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ELECTROMETALLURGY OF SILICON

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Abstract

Several industrial and government laboratories are of the opinion that solar–cell technology will grow into a billion–dollar industry by the year 2000, especially if oil prices rise again. Of the variety of materials that have been investigated as the major component of photovoltaic systems, silicon appears to have an outstanding advantage. The cost factor is the primary importance in photovoltaic development, since the technology to make silicon cells of acceptable efficiency and life time has existed since the early stage of the space program. Electrometallurgy is one of the low–cost processes for the production of silicon, since it allows direct, single–stage production from some abundant, inexpensive source materials such as silica and fluorosilicates. Among several systems, two are given particular attention, using inorganic baths with SiO_2 or K_2SiF_6 as the source of silicon respectively. They appear capable of development to commercial production. Conceptual designs of a commercial–scale cell for silicon production at temperatures above its melting point, and of a pilot plant for plating silicon from an all–fluoride bath are presented.

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Energy Prospects

The major changes in the world energy since the first energy crisis in 1970 have impacted on our community. When oil was $40 a barrel in the mid–1970s, we became obsessed with the energy conservation and a search for alternate energies. Even though the crude oil fell below $15 a barrel during the last several years, our energy security fears continue to haunt us. This time it is not the scarcity, but the abundance of foreign oil and the decline in the domestic production.

The prospects of energy depends on the demand and supply of energy. These, in turn, depend on future energy prices, which are linked to economic factors, political events, and unforeseen circumstances. Although no one can predict the future with certainty, three energy consumption patterns used by the Ford Foundation are as shown in Fig. 1.

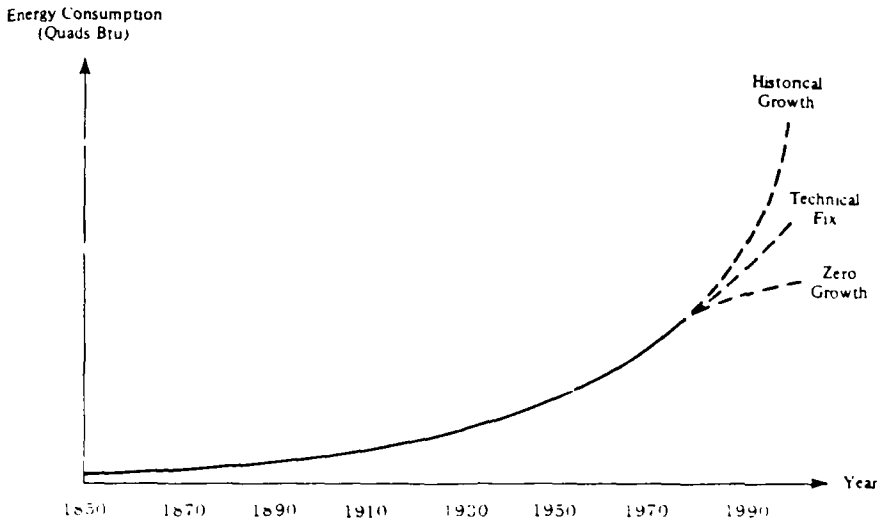

Figure 1 – Patterns of energy consumption.

The first forecast is based on a continuation of a historical exponential growth rate of energy consumption. The second forecast is based on a concerted national effort to use energy more efficiently by introducing energy–conserving technology (technological fix). The final forecast is a tapering off of the rate of increase of energy consumption until zero growth is reached in about the year 2000.

According to a recent report, Energy 2000 (1), the consumption of all forms of energy should increase by about 2% by now and the year 2000 except the oil. Then, the most likely scenario would be technological fix pattern. However, sustained current low oil prices, combined with higher rates of world economic growth than assumed 3% (1) and current low priority to improve the efficiency of energy in industry, building and transportation (2), would certainly favor the historical growth pattern.

The United States is currently importing about 38% of its total oil supply and the figure threatens to pass 50% by the mid–1990s. Furthermore, identified United States reserves are estimated to last only 12 years at current production levels. Coal, in abundant supply over 100 years, is currently accepted as an alternative energy of the future. However, the numerous environmentai problems involved in the mining, transportation, and burning of coal will impose stringent standard on its utilization. While nuclear power, once regarded as the "ultimate" energy solution, is presumably besieged with a bewildering array of problems that considerably endangers its future prospects. Growing doubts over nuclear safety have recently been reinforced by the accident at the Three Mile Island plant in the United States and the Soviet catastrophe at Chernobyl. Radioactive waste disposal is proving to be much more difficult than was indicated by earlier, optimistic pronouncements.

It is very important to note that reserves of our principal energy resources, the fossil fuel (oil, coal and natural gas) and uranium are finite and essentially non–renewable. By far, the world's most important inexhaustible source, however, is solar energy, which can be harnessed both in the direct form of sunlight or in more indirect forms as the energy stored in the wind, plants, and water impounded in elevated reservoirs. Photovoltaic or solar cells, which convert sunlight directly to electricity, belongs tc the former group. The most significant barrier to widespread utilization is the high cost of the fabrication of these devices. However, manufacturing cost reduction similar to those already achieved in related electronic industries could make solar cell economical for an expanding range of applications; a detailed study concerning the economic issues and the economic feasibility was given by Walton and Warren, Jr. (3). It is not clear how much of our future energy needs will be supplied by solar energy. A speculative guess would be about 15% to 33% of the total primary energy use by the year 2000 depending on the commitment made both to improving energy efficiency and the deploying solar technologies. Interestingly, several industrial and government laboratories are of the opinion that solar–cell technology will grow into a billion–dollar industry by the year 2000, especially if oil prices rise again.

Silicon as the Solar Material

Of the variety of materials that have been investigated as the major component of photovoltaic systems, silicon appears to have the outstanding advantages. Although its bandgap and absorbing properties are not ideal, its availability, technological development, low toxicity, and relative ease of fabrication make it the leading contender to satisfy the needs of the solar cell industry in the next decades. Currently, commercially available silicon photovoltaic cells operate at approximately 10–16% sunlight to electricity conversion efficiency. Although, the theoretical efficiency limit is 25% for a single silicon semiconductor device operating at room temperature, the most efficient silicon device yet produced, the point–contact photovoltaic cell, a system of concentrating solar collector lens in conjunction with photovoltaic cell, has achieved an unprecedented 28.2% efficiency. Moreover, an efficiency of 31% was recorded for a new photovoltaic multijunction solar cell which consisted of stacked layers of silicon and gallium arsenide.

It is important to note that semiconductor grade silicon is too expensive if solar cell costs are to be reduced to the level where they are acceptable for domestic or utility applications. Elwell and Feigelson (4) gave an account on the various competing processes for the production of low cost silicon. One of the promising processes is electrometallurgy since it allows direct, single–stage production of silicon from some inexpensive source materials.

Source Materials

Silicon is the Earth's second most abundant element. It occurs primarily in the form of silicate rocks but the most important source mineral for silicon production is its oxide. SiO_2, which is the main constituent of sand. Silica occurs extensively as quartzite, a rocky crystalline variety with typically less than 1% of metallic impurities (Al, Fe, Ti) and often occurring in very high purity. These materials have been used in processes aimed at producing "solar grade" silicon (SGSi) with a purity substantially higher than that of the metallurgical grade (MGSi). The relatively pure lump sources cost around $\$0.50kg^{-1}$ while the less pure Illinois material costs around $\$0.10kg^{-1}$ in bulk.

Another important source of silicon is fluorosilicic acid which is a by–product of phosphate fertilizer production. Silicates occur together with phosphates in the rocks from which the fertilizer is extracted, and the extraction process yields fluorosilicic acid of 98–99% purity and at low cost. The silicon costs less than $\$1\ kg^{-1}$. The acid may be neutralized to form the sodium or potassium salt:

$$H_2SiF_6 + 2KOH \rightarrow K_2SiF_6 + 2H_2O$$

or the dilute acid is reacted with NaF to give hydrofluoric acid as a by–product:

$$H_2SiF_6 + 2NaF \rightarrow Na_2SiF_6 + 2HF$$

Another potential source of silicon which has not been exploited commercially is rice hulls. It is the silica particles in the rice hulls which gives them their stiffness, and United States production alone could yield 100,000 tons of silicon annually if an extraction process could be developed. The hulls can be bought for about $\$0.20kg^{-1}$ and the metallic impurities are comparable with those in a high purity mineral silica. Carbon is, of course, a major constituent and the C:Si ratio in rice hulls is about 4:1.

Processes for the Year 2000 and Beyond

Shortly after the invention of the first battery, the Volta piles, electrolysis was used to produce light metals and it is not surprising that attempts to electrodeposit silicon date back to the mid–19th century. The first attempt on record is that of St. Claire DeVille, who claimed that silicon was produced by electrolysing an impure melt of $NaAlCl_4$, but his material did not oxidize at white heat (for example, see reference (4)). Progress in silicon electrodeposition and the possible applications of electrolytic silicon have been reviewed by a number of authors. Elwell (5) and Fulop and Taylor (6) surveyed the whole field of electrodeposition of semiconductors. Elwell and Feigelson (4) discussed the possible application of electrolysis to produce SGSi, while Rao and Elwell (7,8) considered the prospects for economic electrowinning of silicon for more general applications and for a possible role in industry for the electrolytic production of silicon. A general review of silicon electrowinning and refining was given by Monnier (9) with particular emphasis on the SiO_2/cryolite system. Among several systems, silica–based electrolytes and fluorosilicate–based electrolytes appear capable of development to commercial production.

Silica–based Electrolyte

Since SiO_2 melts at temperatures above 1700°C, a binary or ternary melt composition is required for deposition at about 1450°C and the simplest choice appears to be an alkali– or alkaline earth–silicate system. Electrolysis of molten silicates may produce silicon, silicon monoxide or the metal as the cathodic product. The respective reactions may be represented schematically by the equations:

$$3MSiO_3 \leftrightharpoons 3MO + Si + 2SiO_2 + O_2$$

$$4MSiO_3 \leftrightharpoons 4\,MO + 2SiO + 2SiO_2 + O_2$$

$$2MSiO_3 \leftrightharpoons 2M + 2SiO_2 + O_2$$

Thermodynamic data is in general not available for calculations of the likely reactions in systems of interest. Poris and Huggins (10) made some theoretical calculations. They found that Ca and Mg silicates appeared particularly favorable for Si deposition; Li silicate less promising; while K and Na silicates should yield the alkali metal on electrolysis. It was confirmed experimentally that potassium was liberated on electrolysis of K_2O/SiO_2 melts at 1450°C. Electrolysis of Li silicate melts gave silicon, but not at temperatures above its melting point. Mg and Ca silicates did not yield silicon, and the best results were obtained using the BaO/SiO_2 eutectic (11). BaF_2 was added to facilitate the reaction between $BaCO_3$ and SiO_2 to form the melt, and to lower the melt viscosity. Silicon was also deposited by electrolysis of baths in the $SrO/SiO_2/SrF_2$ system.

The BaO/SiO_2 system has a single eutectic of composition 53% SiO_2/47% BaO by weight and melting at 1370°C. About 15% of BaF_2 was added to this composition and purified melts were electrolysed at about 1450°C in graphite crucible and using graphite electrodes. Applied potentials were normally in the range 1–8 V with currents of 0.1–2.0 A on an immersed area of about 2 cm^2. Silicon has a lower density than the bath, and the molten Si deposits floated around the cathode and gathered into roughly spherical drops, in a horizontal layer near the surface. The largest lump obtained by cooling a melt and dissolving the solidified silicate weighed over 1.6g and contained over 1/3 of the total silicon deposited from a 125g bath. The Faradaic efficiency of deposition was typically 20%, although values as high as 40% were observed. The efficiency tended to decrease with applied potential difference, possibly because of increasing liberation of SiO. This correlation was not firmly established, however, and the SiO could have been evolved because of a slow reaction between the electrodeposited silicon and the silicate bath. Clearly an efficiency in the range 20–40% would not be acceptable for a commercial process but the main limitation could be associated with the small size of the apparatus used. A reverse reaction between anodic and cathodic products is to be expected in a small system, and is known to be significant in Hall–Heroult systems when the anode–cathode separation is less than about 2 cm.

The purity of Si electrowon from the barium silicate melts was about 99.98% by weight, the main impurities being 60 p.p.m. of Ti and 20 p.p.m. each of Al and Fe. Silicon of this purity is close to the quality required to produce 10% efficient solar cells by a single stage of directional solidification. The major impurities originate in the SiO_2 and can be reduced by purification of the silica in HCl gas at about 800°C, or by the use of a purer starting material. The SiO_2 used in this investigation was Illinois Mineral material of 99.5–99.8% purity.

Since electrolytically produced silicon is of lower density than the bath, a modified magnesium (12) or Down's cell for sodium (13) might be suitable. A possible design for a commercial cell for silicon electro–deposition is given in Fig. 2.

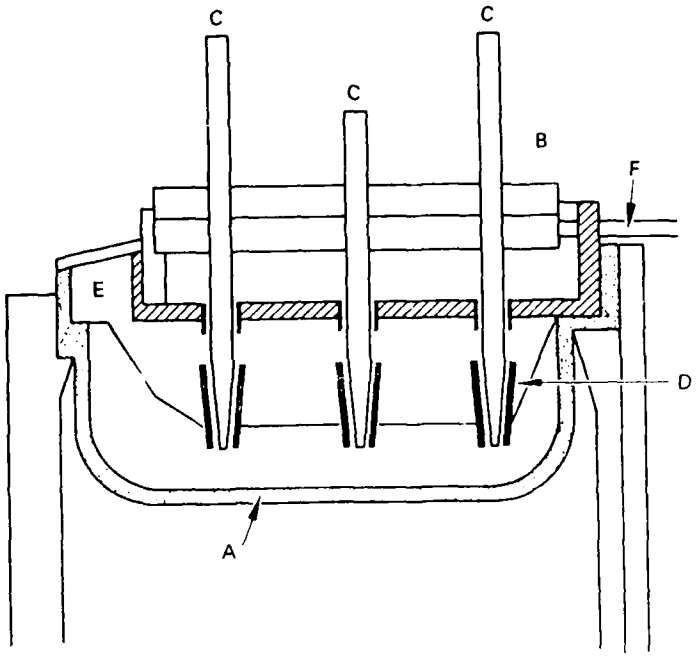

Figure 2 – Schematic of a commercial scale cell for depositing silicon above its melting point, adapted from (12). The steel container (A) is fitted with a ceramic cover (B) through which pass the graphite anodes (C). The silicon is deposited on the cathodes (D) and rises into a collection area (E). Gaseous anodic products are withdrawn through a vent (F).

The cell is of steel construction with the cathode supports welded to the tub–like container that holds the melt. These are fitted with refractory covers, which act as ports for the graphite anodes, metal suction system and solute feed. The anodes are suspended in a manner that permits them to be adjusted independently as the graphite is consumed during electrolysis, to maintain the proper spacing and centering with respect to the cathode. The outside area of the steel container is surrounded by a refractory chamber with arrangements for gas or electric heating. This allows flexibility in adjusting to various electrical loads, especially as the cells are restarted after a complete shutdown. Since a similar system, oxide/cryolite, is used in aluminum electrolysis the cell construction materials used in aluminum cells are generally an appropriate choice. There is, however, the requirement that any materials used must be stable and inert up to 1500°C. Without a protective coat on the steel cathode support, the initial product deposited at the cathode is likely to be iron silicide. If this silicide formation ceased on continued electrolysis, steel would be an inexpensive choice for the silicon production. Otherwise, a suitable coating material on the steel would certainly be required. This coat would also have the role of minimizing the iron contamination of the silicon. Our laboratory experiments (11) suggest graphite as a suitable coating material and inner liner for the steel container.

Alternatively TiB_2, TiC or TiB_2–TiC mixtures, which have been successfully tested in aluminum pilot scale cells (14,15), could be tried as possible coating materials. Although consumable graphite anodes are the initial choice, the inert anodes in development for aluminum cells (15) should also be tested in this system. The silicon produced at the cathode rises into the collection chamber in front of the cell. Molten silicon can be periodically pumped out and cast into ingots. Alternatively, the silicon could be pulled directly from the collection chamber as relatively pure boules because of the additional purification inherent in controlled solidification. Although not shown in Fig. 2, it is desirable to use a diaphragm either to separate the anode and cathode or to act as a hood surrounding the upper region of the anode but immersed 2–3 cm into the melt. The purpose of this arrangement is to minimize the back reaction. To maintain the heat balance in the cell and to control the mass balance in the bath, the cells should be fed semicontinuously through a screw–type feeder, not shown in Fig. 2.

An inert gas atmosphere is required to protect the graphite and to prevent oxidation of the floating silicon. This requirement would add to construction and operating costs but the argon would be recirculated after passing through scrubbers to remove fluoride traces.

The cost of power is an important factor affecting the commercial viability of a silicon plant. Commercial plants could be designed in which most or all of the heat required to maintain the bath at about 1450°C would originate from Joule heating by the deposition current. In a plant with a current 10^5 A at 6 V, a Joule component of 20% would provide 150 kW of "waste" heat which should be ample to compensate for heat losses from a well–insulated container. Plants used for aluminum production normally require active (i.e. forced) cooling. In general, the cost of silicon produced by this method should be comparable with that of aluminum from the Hall–Heroult process.

Fluorosilicate–based Electrolytes

Fluorosilicates as source materials have been investigated intensively but their continued availability as an inexpensive source is dependent on the fertilizer industry. The commercial production of silicon using a fluorosilicate–fluoride system is analogous to the molten salt process for titanium. The latter process was tested successfully on a pilot plant scale (16,17) but did not proceed to full–scale development due to market conditions rather than to any technical problems, at least for the Dow–Howmet cell. It is therefore clear that silicon produced from an analogous system would be attractive to industry only if the product had some special application. Film deposits have shown promise for direct application in low–cost solar cell fabrication and as a corrosion protection coating (7,18), especially at elevated temperatures. Also, electrolytically produced silicon of 4N(99.99%) purity or better (as layer, dendrite, sponge or powder) has the potential to replace MGSi, which needs further purification, as a charge for directional solidification or distillation as a volatile species (e.g. trichlorosilane or tribromosilane) to produce electronic grade silicon.

The deposition of silicon films using K_2SiF_6 began at the Stanford University Center for Materials Research in the early seventies. Although several fluoride solvent systems were studied, only LiF–KF and LiF–KF–NaF melts gave acceptable quality deposits. In early work, cohen (19) showed that single crystal epitaxial layers could be electrodeposited from solutions of K_2SiF_6 in a LiF–KF eutectic and that continuous films could be produced by electrorefining using a dissolving silicon anode. Later work shifted to electrowinning of silicon using an inexpensive graphite anode. The ternary LiF–KF–NaF eutectic or the binary LiF–KF eutectic at 750°C were used as solvents and had the advantage of a high solubility for K_2SiF_6. In the earlier experiments (18,20) silver was chosen as cathode material because of easy nucleation of silicon. Relatively inexpensive graphite substrates, including low grade porous material, were used in later experiments (21,22). Since a low K_2SiF_6 concentration

normally resulted in a non–uniform powdery or dendritic deposit on top of a thin, coherent layer about 2 μm thick (20), the K_2SiF_6 concentration was maintained between 4–20 m/o to grow thicker, continuous silicon deposits. The silicon was electrodeposited at a constant current (10–25 $mAcm^{-2}$) or at a constant potential (–0.74 ± 0.04 V against Pt) for 2–4 days. Well–adherent, coherent and continuous films up to 3–4 mm in thickness were prepared in this study. Growth was columnar with a normal grain size up to 250 μm. The current efficiency for silicon deposition was as high as 80%. The purity of electrodeposited silicon was normally 4N, but the level of impurities in the best samples was less than 10 p.p.m. Undoped samples were normally *n*–type with resistivity up to 3 Ωcm, carrier mobility 100 $cm^2V^{-1}s^{-1}$ and carrier concentration 10^{17} cm^{-3} (23).

Other recently published studies (24–27) on this system have added additional complementary information. Olson and Carleton (24) used a silicon–copper anode to simulate the electrorefining of the metallurgical grade silicon, while Sharma and Mukerjee (26) demonstrated the semi–continuous production of 99.99% pure silicon powder from impure (2.5% impurity) MGSi. Bouteillon *et al.* (25,27) showed that improvements in deposit morphology and the purity of the silicon (impurity levels less than 1 p.p.m.), both during electrowinning and electrorefining, could be achieved by pulsed electrolysis, which is currently practiced in commercial copper electrolytic cells.

The quality, purity and electronic properties of electrolytically produced silicon from the fluorosilicate–fluoride system show promise for commercial applications. However, all the experiments to date have been done on a small laboratory scale. Future study should include pilot plant investigations aimed at solving electrochemical engineering problems. A pilot scale design is shown in Fig. 3, which is adapted from the pilot scale cell for titanium electrowinning developed by NL Industries (17). Both Si and Ti processes involve a molten salt medium and require

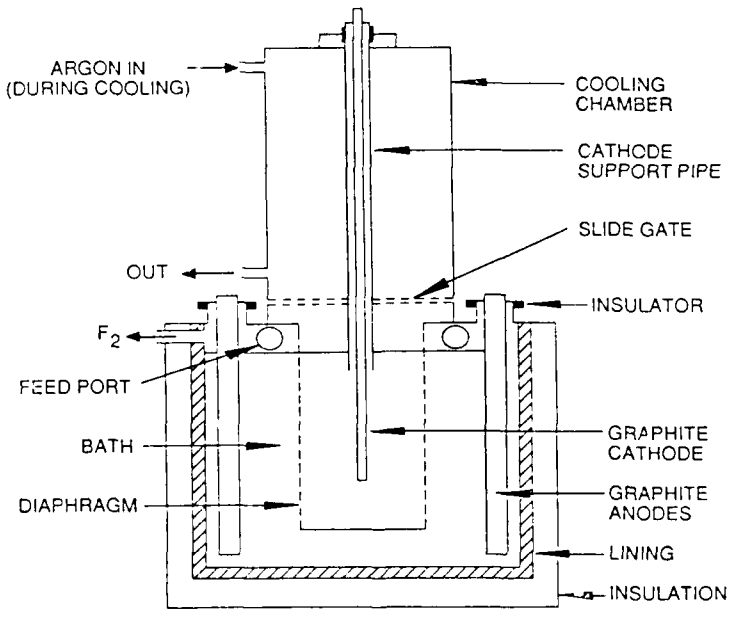

Figure 3 – Design for a pilot cell for electrodeposition of silicon from a fluorosilicate–fluoride bath (adapted from (17)).

four electrons for the reduction from M^{4+} to M, although the actual steps are more complex (27,28). The capital cost, the use of refractory metals and other working conditions are also comparable. The initial choice of electrode materials would be graphite. If it is economically possible, graphite– or silver–coated steel could replace graphite cathodes. The inert electrodes discussed in the preceding section and the new diaphragm materials must be tested thoroughly prior to use even in pilot production cells.

Conclusions

It is obvious that the current low oil prices and the abundance of foreign oil supply, and other fossil fuels may not last forever. Depending on the demand and supply, environmental restrictions, and safety constraints, the cost of energy production will eventually increase. The long term solution, therefore, is to make a commitment now to develop technologies based on the energy from renewable sources such as solar energy to avoid the long gasoline lines and energy shortage by the year 2000. An important requirement of the solar cell development has been to produce a material of acceptable quality and cost.

The availability, low toxicity and high degree of technological development make silicon the most likely material to be used in terrestrial solar cells. Silicon dioxide, SiO_2, occurs in nature as pure deposits which can be mined inexpensively. Although carbothermic reduction is well established as a practical method of producing silicon of metallurgical grade, electrometallurgy offers a viable alternative of producing silicon of significantly higher purity at a cost comparable with that of aluminum. The relative absence of carbon in electrodeposited silicon should offer advantages for some high–grade metallurgical applications, and the electrodeposited silicon should be an attractive starting material for solar applications or as a feed material for the production of semiconductor or detector grade silicon.

The rate of production of silicon as a solid may be too low for commercial viability, and materials such as Na, Mg and Al in the same row of the periodic table are all commercially produced at temperatures above their respective melting points. Designs have been presented for a plant for production of silicon as a liquid, by electrolysis of a barium silicate–fluoride bath. Its rather high melting point of 1412°C is clearly a disadvantage but should not be an impossible hurdle and is, for example, much lower than that of iron. The yield of silicon needs to be improved over that obtained in small–scale laboratory studies but an improvement is to be expected on scale–up. This challenge and that of developing a method for efficient collection of the electrolytically–produced silicon are reasonable and should not require a very high investment.

The alternative of using an all–fluoride bath, with K_2SiF_6 as the source of silicon, may also find a commercial role. The purity and morphology of the deposits from laboratory scale experiments show promise for the direct fabrication of solar cells. The most promising application of this technology is in producing hard, chemically stable coatings on metal surfaces. Also, silicon dendrites, sponge and powder of 4N purity could replace MGSi as the charge to produce higher purity silicon by directional solidification.

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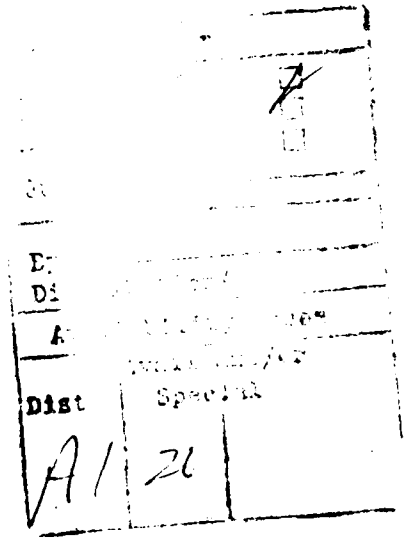

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Several industrial and government laboratories are of the opinion that solar-cell technology will grow into a billion-dollar industry by the year 2000, expecially if oil prices rise again. Of the variety of materials that have been investigated as the major component of photovoltaic systems, silicon appears to have an outstanding advantage. The cost factor is the primary importance in photovoltaic development, since the technology to make silicon cells of acceptable efficiency and life time has existed since the early stage of the space program. Electrometallurgy is one of the low-cost processes for the production of silicon, since it allows direct, single-stage production from some abundant, inexpensive source materials such as silica and fluorosilicates. Among several systems, two are given particular attention, using inorganic baths with SiO_2 or K_2SiF_6 as the source of silicon respectively. They appear capable of development to commercial production. Conceptual designs of a commercial-scale cell for silicon production at temperatures above its melting point, and of a pilot plant for plating silicon from an all-fluoride bath are present.

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