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SOLAR SILICON VIA THE DOW CORNING PROCESS

Quarterly Report No. 7

By
L. P. Hunt
V. D. Dosaj
J. R. McCormick

MASTER

April 1978

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Solid-State Research and Development Laboratory
Dow Corning Corporation
Hemlock, Michigan

U.S. Department of Energy

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Solar Energy

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L. P. HUNT, V. D. DOSAJ
and J. R. McCORMICK

DOW CORNING CORPORATION
Solid-State Research and Development Laboratory
Hemlock, Michigan 48626

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ABSTRACT

Installation of the Direct Arc Reactor (DAR) system was completed. Reactor start-up was initiated after modifications were made as recommended by the safety start-up team. This initial experiment was successful enough to allow us to proceed directly into a series of experiments aimed at establishing baseline operating conditions for the DAR. These experiments use pure quartz and unpurified charcoal as reactants.

Two baseline experiments were completed this quarter. Each has suggested modifications in construction and operation of the DAR to provide for more successful silicon production. The longest experiment (48h) was terminated on schedule after producing 110 kg of silicon. After initial reactor conditioning, silicon was produced at 2.6 kg/h using 28 kWh/kg. After baseline conditions are established, experiments will be performed with pure carbon reductants.

A program was developed with the goal of identifying various carbon reductants having boron and phosphorus concentrations of about 1 ppm or less. This is to be accomplished through subjecting the reductants to chemical and physical processes aimed at enhancing their purity and reactivity.

The necessity is stressed of carrying out a development program for silicon purification by unidirectional solidification. This must be done in parallel with the development program for DAR-silicon production in order to develop the overall Dow Corning Process for solar-grade silicon within the time goals of the LSSA Project. The technology for unidirectional solidification requirements under the Dow Corning Process neither exist nor are they being developed.

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I. INTRODUCTION

This contract began on July 31, 1976. This seventh quarterly report covers activities performed during the three months of January, February and March, 1978.

The objective of this program is to demonstrate the feasibility of a process for the production of solar-cell-grade silicon. This process should have high probability of producing silicon for sale at less than \$10/kg when scaled to 3000 metric tons per year by, or before, 1986.

The program tasks involved in the Dow Corning Process for producing solar-grade silicon (SoG-Si) are diagrammatically presented in Fig. 1. Task A involves obtaining high-purity raw materials in order to minimize the introduction of impurities into the silicon production step. An extensive survey of quartz and quartzite sources has indicated that large quantities of these materials are available at reasonable cost and with sufficient purity (1).

Charcoal, commercially used as a reductant for quartz in Brazil, has been shown to be of higher purity in most trace elements than commercial reductants commonly used in the USA (2). It was further demonstrated that charcoal can be purified at high temperature to reduce impurity levels below the detection limits of emission spectroscopy, i.e., about 10 ppw (2).

Task B is concerned with the reaction of high-purity raw materials to produce high-quality silicon. This is being accomplished through optimization of the SiO_2 reduction process. The feasibility of reacting high-purity quartz with commercial charcoal has been established (2). The produced silicon was purer than commercial silicon by about an order of magnitude for all analyzed elements. Most silicon produced from both high-purity quartz and charcoal has been sufficiently pure to be a good material for final purification in Task C. Difficulties have been incurred, however, in reacting quartz with purified charcoal in a small experimental reactor.

Task C involves final purification via unidirectional solidification to effectively segregate most impurities from the solid into the melt. It is this unidirectionally solidified material that would be supplied to the Large

PROGRAM TASKS

A. Quartz and Carbon Raw Materials

B. Silicon Production via the Reaction $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$

C. Unidirectional Solidification of Silicon

Figure 1. Schematic Diagram of the Dow Corning Process for Producing SoG-Si

Area Silicon Sheet Task. Purification via a Bridgman-type process has been demonstrated (4). The Czochralski process has been used to purify silicon produced in Task B. A polycrystalline ingot pulled from such material was analyzed to have transition metal impurities below their limits of detection of approximately 1 ppba or less (5), essentially equivalent to the concentrations in semiconductor-grade silicon. The best silicon contained 9 ppma boron and 12 ppma phosphorus. These levels must be further reduced through efforts in Tasks A and B.

SoG-Si from Task C was evaluated as solar cells using in-house monies. Single-crystal material (ca. 60-% yield) was produced by float-zoning a Czochralski-pulled ingot which was supplied to Spectrolab for fabrication into cells. Conversion efficiencies at AMO averaged 11 %. Standard cells processed at the same time showed 13 % efficiencies. Further improvements are anticipated when boron levels are reduced through efforts in Task A.

A cost analysis of the Dow Corning Process indicated that the SoG-Si should cost (no profit) \$7.40 (January, 1975 dollars) to produce at a level of about 3000 Mt/y (6). Capital investment would be \$38 million.

II. TECHNICAL DISUCSSION

A. Raw Materials

1. Quartz

Domestic and foreign sources of quartz are available to meet the objective of the Dow Corning Process for producing SoG-Si (3). More detailed work to evaluate these sources is necessary after other tasks in the program have proceeded further.

Quartz used in the Direct Arc Reactor (DAR) was obtained from Malvern Minerals Co. in Little Rock, Arkansas. The semiclear crystals analyzed by emission spectroscopy as follows: Al=10, B=5, Fe=10, and P<10 ppmw.

2. Carbon

A program was initiated to identify a high-purity reductant for use in the DAR. This was deemed necessary since only 11-% efficient solar cells could be fabricated from Dow Corning Process silicon (12 ppma B and 9 ppma P) which resulted from using purified charcoal in the DAR.

The carbon program consists of investigating various types of carbon reductants after changes have been made in their chemical and physical properties. Chemical composition and reactivity during quartz reduction are of high interest. The program involves interaction between Dow Corning and a major carbon corporation, a major research center, and a material pelletizer.

Present goals for B and P in Dow Corning Process silicon are 2 and 1 ppma, respectively (6). These concentrations translate into 4 ppma, each in carbon when impurity yields are considered in the DAR (3).

B. Silicon Production

1. Introduction

A pre-start-up safety inspection of the Direct Arc Reactor (DAR) and its associated silica dust recovery system resulted in improvements for minimizing electrical hazards and atmospheric dust.

The DAR is similar to the schematic shown on p. 17 of Quarterly Report No. 2 (2). One main difference is that the Dow Corning reactor is larger than the one previously used at Elkem-Spigerverket A/S in Norway. The DAR has an inside diameter of 600 mm and has an electrical rating of 200 kVA. The electrical input to the furnace during a typical run is about 100 kW (2500 A at 40 V).

Another significant difference between the two reactors is that the Dow Corning reactor was designed with the proper reactance, thereby allowing for much easier control of the carbothermic reduction reaction. In fact, control is so much improved that we recommend retesting of high-temperature purified charcoal which was an unsuccessful reductant in the past.

2. Start-up Experiment

The purpose of the initial experiment was to check out the overall operation of the DAR system: transformer and associated electrical circuits, electrode positioner and hydraulic system reactor pot and water-cooling system, the reactor control center, and foremost the capability of reducing quartz with carbon. Start-up was successful with only minor problems being experienced.

Commercial raw materials were used in order to assure minimal problems during start-up. The percentage carbon and material balance of the various reductants are listed below. The average carbon content of the mixture was 90-% of stoichiometry. The 15-cm-diameter electrode was consumed at a rate of 0.8 cm/h. The quartz was a high-purity semiclear

Reductant	Carbon (%)	Stoichiometric Material Balance (kg/kg Quartz)
Coal	54	0.56
Coke	82	0.047
Wood Chips	20	0.30

variety from Arkansas that had been used in earlier experiments (4).

A 36-hour experiment (DAR-200-1) was carried out. The reactor was tapped once every two hours. Taps ranged from 2-12 kg each with the average being 6 kg. The average production rate of silicon during this period was 3.4 kg/h. One batch of silicon was tapped directly into a quartz crucible and produced a crack-free 10-cm-diameter x 65-cm ingot (11.8 kg).

The experiment terminated after 36 hours due to operator inexperience. Energy usage averaged 63.9 kWh/kg Si over the entire run. If this corrected for actual silicon production time, energy consumption was 22 kWh/kg, which is about correct for a small-scale reactor when compared to commercial units which use about 12-14 kWh/kg.

The silicon analyzed to be 98.4-% silicon, equivalent to commercial material.

Based upon the above results, reactor start-up was deemed to be very successful.

3. Baseline Experiments

A series of baseline experiments are being performed to establish normal operating conditions and parameters for the DAR. This information will then be used as the base from which to compare the results of tests on unique carbon reductants, as described in the Raw Materials section.

Baseline experiments are employing Arkansas quartz and unpurified charcoal in order to determine parameters such as correct SiO_2/C ratio, energy consumption, electrode diameter, raw material utilization rate, silicon production rate, etc. Design modifications are being made in the reactor interior with respect to its size and materials of construction. Design of the reactor tapping spout is also being improved upon.

Experiment DAR-200-2

The first baseline experiment was carried out with charcoal having 76-% fixed carbon. The average carbon content of the charge was 96 %

during the 30-h experiment. After a 5-h conditioning period, silicon was removed at a rate of 1.7 kg/h. A total of 42.6 kg of silicon was produced. The average energy consumption during silicon production was 34 kWh/kg Si. Electrode consumption was high at 1.8 cm/h.

The experiment was terminated prematurely due to difficulties in removing silicon from the reactor. An estimated 10 kg of silicon was found in the reactor hearth when it was excavated after cool down.

b. Experiment DAR-200-3

This experiment was run with the same charcoal and quartz using an improved silicon removal technique and a more optimized carbon content of the charge (91 %). After the reactor was conditioned for 6.5 h, silicon was produced for 41.5 h for a total run time of 48 h. The experiment was terminated as scheduled.

After reactor conditioning, 109.7 kg of silicon were produced at an average rate of 2.64 kg/h. Silicon was periodically removed in quantities ranging from 1-16 kg. The energy usage during this period was 28.1 kWh/kg Si. Electrode consumption was 1.1 cm/h.

Reactor operation was much easier using an electrode voltage in the range of 50-60 V as opposed to around 40 V in the previous experiment.

c. Silicon-Purification

Silicon produced in the DAR is purified by segregating impurities from the solid to liquid phase during unidirectional solidification. This process step reduces most impurities to a part-per-billion level or less (5).

Cost analyses in previous quarterly reports (3,6) indicated the need to develop a Czochralski-type process of unidirectional solidification capable of producing 20 to 30-cm ingots using a sequential or a continuous growth and melt replenishment technique. This need exists for two reasons. First, silicon purification is as much of a part of the overall Dow Corning Process as is silicon production. Second, Czochralski

technology in the semiconductor industry is capable of producing only 10-cm ingots commercially and 15-cm ingots experimentally; both with limited sequential melt replenishment. Therefore, if the Dow Corning Process is to succeed, the silicon purification step must be developed in addition to the silicon production step. Growth of ingots must be increased from the current diameters of 10-15 cm to required diameters of 20-30 cm.

Some required ingot growth technology is currently being developed by Hamco, Siltec, Texas Instruments, and Varian under JPL contract. Various techniques of melt replenishment are being investigated. However, all work is being done in currently available machines at diameters of about 12.5 cm, far below the requirements of the Dow Corning Process.

JPL has chosen to fund the silicon production and purification steps in series rather than in parallel. Therefore, work on the purification step will be limited to purifying silicon from the DAR using small-scale Czochralski machines in the laboratory. This purification will be performed on silicon from production experiments using purified carbon reductants.

III. CONCLUSIONS AND RECOMMENDATIONS

A program was developed to provide a carbon reductant capable of meeting the anticipated goals for boron and phosphorus impurity concentrations in silicon produced in the DAR.

Start-up of the DAR was very successful. The second baseline experiment ran for 48 hours, as scheduled, and produced 110 kg of silicon.

Further experiments are required to define the baseline operating conditions of the DAR in order to properly evaluate future reactions with purified reductants.

A development effort must be funded to develop high-capacity, low-cost purification of DAR-silicon via unidirectional solidification. Sequential or continuous melt replenishment processes in machines capable of pulling 20 to 30-cm-diameter ingots do not exist today, nor is there a

program directed at meeting this goal. The purification step must be developed in parallel with the silicon production step in order for the Dow Corning Process to meet the time goals of the LSSA project.

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2. Ibid., Quarterly Report No. 2, ERDA/JPL-954559-76/2.
3. Ibid., Quarterly Report No. 4, ERDA/JPL-954559-77/2.
4. Ibid., Quarterly Report No. 5, ERDA/JPL-954559-77/3.
5. Ibid., Quarterly Report No. 3, ERDA/JPL-954559-77/1.
6. Ibid., Quarterly Report No. 6, DOE/JPL-954559-78/4.

V. PROGRAM SCHEDULE

The program is proceeding according to schedule.

VI. PLANS

Future plans were presented in responses to statements of work on September 23, 1977 and on February 24, 1978.

VII. NEW TECHNOLOGY

No reportable items of new technology have been identified.

VIII. ACKNOWLEDGEMENT

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