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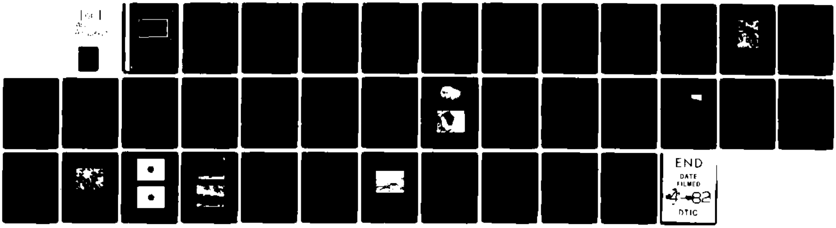

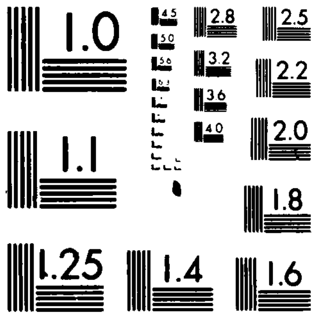

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Final Technical Report

on

PREPARATION AND CHARACTERISTICS OF SINGLE CRYSTALS AND EPITAXIAL LAYERS OF SILICON CARBIDE BY MOLTEN SALT ELECTROLYSIS

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Thin layers of SiC were electrodeposited from Li_2CO_3/SiO_2 melts onto α-SiC substrates at 1000° - 1050°C using potential differences around -0.5V versus polycrystalline SiC anodes. The layers appear to be epitaxial. Although conditions were found under which the melt exhibited good long term stability, attempts to grow bulk SiC crystals were handicapped by delamination of the seed crystals. Attempts to electrodeposit SiC from $K_2SiF_6/Li_2CO_3/LiF/KF$ and $SiO_2/Na_2CO_3/NaBO_2/LiF$ melts yielded botryoidal deposits containing excess carbon.

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TABLE OF CONTENTS

Page

I. INTRODUCTION

Silicon carbide is a material of great interest and potential importance for semiconducting devices which can tolerate high temperatures and radiation levels. It is currently grown by a vapor transport method in few laboratories but severe problems are normally encountered in preparing reproducibly crystals of adequate size and purity for device applications.

The aim of this investigation was to develop a process for the production of layers and bulk crystals by electrolysis of molten salts. Ideally the process should produce the cubic β-phase since it takes place at temperatures much lower than those normally used to grow SiC.

II. PRINCIPLES OF MOLTEN SALT ELECTROCRYSTALLIZATION OF SiC

The electrodeposition of SiC requires the simultaneous cathodic deposition of silicon and carbon under conditions where reaction to form SiC will occur. In this study sodium or lithium carbonate have been preferred as the source of carbon by the overall reaction

$$Li_2CO_3 \rightarrow Li_2O + C \text{ (cathode)} + O_2 \text{ (anode)} \qquad 1\text{ (a)}$$

and SiO_2 or K_2SiF_6 have been used to give silicon, e.g. by the reaction

$$K_2SiF_6 \rightarrow 2KF + Si \text{ (cathode)} + 2F_2 \text{ (anode)} \qquad 1\text{ (b)}$$

The actual cathodic reaction involves electron transfer prior to the combination of Si and C to form silicon carbide:

$$CO_3^{2-} + 4e \rightarrow C + 3O^{2-} \qquad 2\text{ (a)}$$

$$SiF_6^{2-} + 4e \rightarrow Si + 6F^- \qquad 2\text{ (b)}$$

$$Si + C \rightarrow SiC \qquad 2\text{ (c)}$$

An ideal system for electrodeposition is one in which the carbonate and fluorosilicate (or SiO_2) are present in high concentration. The viscosity of the melt should be low, and the melt components should all be stable at the deposition temperature so that the composition does not change appreciably during deposition. Alkali metal salts are normally preferred since deposition potentials for crystallization of the metal are relatively high.

A literature survey of the crystal growth of SiC from solution showed that temperatures below 1400°C are rarely used, although vapor growth has been achieved at approximately 1050°C. The maximum temperature for electrodeposition of SiC is determined primarily by the stability of the carbonate, which has been studied as an important factor in this investigation. A maximum temperature of 1200°C has been employed to date, the minimum temperature being 750°C since the formation of well-crystallized SiC is unlikely at lower temperatures.

III. APPARATUS

The electrodeposition of SiC has been carried out in a variety of apparatus, some of which was described in our previous reports. Of particular interest is a new furnace design which permits more reliable operation at relatively high temperatures (up to 1200° in this study, but with a 1500° capability). This type of furnace was developed with support from this contract and from the Department of Energy; two furnaces were built, one being used in this program, the other for electrodeposition of silicon at temperatures above its melting point.

Figure 1 shows a diagram of the completed furnace. The heating element is made of graphite with dimensions of 11.4 cm OD and 11.1 cm high with a wall thickness of 0.95 cm. The element is slotted so that it acts as two parallel folded linear elements of length 66 cm, width 2.5 cm, and depth 0.95 cm. The element is supported on two "D" shaped graphite supports which are sections of a circle 16.5 cm in diameter. These supports, which have an overall height of 6.7 cm, have a wall thickness of 1.4 cm and have the major part of their vertical walls removed to lessen heat transfer and to allow access to the mounting bolts. The supports also act as heat shields to reduce radiation to the bottom plate and are grooved on their top surface to hold a ceramic ring which insulates the two graphite heat shields. The element supports are attached to two water-cooled power feedthroughs made from copper 3.8 cm in maximum diameter and of 1.3 cm diameter where they are attached to the element support. The power feedthroughs are insulated from the bottom plate by Teflon spacers and sealed by Viton O-rings. The two graphite heat shields are 0.48 cm thick. The inner shield is 13.3 cm OD and 12.1 cm high while the other one is 16.5 cm OD and 14 cm high with a 7.6 cm opening in the top. The outer heat shield is of fused silica (22.9 cm

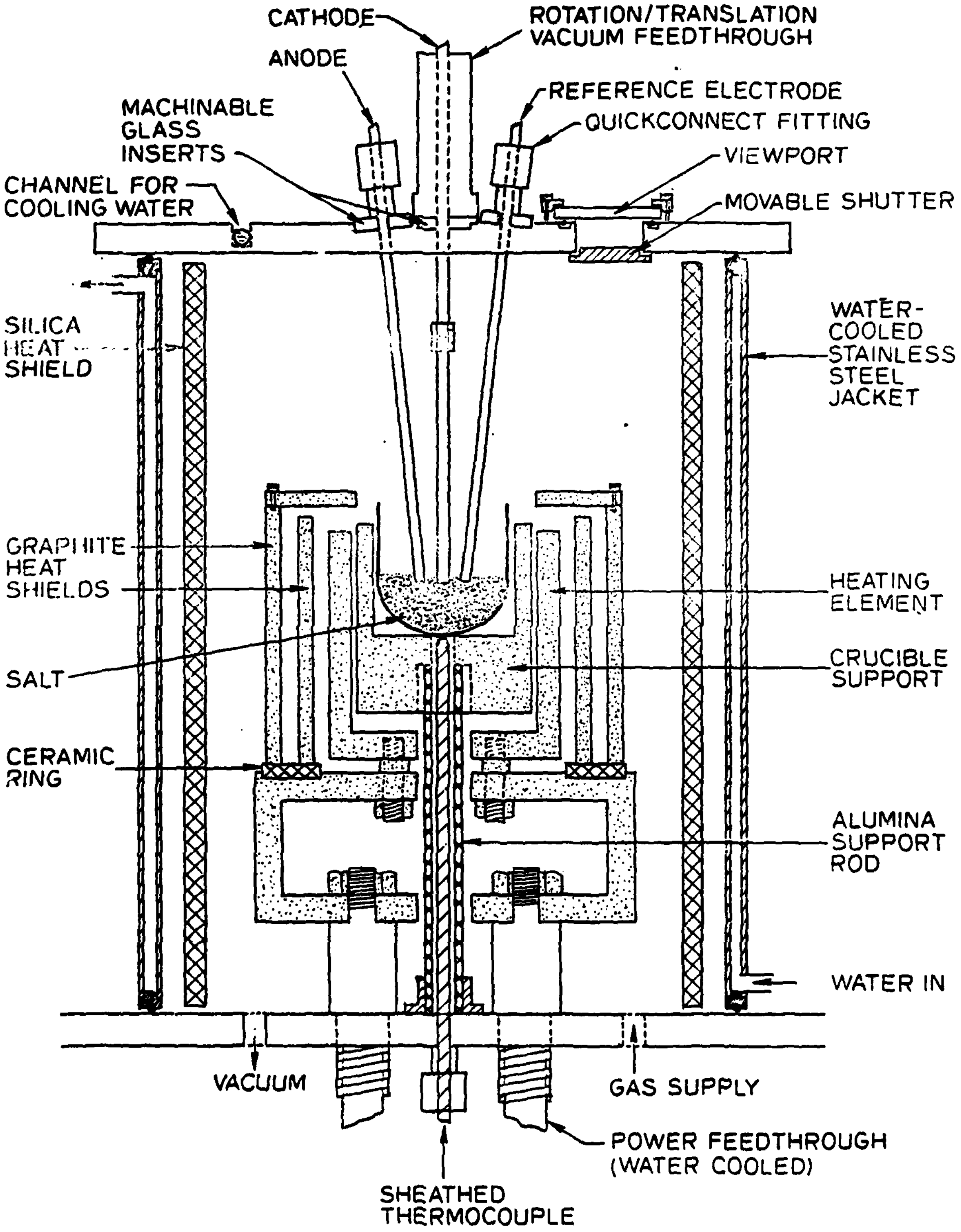

Fig. 1. Furnace used for electrodeposition of SiC from Li_2Co_3/SiO_2 (diagrammatic).

diameter, 34.9 cm high, and 0.4 cm thick) and is surrounded by a water-cooled stainless steel jacket (26.2 cm ID, 27.9 cm OD, 35.2 cm high).

The crucible is held in a graphite crucible holder which is supported by an alumina tube 1.9 cm in diameter and 17.1 cm high. The holder has an axial hole to allow a thermocouple to contact the bottom of the crucible. This thermocouple is used for both measurement and control of temperature.

The whole furnace assembly rests on a 1.3 cm thick, 32.4 cm diameter brass plate. This plate has fittings for the thermocouple and for vacuum and gas (usually argon) connections. Water cooling is provided by copper tubing (0.64 cm OD) soldered into grooves machined in the plate. This method of cooling was chosen over internally machined water channels because of its simplicity and ease of execution. The entire plate is nickel plated for corrosion resistance. The furnace is closed by a 1.9cm thick brass plate. The plate is machined to accept three electrodes. The center electrode (cathode) passes through a rotary vacuum feedthrough (Varian), the other two electrodes pass through Quick Connect fittings. The outer electrodes are inclined at 6° to the vertical by machining a recess in the top plate. All three electrode fittings are mounted on Corning machinable glass inserts to provide electrical insulation. The machinable glass is sealed to the metal using epoxy which appears to have a good lifetime if the fittings are individually cooled. A 5 cm diameter sapphire window sealed by O-rings provides a view of the interior of the apparatus. This window is protected from condensation and fogging by a movable shutter controlled through a Quick Connect fitting. This plate is cooled in the same manner as the bottom plate. Vacuum sealing of the system is provided by O-rings carried in groves at the top and bottom of the outer jacket.

The system is evacuated by a rotary vacuum pump which is capable of bringing the manifold vacuum down to 20 μm of mercury. The furnace is normally evacuated, then a flow of argon gas introduced during deposition. The two-way valve connecting the chamber to the pump or inert gas supply is bypassed by a 1 psi relief valve to prevent excessive pressure buildup in the furnace. The argon is admitted through a needle valve and its rate of flow is monitored by a flowmeter.

A transformer was wound to provide 20 volts AC at 1000 amps from a 208 volt supply. The output of this transformer is carried to the furnace on leads consisting of two lengths each of 6 cm wide x 0.5 cm thick copper braid. The input to the transformer is controlled by a Eurotherm type 962 phase-fired SCR unit with a capacity of 120 amps at 240 volts. This unit is controlled by a Eurotherm 919 digital temperature controller. The sensing element is a Pt-30% Rh. Pt-6% Rh thermocouple and a digital temperature display is also provided. A flow switch is used to shut down the power if the cooling water flow falls below 1.5 gallons/minute.

IV. EXPERIMENTAL DATA

A. Choice of Melt System

The problem of choosing a suitable system for electrodeposition of SiC proved much more difficult that had been anticipated. Thermodynamic analysis (1) indicates that carbon is the most likely product of electrolysis of lithium carbonate solutions at lower temperatures, with CO evolution predominating above ∿1200K. The same analysis predicted that CO or CO_2 would be produced on electrolysis of Na_2CO_3. Lithium carbonate therefore appeared the most promising source of cathodic carbon. Extensive studies in our laboratory had shown that silicon could be electrodeposited from either SiO_2 or K_2SiF_6, and the major problem forseen was that of adjusting the composition of a melt to give SiC without excess C or Si. The systems investigated are described below.

1. $K_2SiF_6/Li_2CO_3/LiF/KF$

This system was initially considered of particular promise since silicon had been deposited as epitaxial layers from K_2SiF_6/LiF/KF solutions, and it was confirmed experimentally that carbon can be readily deposited from Li_2CO_3 alone or with addition of the LiF/KF eutectic at temperatures of 700° - 800° C. It was found possible to deposit SiC from solutions containing about 5 m/o K_2SiF_6 and 20 m/o Li_2CO_3 at 750°C, with deposition potentials in excess of -1.6V (versus platinum) and current densities of about 30 mA cm^{-2}. Lowering the current density in attempts to improve the morphology normally led to the complete absence of any deposit.

Melts containing less than 10 m/o of Li_2CO_3 with 5 m/o K_2SiF_6 gave silicon on electrolysis. The SiC deposited from a Li_2CO_3 concentration of 20 m/o were always contaminated with excess carbon. Melts containing 30 m/o Li_2CO_3 yielded graphite only even when the K_2SiF_6 concentration was increased to 10 m/o. In the critical composition range for SiC formation, the phase(s) deposited were sensitive to the choice of deposition potential. An additional disadvantage was that the morphology of the SiC was very poor, mainly irregular nodules rather than clearly crystalline material.

2. $\underline{SiO_2/Na_2CO_3/NaBO_2/LiF}$

The use of borate/carbonate melts for the preparation of refractory carbides was introduced by Weiss (2) who was able to prepare carbides of iron, molybdenum, and tungsten by adding Fe_2O_3, MoO_3, or WO_3 to melts containing Na_2CO_3 and $NaBO_2$, with LiF added to lower the viscosity. In our work similar compositions were used with SiO_2 replacing the above oxides.

The ratio of Na_2CO_3 to SiO_2 chosen on the basis of Weiss' work was 4.2 to 1. It was confirmed that SiC could be electrodeposited from this system. The deposits contained excess carbon which was determined quantitatively by oxidation in air at 700°C, at which temperature the carbon is completely removed as CO_2 while the SiC is stable against oxidation. The ratio of Na_2CO_3 to SiO_2 was lowered systematically to 0.53 but the concentration of excess graphite was found to be remarkably insensitive to the carbonate to silica ratio in the melt (see Table I). As in the case of the K_2SiF_6/Li_2CO_3 melt, the morphology of the deposit (see Fig. 2) and its crystallinity (as determined by x-ray powder photography of the deposited material) were generally poor.

3. $\underline{SiO_2/Na_2B_4O_7/KF/NaF}$

A similar system to that described above has been used successfully to deposit tantalum and niobium carbides, using $Na_2B_7O_7$ in place of $NaBO_2$ and KF/NaF in place of LiF. This was investigated to see whether improved results could be obtained compared with those summarized in Table I. Typical compositions investigated were from about 18.5 m/o $Na_2B_4O_7$; 18.5 m/oNa_2CO_3; 27 m/o KF; 27 m/o NaF; 9 m/o SiO_2 and 10 m/o $Na_2B_4O_7$, 20 m/o Na_2CO_3: 30 m/o KF; 30 m/o NaF; 10% SO_2. Further variation was also made in the SiO_2 to Na_2CO_3 ratio.

In no case was SiC successfuly deposited. The initial deposits appeared to be a silicon boride, but increasing the Na_2CO_3 concentration by a factor up to 4 led to a whiskery deposit, mainly carbon but with minor

Fig. 2. Scanning electron micrograph of deposit from $SiO_2/Na_2CO_3/NaBO_2/LiF$ melt (485X).

TABLE I. DEPOSITIONS FROM $SiO_2/Na_2CO_3/NaBO_2/LiF$ SYSTEM

	Melt Composition (m/o)				Ratio Na_2CO_3: SiO_2	Deposit Potential V_d (V)	Deposit
	$NaBO_2$	LiF	Na_2CO_3	SiO_2			
(1)	13.8	70.3	12.9	3.1	4.1	.75	Cohesive, poor morphology; 55% excess carbon
(2)	14.6	74.8	7.3	3.3	2.2	.50	Less cohesive than (1) poor morphology; 50% excess carbon
(3)	14.9	75.5	4.4	5.2	.85	1.21	Smooth, flaky, poorly cohesive; low efficiency; 48% excess carbon
(4)	15.1	76.7	2.8	5.3	.53	1.4	Powdery deposit, poor crystallinity 50% excess carbon
(5)	13.5	76.2	6.7	3.5	1.9	1.1	Li_2SiO_3; no SiC.

quantities of other unidentified phases.

When an intermediate Na_2CO_3 to SiO_2 ratio was used, a small powdery deposit was obtained which could not be positively identified.

4. SiO_2/Li_2CO_3

The binary system SiO_2/Li_2CO_3 has the advantages of simplicity and that the elements to be deposited are present in high concentration. Lithium carbonate melts at 723°C and, according to the Handbook of Chemistry and Physics (CRC Press), decomposes at 1310°C at one atmosphere pressure. In practice, however, this decomposition temperature is greatly lowered by contact with carbon or metals. The temperature range over which deposition can proceed is therefore limited at its upper boundary by the stability of the carbonate, which depends on the container and electrode materials. The lower limit is fixed by the requirement that the $SiO_2:Li_2CO_3$ ratio be sufficiently high for the formation of SiC without excess carbon, and the crystal quality of the deposit is likely to decrease with decrease of temperature rather than the reverse.

This system gave, from its introduction into the program, the best SiC deposits and a major part of the latter stage of this investigation consisted of a study of the optimum deposition conditions for this system. This aspect will be discussed in the next section, and Section C will focus on the deposits and their characterization.

B. Optimization of Deposition Conditions

1. Crucible Material

The influence of the crucible material on the decomposition of lithium carbonate was studied by two methods. The simplest was by the use of thermogravimetric analysis using a Du Pont DTA/TGA apparatus. Fig. 3 shows several traces obtained with different crucible materials. In each case the evolution of CO_2 from Li_2CO_3 occurs a little above its melting point (723°C) and increases as the temperature is raised. The weight of Li_2CO_3 is different in each case and so the weight loss data should be referred to constant weight of Li_2CO_3. However, even the comparison at constant Li_2CO_3 is not quantitatively valid since the area of contact between powder and crucible will influence the decomposition kinetics. The data do suggest, however, that vitreous carbon is the most suitable crucible material.

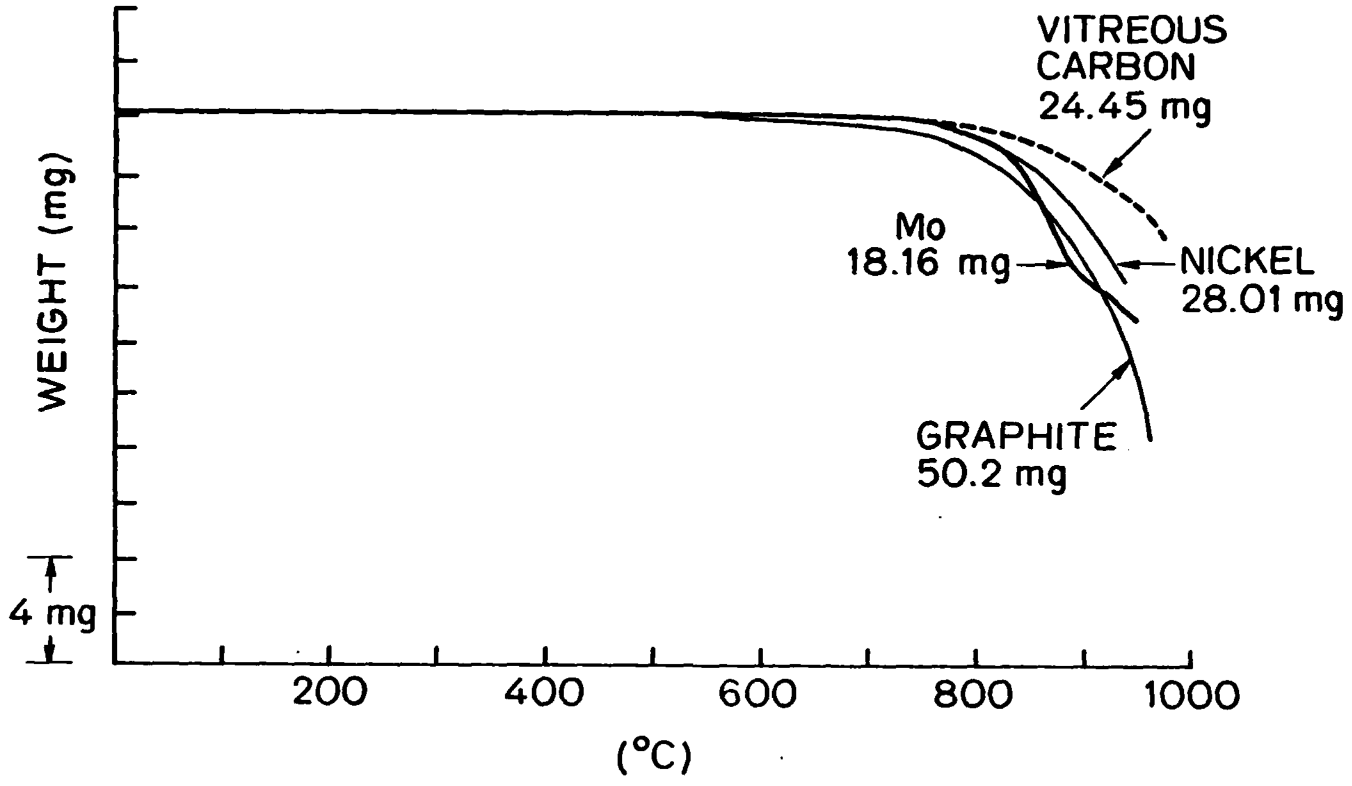

Fig. 3. Thermogravimetric data showing weight loss of lithium carbonate contained in various crucibles. The weight of Li_2CO_3 is shown for each trace.

The alternative procedure used to compare various crucible materials consisted of heating a weighed sample of lithium carbonate rapidly to 1000°C, holding it at this temperature for an hour, then cooling rapidly to room temperature and re-weighing. The results of this study are given in Table II. The data confirm that vitreous carbon is the best crucible material in terms of stability of the carbonate, but these crucibles were covered by a large number of very fine cracks, suggesting local reactivity. In addition, failure of the crucibles always occurred during cooling and occasionally during the heating stage because of stresses resulting from thermal expansion mismatch between the crucible and the melt. In one case the melt ran out through a crack in the crucible causing extensive damage to the furnace. Because of this cracking of vitreous carbon, zirconium crucibles have been preferred for later studies.

The zirconium concentration in SiC crystals was found to be around 0.02 wt%. Although this is significant, it should be compared with 0.03 - 2.0 wt % nickel found in material deposited in Ni crucibles.

SiC-coated graphite crucibles were tried but the coating was found to peel off the crucible on the first use. Silicon carbide crucibles would clearly be preferable to zirconium but are very expensive.

2. Melt Preparation

Both lithium carbonate and SiO_2 absorb moisture from the atmosphere to some extent and heating in vacuum to about 300° has been used for dehydration. A more serious problem is the frothing which occurs as the temperature of the mixed powders is raised through the melting point of the Li_2CO_3. This very rapid evolution of CO_2 can result in a weight loss much larger than that expected if all the SiO_2 is to react to form Li_4SiO_4:

$$2Li_2CO_3 + SiO_2 \rightarrow Li_4SiO_4 + 2CO_2 \qquad (3)$$

The additional weight loss of Li_2CO_3 with increasing SiO_2 concentration is illustrated in Fig. 4.

Melts prepared by heating powder samples through the melting point of Li_2CO_3 were useable and tended to lose CO_2 (and presumably Li_2O) at a severe rate throughout electrodeposition, leading in some experiments to the precipitation of lithium silicate on the cathode, in addition to the SiC.

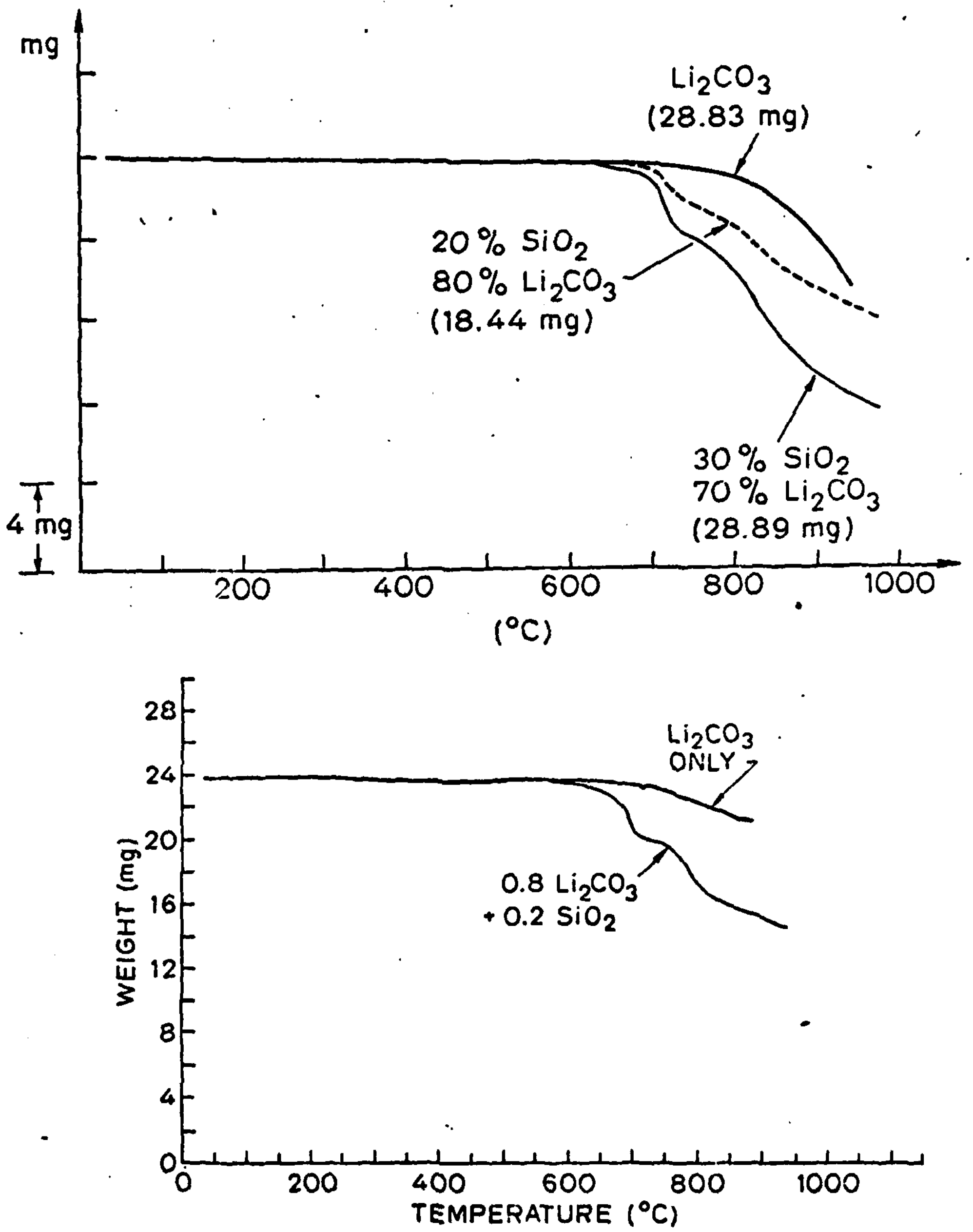

Fig. 4. Thermogravimetric traces showing the influence of SiO_2 on evolution of CO_2 from lithium carbonate. (a) Nickel crucible (b) Glassy carbon crucible.

TABLE II: WEIGHT LOSS OF LITHIUM CARBONATE IN VARIOUS CRUCIBLES

Crucible Material	Weight Loss (%)	Reactivity
Vitreous carbon #1	12.5	Low but cracked
Vitreous carbon #2	12.3	
Vitreous carbon #3	8.5	
Zirconium	16.3	Low
Silicon nitride	50.9	High
Titanium carbide	50.9	High
Niobium	65.0	High
Magnesium oxide	85.1	Very High

A study was therefore undertaken of a two-stage melt preparation process involving a prior sintering of lithium silicate Li_4SiO_4 at a temperature below the melting point of lithium carbonate (723°). Additional lithium carbonate powder was then added to the silicate to form the chosen melt composition. It was confirmed by x-ray diffraction that the sintering reaction to form Li_4SiO_4 was completed in 24 hours at 675°C in air or argon. The major difficulty with this procedure was that the silicate densified to form a hard mass which was dissolved very slowly by the lithium carbonate on heating above 723°C. The frothing of the carbonate on fusion of the powder, although reduced, was not eliminated completely.

An improved procedure was therefore introduced in which the Li_2CO_3 and SiO_2 powders were mixed in the required proportions, dehydrated in vacuum and then sintered at ∿700°C for at least 4 hours prior to fusion This procedure achieved the required aim of reacting the SiO_2 without violent evolution of CO_2, but prevented the formation of a dense solid mass which was difficult to melt. The total weight loss in the whole duration of a typical experiment with powders prepared in this way was 16 - 22g, compared with 13.6g expected for all the SiO_2 to react according to equation (3). Since the weight losses quoted include SiC deposited, oxygen liberated and salt adhering to the deposits, this loss was considered acceptable. The problem of precipitation of silicate on the cathode was eliminated by this procedure. Moreover the weight loss was substantially independent of the duration of the experiment, so that long-term experiments became feasible.

3. Electrode Materials

In the early stages of this investigation, a cathode other than SiC was preferred so that the synthesis of SiC could be demonstrated. Nickel was chosen for convenience and because of its relatively low reactivity with the melt. Nickel suffers from the disadvantage that it reacts with silicon to form nickel silicides, but the concentration of silicides in the deposits was found to be low. The successful synthesis of SiC in this system was demonstrated using a nickel cathode and graphite anode.

Silicon was also used as cathode but reacts rather rapidly with the melt. The most appropriate choice of electrodes appears to be silicon carbide itself. Polycrystalline SiC was obtained from the RIC/ROC Chemical Company and found to be very stable against chemical attack by the melt. "Globar" heating element material, which is mainly SiC but with a binder, was found to be unsuitable because of its high reactivity. An extensive search for single crystal SiC at reasonable cost (some suppliers require \$75 for a 1 cm^2 crystal platelet) led eventually to the location of a retailer who can supply plate-like crystals of 6H polytype over 1 cm^2 in area. These crystals are formed as an accidental by-product of the formation of SiC powder for abrasive applications, and examples of a cluster of crystals and an individual crystal cleaved from a polycrystalline matrix are shown in Fig. 5. The matrix attached to a crystal is used to locate the material in a graphite holder, the single crystal portion being immersed in the melt to act as cathode. During deposition the melt tends to creep up the crystal and support because of its strong wetting action, and this makes an exact specification of current density difficult. This wetting action also leads to contamination of the deposited material with nickel from the wire used to secure the crystal, but this problem could be alleviated by the use of an all-graphite support. Polycrystalline SiC has been used as the anode for most experiments aimed at establishing the optimum conditions for deposition. A graphite or platinum anode was used for experiments on electrowinning - the demonstration that the melt can yield SiC without a dissolving SiC anode.

4. Melt Composition

The earliest experiments were made with melts of composition 0.6 Li_2CO_3; 0.4 SiO_2, the rather high SiO_2 concentration being used to reduce the possibility of excess graphite in the deposit. Melts containing such high concentrations of SiO_2 are very viscous at 1000-1100°C and the SiO_2 concentration x in the system $(1-x)\ Li_2CO_3 \cdot x\ SiO_2$ has been varied in the range $0.1 \leq x \leq 0.3$ in an attempt to find an optimum composition. A high solute concentration is favorable for stable deposition but a high viscosity is an adverse factor (3), so the best deposits are expected when these factors are balanced.

It was found that deposits from melts with a SiO_2 concentration of 0.10 were irregular in texture with poorly formed grain structure.

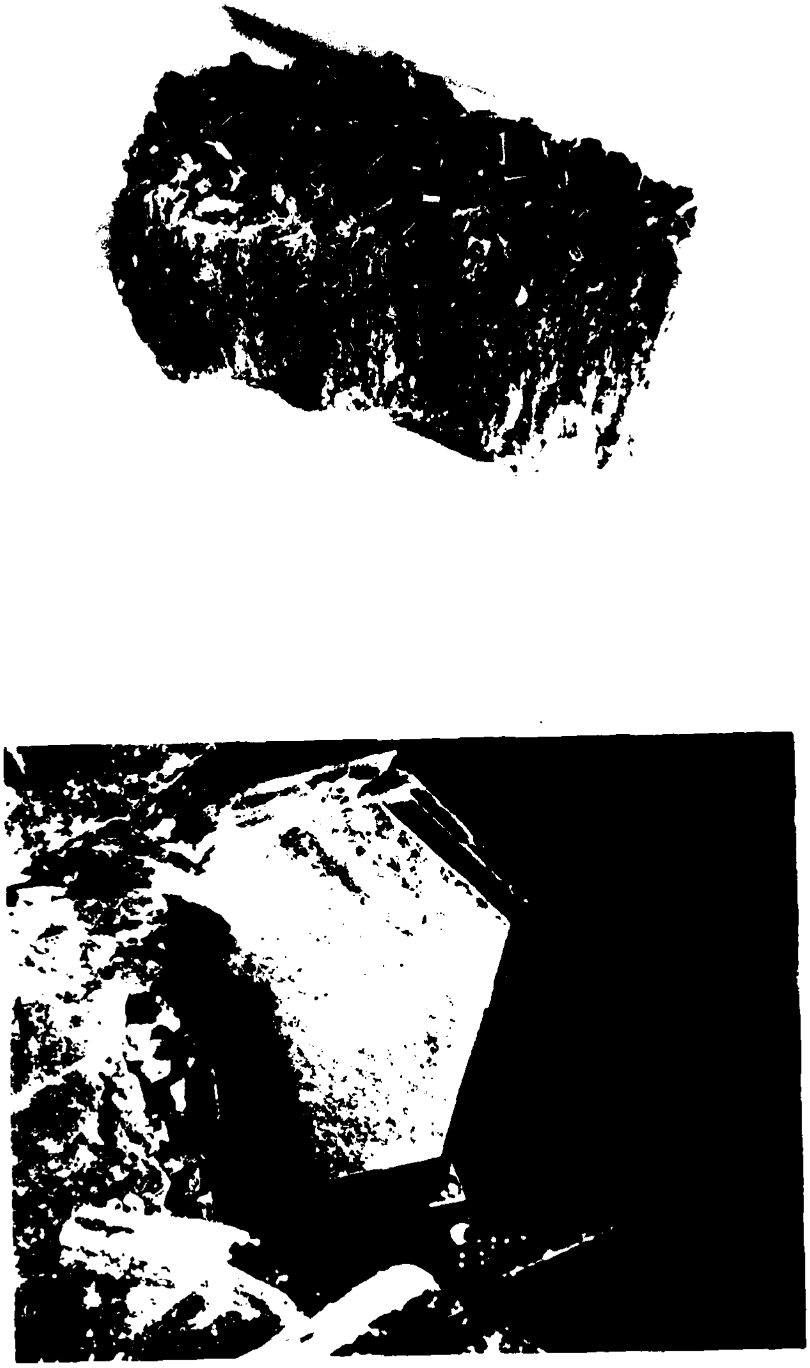

Fig. 5. (a) cluster of silicon carbide seed crystals
(b) individual α-SiC crystal

Melts with $x \sim 0.20$ have given clearly polycrystalline deposits and also textured deposits which may be epitaxial. Increasing the concentration to 0.30 led to a decrease in grain size. It was concluded that the range $0.15 < x < 0.25$ is optimum for SiC deposition, and the most recent work has been concentrated at the lower end of the range.

Since the viscosity of Li_2CO_3/SiO_2 melts at $T \sim 1050°C \pm 100°C$ is high for electrodeposition even with $x = 0.15$, fluoride additions have been used in order to lower the melt viscosity. When 10% NaF was added, the volatility was found to be excessively high at $T \sim 1050°C$ and damage occurred to the silica heat shield surrounding the furnace element. An additional detrimental effect was the occurrence of fine whisker-like deposits on the SiC grains. The nature of these whiskers has not been established, but high NaF additions have not been used subsequently. LiF has a lower vapor pressure and the addition of 1% lithium fluoride has been used during the later stages of this program. A major disadvantage of LiF is its low solubility in water which makes small traces adhering to a deposit difficult to remove by dissolution. A concentration of 1% was found, however, to have beneficial effect on the morphology of the deposit, presumably because of a significant lowering of the melt viscosity.

5. <u>Temperature</u>

It was not found possible to electrodeposit SiC at temperatures below 950°C. This limit is probably set by the tendency of lithium silicates to deposit on the electrodes due to the cooling effect of thermal conduction along the graphite rods. This thermal deposition of lithium silicate is clearly more likely to occur at lower temperatures and at higher SiO_2 concentrations. The lower temperature limit for electrodeposition may therefore be composition-dependent and is probably not a fundamental effect associated with the reaction between electrodeposited silicon and carbon.

The highest temperature at which SiC deposition has been achieved is about 1225°C. This limit was mainly dictated by practical considerations and the influence of temperature should be investigated in more detail with a fixed melt composition. It is, however, encouraging that the rate of CO_2 loss at this temperature is not so rapid that SiC deposition becomes impossible.

Unless otherwise specified, all experiments reported below were performed at melt temperatures between 1000°C and 1050°C.

6. Deposition Potential

The voltammograms of Fig. 6 do not provide useful information on the choice of operating potential difference between anode and cathode. It would normally be expected that a slow-scan voltammogram would show separate "waves" for Si and C deposition. Stability considerations (3) normally favor a low current density and our earlier work at $T \sim 750$°C was handicapped by the apparent failure of SiC to deposit unless large current densities were used. High current densities ($\gtrsim$ 50-100 mA cm^{-2}) frequently result in very irregular morphologies (e.g., dendritic growth) with high concentrations of solvent inclusions. However, it was occasionally found possible to deposit coherent layers at even higher current densities. (See Fig. 7.)

Better surface morphologies have been obtained at a deposition potential of -0.5V (vs SiC) and this value has been preferred for investigations of the influence of composition on the quality of the electrodeposit. The corresponding current density is typically from 30 to 50 mA cm^{-2}. The deposition time is normally 1½ - 3 hours.

7. Summary - Optimum Deposition Conditions

Table III summarizes the results of the series of experiments aimed at optimizing the conditions of electrodeposition of SiC from Li_2CO_3/SiO_2 melts. This table is the culmination of a fairly intensive investigation and we believe that it is unlikely that better conditions would be discovered with this system.

C. Characterization of Deposits

The main aim of the investigation was to prepare bulk crystals of SiC, ideally of the β-phase. Initially it was decided to concentrate on determining the optimum conditions for growing a thin layer on a suitable seed, using a growth period of 1 1/2 - 3 hours. Once such conditions had been found, the second stage would be to grow a crystal by using the same deposition for a much longer time, sufficient to grow a crystal 5-10 mm in thickness.

Fig. 7 shows one particularly successful attempt to deposit a layer at high temperature (1225°C) and current density (500 mA cm^{-2} at 0.95V). The deposition efficiency was 20%. It was unfortunately not possible to reproduce this result and lower values of both current density and temperature were normally found to be required for deposits showing a regular

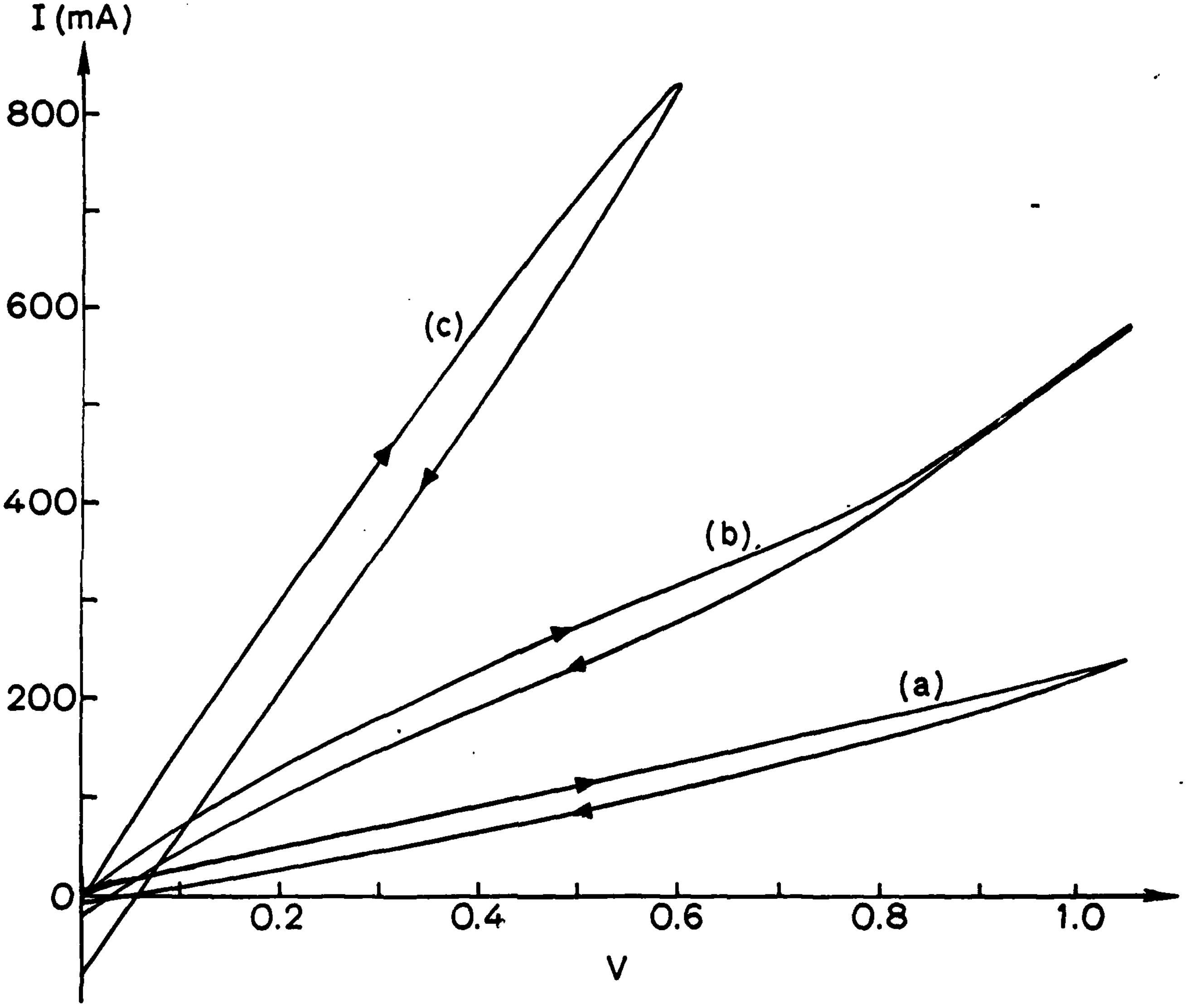

Fig. 6. Slow scan voltammograms using SiC anode and cathode at 1000°C (a) Li_2CO_3 only (b) 0.9 Li_2CO_3+ 0.1 SiO_2 (c) 0.8 Li_2CO_3 + 0.2 SiO_2

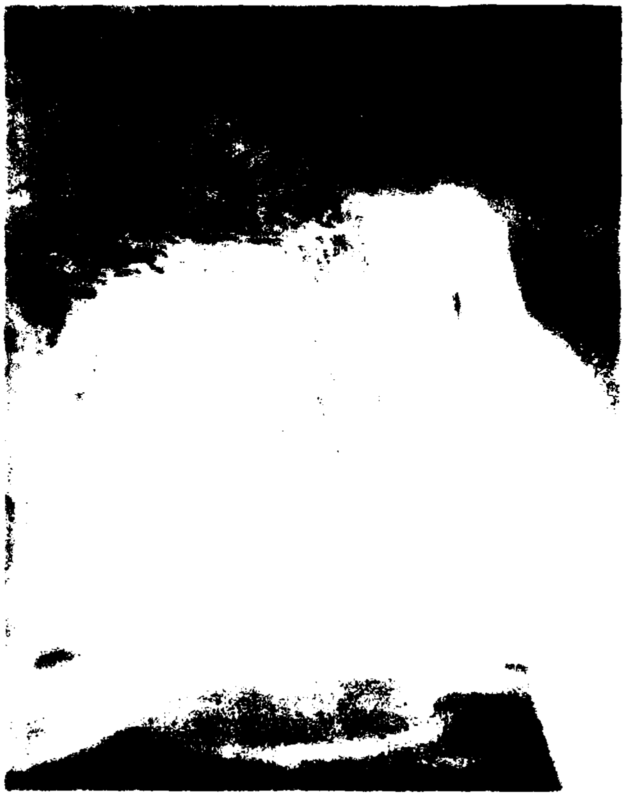

Fig. 7. Cleaved cross-section of SiC deposit on α-Sic substrate at -0.95V (vs SiC) at current density of ∿ 500 mA cm^{-2} and 1225°C. (400X)

TABLE III: OPTIMUM CONDITIONS FOR DEPOSITION OF SiC FROM Li_2CO_3/SiO_2 MELT SYSTEM

1.	Crucible material	Zirconium (or vitreous carbon)
2.	Melt composition (by weight)	Li_2CO_3 84.2% SiO_2 14.8% LiF 1.0%
3.	Cathode materials	Cathode = SiC Anode = SiC (or graphite)
4.	Temperature	1050 ± 50°C
5.	Melt preparation procedure	(a) Dehydrate in vacuum at ∿300°C (b) Sinter at ∿700° to react SiO_2 (c) Melt down
6.	Deposition conditions	Potential −0.50 ± .10V (vs SiC) Current density 30 - 50 mA cm^{-2}

TABLE IV: INTENSITY DATA FOR SiC X-RAY DIFFRACTION PATTERNS

d(Å)	Experimental Data	α(6H)						
		*	+	β	2H	4H	15R	33R
2.63	25	50	70	-	60(2.67)	40(2.67)	40	50
2.60	-	20	-	-	-	-	-	-
2.57	15	20	-	-	-	50	70	-
2.51	100	100	100	100	100	40	70	100
2.48	-	20	20	-	-	-	-	-
2.40	-	-	20	-	-	-	60	-
2.36	30	40	10	-	80	50	-	60
2.34	-	30	-	-	-	-	50	-
2.18	30	20	10	10	-	-	10	30
2.15	-	20	-	-	-	-	-	-
2.09	-	-	-	-	-	30	30	20
2.00	-	-	30	-	-	-	10	20
1.865	15	-	-	-	-	-	-	20(1.69)
1.84	20	-	-	-	20	20	-	20(1.64)
1.60	-	-	-	-	-	40	50	-
1.55	10	50	80	-	-	60	-	30
1.54	15	50		60	-	-	90	80
1.50	-	-	30	-	-	-	-	10
1.42	85	20+20	30+20	-	-	50	40	30+30
1.31	85	50	70	60	-	70	80	70
1.29	-	-	-	-	-	40	20+20	30
1.26	10	10	30	10	-	30	20	30

*Thibault, Am. Min. 93 (1948) 588.

+P. T. B. Shafer, Acta Cryst., b25 (1969) 477.

morphology, as discussed in the previous section.

Fig. 8 shows deposits made under the conditions set out in Table III. The deposits in this case show a regular texture and attempts were made to determine whether the layers were epitaxial. Fig. 9 shows a comparison between a back reflection Laue photograph on the substrate material and on the sample shown in Fig. 8. Apart from the obvious change in orientation in the {0001} plane there are no differences between the two photographs. This is not conclusive evidence that the layer is epitaxial but the absence of rings which are seen in Laue photographs of clearly polycrystalline layers is a promising result when combined with the textured appearance of Fig. 8 (a). It was hoped to test for expitaxial layer formation using a Reed camera which is more sensitive to this surface films (∿20 μm in this case) but this camera has not been in operation during the later stages of our program.

Deposits scraped from α-SiC seeds, powdered and examined by x-ray diffraction, were found to be of the α- rather than the β- phase. Table IV shows d-spacings and intensity data for a typical deposit compared with literature data, mainly from the ASTM file, for several of the more common polytypes. Although agreement between the experimental data and the literature data for the α(6H) form are not perfect, it is as good as that between the two sets of literature data quoted for this phase. There is also fair agreement between our data and that of the 33R polytype, but the two lines at d-spacings of 1.865, 1.84Å do not correspond to those at d = 1.69 and 1.64Å in the 33R pattern.

The α-form is the most common SiC polytype although it is not the equilibrium form, and β-SiC is often obtained (by vapor growth) at relatively low temperatures such as those used in this investigation. The phase deposited is likely to be influenced by the substrate material, but β-SiC was not formed in this investigation even when nickel was used as the cathode material.

Attempts to proceed to the next stage of the program, namely to deposit a thick layer of SiC using a long deposition time, were handicapped by delamination of the seed crystals. This effect is illustrated in Fig. 10(a) which shows the end view of a crystal which has expanded tenfold in thickness by delamination of {0001} layers. Fig 10 (b) shows a high-magnification view of a space between layers on another seed where this effect was not quite so strong. The spaces which open up between layers as the crystals are held in the melt can trap solvent which solidifies in these spaces on removal of

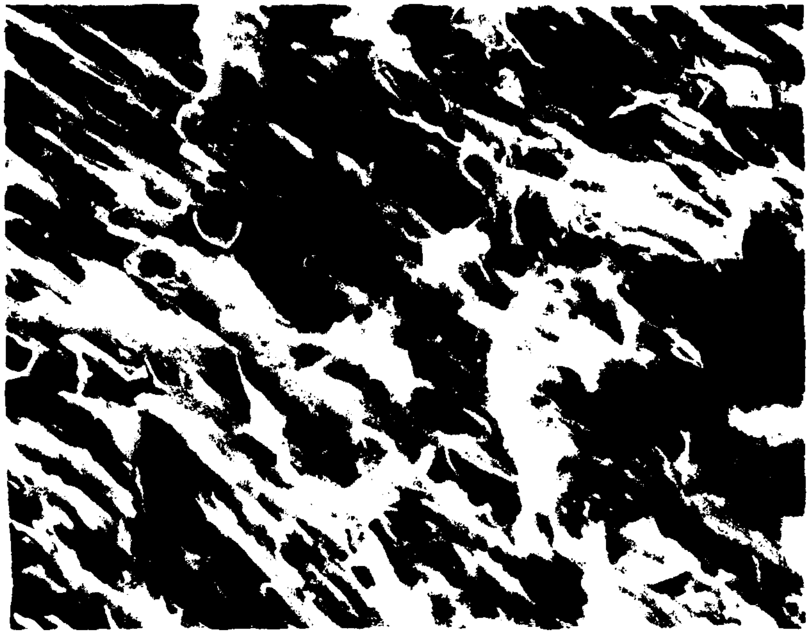

Fig. 8. Deposit on $\{0001\}$ plane of α-SiC under optimum conditions specified in Table III. (in this case $x = 0.20$; $V = 0.50V$ vs SiC; $t = 3$ hrs.)

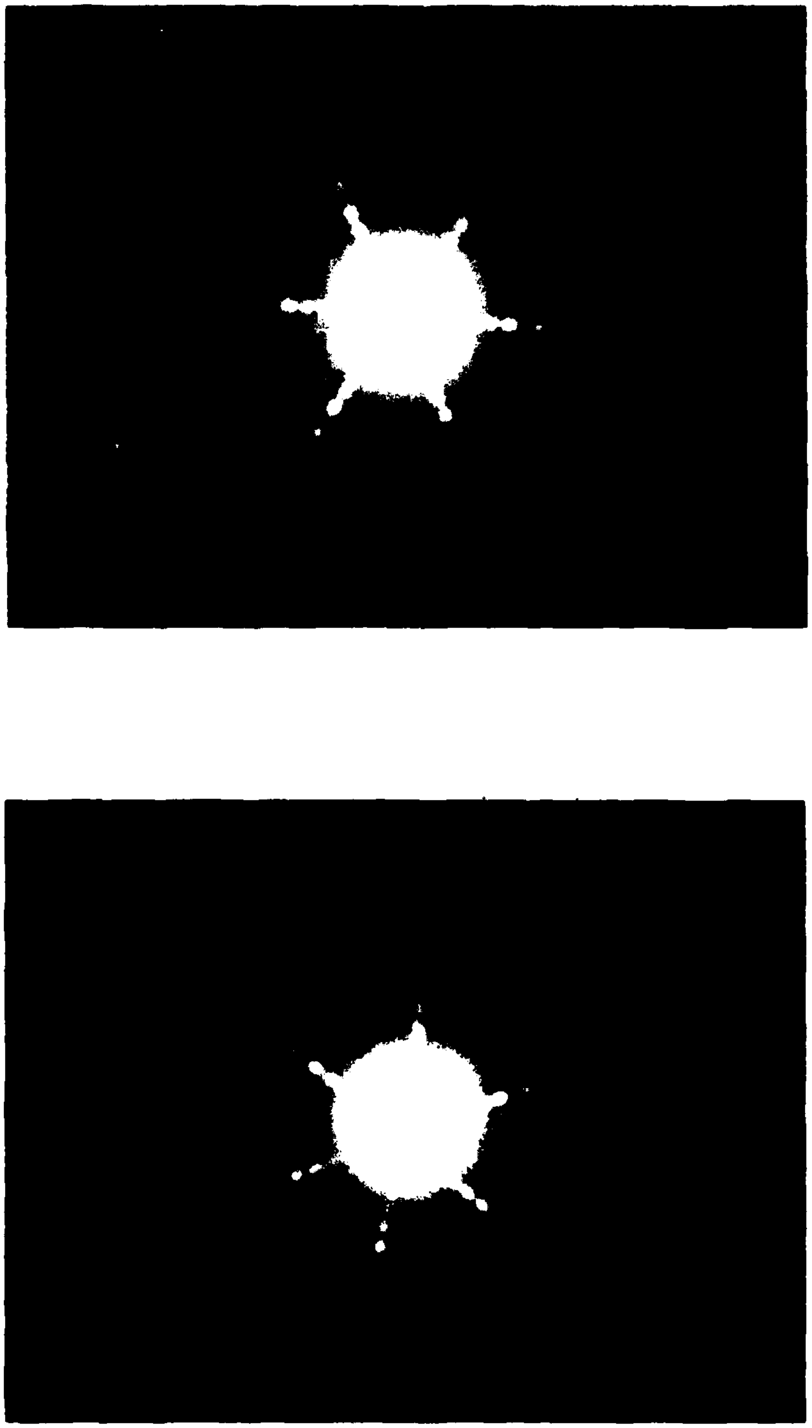

Fig. 9. Back reflection Laue photographs of (a) substrate material (b) layer deposited under conditions specified in Table III.

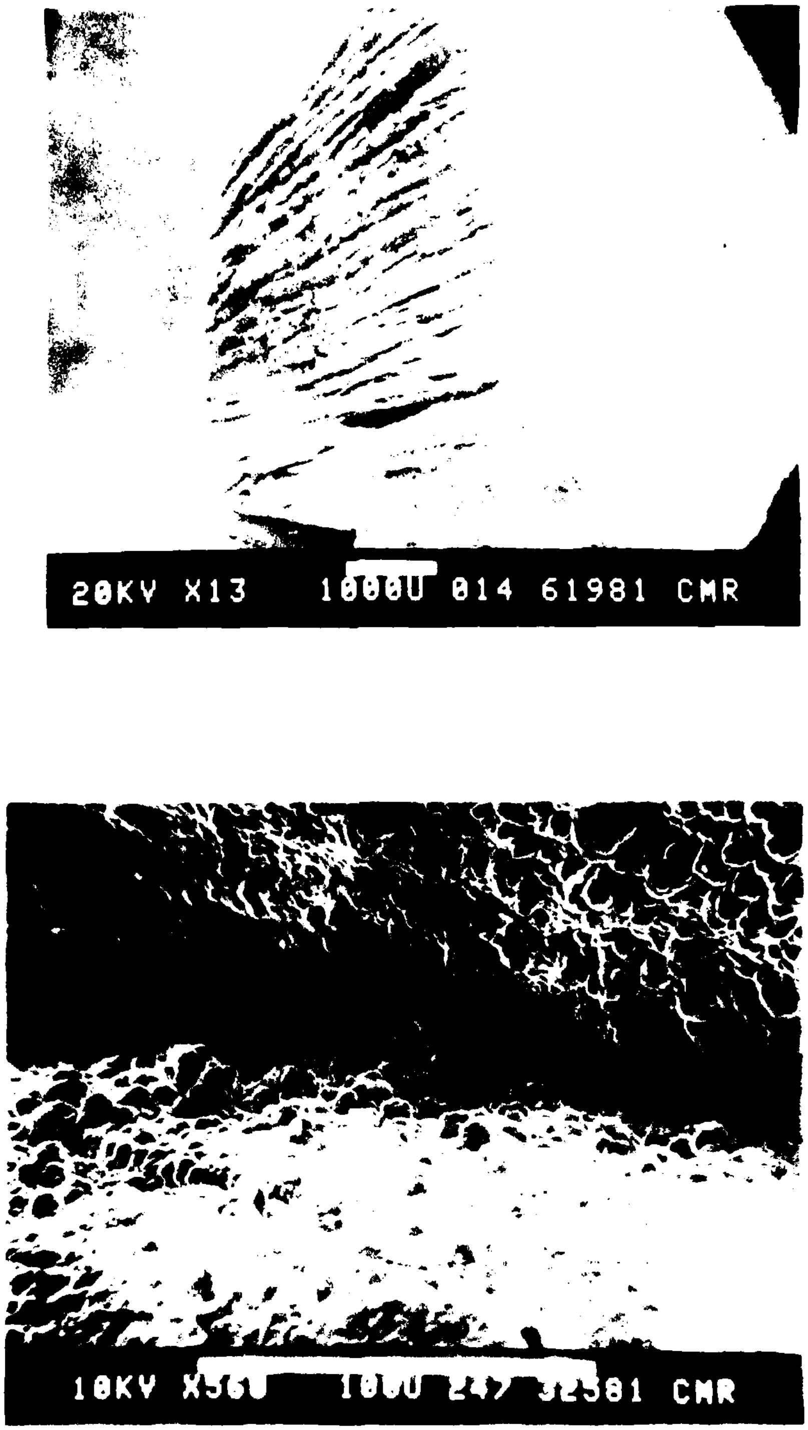

Fig. 10. (a) End view of seed crystals showing extreme delamination
(b) 20μm void between layers due to delamination.

TABLE IV: INTENSITY DATA FOR SiC X-RAY DIFFRACTION PATTERNS

d(Å)	Experimental Data	α(6H)		β	2H	4H	15R	33R
		*	+					
2.63	25	50	70	-	60(2.67)	40(2.67)	40	50
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2.57	15	20	-	-	-	50	70	-
2.51	100	100	100	100	100	40	70	100
2.48	-	20	20	-	-	-	-	-
2.40	-	-	20	-	-	-	60	-
2.36	30	40	10	-	80	50	-	60
2.34	-	30	-	-	-	-	50	-
2.18	30	20	10	10	-	-	10	30
2.15	-	20	-	-	-	-	-	-
2.09	-	-	-	-	-	30	30	20
2.00	-	-	30	-	-	-	10	20
1.865	15	-	-	-	-	-	-	20(1.69)
1.84	20	-	-	-	20	20	-	20(1.64)
1.60	-	-	-	-	-	40	50	-
1.55	10	50	80	-	-	60	-	30
1.54	15	50		60	-	-	90	80
1.50	-	-	30	-	-	-	-	10
1.42	85	20+20	30+20	-	-	50	40	30+30
1.31	85	50	70	60	-	70	80	70
1.29	-	-	-	-	-	40	20+20	30
1.26	10	10	30	10	-	30	20	30

*Thibault, Am. Min. 93 (1948) 588.

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the crystal. This effect was observed even in the absence of a potential difference between electrodes. The delamination clearly interfered with the growth of good quality films, as may be seen by the example in Fig. 11 which shows the tendency of small plate-like crystals to nucleate in the spaces between layers. Attempts to deposit over periods longer than 3 hours were particularly adversely affected by delamination and it was concluded that the seeds were highly unsuitable for the growth of bulk crystals.

Attempts to obtain high quality SiC seeds from Dr. Y.M. Tairov Leningrad Electrotechnical Institute, from Westinghouse and SRI International were not successful. Better quality seed crystals grown by Dr. A. Addamiano of the Naval Research Laboratory were located only after termination of the contract. It is, however, intended to investigate the use of these seeds for a small study of electrodeposition of SiC using internal funding.

D. <u>β-SiC Seeds</u>

Attempts were made to electrodeposit β-SiC on β-SiC seeds. These polycrystalline seeds were grown by Professor R. F. Davis of North Carolina State University by chemical vapor deposition onto graphite which was subsequently removed. The material contains traces of the 15R polytype and of free carbon.

When used as cathodes under conditions similar to those described above, the β-SiC exhibited a remarkable behavior which has not been seen on other material and is difficult to understand. The material appears to have a strong affinity for lithium carbonate which formed a thick (1-2mm) white layer around the cathode, and was enclosed in turn by a black electrodeposit. X-ray diffraction of this deposit mainly showed Li_2CO_3, but with traces of what was probably α-SiC but definitely not the cubic β phase. Only a limited number of experiments could be performed in this series since only 5 β- substrates were available. The voltammogram was similar to that using an α-SiC substrate and no convincing explanation can be advanced for the unusual behavior of the β-SiC cathodes.

E. <u>Electrowinning</u>

As mentioned above, most experiments were performed using a polycrystalline α-SiC anode because of the low reactivity of this material with the melt. Such experiments in which the anode dissolves during the course of the experiment and the same material deposits on the cathode are referred to as "electro-refining", the normal aim being to achieve purification of the source material during transfer between the electrodes. The alternative

Fig. 11. Small crystals nucleated at space between layers on delamination of seed crystal.

process, known as electrowinning, involves the synthesis of the material from the melt which means that the electrode is of some alternative material. A few experiments were therefore performed to determine whether electrowinning of SiC was feasible from the Li_2CO_3/SiO_2 melt. Electrowinning could be used as a means of coating materials with SiC to form a protective layer, or to synthesize powder for abrasive purposes. In the latter case, a high potential could be used in principle since the morphology of the deposit would be unimportant.

Electrowinning experiments were performed under conditions similar to those set out in Table III except that a graphite or platinum anode was used and the potential difference (and current density) were higher than those used in experiment aimed at producing an epitaxial layer.

It was generally found that the use of high potentials led to massive deposits, but mainly of solidified salt trapped between black particles. X-ray diffraction of these deposits showed mainly Li_2CO_3, and this material is difficult to separate from the SiC because of its low solubility in water or acids.

It was therefore concluded that high deposition rates are unfavorable for electrowinning because of the difficulty of removing trapped solvent. Although electrowinning at slow rates could presumably be used, it seems less attractive than electrore fining and is not a viable alternative to present commercial practice as a means of making SiC powder for abrasive applications.

V. <u>Conclusions</u>

The major achievements of this investigation were as follows:

1. The electrodeposition of silicon carbide was achieved for the first time.
2. A melt system, Li_2CO_3/SiO_2 was identified which is capable of yielding silicon carbide as a single phase on electrolysis. A procedure was established for the preparation of a stable melt, which should permit operation over periods, possibly of several days, required for deposition of bulk crystals of SiC.
3. A set of parameters was identified which appear to be optimum for the deposition of SiC from this system.
4. There is evidence for expitaxial layer deposition of SiC on α-SiC substrates.

The major problem in using this technique to grow bulk crystals of α-SiC is delamination of the seed crystals which were grown as a by-product of abrasive material fabrication. An alternative seed material would be required for growth of bulk crystals by this method. The growth of β-SiC by this process appears particularly difficult.

The general conclusion must be reached that electrodeposition is not an easy route to the fabrication of bulk crystals of silicon carbide. The vacuum sublimation method of Tairov and Tsvetkov (4), the result of over a decade of development, has recently given cm^3 crystals which are clear in thin section. It is claimed that crystals of controlled polytype (α or β) can be grown by changing the growth kinetics and this process, although not without its problems, appears more attractive than electrodeposition for further development as a method of growing bulk material.

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8