

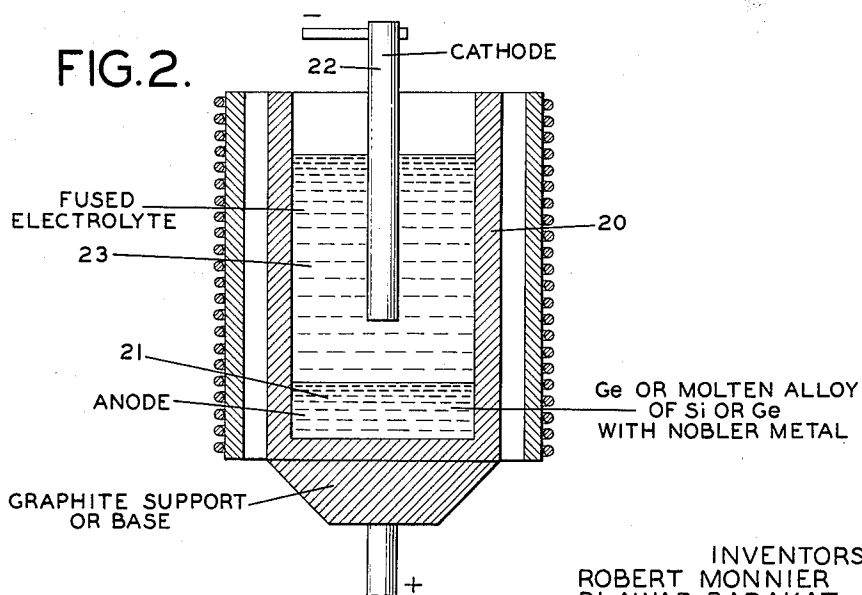
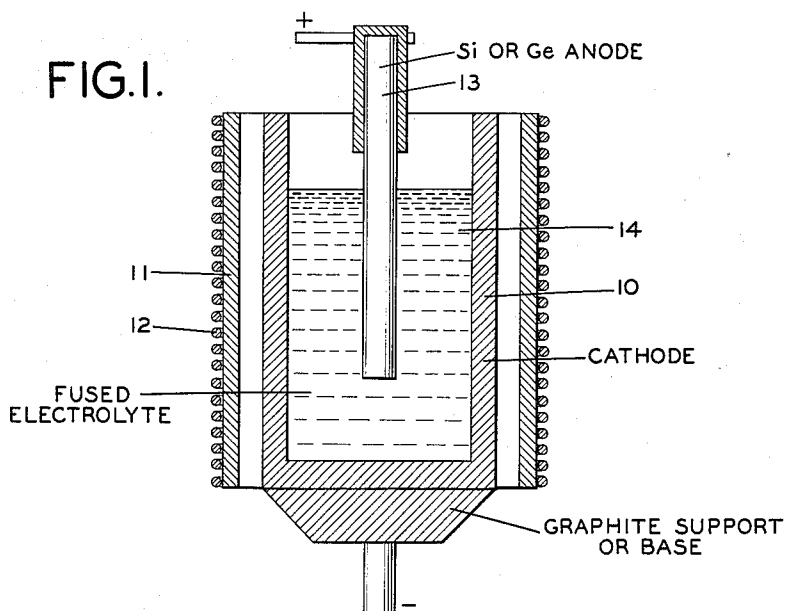
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REFINING OF SILICON AND GERMANIUM

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REFINING OF SILICON AND GERMANIUM

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This invention relates to the production of high purity silicon and germanium and, more particularly, to the refining of silicon and germanium by electrolysis with fused electrolytes.

Heretofore, the silicon and germanium suitable to be ultra-purified by zone-refining, crystal growing, etc., were prepared by elaborate chemical processes of very high cost and at low production rate and requiring very skillful control.

It has also been suggested that silicon can be produced by an electrolytic process with an electrolyte composed of a fused bath of alkali metal chloride salts and an alkali metal fluosilicate utilizing silicon carbide as the anode and depositing the silicon removed therefrom on the cathode of the electrolytic cell. This process has not been used, and it is not suitable, for the production of high purity silicon. When using commercial grade SiC as the anode, the purity of the silicon deposited on the cathode is only about 92% and, therefore, of lower purity or quality than commercial grade silicon (96% to 98% silicon) which is produced in electric furnaces. Inasmuch as the initial cost of commercial grade SiC is higher than the electric furnace silicon, the SiC process is non-competitive. Even when using highly purified SiC, a very costly material, the silicon obtained by electrolysis is only about 99.3% pure and cannot be used for many of the purposes requiring high purity silicon. Furthermore, during the electrolysis, the electrolyte is quickly contaminated by the carbon of SiC, and by little particles of SiC originating from the anodic attack.

In accordance with the present invention, we have provided a process of refining crude or impure silicon or germanium by using it as the anode in an electrolytic cell containing a fused salt electrolyte and depositing silicon or germanium having a purity of 99.9%, or even as high as 99.99%, depending upon the purity of the metal of the anode, on the cathode. The discovery that silicon and germanium can be purified by electrolysis is surprising for the reason that it was generally believed that the compounds of these elements in a molten state gave no or very few cations. However, we do not wish to be limited by any theory of operation.

It has been discovered that silicon or germanium can be used as a solid or a liquid anode with equally satisfactory results. Thus, a solid anode may be formed of electric furnace grade silicon or silicon derived by electrolysis in a fused electrolyte. A solid anode of electric furnace grade silicon, for example, enables the production of refined silicon of 99.6% purity. Using silicon of 99% to 99.9% purity, high purity silicon of 99.99% purity and higher can be obtained in accordance with the present invention. Solid anodes may also be formed of alloys of silicon or germanium with nobler metals. However, the alloying metal tends to collect in the electrolyte and contaminate it, thus necessitating the treatment of the electrolyte to recover the alloying metal if it is expensive. Moreover, it is difficult to recover completely the alloying metal.

Also, excellent results are obtained with liquid anodes composed of an alloy of silicon or germanium with another metal nobler in our operating conditions and provided it is in a liquid state at the temperature of the electrolysis. Gold and silver can be used as an alloying metal,

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but they are expensive and losses unavoidably occur. For commercial purposes copper alloys are most suitable.

Inasmuch as germanium has a melting point below 960° C. and a density of 5.35, it can be used as a solid anode or melted to form a liquid anode since the cell may readily be operated at a temperature of 1000° C. or higher. Inasmuch as silicon has a melting point of 1420° C., it is not practical to operate the cell at a high enough temperature to maintain the silicon in a molten condition. For that reason, when silicon is used as a molten anode, and electrolysis is conducted at 1000° C. or below, a liquid alloy of silicon with a nobler metal such as copper is used. In the case of germanium with a liquid anode, to prevent the germanium from falling in the anode, it is necessary to electrolyze at a temperature a little above the melting point of the germanium, thus the germanium solidifies on the cathode in the bath, which is a little cooler than the electrolyte.

The cathode of the electrolytic cell may be formed of any suitable material capable of withstanding the high temperatures encountered in the cell, such as carbon, graphite or silicon carbide which is treated in such a manner as to render it conductive. With solid anodes formed of silicon or germanium or the solid alloys thereof referred to above, the cell itself may serve as the cathode when formed of conductive and non-reactive material such as carbon or graphite. With liquid (molten) electrodes formed of germanium, and silicon or germanium alloys, the cell is either composed of or provided with a conductive material such as carbon or graphite to conduct current to the molten pool of metal in the cell. In such a cell or even in cells having separate solid anodes, a separate cathode formed of carbon, graphite or other conductive and non-reactive material can be used.

The electrolyte may be any of several different types. One suitable type is composed essentially of a cryolite of the general formula Me_3AlF_6 , in which Me is an alkali metal. Cryolite may be used alone or with alkali metal fluorides, alkaline earth metal fluoride or aluminum fluoride. Also alkali metal fluorides, alkaline earth fluorides and mixtures thereof are satisfactory.

A second suitable electrolyte is composed of a fluoride, that is, an alkali metal fluoride, an alkaline earth metal fluoride, or a mixture of the same, or a cryolite with or without other fluorides, the electrolyte also containing an oxide preferably of the element to be defined. In the refining of silicon, the most suitable oxide is silica.

A third type of electrolyte is composed of alkali metal or alkaline earth metal chlorides, or a mixture of the same, containing an alkali metal or alkaline earth metal fluoride or fluosilicate.

An important characteristic of these types of electrolytes is the absence of any constituents which would give cations with a discharge potential, under the electrolyzing conditions, lower than that of silicon and germanium, respectively. Alkali metal or alkaline earth metal chlorides, without fluorides, are not satisfactory with silicon for the reason that they react with the silicon to form silicon chlorides which evolve from the bath. When fluorides are present in the bath, the silicon is probably retained as a double fluoride. Of the three types of electrolytes, the fluorides with added oxides are the most effective. The oxides may be present within their range of solubility. However, in certain cases the presence of an excess of oxide permits the continuous dissolving of the oxide in the electrolyte during the operation. Conveniently, up to 10% silica may be added to the electrolyte used in the refining of silicon.

The cell temperature must be maintained high enough to melt the electrolyte used. Most suitably, the cell temperature will be maintained in the vicinity of 1000° C., although the cell temperature may be maintained within

a range of 500° C. to 1000° C. with electrolytes composed of chlorides and fluorides. The other classes of electrolytes referred to above operate to best advantage between 800° C. and 1100° C.

The cathodic current density maintained in the cell is between about 5 and 150 amperes per square decimeter. For greatest efficiency the current density should be between 25 and 80 amperes per square decimeter. A suitable potential is applied between the electrodes to maintain the current density in the range indicated.

The cell in which electrolysis is conducted should be made of a material, or at least coated with a material, which is resistant to corrosion under the working conditions. Carbon, graphite, boron nitride, or silicon carbide with a bonding agent not attacked by fused fluorides, such as silicon nitride, are suitable. If desired, when using a solid anode of the metal to be refined, a graphite crucible or cell may be used and connected in the electrical circuit to form the cathode of the cell. The anode is mounted preferably for progressive movement into the electrolyte to provide a continuing supply of the element which is refined and deposited on the cell wall from which it can be removed. When the element is obtained in the solid state as is the case for silicon, and also for germanium when operating at a temperature below its melting point (958.5° C.), then the element is deposited mainly on the walls of the cell but some of it is also found in the mass of the electrolyte. In such conditions, if it is desired to recover all the metal formed, it is necessary to treat all the content of the crucible. In case the operation is with germanium and the electrolyte is above its melting point, the metal is in a molten state in the bottom of the crucible and it could be recovered easily without carrying to much of the bath with it. Alternatively, the cell may be provided with a movable anode of the element to be refined and a movable cathode formed of carbon or graphite or the like on which a layer or ball of the refined element and electrolyte is deposited. Obviously, with mobile cathodes the conditions of operations must be such that the elements must deposit in a solid state. When a sufficient amount of the refined element has been deposited, the cathode is removed from the cell and replaced with a different cathode.

When the anode is a molten alloy of the metal to be refined, it is in a molten condition below the electrolyte and in contact with the bottom of the cell. A graphite or similarly conductive cell serves to conduct the current to the anode. A cathode formed of graphite or carbon is mounted removably in the cell to enable it to be removed for recovery of the silicon thereon. In a continuous operation, additions of the element are made to maintain the concentration of the element in the molten anode reasonably constant.

Any suitable means may be used for heating the cell, such as electric resistance heaters, and the cell also may be heated only by the current flowing between the anode and the cathode. For this last type of heating, it is necessary to electrolyze with a sufficiently high current density, which is not possible if the recommended current densities are not exceeded, unless the size of the cell is large enough to withstand for example 1000 A. The temperature of the cell is maintained by changing the distance between the electrodes. The deposited metal, whether found in the cathodic ball, on the walls of the cell, scattered in the bath or collected in the bottom of the crucible, must be separated from the electrolyte clinging to it. For such an operation several methods could be used: the pulverized mass is treated with a dilute solution of caustic soda or aluminum chloride, or even in certain cases only with hot water thus dissolving the cryolites and the fluorides and leaving the metal intact. It is also possible to take advantage of the difference of densities between the metals and adjoining masses, to utilize mechanical methods such as centrifugation, separation by vibrations, hydrodynamique separations etc.

It is also possible to distill or sublime the cathodic mass in vacuum. The fluorides present, being much more volatile than the silicon or germanium with which they are mixed, are easily separated and recovered. Certain processes combining the chemical treatment and the mechanical or physical separation can be adapted to this operation.

While the process is primarily intended to be used for the production of high purity silicon and germanium, various grades of silicon can be produced by using silicon of different purities as the anode. Products refined in accordance with the present invention have a purity of 99.9% or higher. Such products are suitable, after a physical ultra-purification such as single crystal growing, zone-refining etc., for the use in semi-conductors, such as for example transistors, diodes and rectifiers. However, the product obtained by the process of this invention can be used directly with no further ultra-purification for the manufacture of silicones, special alloys, optical elements for use with infrared radiation, solar batteries, and the like.

For a better understanding of the present invention, reference may be had to the accompanying drawings in which

FIGURE 1 is a view in section of a typical cell having a solid anode for practicing the invention, and

FIGURE 2 is a view in section of a cell having a molten anode and a separate cathode.

As shown in FIGURE 1, a typical cell includes a graphite crucible 10 having a refractory cylinder 11 around it, containing a resistance heating element 12 for heating the crucible and its contents. Movably mounted for introduction into the crucible 10 is a rod 13 of the element to be refined and forming the anode of the cell. In this cell, the crucible 10 is connected to the negative pole of the source of direct current and forms the cathode of the cell. The electrolyte 14 is melted in or introduced into a molten state into the cell to a depth sufficient to immerse at least the lower portion of the anode 13. The top of the crucible need not be covered.

FIGURE 2 shows a typical cell in which the molten metal to be refined or an alloy of such metal serves as the anode. A crucible 20 is formed of carbon or graphite and connected to the positive terminal of a D.C. source and a pool 21 of the molten metal or alloy is in contact therewith and forms the anode of the cell. A separate cathode rod 22 of carbon, graphite or the like is movably mounted in the crucible with its lower end spaced from the pool 21 and immersed in the molten electrolyte 23.

In either type of cell, when current is passed between the anode and the cathode, the refined metal is deposited on the cathode.

The following examples illustrate typical processes embodying the present invention.

Example 1

200 g. of Na_3AlF_6 and 4 g. of silica were heated in the graphite crucible until they melted and a temperature close to 1000° C. was attained. A cylindrical anode made of commercial grade, electric furnace silicon (98.2% silicon) was placed in the center of the crucible. The anode was prepared by melting and then cooling and solidifying silicon in a graphite mold having one closed end which serves as a terminal for connecting the anode to a source of direct current. A direct current was passed through the cell between the anode and the crucible which served as the cathode. The current density was about 100 A./dm.².

After four hours of electrolysis, the anode was removed, a strong attack being noticed on it, and the crucible was drained together with the deposit on its wall. The contents of the crucible were pulverized and immersed in a 13% solution of aluminum chloride until the electrolyte mixed therewith was dissolved. The residue was treated with a solution of hydrofluoric acid and then

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hydrochloric acid and filtered. 6 g. of silicon crystals of a purity of 99.9% were obtained.

The current efficiency in the operation was about 60%.

Example 2

Operating in the manner described in Example 1, an electrolyte composed of 12 parts NaF, 43 parts KF and 45 parts LiF, expressed in percent mol, was melted in a graphite crucible. 1% of K_2SiF_6 is added to the mixture before, during or after melting. The temperature of the electrolyte is maintained at about 550° C. A solid electrode composed of 98% to 99% germanium to be refined was introduced in the fused bath and a direct current was passed between the anode and the cell as a cathode at a current density of 100 A./dm.².

After four hours of electrolysis, the anode was removed and the contents of the crucible removed, pulverized and treated with boiling water acidified with hydrochloric acid to dissolve the soluble components.

The germanium obtained after filtration and drying was 99.9% pure.

Example 3

Operating in the manner described in Example 1, 200 g. of Na_3AlF_6 and 4 g. of silica are melted to form an electrolyte. An alloy of copper and silicon containing 16% silicon and prepared from electrolytic copper and 99.9% pure silicon which was obtained by direct electrolysis, was melted and poured into the crucible and covered with the molten electrolyte. A graphite rod was immersed in the bath in spaced relation to the molten alloy. In this cell the crucible is connected to one pole of a D.C. current source and the rod to the other pole so that the molten alloy therein forms the anode and the graphite rod, the cathode. The temperature of the cell is maintained at 1000° C. A current density of 50 A./dm.² was maintained for a period of four hours. A ball is formed around the cathode and is removed and treated to eliminate the electrolyte clinging to the cathode in the same manner as described in Example 1.

Silicon of purity above 99.99% is obtained with a current efficiency better than 80%.

Example 4

The bottom of a cavity furnace similar to that used for refining aluminum and in which temperature is maintained by the passage of direct current through the furnace was coated with carbon. The bottom of the cavity had a surface area of 100 dm.². The positive terminal of a source of direct current was connected to the carbon coating. A copper-silicon alloy containing 16% commercial grade silicon (98.2%) was poured into the furnace and then covered with a fused electrolyte containing, expressed in percent mol, 71% Na_3AlF_6 , 27% NaF and 2% SiO_2 . A pure graphite cathode of a cross-section of 40 dm.² was immersed in the electrolyte. A 2000 A. direct current was passed between the anode and cathode providing a current density of about 50 A./dm.². The furnace was maintained at a temperature close to 900° C. by adjusting the distance between the electrodes. At fixed intervals the cathode was changed. The ball of refined silicon formed around the cathode was removed and treated in the same manner as in Example 1.

The silicon obtained in this manner was 99.9% pure and the current efficiency was close to 80%.

From the foregoing examples it will be clear that a method is provided which enables the preparation of germanium and silicon of high purity at high efficiency and improved production rates. It will be understood that the methods and apparatus are susceptible to considerable modification and that the examples of the method and apparatus are illustrative.

We claim:

1. A method of refining impure silicon and germanium comprising passing a current between a cathode and an

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anode through a molten salt electrolyte containing a fluoride, said anode being composed of a metal of the class consisting of impure metallic silicon and germanium, alloys of impure silicon with nobler metals than silicon and alloys of impure germanium with nobler metals than germanium to deposit on said cathode at least 99.9% pure metal of the class being refined consisting of silicon and germanium.

2. The method set forth in claim 1 in which said anode is solid and said electrolyte is maintained at a temperature less than the melting point of said anode.

3. The method set forth in claim 1 in which said anode is an alloy which is molten at electrolyte temperature.

4. The method set forth in claim 1 in which said electrolyte comprises at least one fluoride of the class consisting of alkali metal and alkaline earth metal fluorides and up to about 10% of an oxide of metal being refined of the class consisting of silicon and germanium.

5. The method set forth in claim 1 in which said anode is a molten alloy of copper and silicon containing less than 35% of silicon.

6. The method set forth in claim 1 in which said anode is molten germanium at the temperature of said fused electrolyte.

7. The method set forth in claim 1 in which said electrolyte comprises at least one cryolite with the general formula Me_3AlF_6 in which Me is an alkali metal or alkaline earth metal and up to 10% of an oxide of metal being refined of the class consisting of silicon and germanium.

8. A method of refining silicon comprising passing a current at a current density of between 5 and 150 amperes per square decimeter between a cathode and an anode through a molten salt electrolyte containing a fluoride, said anode being composed of 96% to 99.9% silicon and maintaining the temperature of said electrolyte between about 500° C. and 1100° C. to deposit on said cathode silicon of higher purity than said anode.

9. The method set forth in claim 8 in which said molten electrolyte contains up to 10% of silica.

10. A method of refining germanium comprising passing a current at a current density between 5 and 150 amperes per square decimeter between a cathode and an anode through a molten salt electrolyte containing a fluoride, said anode being composed of 96% to 99.9% germanium, maintaining the temperature of the electrolyte below the melting point of germanium to deposit on said cathode germanium of higher purity than said anode.

11. A method of refining silicon comprising passing between a current at a current density of between 5 and 150 amperes per square decimeter between a cathode and an anode through a molten salt bath containing a fluoride, said anode being composed of a molten alloy of 96% to 99.9% pure silicon and a nobler metal, said alloy containing less than 50% silicon, and maintaining the temperature of the bath above the melting point of said alloy to deposit on said cathode silicon of a higher purity than the silicon of said anode.

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