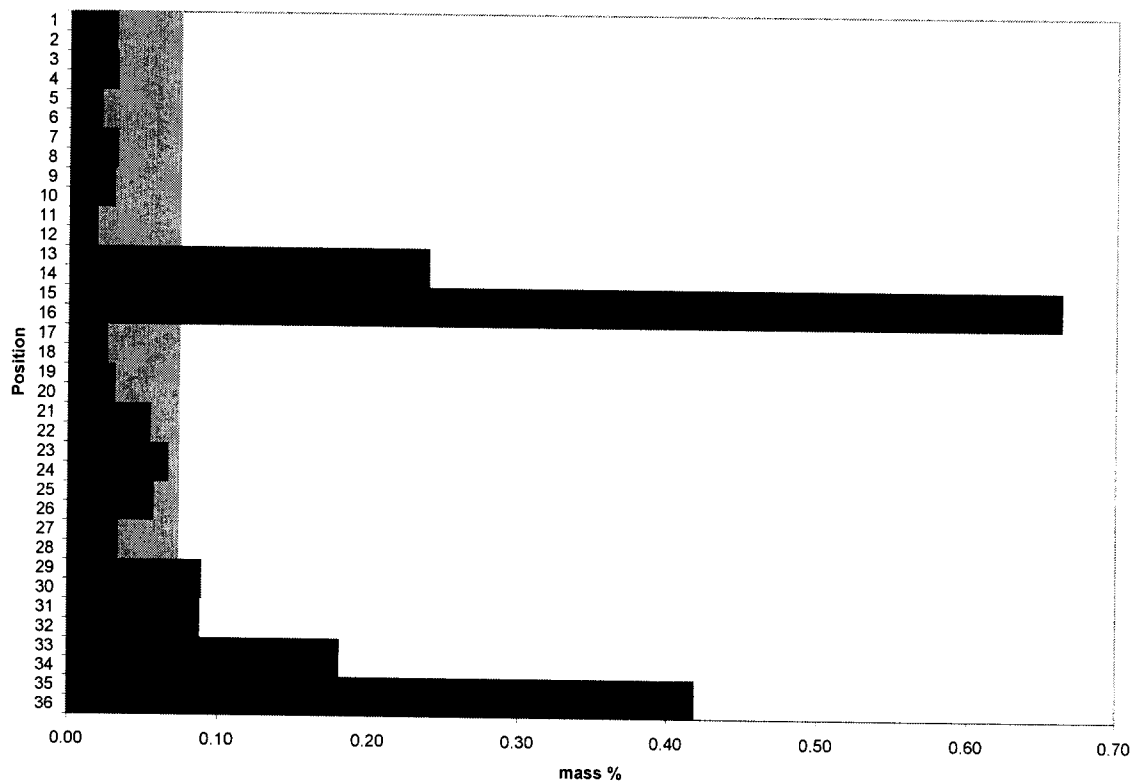
FIG. 8B
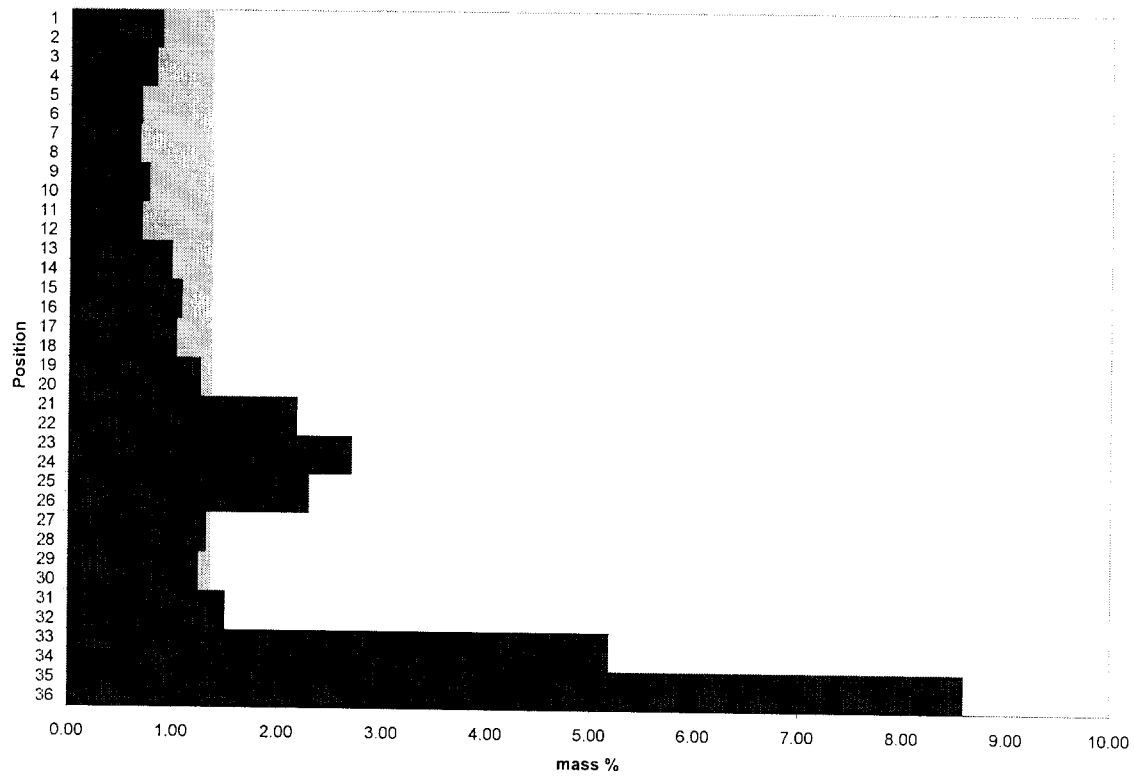
Iron distribution

FIG. 8C

Manganese distribution
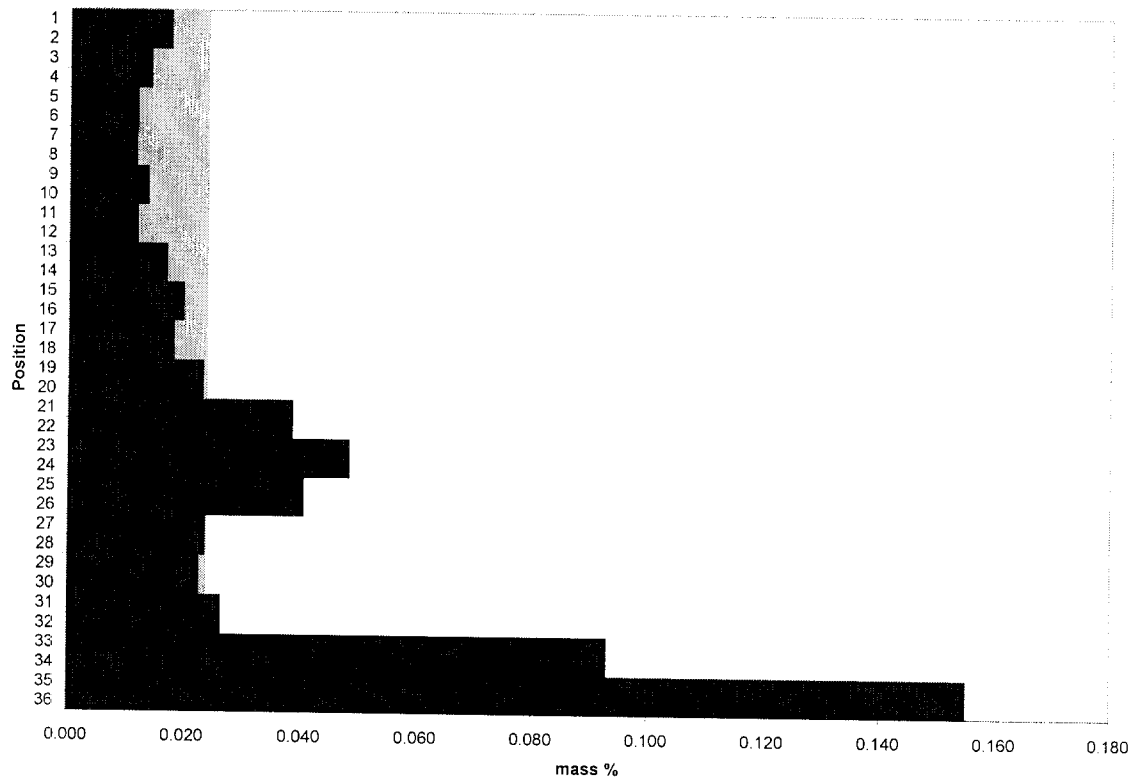
FIG. 8D

Nickel distribution
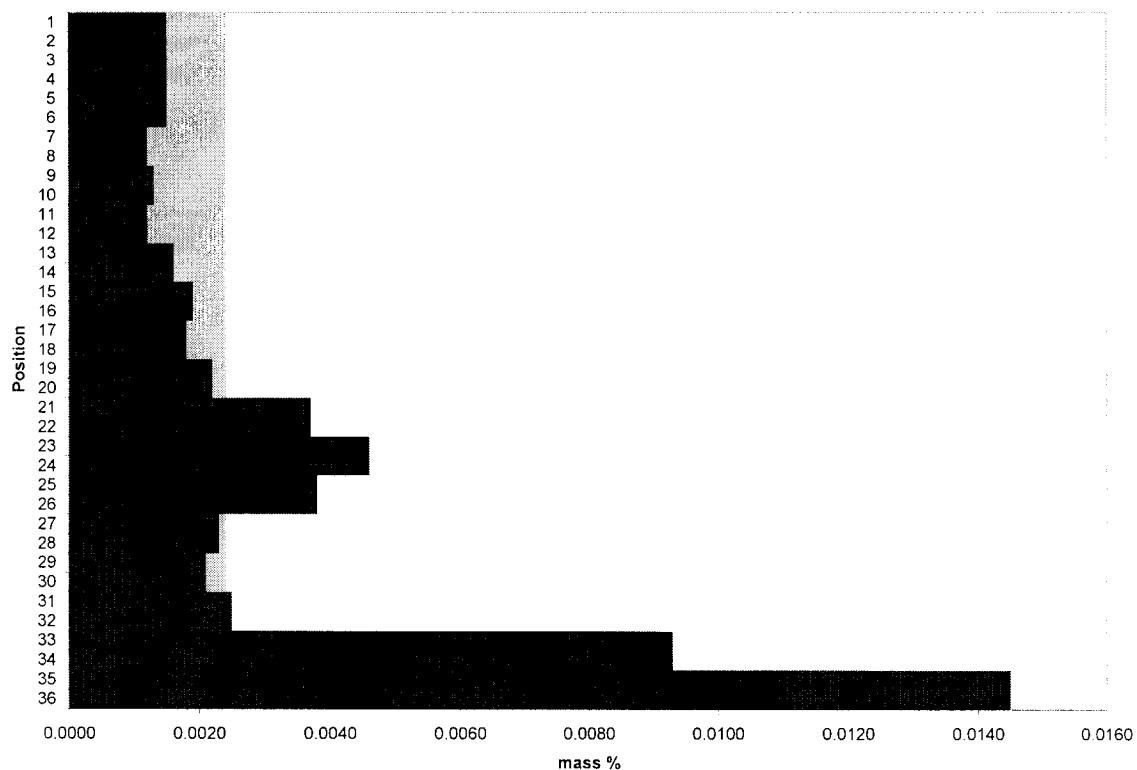
FIG. 8E

Phosphorus distribution
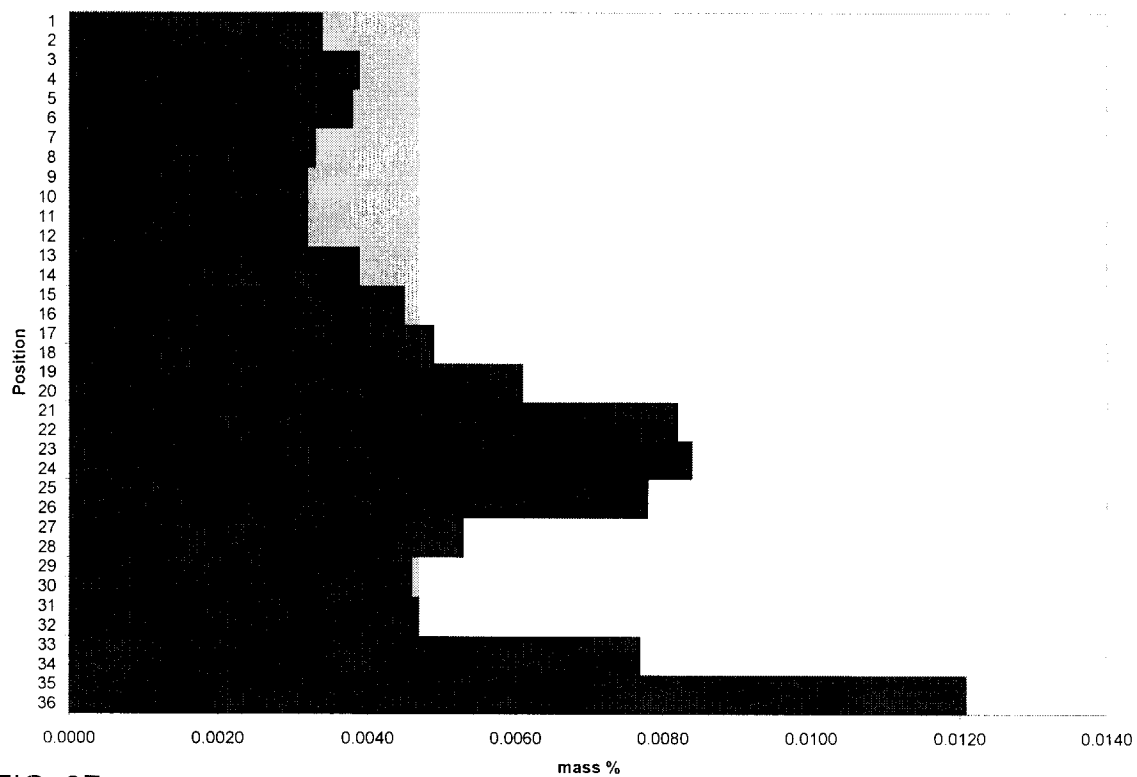
FIG. 8F

Titanium distribution
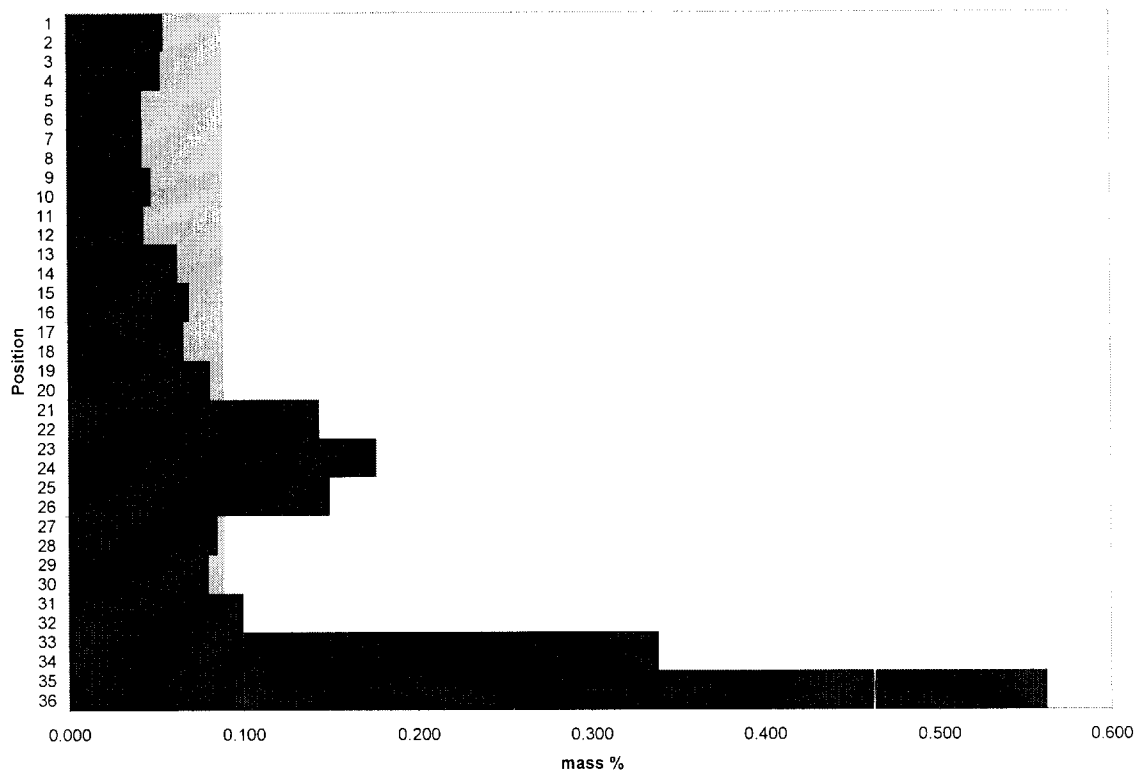
FIG. 8G

Boron distribution
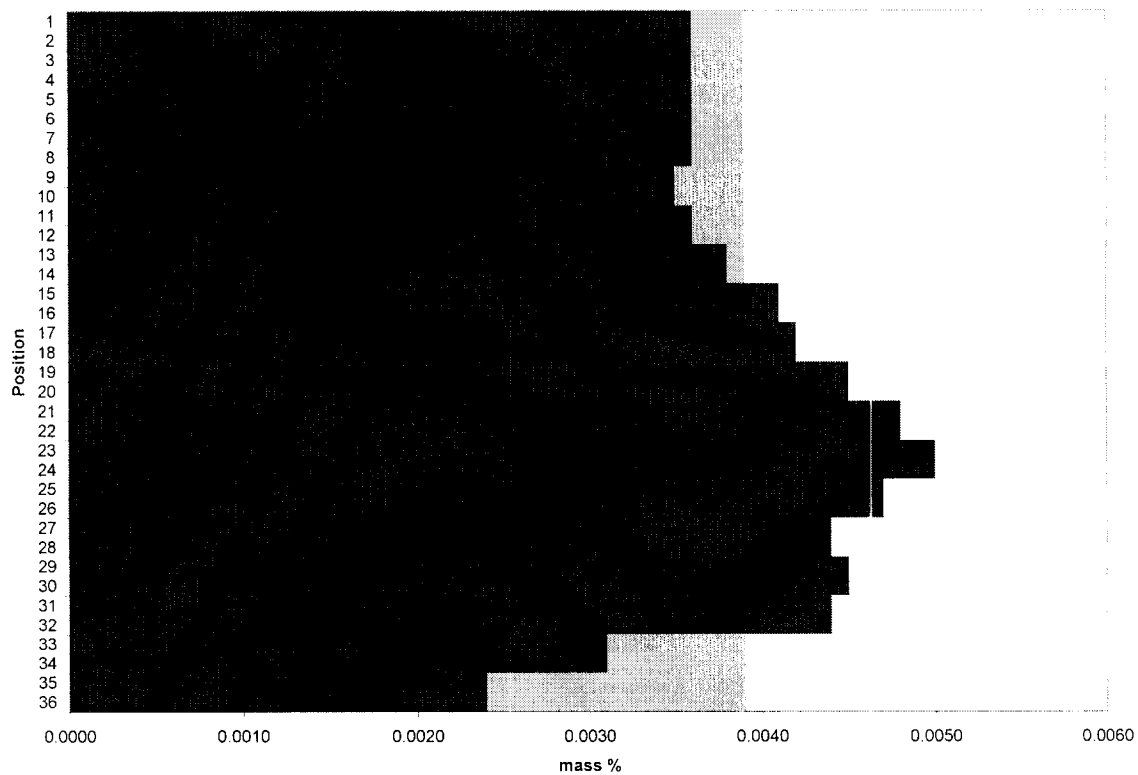
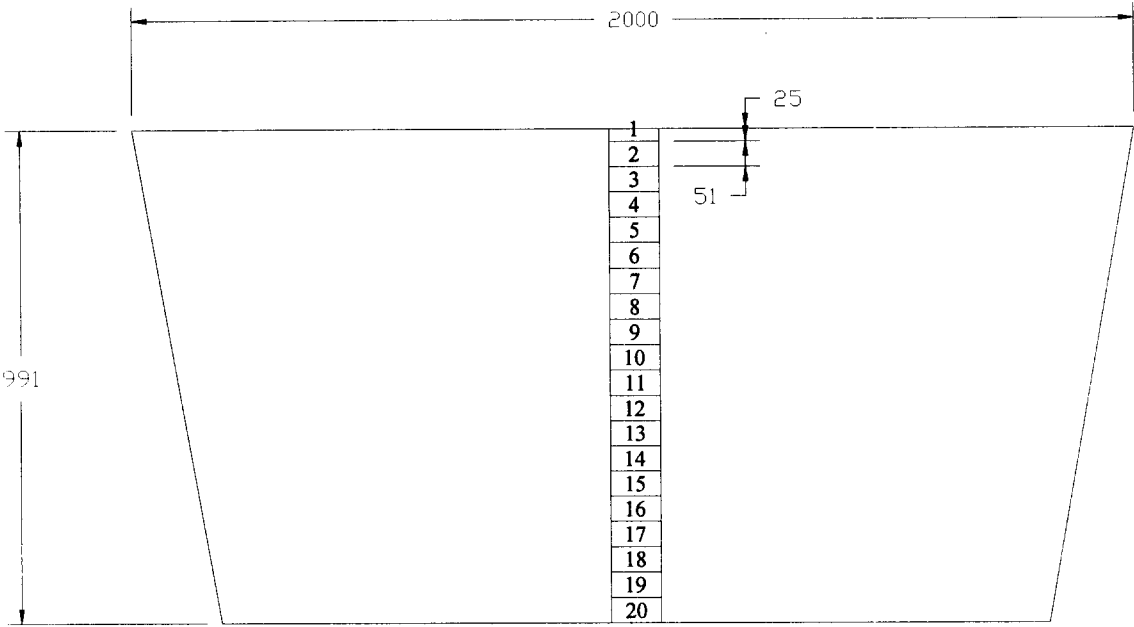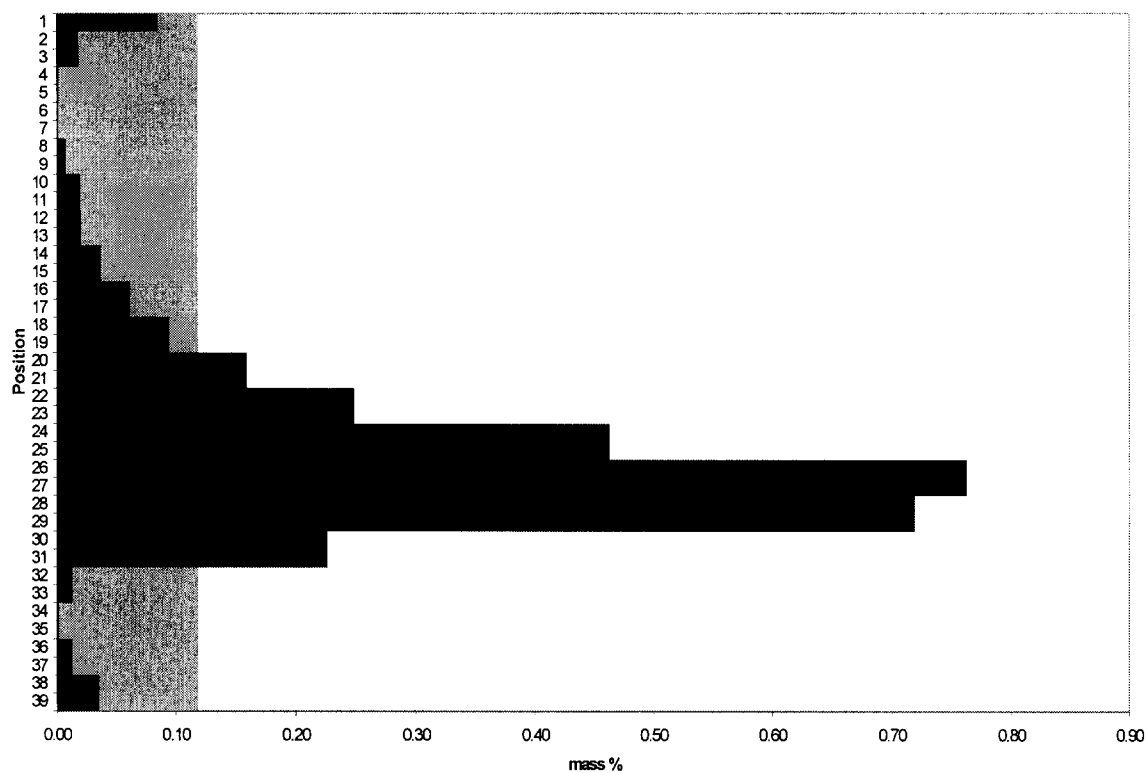FIG. 8H

FIG. 9
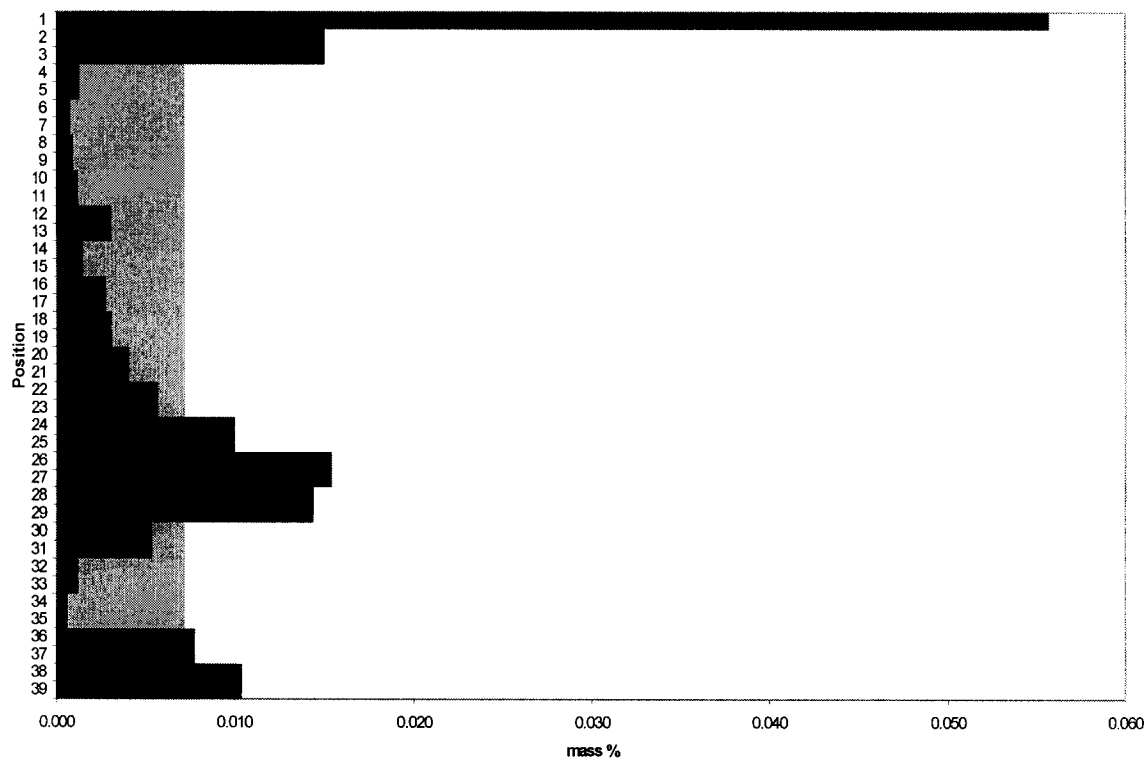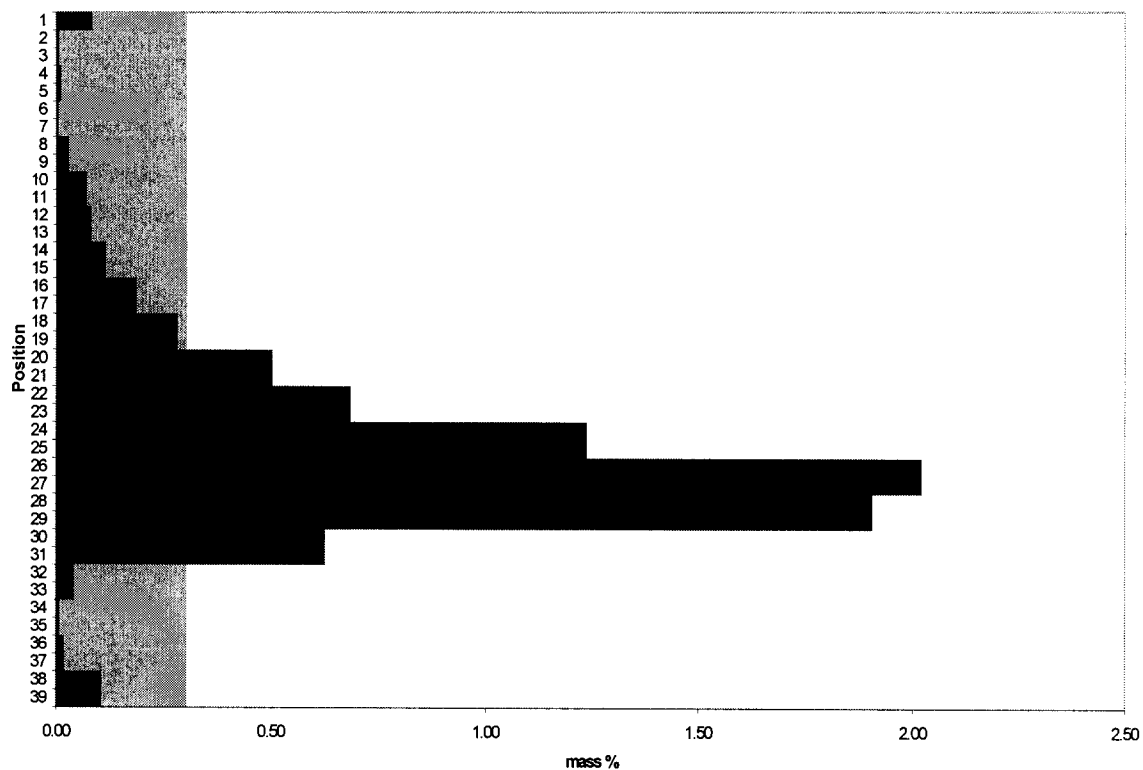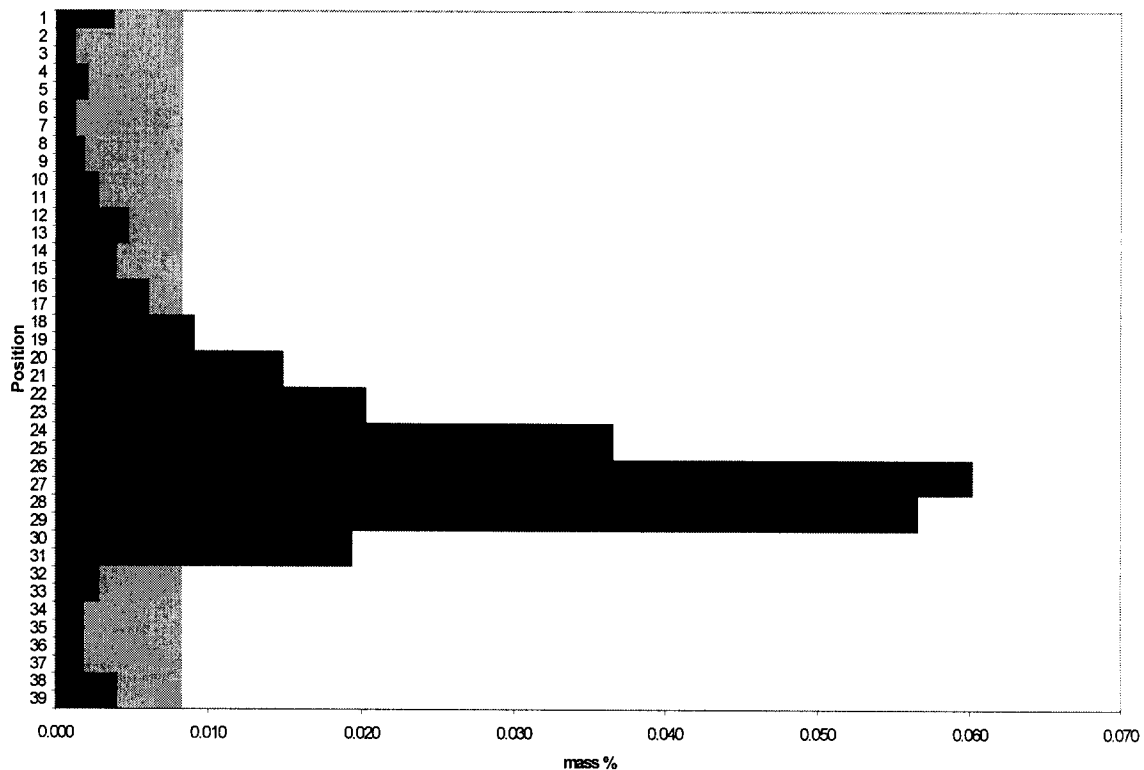
Aluminum distribution

FIG. 10A

Calcium distribution

FIG. 10B

Iron distribution
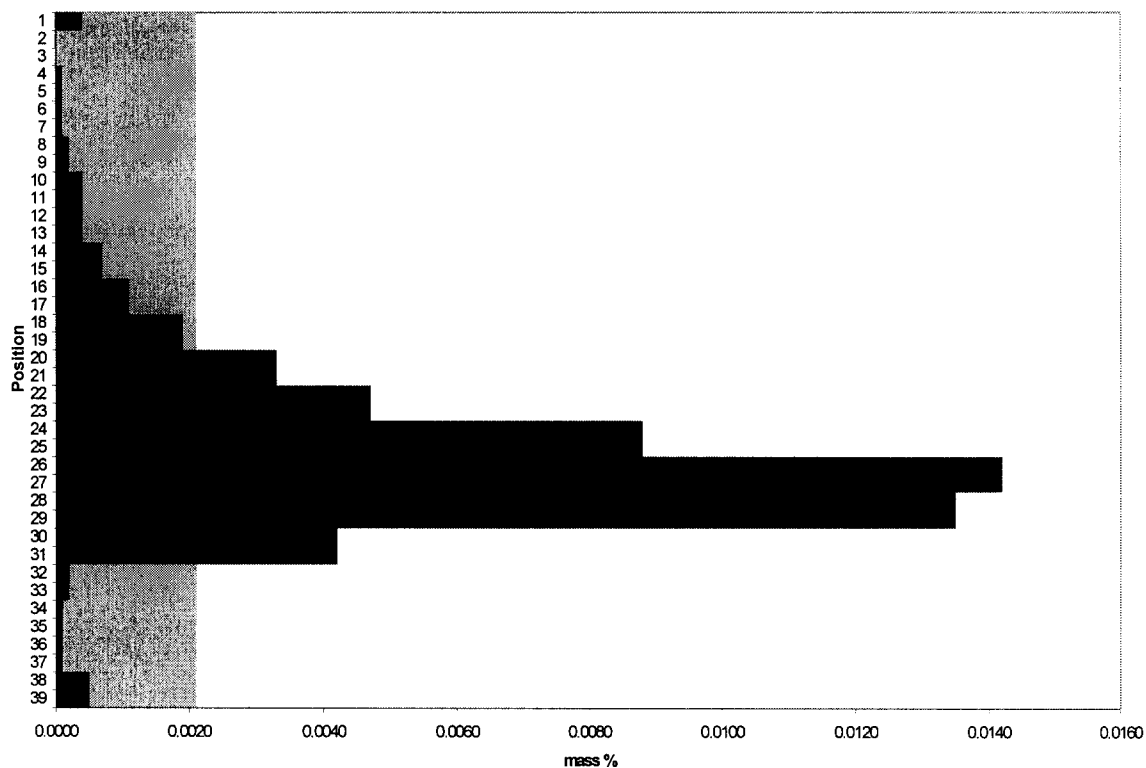

FIG. 10C

Manganese distribution

FIG. 10D

Nickel distribution

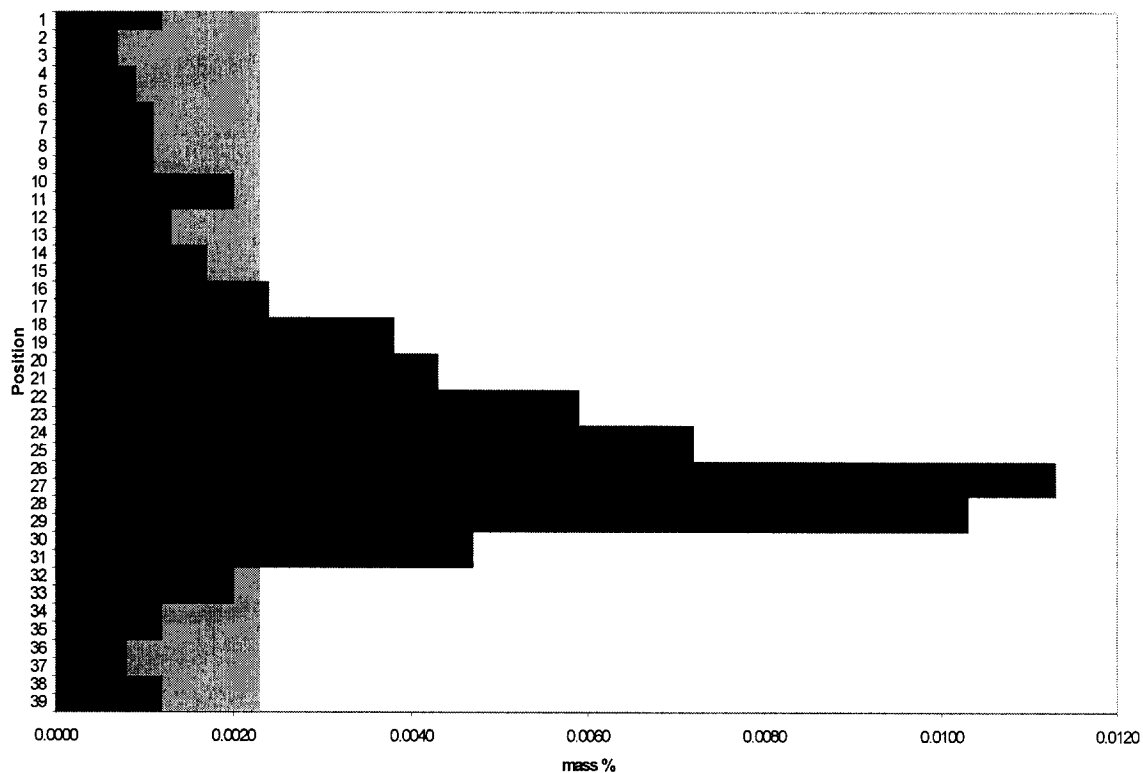FIG. 10E

Phosphorus distribution

FIG. 10F

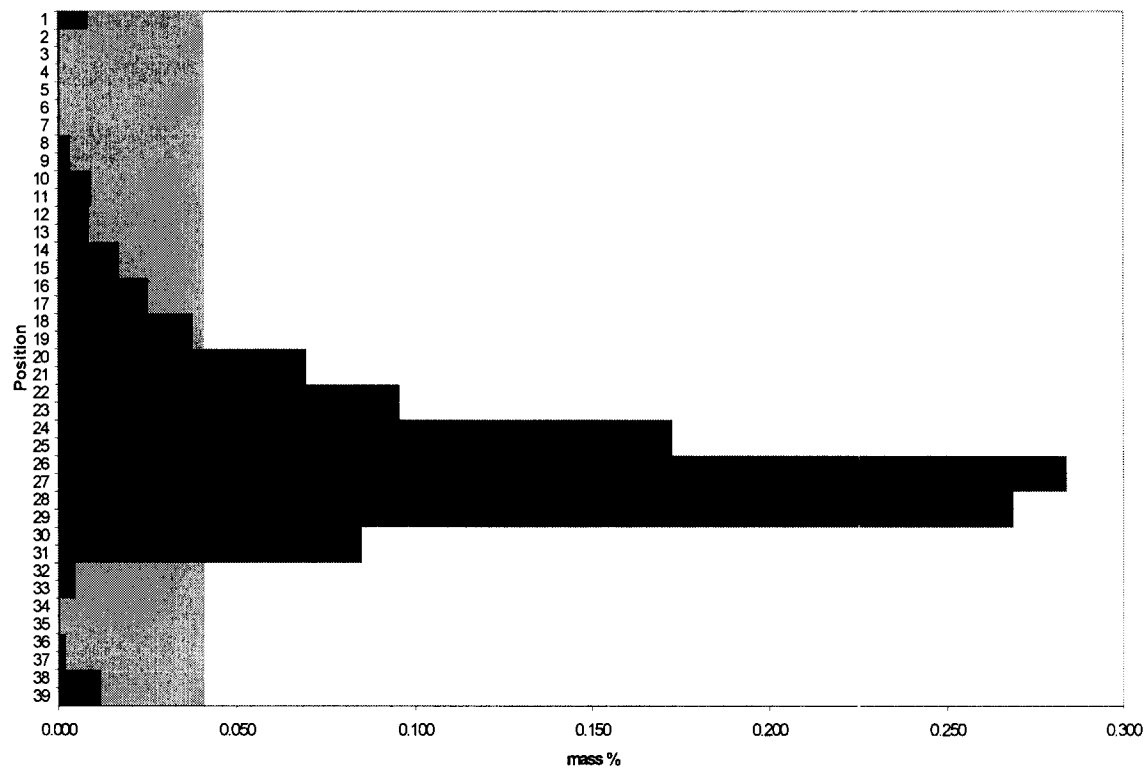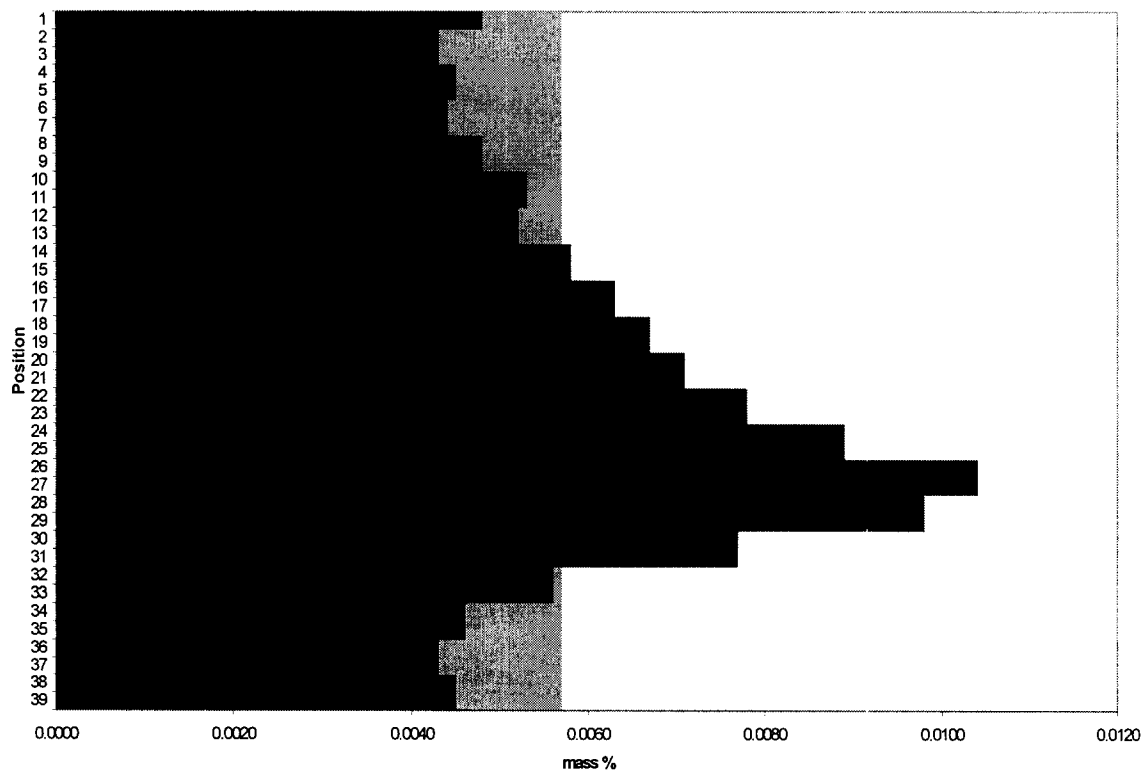*Titanium distribution*

FIG. 10G

Boron distribution

FIG. 10H

A.	CLASSIFICATION OF SUBJECT MATTER

IPC: *C01B 33/037* (2006.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B 33/037 (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Delphion, Google Scholar, Canadian Patent Database (silicon, melt, molten, unidirectional solidification, opening, pour, refining, purification)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 012 865 (R.A. PELLIN) 12 December 1961 (12-12-1961) Whole Document.	1-17
A	US 4 094 731 (KEYSER ET AL.) 13 June 1978 (13-06-1978) Whole Documjent.	1-17

[ ] Further documents are listed in the continuation of Box C.	[X] See patent family annex.

*	Special categories of cited documents :	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
5 May 2008 (05-05-2008)	5 June 2008 (05-06-2008)

Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer Stewart Parsons 819- 997-4378

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