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PROCESS FOR PURIFICATION OF SILICON

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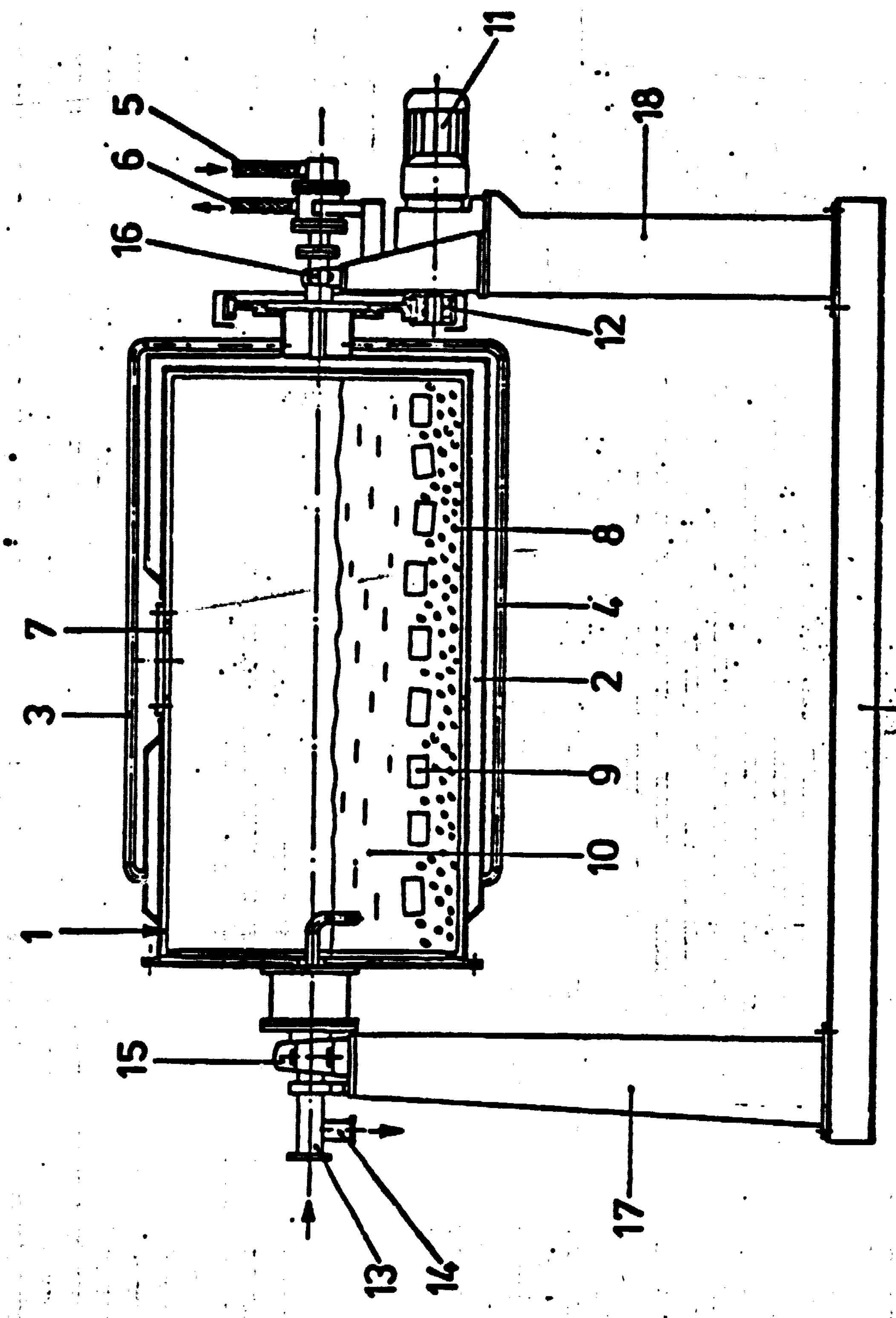

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PROCESS FOR PURIFICATION OF SILICON

Patent Claims

1. Process for purification of metallurgically pure silicon with a silicon content of more than 95% by weight by leaching silicon is an acidic solution which is substantially not corrosive, characterized by the fact that a treatment of the silicon granulation to be purified, leading to a continuous reduction in particle size, is superimposed on the previously known chemical purification step.

2. Process as in Claim 1, characterized by the fact that the silicon granulation is ground during the action of the aqueous acid solution.

3. Process as in Claims 1 and 2, characterized by the fact that grinding elements of polycrystalline silicon are used.

4. Process as in one or more of Claims 1 to 3, characterized by the fact that a rotating ball mill is used.

5. Process as in Claim 4, characterized by the fact that the rate of rotation of the ball mill is 5 to 15 revolutions per minute.

6. Process as in one or more of Claims 1 to 5, characterized by the fact that the mechanochemical purification of the silicon granulation is performed at a pressure of 1 to 1.8 bar.

7. Process as in one or more of Claims 1 to 6, characterized by the fact that the mechanochemical purification of the silicon granulation is performed at a temperature of 20 to 80°C.

8. Process as in one or more of Claims 1 to 7, characterized by the fact that an oxidant which does not dope silicon is added to the aqueous acid solution.

9. Process as in Claim 8, characterized by the fact that air is injected as the oxidant.

10. Process as in one or more of Claims 1 to 9, characterized by the fact that the aqueous acid contains 4 to 7 moles of acid per liter.

11. Process as in Claim 11, characterized by the fact that hydrochloric acid is used as the aqueous acid.

12. Process as in Claims 10 and 11, characterized by the fact that the aqueous acid is composed of a mixture of hydrochloric acid and hydrofluoric acid.

13. Process as in one or more of Claims 1 to 12, characterized by the fact that the silicon granulation is mixed with from 0.8 to 1.2 times its weight of acid.

The object of the invention is a process for purification of metallurgically pure silicon having a silicon content of more than 95% by weight by leaching with an acidic solution which substantially does not attack silicon.

In energy considerations of recent years, generation of electricity by direct conversion of solar energy into electrical energy has become increasingly important. But, in order to make silicon solar cells, for instance, economically competitive, it is essential to make a substantial reduction in the cost of the raw material of required purity, which exists on the earth in essentially inexhaustible quantity. Gas phase purification, such as is standard today in production of silicon for the electronic industry, is immediately ruled out because such a process is too energy-intensive and, therefore, too expensive by a considerable factor. In addition, the purity requirements for silicon to be used in solar cells are not as great as those for 'wafer silicon' to be used in production of expensive components.

It is metallurgically well known, to be sure, that pure silicon can be purified with corrosive acids or acid combinations; but with the previously known processes, one either gets material with inadequate purity for manufacture into solar cells, or extremely long processing times are needed (see, for instance, L. P. Hunt et al., "Purification of Metallurgical Grade Silicon to Solar Grade Quality", Solar Energy, Proc. Intern. Symp., 1976, and Swiss Patent 567 435).

The invention is, then, based on the problem of purifying metallurgically pure silicon having a silicon content greater than 95% by weight, in a short time, enough that it can be used for manufacture of solar cells, for example.

This problem was solved by combining a mechanical treatment leading to continuous particle size reduction of the silicon granulation to be purified with the chemical purification step, which was itself well known.

This mechanical treatment is preferably performed by grinding, as in ball mills or tube mills, which are best coated internally with polytetrafluoroethylene, polypropylene, or other suitable plastic which is resistant to acid and which does not liberate impurities which dose silicon.

The grinding elements may be, for instance, spherical or cylindrical bodies of ceramic, or, preferably, silicon carbide or polycrystalline silicon.

The size reduction of the silicon granulation used during the action of the aqueous acids can also, within the meaning of the invention, be attained, for example, by counter-rotating pairs of rolls of steel coated with the above-mentioned plastics.

The silicon to be purified is conveniently used as a granulation with a particle size distribution in the range of 0.1 to 2 mm. It is usually advantageous to use a granulation which has already been pretreated in a known manner by action of aqueous acid.

In the preferred ball or tube mills, the silicon granulation is mixed with 0.5 to 2 times, and preferably 0.8 to 1.2 times its weight of aqueous acid solution. The aqueous acid solution may contain 3 - 10 mole, and preferably 4 - 7 mole pure acid per liter. Suitable acids are, as examples, sulfuric acid or hydro-halogen acids such as hydrochloric acid and hydrofluoric acid in particular, which can be used alone or mixed.

During the mechanochemical purification of the silicon granulation, it is desirable to keep the mill at a pressure of about 1 - 5 bar, preferably 1 - 1.8 bar, and at a temperature of 10 - 90°C, preferably 20 - 80°C. The speed of mill rotation is 0.5 to 50 revolutions per minute, and preferably 5 - 15 revolutions per minute.

The purifying action can be increased sometimes by addition of oxidants, such as hydrogen peroxide, ammonium persulfate, or other oxidizing materials which do not cause dosing of the silicon granulation being purified, and which can remain, decomposed or undecomposed, in the solution or are drawn off as gas. Such chemical oxidants should be at most 2 mole percent based on the silicon content, and preferably at 0.8 - 1.3 mole-%. Air has proved to be the preferred oxidant. It is blown in at a rate of 0.2 to 5 standard cubic meter per hour per unit volume of mill, and preferably at 0.4 - 0.8 standard cubic meter per hour per unit volume of mill. The advantageous effect of the air is particularly that it causes added mixing of the reaction material. Also, of course, it is cheaper than the chemical oxidants listed above.

The invention is explained by means of the figure, showing a tube mill such as can be used to carry out the process of the invention:

A cylindrical steel drum 1 coated with polypropylene, for example, is surrounded by a heating jacket 2 through which a heating fluid can be pumped by means of the pipe connections 3 and 4. These are connected through the axle with the input and exhaust lines 5 and 6. It is filled through the opening 7 with the silicon granulation to be purified, 8, with the grinding elements, 9, and with the acid solution, 10, so that the drum 1 is almost half full. The electric motor 11 working through the gear drive 12 rotates the drum about its longitudinal axis. The end of drum 1 opposite the gear drive, 12, has a coaxial tube through the axle, and air can be blown into the drum through the inner tube 13, with air or exhaust gas exiting again through the outer tube 14. The drum 1 with bearings 15 and 16 stands on the supports, 17 and 18, which are solidly anchored in the base, 19. The time of treatment for the raw silicon charge placed in the drum depends on the level of purification. Through the steady rotation of the drum, the crude silicon used is ground by the grinding elements, made of polycrystalline silicon, for instance, so new grain faces are continuously exposed. The impurities, preferentially excluded into the grain faces, can be treated through reaction with the corrosive acid mixture.

After termination of the mechanochemical treatment, the entire charge is cooled and dumped. The silicon is filtered off. The grinding elements, much larger than the largest particles of the treated silicon granulation, are also removed. The silicon, purified in this manner, is further processed after drying. In the further processing it may be melted and cast into plates or rods or other shapes, or it may be used as the raw material for for subsequent segregation processes, such as zone purification or crucible pulling processes. Even without these further purifications, the silicon can be used directly wherever its electrical properties are not important, as in alloys, for instance.

Example 1:

A tetrafluoroethylene jar insert with a volume of about 250 cm^3 and with a cover is fitted into the stainless steel jar of a ball mill. The grinding elements are three cylindrical polycrystalline silicon pieces with a diameter of 30 mm and a length of about 35 mm, with ground edges. Then silicon granulation with a particle size between 0.2 and 1.5 mm is added. The silicon granulation has already been pre-purified by leaching with hydrochloric acid and contains impurity levels of 400 ppm iron and 250 ppm aluminum by weight, along with the usual impurities, boron, phosphorus, titanium, chromium, vanadium, manganese, nickel, copper, calcium and magnesium. This silicon granulation is then mixed with 100 ml 18% aqueous hydrochloric acid and 5 ml 40% aqueous hydrofluoric acid. The mill is rotated at about 30 revolutions per minute. The temperature of the salt solution is 20-25°C. After 5 hours the mill is turned off and the silicon separated. After drying, the iron and aluminum contents were determined by analysis: the iron content had diminished to 20 ppm and the aluminum content to 50 ppm by weight.

Example 2:

A polypropylene cylinder with a volume of 2.12 m^3 was fitted into a steel drum with an inside diameter of 100 cm and a length of 270 cm. The polypropylene cylinder was then filled with 500 kg granulated crude silicon with a mean particle size of 0.2 - 1.5 mm, 500 kg 18% aqueous hydrochloric acid, and 25 kg 40% aqueous hydrofluoric acid, as well as about 500 grinding elements of polycrystalline silicon cylinders of various dimensions, with diameters between 18 and 75 mm, and with lengths between 20 and 50 mm. Then the drum was rotated at 12 revolutions per minute. The temperature in the drum was adjusted with the heating jacket to about 80°C. Air was blown into the drum through the axial air inlet at 1 m^3 per hour. After a treatment period of 6 hours the process was stopped. The silicon was separated and dried, and the contents of the major impurities, iron and aluminum, were again determined. The iron content had dropped from the previous 400 ppm by weight to about 10 ppm, and the aluminum content had dropped from 250 ppm to less than 20 ppm.