The invention relates to a method for thermally processing α-spodumene, i.e. lithium aluminum silicate, by which treatment it is transformed into β-spodumene, which is more advantageous for further processing. In the method, concentrate or ore with a grain size of 20-1,000 μm is processed in a fluidized bed reactor, at a temperature of 800-1,000 °C, by using an oxygenous gas as the fluidizing gas.
Method for processing spodumene

FIELD OF INVENTION

The invention relates to a method for thermally processing α-spodumene, or lithium aluminum silicate, by which treatment it is rendered in a form more advantageous for further processing, i.e. soluble β-spodumene.

BACKGROUND OF INVENTION

The largest lithium users at present are glass and ceramic industry as well as battery industry, the share of which is constantly growing, because lithium batteries have a significant role in the development of electric automobiles, for example. Part of the lithium is used as lithium carbonate, or it is at least a commercial intermediate product. Lithium is typically used for instance in the batteries of videos, cameras and mobile phones. Natural lithium-containing minerals are mainly spodumene, petalite and lepidolite. In salt lakes, the hypolimnion may also contain lithium, but there the decisive factor with respect to industrial production is the lithium-magnesium ratio. Likewise, also sea water contains lithium. Lithium is produced by heating and further leaching for example ores or concentrates, such as spodumene, i.e. lithium aluminum silicate (LiAlSi$_2$O$_6$) or petalite (LiAlSi$_4$O$_{10}$). In the first recovery step of lithium, the α structure of spodumene is transformed into a soluble β structure. This can be carried out by thermal heating. It has been found out that the alpha structure is converted into a beta structure when the temperature is 850-1 000° C. To summarize: in lithium recovery, lithium mineral is concentrated, whereafter the treatment of the concentrate generally includes transformation of the crystal structure at a high temperature, pressure leaching, carbon dioxide treatment, as well as filtering and cleaning of the created lithium bicarbonate LiHCO$_3$. 
From the Canadian publication CA 1297265, there is known a process for producing lithium carbonate. According to said publication, the material is thermally treated in a circulating fluidized bed reactor, which requires a high free-space velocity for the gas in the reactor. The concentrate or ore is fed into the process as coarse material, with a grain size of 1-10 millimeters approximately. In order to make said material circulate in a way characteristic for a circulating fluidized bed, a large gas flow is required. The heating of a large gas flow in turn demands a large quantity of energy. In order to maintain the temperature on the level required by the conversion throughout the whole process, oxygenous gas must be added on different levels. For keeping the gas temperature on a sufficiently high level, a large number of lances is needed for fuel supply. In addition, the high energy demand and large quantity of fuel increase CO₂ emissions.

OBJECT OF INVENTION

The object of the invention is to introduce a new, more efficient, more environmentally friendly and energy-efficient way for treating spodumene, particularly for processing it thermally in a fluidized bed reactor, so that a desired structure is obtained for spodumene with respect to further processing.

SUMMARY OF INVENTION

The essential novel features of the invention are apparent from the appended claims.

The invention relates to a method for thermally processing a-spodumene, i.e. lithium aluminum silicate, by which treatment it is transformed into β-spodumene, which is more advantageous for further processing; according to said method, concentrate or ore with a grain size of 20-1,000 µm is
processed in a fluidized bed reactor, at a temperature of 800-1,000 °C, by using an oxygenous gas as the fluidizing gas. According to the invention, heat transfer to the nuclei of the particles to be processed takes place more rapidly in a fine-grained material than in a coarser material, in other words the delay caused by the heating of spodumene in the reactor is shorter with a finer material, i.e. when the concentrate grain size is advantageously 20-1,000 μm.

According to an embodiment of the invention, oxygenous fluidizing gas is fed into the fluidized bed reactor, depending on the grain size of the feed, so that the free-space velocity of gas is 0.3-1 m/s.

The oxygen content of the oxygenous fluidizing gas to be fed in the fluidized bed reactor equals the oxygen quantity required by the oxidation of the fuel needed for heating the fluidized bed.

According to an embodiment of the invention, the fluidized bed is a bubbling bed. When operating according to the method of the invention, heat transfer in the suspension bed is effective. The energy consumption in the process is minimized in many different ways. When using a bubbling bed, where the gas velocity and at the same time the gas flow is small, the heated gas flow is not too large. According to the invention, the energy from the hot exhaust gas is used for drying and preheating the feed, which reduces the quantity of fuel needed in the reactor. The energy content of the hot product removed from the fluidized bed reactor is used for preheating the process gas, which reduces the quantity of fuel needed in the reactor.

According to an embodiment of the invention, the delay of spodumene in the fluidized bed is no more than one hour, preferably 15 minutes to 1 hour.

The energy contained in the hot gas discharged from the fluidized bed reactor is utilized in the drying and preheating of the material to be fed in the fluidized bed reactor. According to the invention, at least part of the dust
conveyed along with the gas discharged from the fluidized bed reactor, which dust is recovered by a cyclone and a fiber filter, is returned to the bubbling fluidized bed. According to the invention, liquid, gaseous or solid fuel is fed to the bubbling fluidized bed by lances.

According to a preferred embodiment of the invention, the energy contained in the hot product discharged from the fluidized bed reactor is utilized in the preheating of the combustion/fluidizing air to be fed in the fluidized bed reactor, in the fluidized bed cooler of the product.

Dust is recovered from the hot, oxygenous gas discharged from the fluidized bed cooler prior to feeding the gas to the fluidized bed reactor. The dust obtained from the fluidized bed cooler is combined in the product.

According to the invention, the temperature of the fluidized bed is chosen according to the impurity contents of the spodumene and the fuel, by avoiding an excessive formation, i.e. over 15%, of molten phases in the bed.

While using a bubbling fluidized bed according to the invention, where the employed feed is fine-grained concentrate or ore, and by making use of the energy flows contained in the hot exhaust gas and the hot product, there is advantageously achieved, with relatively low energy consumption, an effective thermal conversion of spodumene.

LIST OF DRAWINGS

An arrangement according to the invention is described in more detail with reference to the appended drawing, where Figure 1 illustrates the invention as a block diagram.

DETAILED DESCRIPTION OF INVENTION
According to the invention, spodumene concentrate or ore, i.e. lithium aluminum silicate, is processed thermally in a fluidized bed reactor in order to convert it to a desired soluble form for separating lithium. The filtered lithium concentrate (moisture in concentrates being generally ~10 %) is conducted in the process line in countercurrent to the hot process gas to be removed from the fluidized bed reactor. Now the hot gas is in direct contact with the concentrate. The concentrate is dried and heated while the gas is cooled, i.e. the concentrate is dried and preheated prior to being thermally processed in the fluidized bed reactor, in a bubbling fluidized bed.

In the bubbling bed of the fluidized bed reactor, the lithium concentrate is subjected to conversion, i.e. the a-spodumene is, owing to the effect of heat, converted to soluble β-spodumene. This change takes place when the temperature is 800-1,000 °C, but yet so that the formation of molten phases formed by impurities is minimized by selecting the temperature. According to the invention, the grain size of the lithium concentrate fed in the fluidized bed reactor is 20-1,000 μm. The delay of the material in the fluidized bed is preferably less than 1 hour, when the free-space velocity of the gas is 0.3-1 m/s. In the fluidized bed, the fuel fed therein (can be gaseous, liquid or solid) reacts with the oxygenous fluidizing/process gas. The process gas in a fluidized bed reactor is composed of gas and air that was used for cooling the fluidized bed reactor product and preheated in the process. When burning, the fuel must generate sufficient energy for heating both the spodumene and the gas in the fluidized bed reactor. Dust is recovered in a cyclone from the gas exhausted from the fluidized bed reactor. The energy content of dust-free gas is utilized for drying and preheating the concentrate. The thermal capacity of the product treated in the fluidized bed reactor is made use of in a fluidized bed cooler, where the energy contained in the product is transferred in the gas, and the cooled product is removed. Air is fed as fluidizing gas into the multiblock fluidized bed cooler, and the hot spodumene product removed from the fluidized bed reactor is also fed in said cooler. Fluidizing air is heated as the spodumene is cooled. The hot
oxygenous gas exhausted from the fluidized bed cooler is conducted to the process reactor as fluidizing and combustion gas. The products must be cooled in order to improve the wear of the conveyors and to make the processing easier.

EXAMPLE

In the example below, the invention is discussed with reference to the energy balance in the conversion process of a-spodumene taking place in a fluidized bed reactor. Spodumene concentrate is fed to be processed in a fluidized bed reactor. In order to facilitate the desired conversion from a-spodumene to β-spodumene, energy is needed for raising the temperature. The temperature is raised to 950 °C, in which case the methane demand is 55 Nm³ per ton of spodumene concentrate. For burning the methane, there is needed 110 NM³ oxygen, which equals 524Nm³ when calculated as air. In that case the size of the furnace is defined according to the feed quantity and spodumene grain size, so that the bed forms a bubbling bed (free-space velocity according to grain size 0.3-1 m/s), and there is sufficiently oxygen for oxidizing the fuel needed in the heating of spodumene. When, according to the example, 524 Nm³ air is cooled from 950 °C to 200 °C, the quantity of released energy is 156 kWh, which is made use of in the drying and preheating processes. As one ton of spodumene exhausted from the fluidized bed reactor at the temperature of 950 °C is cooled down to 70 °C, the quantity of released energy is 300 kWh, which is made use of in the preheating of the process gas.

For a person skilled in the art, it is obvious that along with the development of technology, the principal idea of the invention can be realized in many different ways. Thus the invention and its embodiments are not restricted to the above described examples, but they may vary within the scope of the appended claims.
CLAIMS

1. A method for thermally processing a-spodumene, i.e. lithium aluminum silicate, by which treatment it is transformed into β-spodumene, which is more advantageous for further processing; characterized in that concentrate or ore with a grain size of 20-1,000 \( \mu \text{m} \) is processed in a fluidized bed reactor, at a temperature of 800-1,000 °C, by using an oxygenous gas as the fluidizing gas, when the temperature of the fluidized bed is chosen according to the impurity contents of the spodumene and the fuel, by avoiding an excessive formation, i.e. over 15%, of molten phases in the fluidized bed.

2. A method according to claim 1, characterized in that oxygenous fluidizing gas is fed into the fluidized bed reactor, depending on the grain size of the feed, so that the free-space velocity of gas is 0.3-1 m/s.

3. A method according to claim 1 or 2, characterized in that the oxygen content of the oxygenous fluidizing gas to be fed in the fluidized bed reactor equals the oxygen quantity required by the oxidation of the fuel needed for heating the fluidized bed.

4. A method according to claim 1, 2 or 3, characterized in that the fluidized bed is a bubbling bed.

5. A method according to any of the claims 1-A, characterized in that the delay of spodumene in the fluidized bed is no more than one hour, preferably from 15 minutes to 1 hour.

6. A method according to claim 1, characterized in that the energy contained in the hot gas discharged from the fluidized bed reactor is utilized in the drying and preheating of the material to be fed in the fluidized bed reactor.
7. A method according to claim 1, characterized in that at least part of the dust that is recovered by a cyclone and a fiber filter from gas exhausted from the fluidized bed reactor is returned to the bubbling fluidized bed.

8. A method according to claim 4, characterized in that liquid, gaseous or solid fuel is fed to the bubbling fluidized bed by lances.

9. A method according to claim 1, characterized in that the thermal energy contained in the hot product discharged from the fluidized bed reactor is made use of in the fluidized bed cooler of the product, in preheating the combustion/fluidizing air to be fed in the fluidized bed reactor.

10. A method according to claim 9, characterized in that dust is recovered from the hot, oxygenous gas discharged from the fluidized bed cooler prior to feeding the gas to the fluidized bed reactor.

11. A method according to claim 9 or 10, characterized in that the dust obtained from the fluidized bed cooler is combined in the product.
### A. CLASSIFICATION OF SUBJECT MATTER

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)

IPC: B01 J, C01 D, C22B, F23C

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

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, XPESP, COMPDX, INSPEC, Chemical Abstracts, Metadex

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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CLASSIFICATION OF SUBJECT MATTER

Int.Cl.
C01D 15/00 (2006.01)
C22B 26/12 (2006.01)
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