Electrophoretic deposition [EPD] applied to reaction joining of silicon carbide and silicon nitride ceramics

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Electrophoretic Deposition (EPD) was used to deposit a mixture of SiC or Si_3N_4 "filler" and reactive carbon (graphite and carbon black) particles onto various SiC or Si_3N_4 parts in preparation for reaction bonding. The particles had gained a surface charge when mixed into an organic liquid consisting of 90 w % acetone + 10 w % n-butyl amine to form a slurry. The charged particles then moved when placed under the influence of an electric field to form a "green" deposit on the ceramic parts. The green parts were then dried and subsequently joined using a reaction bonding method. In this reaction bonding, molten Si moves into the joint via capillary action and then dissolves carbon and precipitates additional SiC. An optimum mixture of SiC "filler" to C powder ratio of 0.64 was identified. Residual un-reacted or "free" Si was minimized as a result of selecting powders with well-characterized particle size distributions and mixing them in batch formulas generated as part of the research. Image analysis of resulting microstructures indicated residual "free" Si content as low as 7.0 vol % could be realized. Seven volume percent compares favorably with the lowest "free" Si levels available in experimental samples of bulk siliconized (reaction-bonded) SiC manufactured using conventional reaction-bonding techniques. The joints retained the residual silicon over a large number of high-temperature thermal cycles (cycling from below to above the melting point of silicon). Comparisons to commercial reaction-bonded SiC indicated the majority of residual silicon of the joint was retained in closed porosity. This infers that parts made with these joints might be successfully utilized at very high temperatures. It was demonstrated that the EPD technique could be applied to butt, lap, and scarf type joints, including the capability to fill large gaps or undercut sections between parts to be joined. The overall results indicate that EPD, combined with reaction bonding, should allow for the fabrication of large complex structures manufactured from smaller components consisting of silicon carbide or silicon nitride. © *2000 Kluwer Academic Publishers*

1. Introduction
1.1. Background information
Researchers at the Idaho National Engineering & Environmental Laboratory (INEEL) have previously demonstrated that reaction bonding techniques have considerable potential for joining SiC parts [1]. In the most common version of this technique, carbon or graphite powder and ceramic fillers (e.g. SiC powder) are placed in the gap of a joint at room temperature. This is followed by reaction with molten silicon at high temperatures. The molten silicon dissolves the carbon and subsequently silicon carbide grains are precipitated. Residual un-reacted silicon, sometimes called "free" silicon, typically results. Fabrication of joints using reaction bonding is attractive since the joining materials are compatible with SiC, processing can be carried out in short times at temperatures <1500 °C, and joints

with excellent mechanical properties can be produced. In addition, similar to brazing processes, large external pressures are not required, thus making the process inexpensive and practical compared to other ceramic joining methods.

Reaction bonding was first used by Iseki *et al.* [2], in 1983, to join bulk reaction-bonded SiC (RBSC) ceramics. It was later extended, by INEEL researchers under U.S. DOE sponsorship, to the joining of pressureless-sintered SiC and SiC/SiC composites [1, 3]. Since 1986, extensive development of the reaction bonding technique has taken place at the NASA Lewis Research Center [4–11].

Details of the progress made at the INEEL, using reaction bonding (compositions, microstructures, etc.), is described in several papers [12–15]. Much of this work utilized lap or butt type joints; with the placement of

thin tape-cast precursor strips (a technique pioneered at the INEEL) as filler material in the joint. Four-point bending tests of reaction bonded joints showed average room temperature strengths of 327 MPa that increased slightly with increasing test temperature up to 1200 °C (this is comparable to the strength reported for bulk pressureless sintered α-SiC) and then fell to 208 MPa at 1400 °C. Weibull modulus (m) values were $m = 5$ at room temperature and $m = 7$ at 1200 °C. Single edge notched beam (SENB) fracture toughness tests yielded K_{Ic} values of 2.8 and 7 MPa $\cdot$ m$^{1/2}$ at room temperature and 1200–1400 °C, respectively. The fracture toughness values were comparable to those measured for bulk SiC. The previous INEEL work identified challenges that need to be overcome before reaction bonding can be effectively utilized for large industrial applications:

(1) Production of consistently high quality microstructures and consistent properties in the joint.

High quality microstructures result from controlling the density of the precursor materials to result, after Si infiltration and reaction bonding, in a structure that is fully dense (low porosity) with the lowest free Si content possible (e.g. 7–8 vol %). This is necessary to retain good mechanical properties (strength and creep resistance) at temperatures exceeding the melting point ($\cong$1410 °C) of the residual silicon. In addition, free-silicon can be detrimental to mechanical properties at lower temperatures since cracks can initiate and propagate along weak silicon/silicon-carbide interfaces. Producing a low fraction of residual silicon has proved to be difficult when using tape-cast precursors because the large organic binder content (e.g. 30 vol %), necessary for flexibility, always resulted in excess porosity. This porosity is subsequently filled with residual Si (typically >30 vol %). Various researchers have recently focused on the use of polymer adhesives to hold parts together at room temperature. The polymers can then be "charred, carbonized, or pyrolyzed" in an inert atmosphere to produce either carbon or pre-ceramics that can subsequently react with molten silicon [16, 17] at high temperatures. The large shrinkage of some precursors (e.g. polymeric precursors) during carbonization is a large problem with 3-D joints (e.g. tube in flange) because the rigid parts typically can only move in one dimension. Therefore, shrinkage cracks or delaminations develop within the precursor or along the ceramic/precursor boundaries; these cracks are filled with residual silicon rather than new SiC (formed by reaction of Si with the pyrolyzed carbon). Also, achieving sufficient carbon yields from the precursors to avoid large volumes of residual silicon is a problem.

(2) Engineering of fabrication methods suitable for dense, three-dimensional joints.

Butt type joints do not yield optimum strength 3-D joints because they are not well supported (as with a flange), and they are susceptible to brittle fracture (cracks originating at OD flaws) during shear or bend loading. Also, these type joints generally need some applied pressure during joining, and the butt configuration makes part alignment and "fixturing" to hold parts in alignment difficult on large structures. "As-fired" ceramic parts are almost always slightly warped and

circular cross-sections are "out-of-round" (unless parts have been diamond- ground to specific tolerances). This makes fitting of parts (to be joined) almost impossible for structures with large dimensions. Even parts ground to a warp specification of less than 0.001 m/m could be off-alignment by 0.003 m at the end of 3.048 m long tubes intended for constructing modules for large ceramic heat exchangers (e.g., designed for an advanced coal burning power plant). Un-ground parts would have much larger dimensional deviations and alignment of ceramic parts cannot be adjusted by plastic bending (possible for metal tubing).

1.2. A new approach

After consulting with design and engineering firms, the authors have created a new concept to utilize reaction bonding to form 3-D joints using SiC parts to form large structures. Instead of butt type joints, the joints will be "scarf" joints supported by flanges or sleeves or butt-lap joints when the use of flanges or sleeves is not practical. A "scarf" joint is a modified butt joint where the bonding surfaces are angled to increase the bonding area and provide for self-alignment of the parts during assembly and joining. For tube-in-flange joints, complementary angles will be ground into both the tube and flange (or sleeve) ends. The Electrophoretic Deposition (EPD) technique was chosen to replace tape casting of the precursors. EPD allows particles to be directly deposited from a liquid/powder slurry [18]. It was hoped that the use of EPD would result in very densely packed powder coatings in order to minimize "free" silicon after the reaction bonding process. Coatings could be deposited on the OD of the tubes (prior to joining) or deposited to fill the entire gap [19] between mating parts (particularly useful for mis-aligned parts).

It was necessary to refine the EPD process for slurries of carbon and/or graphite powders with SiC [20] or Si_3N_4 "filler" powders using the specific configurations and materials necessary for reaction bond joining of either SiC or Si_3N_4-based ceramic tubes and bars. This development involved several tasks:

(1) Develop thin metal surface coatings for nonconducting ceramics so the ceramic parts function as electron-conducting electrodes for particle deposition in the EPD process.

(2) Optimize an organic-liquid/powder slurry composition such that high density "green" powder compacts result.

(3) Determine if the EPD technique can be used to deposit coatings to fill relatively large gaps between parts that are to be joined.

(4) Perform reaction bonding (with molten silicon) utilizing the EPD coatings and minimize residual "free" silicon in the joints.

(5) Examine the microstructure of joints created using the EPD/Reaction bonding process.

(6) Measure the strength of joints resulting from the EPD/Reaction bonding process.

(7) Determine how robust EPD/Reaction bonded joints will be in high temperature applications; including potential damage from thermal cycling above and

below the melting point of silicon and loss of gas-tightness due to loss of silicon (near or above its melting point).

2. Experimental procedures
2.1. Thin metal surface coatings for non-conducting ceramics

A schematic of the EPD process is shown in Fig. 1. Particles within the slurry must possess a surface charge (i.e., zeta potential). In order to form a deposit, the charged particles move in response to the voltage gradient established between two electrodes. The electrodes must be electrical conductors in order to establish a DC voltage differential (e.g. 20–200 volts). If the particles have a positive surface charge they will move towards the negative electrode, if the particles have a negative surface charge they will move towards the positive electrode. In order for particles to accumulate into a deposit, the electrodes must transfer charge (act as current collectors) with the result that a small current flows in the circuit. Some silicon-based ceramics are not electrically conductive (e.g. sintered SiC, sintered Si_3N_4, CVD SiC) while others have some conductivity (e.g. reaction-bonded SiC with a high free Si content). In order for EPD to work with the non-conductors, these ceramic compositions were coated with a thin, "metallic" surface coating. Candidate conductors were: C, Au, Cu, Mo, Pd, Nb. The conductors were selected because a very thin coating (e.g. nanometers) would later dissolve into the molten silicon and either form a very small amount of silicon carbide, silicon alloy or silicon intermetallic. Coating experiments were conducted using: C (10–100 nanometers using carbon-arc vacuum vapor deposition), Au (using vacuum physical vapor deposition), and Cu (using a direct metallization / "electroless" process that utilized a 10 angstrom palladium undercoat [21]).

2.2. EPD slurry compositions

Experiments were designed to vary the relative amounts of components of the slurry and to examine the resulting coatings (after drying) and joint microstructures (after reaction bonding). The composition of the organic liquid used for the slurries was 90 vol % acetone mixed with 10 vol % *n*-butylamine. The *n*-butylamine increases the base character of the surface of the powders (negative charge on the powder particles) via proton-exchange reactions. This results in a negative direction of electrophoretic mobility, where both SiC and C particles are deposited on the positive electrode. The voltage normally used was between 5 and 20 volts. A typical anode to cathode spacing of 6.35 E-003 m resulted in currents between 1 and 15 mA using 1.27 E-002 m × 1.27 E-002 m test pieces.

Table I lists the materials used for the various experiments. The compositions shown in Table II were to provide an initial "scoping" of slurry parameters, including SiC filler to C ratio and various sources of C. The compositions shown in Table III provided for more refinement of these variables; with attempts to use a mixture of particle sizes to increase the "green" packed density of the coatings. An organic binder was sometimes added to the slurry in an attempt to increase the strength and crack resistance of the "green" deposit; it was added as a weight percentage of the total weight of dry solids (ceramic fillers plus C black plus graphite) used in the slurry. The solids were added to 200 ml of 90 acetone/10 *n*-butylamine liquid using about 10 wt % solids with 90 wt % liquid. In some experiments, after the coating was dried, an attempt was made to increase the carbon or SiC loading by "wicking" in a liquid polymer precursor from the surface into the interior via capillary action (noted under the "Comments" column as a "Dip").

Table IV gives the various experimental compositions when silicon nitride powder was substituted for the silicon carbide as the filler powder. The idea was to develop an EPD slurry that could be used for joining silicon nitride parts [22]. The resulting joint was designed to contain crystal grains of SiC, Si_3N_4, and residual Si.

The experiments tabulated in Table V utilized SiC or Si_3N_4 fillers, but emphasized carbon black as the carbon source.

2.3. EPD technique to deposit coatings into a large gap between parts

An experiment was conducted to join a Hexoloy SiC tube (with thin gold coating) into an over-sized hole that was diamond-drilled into a Crystar SiC plate. The tube was suspended in the hole (not well centered), while the entire plate and end of the tube were immersed in the slurry for EPD coating (composition similar to that of "T" in Table III.) Portions of the parts, where
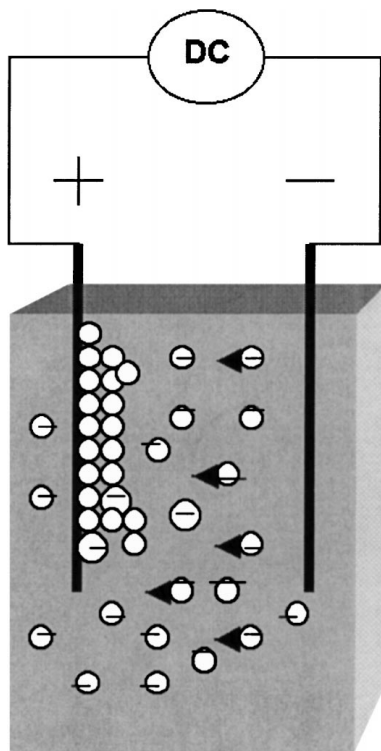

Figure 1 Schematic of electrophoretic deposition of particles from slurry.

TABLE I Materials used for experiments

Material	Trade name	Manufacturer	Characteristics
Sintered SiC	Hexoloy SA^{TM}	Carborundum/St. Gobain Company, Box 1054, Niagara Falls, NY 14302-1054	Sintered alpha, 3.07 g/cc, 380 MPa strength at RT, E2-E6 ohm-cm resisitivity@RT
Siliconized SiC	Crystar^{TM} Si/SiC	Norton /St. Gobain Electronics, 1 New Bond Street, Worcester, MA 01615-0316	Reaction bonded, bi-modal mix, large grain size, 3.05 g/cc, 170 MPa strength@RT, 1 ohm-cm resistivity@RT, 13–15 vol % Si
Siliconized SiC	NT 230 SC 7-7 (experimental)	Norton St. Gobain Electronics, 1 New Bond Street, Worcester, MA 01615-0136	Reaction bonded, tri-modal mix, fine-grained experimental grade, 7–8 vol % Si
Si$_3$N$_4$	AS800	Allied Signal Inc. Attn: Charles Gasdaska Bldg CTC-2, Box 1021, Morristown, NJ 07960	High Temperature Grade
CFCC tube	CMC-Nicalon/E-SiC with CVIP (experimental)	Allied Signal (formerly DuPont Lanxide Composites) 1300 Marrows Road Newark, DE 19714-6077	Nicalon/Enhanced SiC with a pyrocarbon interface, outside surface coated with oxidation protective coating, ID surface with CVI-SiC seal
Carbon black	Carbon Lampblack # C-198	Fisher Scientific Co., 711 Forbes Ave., Pittsburg, PA, 15219	Tri-modal particle size measured with Coulter LS Particle Size Analysis at 0.6 (largest peak), 3, 10 microns (possibly agglomerated)
Graphite powder	Grade 7 × 99	Cummings-Moore Graphite Co., 1646 North Green Ave., Detroit, MI, 48209	Mean particle size of 13.4 micron measured with Coulter LS Particle Size Analysis
SiC powder	Cerac # S-1169	Cerac Inc. Box 1178, 407 N. 13th St. Milwaukee, WI 53233	−325 Mesh, 99% typical purity, 10 micron measured mean particle size
SiC powder	Starck A-1	Hermann C. Starck Inc. 280 Park Avenue New York, N.Y. 10017	Medium fine alpha-SiC powder, 0.8–1.5 micron factory (1.2 micron measured mean) particle size, 4–6 m^2/g
SiC powder	Starck A-10	Hermann C. Starck Inc. 280 Park Avenue New York, N.Y. 10017	Very fine alpha-SiC powder, <0.8 micron factory particle size (1.37 mean, 0.55 median measured), 14–17 m^2/g
Si$_3$N$_4$ powder	Cerac # S-1068	Cerac Inc. Box 1178, 407 N. 13th St. Milwaukee, WI 53233	−325 mesh, 2 micron typical, 99.9% purity
Acetone	Dimetyl ketone product # A18-4	Fisher Scientific Co., 711 Forbes Ave., Pittsburg, PA 15219	Certified A.C.S. Grade
Butylamine	Butylamine, 99%, Product # B8,898-5	Aldrich Chemical Co., 1001 West St. Paul Ave., Milwaukee, WI 53201	Certified A.C.S. Grade

TABLE II Slurries for EPD experiments—scoping study

Sample ID	SiC : C ratio	Wt % SiC source	Wt % C source	Substrate type/coat	Comments
A$_{AU}$	2 : 1	66.7 Cerac	33.3 graphite	Hexoloy/Gold	
B$_{AU}$	2 : 1	66.7 Cerac	33.3 graphite	Hexoloy/Gold	Furfural Alcohol Resin Dip
D$_{AU}$	0.64 : 1	39 Cerac	61 graphite	Hexoloy/Gold	
R$_1$	0.64 : 1	39 Cerac	61 graphite	Crystar	
R$_2$	0.64 : 1	35.1 Cerac 3.9 A-10	61 graphite	Crystar	
R$_3$	0.64 : 1	35.1 Cerac 3.9 A-10	54.9 graphite 6.1 C black	Crystar	
R$_{3.5}$	0.64 : 1	39 Cerac	61 graphite	Crystar	
R$_4$	0.64 : 1	39 Cerac	61 graphite	Crystar	Furfural Alcohol Resin Dip

coating was not desired, had been previously dipped into molten paraffin wax. The tube was 6.35 E-003 m diameter with a 3.175 E-003 m wall and the plate was 7.938 E-003 m thick. The hole had a 1.588 E-003 m diameter.

2.4. Reaction bonding (with molten silicon) utilizing the EPD coatings

Reaction bonding took place at 1450 °C and took approximately 15 minutes. Several examples were joined, including:

TABLE III Slurries for EPD experiments—refining parameters

Sample ID	SiC : C ratio	Wt % SiC source	Wt % C source	Substrate type/coat	Comments
L	0.51 : 1	26.9 A-1 3.4 Cerac 3.4 A-10	15.3 C black 51.0 graphite	Hexoloy/Gold	6.9% binder
R	0.48 : 1	25.8 A-1 3.2 Cerac 3.2 A-10	19.4 C black 48.4 graphite	Hexoloy/Gold	8.5% binder Ceraset SN Dip
S	0.48 : 1	25.8 A-1 3.2 Cerac 3.2 A-10	19.4 C black 48.4 graphite	Hexoloy/Gold	8.5% binder Furfural Alcohol Resin Dip
T	0.64 : 1	39.0 A-10	14.0 C black 47.0 graphite	Hexoloy/Gold	3.0% binder
U	0.64 : 1	39.0 A-10	14.0 C black 47.0 graphite	Hexoloy/Gold	3.0% binder Ceraset SN Dip
V	0.64 : 1	39.0 A-10	14.0 C black 47.0 graphite	Hexoloy/Gold	3.0% binder Furfural Alcohol Resin Dip

TABLE IV Slurries for EPD experiments—silicon nitride compositions

Sample ID	Si_3N_4 : C ratio	Wt % Si_3N_4 source	Wt % C source	Substrate type/coat	Comments
N1	2.5 : 1	45.4 Cerac	22.6 graphite 6.1 C black	AS800/Gold	15.8% binder
N2	1.8 : 1	64.0 Cerac	25.7 graphite 10.3 C black	AS800/Gold	14.1% binder
N3	1.8 : 1	64.0 Cerac	25.7 graphite 10.3 C black	AS800/Gold	14.1% binder —Slurry cooled with liquid N2
N4	0.8 : 1	45.4 Cerac	40.0 graphite 14.6 C black	AS800/Gold	10.0% binder

TABLE V Slurries for EPD experiments—emphasizing carbon black (CB) as carbon source

Sample ID	SiC : C ratio	Wt % SiC source	Wt % C source	Substrate type	Comments
N5	1.80 : 1	31.2 Cerac 31.2 A-1	34.7 C black	Crystar	2.9% binder
N6	1.20 : 1	25.6 Cerac 25.6 A-1	42.7 C black	Crystar	6.1% binder
N7	0.86 : 1	21.7 Cerac 21.7 A-1	50.6 C black	Crystar	6.0% binder
N8	0.64 : 1	18.2 Cerac 18.2 A-1	56.5 C black	Crystar	7.1% binder
N9	1.28 : 1	26.0 Cerac 26.0 A-1	40.5 C black	Crystar	7.4% binder
N10	1.28 : 1	23.9 Cerac 23.9 A-1	37.3 C black 8.0 graphite	Crystar	6.8% binder
	Si_3N_4 : C ratio	Wt % Si_3N_4 source			
N11	1 : 1	47.5 Cerac	47.5 C black	AS800/Gold	10.2% binder
N12	0.55 : 1	33.1 Cerac	59.8 C black	AS800/Gold	7.1% binder

(1) A thin-walled Hexoloy SiC tube was joined (end-to-end) with a thick-walled Hexoloy SiC tube of larger diameter (Sample 5–8 SiC 7°). One tube was 1.270 E-002 m diameter with a 3.175E-003 m wall and the other tube was 1.488 E-002 m diameter with a 4.763 E-003 m wall. The ends were ground into a butt-scarf configuration using a 7° angle. Based upon positive exploratory results, an EPD composition similar to "T" (See Table III) was utilized. This composition had a SiC : C ratio of 0.64 : 1 comprised of 14.0 w % Carbon black, 46.9 w % graphite, and 39.0 w % Starck A-1 SiC with 3 w % binder. The end of the smaller tube was coated and then pushed against the larger tube. Silicon was wicked into the joint (from the OD) via capillary action after the Si was melted during the heating process.

(2) Rectangular bars ($3 \times 4 \times 20$-30 E-003 m) of AS800 Si_3N_4 were butt joined. Based upon positive exploratory results, EPD composition "N11" (see Table V) was utilized.

2.5. Microstructure of joints

An EPD composition similar to composition "T" (See Table III) was used to join Crystar Siliconized SiC to Hexoloy sintered SiC pieces (sample ID "CAT"). This composition had a SiC : C ratio of 0.64 : 1 comprised of 14.0 w % Carbon black, 46.9 w % graphite, and

39.0 w % Starck A-1 SiC with 3 w % binder. After joining, standard ceramographic techniques were used to prepare samples for optical microscopy. A "Bausch & Lomb Research II Metallograph" was used to take photographs at up to 400 X magnification. These photographs were then converted into digital images at 300 pixels per inch, using a "Hewlett Packard Scan-Jet 6100 C" image scanner. The digital images were analyzed using "Image Pro" software [23] on a personal computer (Microsoft NT operating system). The samples were analyzed (on an area percentage basis) for different phases (e.g. SiC, Si, porosity).

2.6. Fabrication of tensile strength specimens using the EPD/reaction-bonding process

Tensile strength test specimens were fabricated by cutting sections (5.08 E-002 m diameter × approx. 8.89 E-002 m long) from the CFCC tube. These tube sections were butt-scarf (7° taper) joined (at both ends) to specially ground thick-walled Hexoloy headers. The assembly then contained two joints. The overall bonding of the joints was evaluated using radiography with fine-grained film. The assembly was designed to be pulled in tension using an Instron testing machine with attachment and centerline alignment facilitated by special grips fabricated as scaled-up (proportionally larger dimensions) version of those specified in ASTM F19-64 [24] for tensile testing metal to ceramic seals.

2.7. EPD/reaction-bonded joints in high temperature applications

EPD of composition "N10" (see Table V) combined with reaction bonding was used to join Crystar siliconized SiC pieces. These joined pieces were then exposed to 42 thermal cycles (1340 °C to 1480 °C) during about 100 hours in an inert gas (helium) atmosphere.

3. Results
3.1. Thin metal surface coating results

All of the coating materials (Au, Cu/Pd, C) resulting in sufficient surface conductivity such that EPD coatings could be deposited. The C coating was soft and easily scratched or removed such that poor contact to lead wires resulted. The Au and Cu/Pd coatings both worked very well. Since Au coatings were easy to apply, using equipment readily available in our laboratory, they were utilized for the remaining tests with non-conducting ceramics. The Cu/Pd coating would be the preferred choice for large production rates due to its low cost when applied to large surface areas or a large number of parts.

3.2. EPD slurry composition results

When the EPD system was working well, deposits of 5.08 E-004 m were made within 2 minutes. Deposition rates diminished as the organic liquid mixture slowly adsorbed water from the atmosphere (over a period of

TABLE VI Microstructure observations

| Sample ID	Observations
A_{AU}	More carbon needed.
B_{AU}	More carbon needed.
D_{AU}	SiC : C ratio OK.
R_1	SiC : C ratio OK.
R_2	SiC : C ratio OK. Addition of fine SiC was helpful.
R_3	SiC : C ratio OK. Addition of fine SiC was helpful. C black addition reduced residual Si.
$R_{3.5}$	SiC : C ratio OK.
R_4	SiC : C ratio OK.
L	Large cracks during drying of EPD coating—up to 1.194 E-003 m. Large voids filled with Si; more free Si in coating than desired. Good adhesion at interface of EPD to substrate, but some areas of unreacted Si.
R	Large cracks during drying of EPD coating—up to 1.295 E-003 m. Complete separation of EPD coating from substrate. Only outer skin of EPD was reaction bonded.
S	Large cracks during drying of EPD coating—up to 1.321 E-003 m. Similar to "L" and "R", but deeper penetration of reaction bonding from outside.
T	Good EPD coating—needs 8 pin pricks to produce cracking (7.87 E-004 m). Some voids within the EPD—some filled with free Si, some empty. Better reaction of Si with the carbon. Some interface separation of coating from substrate. Low in unreacted carbon.
U	"T" shaped crack (1.041 E-003 m) due to drying of EPD coating. Very similar to "R" with lack of penetration of Si into the coating. Low in unreacted carbon.
V	Good EPD coating—needs 7 pin pricks to produce cracking (9.906E-004 m). Equal or better than "T" with good adhesion of coating to substrate. Some voids in coating filled with Si. Low in unreacted carbon.

days). Deposition rates diminished rapidly when the thickness of the deposit became quite large (>approx. 2.54 E-003 m). Table VI gives microstructure observations resulting from test joins using the EPD mixtures noted in Table II and Table III.

Based upon sample appearance and microscopic observations, slurry composition "T" and "U" (from Table VI) produced reaction-bonded layers with the best structures. Organic precursors only penetrated the surface of the coatings and did not enhance (e.g., lower the residual Si content) the reaction-bonded microstructures. Therefore, EPD compositions very similar to "T" were adopted as a "standard" mixture for joining experiments.

3.3. Results of EPD to deposit coating into a large gap

Fig. 2 shows the microstructure that resulted when EPD (composition "T") was used to fill the large gap between the ceramic tube inserted into an oversized hole in a plate and then reaction bonded. The figure shows a cross-section where the largest gap filled was 5.6 E-003 m (due to tube not be centered in the hole). The reaction-bonded microstructure was very fine, however this structure was penetrated by relatively large "rivers

Sintered α-SiC (Carborundum's Hexaloy)

← **EPD Coating**

← **EPD Coating**
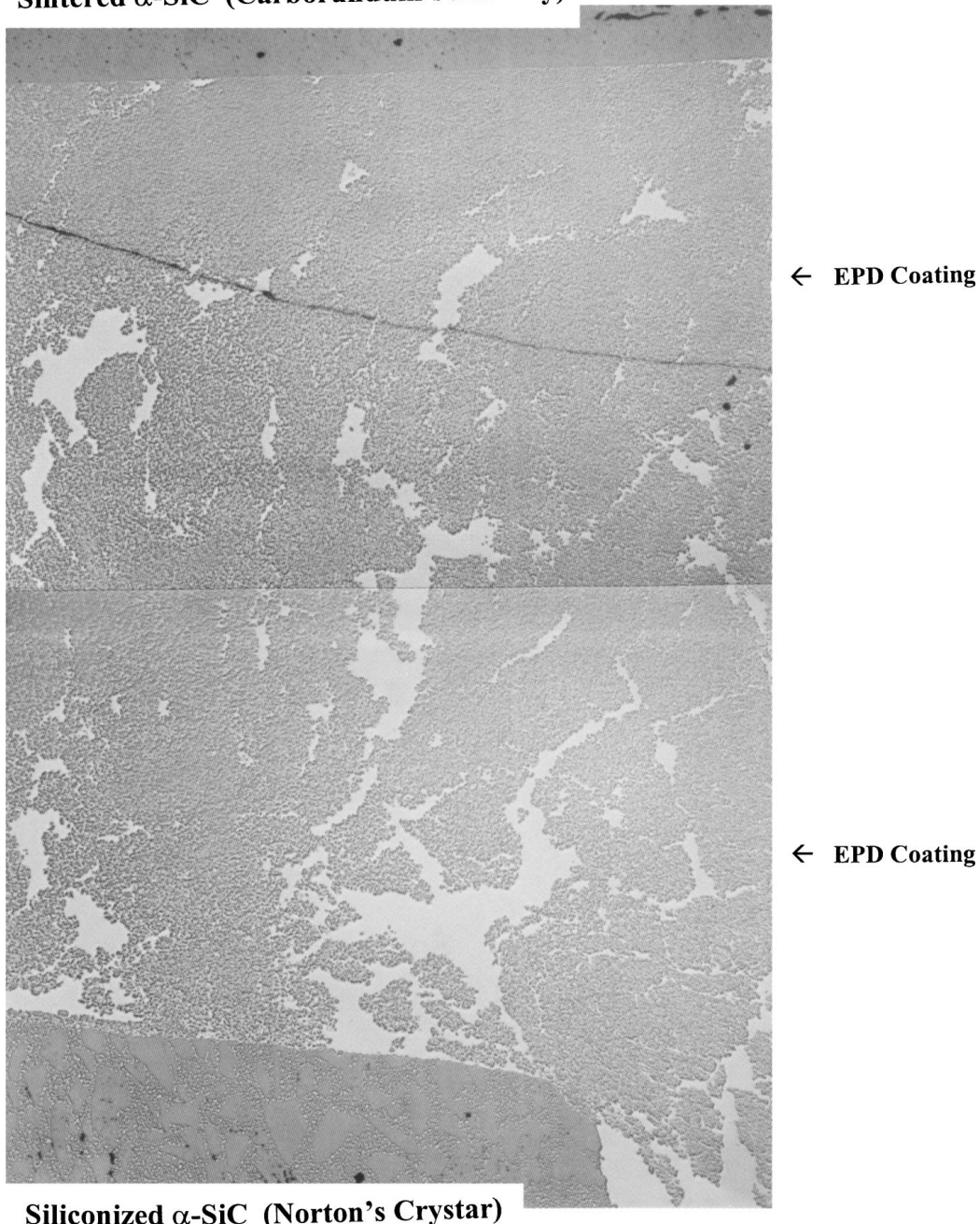
Siliconized α-SiC (Norton's Crystar)

Figure 2 Resulting microstructure when EPD was used to fill in large gap. Hexoloy SiC tube joined into a crystar SiC plate with over-sized hole, Gap = 5.6 mm (0.22 inch) 25 × magnification.

and lakes" of silicon (lighter color). It was determined that the large silicon structures resulted from shrinkage cracks in the EPD coating that were formed during drying of the coating. Subsequent experiments indicated that the cracking could be minimized by slower drying, smaller gaps, and drying of coatings only bonded at one interface.

3.4. Results of reaction bonding (with molten silicon) with EPD coatings
3.4.1. Joining of Hexoloy SiC tubes
The thin-walled Hexoloy SiC tube joined (end-to-end) with a thick-walled Hexoloy SiC tube (of larger diameter) using composition "T" resulted in an excellent joint. The resulting microstructure is shown in Fig. 3.

The microstructure showed extremely fine grain structure and a low level of residual silicon. Especially low residual silicon levels were observed in the vicinity of pore clusters. No shrinkage cracks (filled with Si) were observed. However, there were small regions at the EPD/substrate interfaces where some de-lamination of the coating that subsequently filled with "free" silicon during the reaction bonding process.

3.4.2. Joining of Si₃N₄
Rectangular bars ($3 \times 4 \times 20$ to 30 E-003 m) of AS800 Si_3N_4 were butt joined using composition "N11". The resulting microstructure was examined using an "Environmental" Scanning Electron Microscope [25] as shown in Fig. 4. This technique requires no conductive
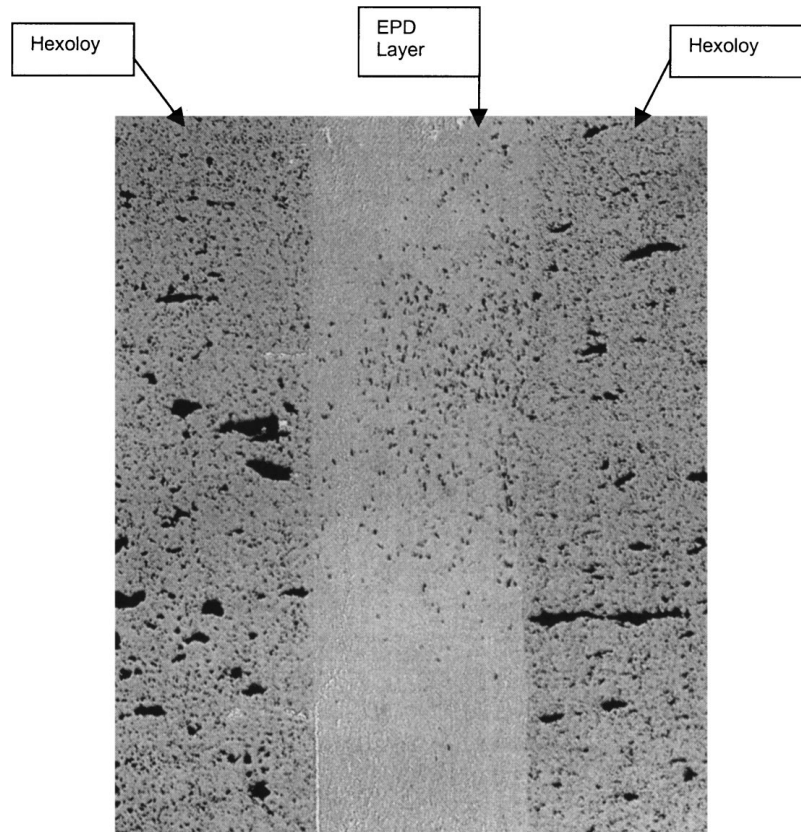
Figure 3 Butt/Scarf EPD joint between Hexoloy tubes (sample 5–8 SiC 7°, 100 × mag).

coating on the surface and can qualitatively distinguish SiC grains from Si_3N_4 grains. These very small crystal phases are identified in the 8000 X magnification SEM micrograph in Fig. 4.

3.5. Resulting microstructures of joints
Image Analysis results for Crystar SiC are shown in Fig. 5. The grain size and free Si content can be compared with the experimental grade NT230 (SC7-7) as shown in Fig. 6. The 14.55% Si measured for the Crystar fits very well into the 13–15% range claimed by the manufacturer. However, the experimental value of 11.17% for the NT230 (SC7-7) was somewhat higher than the 7–8% claimed by the manufacturer. By comparison, the EPD coating values for residual Si generally ranged from about 7% to 11% as illustrated in Figs 7 and 8. Some isolated areas showed free Si content somewhat lower than 7% . These low Si areas generally were associated with an increase in local porosity; this lowering of free Si appeared to be compensated by an area higher in Si elsewhere in the sample. The low residual Si for EPD joints can be contrasted with free Si contents of 41% for tape cast/reaction bonded joints (as shown in Fig. 9). As illustrated by the two different samples of Fig. 9, the high residual free Si content of tape-cast joints did not vary with SiC filler particle size.

3.6. Results of tensile strength specimen fabrication using the EPD/reaction-bonding process
Fig. 10 shows a radiograph that was made of the SiC composite tube joined to the special Hexoloy SiC

"header" to fabricate a tensile test specimen. The joint appears to be well-bonded, except in one area; this section has been magnified and the contrast enhanced in the small photograph. It is thought that this area did not receive full infiltration of molten Si that was placed on outside perimeter of the joint. This lack of bonding region points out the importance of strategically placing sufficient Si around the exterior of the joint to result in an even distribution of molten Si within the join for reaction bonding. Lack of bonding would result in a large strength-limiting flaw when the entire structure is tested in tension.

3.7. Results for EPD/reaction-bonded joints exposed to high temperatures
Fig. 11 shows the microstructure that resulted from thermal cycle testing (above and below the melting point of Si). The residual "free" Si completely evaporated from the open porosity of the Crystar siliconized parts (a small amount remained in the closed pores). By contrast, most or all of the free Si remained in the EPD reaction bonded joint (evidently in closed pores).

4. Discussion of results
It was obvious that a wide range of SiC : C ratios could be deposited using the EPD technique. Successful reaction-bonded joints were fabricated using SiC : C ratios that varied from 2 : 1 to 0.48 : 1. However, the best microstructures were consistently obtained with a SiC : C ratio of 0.64 : 1. Attempts were made to select the SiC and C source materials such that the variations
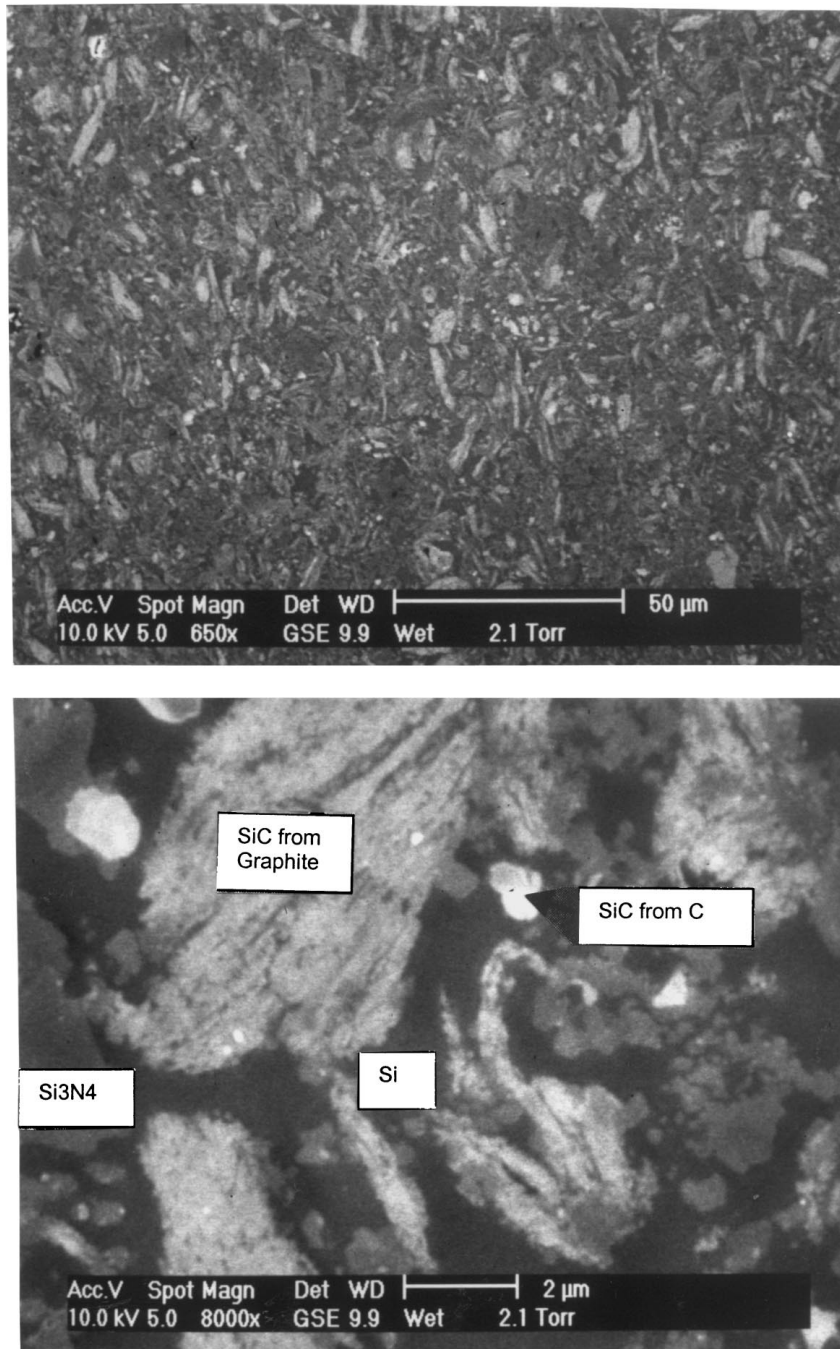
Figure 4 Microstructure of EPD joint containing Si$_3$N$_4$ filler.

in particle sizes would result in high "green" packed densities for the coatings. This high "green" density helped create a low volume fraction of residual "free" silicon after the silicon reacted with the carbon. Attempts to fill in pores in the "green" coating with polymeric precursors that would create additional fine carbon (after pyrolization) were unsuccessful because the precursors did not deeply penetrate from the exterior of the dried "green" coatings. These liquid precursors also tended to reduce the "green" density by moving the particles further apart as the liquid penetrated the packed powder assembly. Therefore, the experiments using polymeric precursors were abandoned. However, the use of about 3–6% organic binder (dissolved in the organic solvents of the slurry) was very helpful. After the EPD deposits dried, the organic binder imparted

strength and toughness to the coatings that allowed the coatings to remain intact and adhered to the ceramic substrates during subsequent handling.

It may be possible to further increase the green density of the EPD coatings with the intended result that shrinkage during drying is minimized (in order to reduce cracking of deposits filled into large gaps between parts) and the residual silicon level be reduced to even lower levels. However, it might not be possible to reduce the residual silicon to a level much lower than 7 vol % because this is the approximate volume level where residual open porosity is eliminated and only closed porosity remains. Open porosity is necessary to "wick" the molten silicon from outside the joint into the center of the porous particle assembly via capillary action. If higher "green" densities are desired for filling
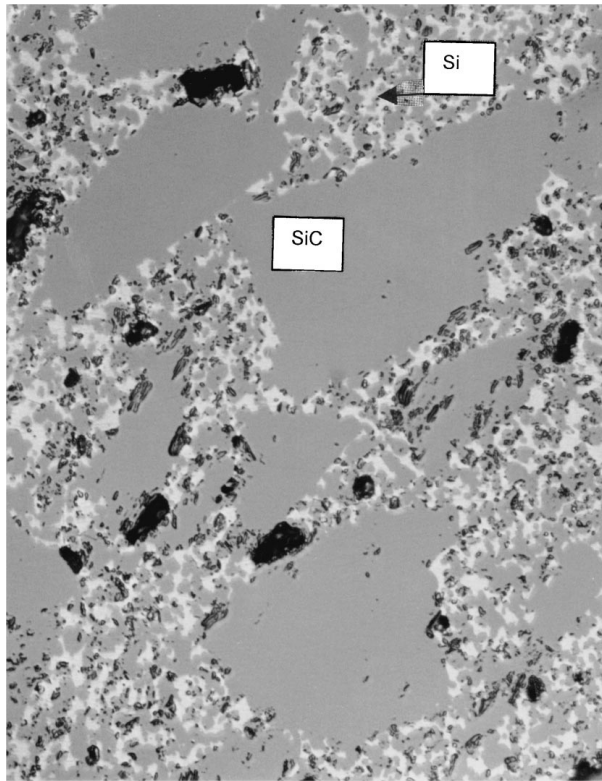
Figure 5 Crystar siliconized SiC (400 × mag). Image analysis: 14.55% Si, 8.10% porosity, 77.05% SiC.
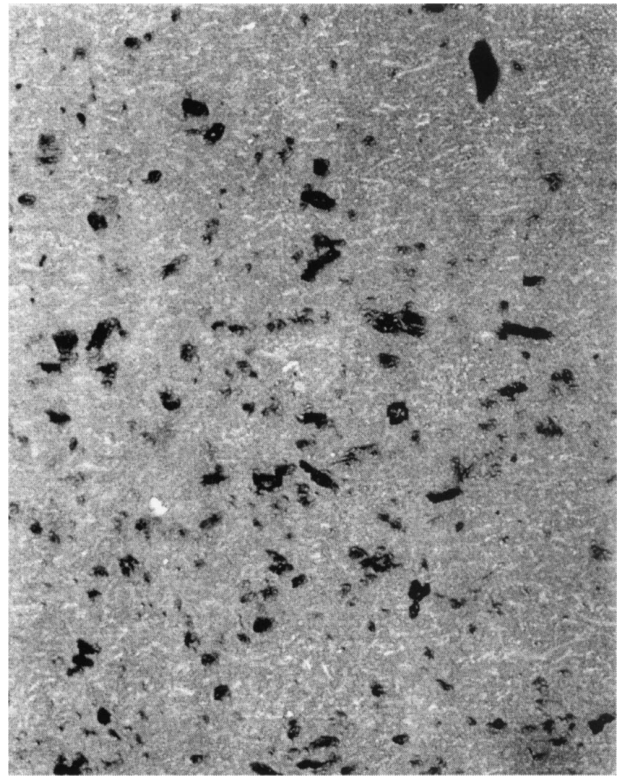

Figure 7 EPD joint (sample CAT -1 area 2, 400 × mag). Image analysis: 7.11% Si, 3.18% porosity, 89.7% SiC.
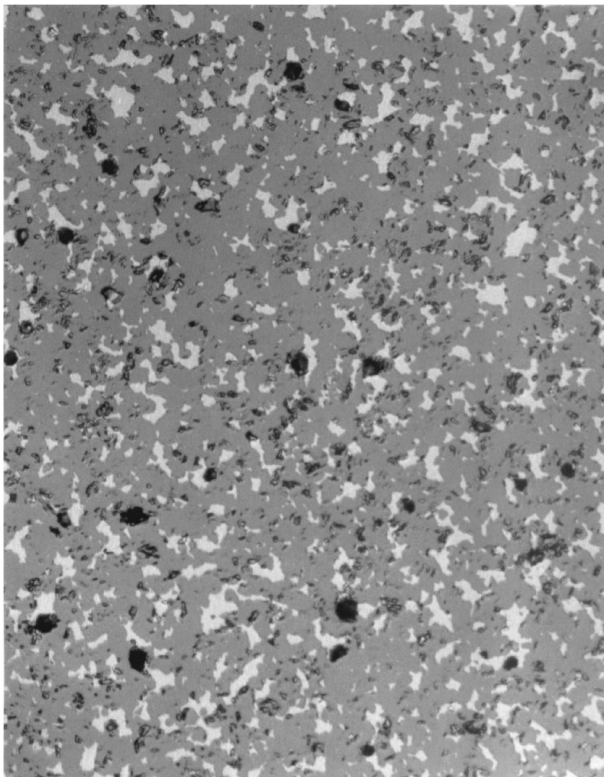

Figure 6 Siliconized SiC grade NT230; SC7-7 experimental (400 × mag). Image analysis: 11.17% Si, 4.18% porosity, 84.63% SiC.
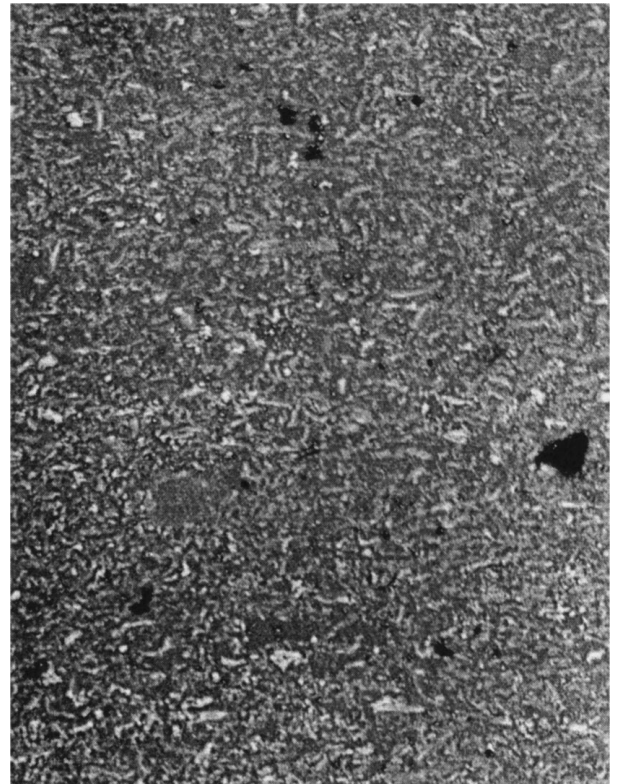

Figure 8 EPD joint (sample CAT-1 area 1, 400 × mag). Image analysis: 11.20% Si, 1.84% porosity, 86.96% SiC.

in large gaps while preventing cracking, the EPD process can be controlled and varied in a number of ways:

(1) Carefully select the particle sizes of the SiC or Si_3N_4 filler, graphite, and carbon black. Tri-modal particle size mixtures can result in very high packed den-

sities; however, the particle sizes should be at least an order of magnitude different at each of the three sizes to maximize the effect. The variation in mean particle size between the favored SiC sources utilized in this study (e.g. Starck A-1 compared to A-10 grade) really was only about 2 : 1. Interestingly, using a gradation
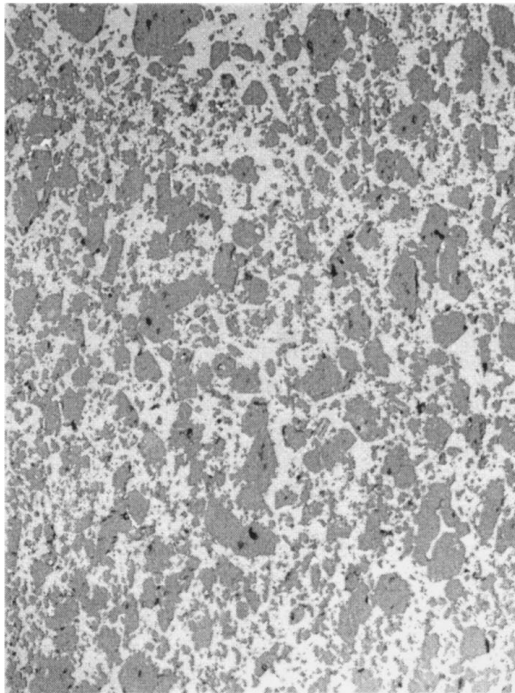
Sample 8B427

(a)
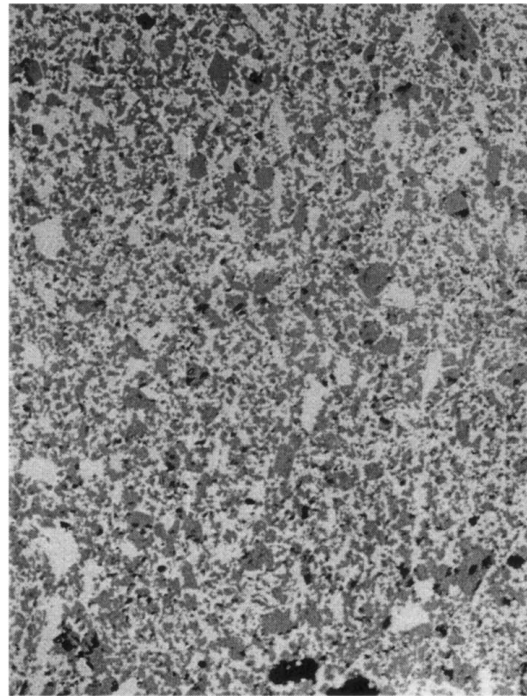
Sample 20 6-6-96

(b)

Figure 9 Tape cast joints (343 × mag). (a) Image analysis 8B427: 41.83% Si, 0.70% porosity, 57.47% SiC; (b) Image analysis 20 6-6-96: 41.14% Si, 2.12% porosity, 56.747% SiC.
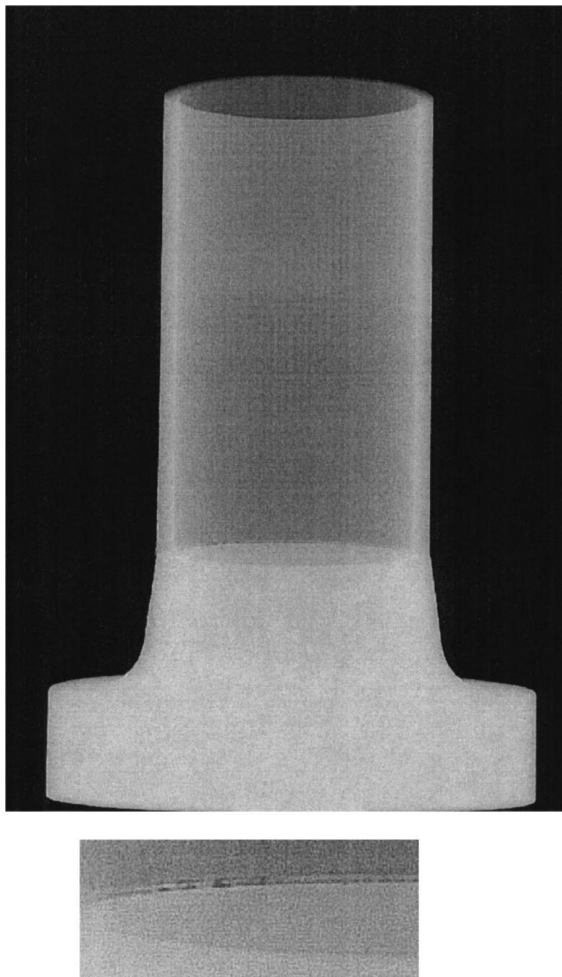

Figure 10 Radiograph of EPD join of SiC composite tube to Hexoloy "Header"—enlargement shows lack of complete bond in one area of the interface.

of SiC particle sizes that included Cerac SiC 10 micron particles (e.g. Cerac : A-1 mean size ratio 10 : 1) in Samples "L", "R", and "S" wasn't helpful because the resultant EPD coatings tended to crack (indication of excess shrinkage). It is possible that the large Cerac particles tended to settle very quickly from the slurry due to the low viscosity of the EPD solvents utilized. Better results were obtained by using 100% fine A-10 SiC powder with graphite and carbon black (e.g. sample "T"). Laser particle size analysis of A-10 powder indicated a tri-modal particle size distribution with small 4 vol % peaks at 10 micron and 2 micron, with a larger 20 vol % peak at 0.6 micron.

(2) The voltage of the EPD process can be increased, to speed lateral movement of large particles.

(3) The solvent composition could be altered to affect the charge on the particles and possibly increase the viscosity.

(4) The EPD electrode gaps and part geometry can be modified and improved.

(5) The organic binder composition and volume % in the slurry can be adjusted to affect the viscosity (without the binder occupying too much volume in the dried coating).

(6) Polymer precursors could be used to "backfill" cracks in dried coatings and increase the carbon and/or SiC density. However, viscosity adjustments and improved impregnation techniques would have to be developed.

(7) The wt % loading of the particles in the slurry could be optimized. However, it is not clear that a large increase in the slurry loading would result in an increase in the green density of the EPD deposit.
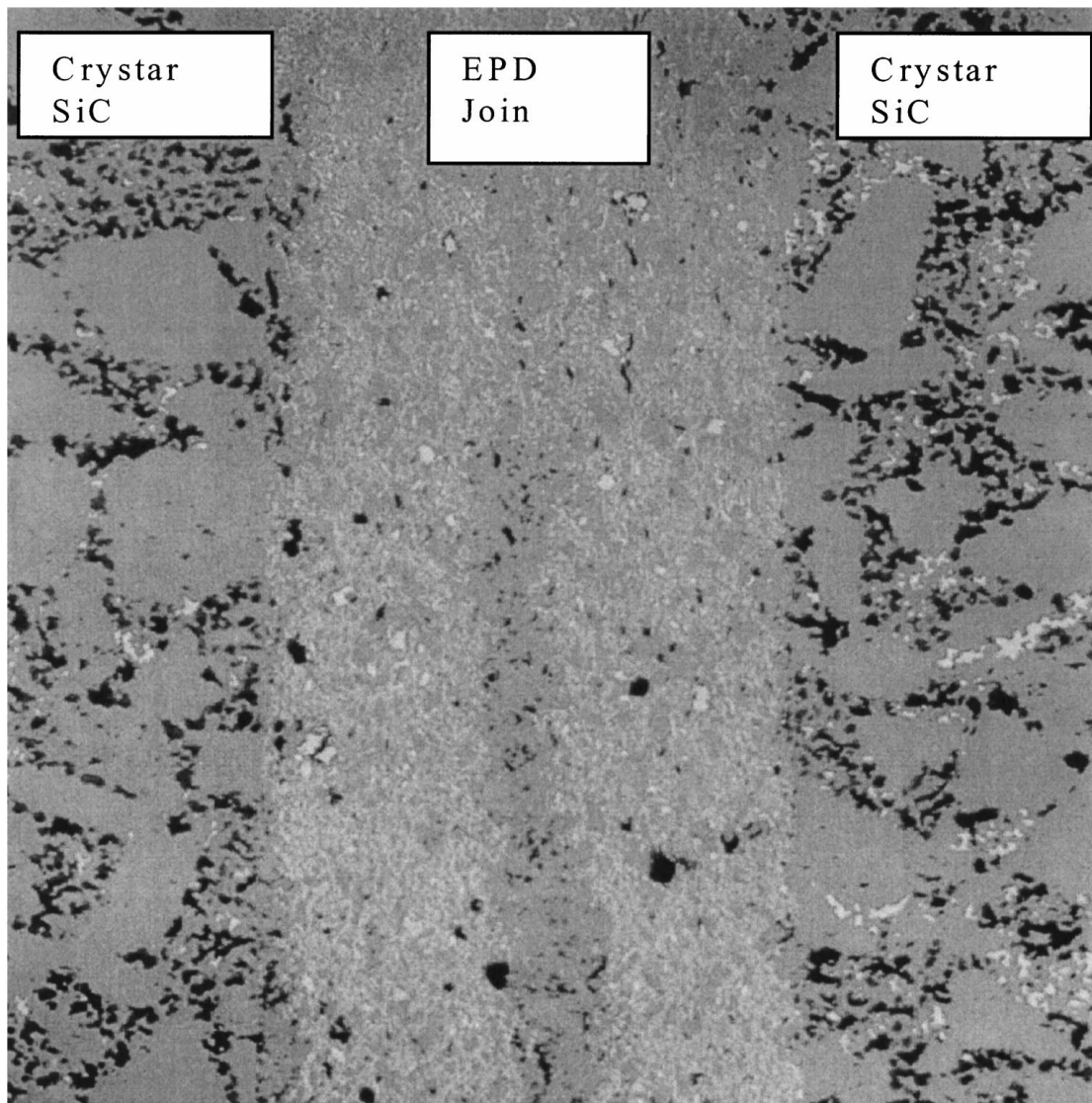
Figure 11 EPD join of crystar SiC after extensive thermal cycling at high temperatures (sample TC3-1).

(8) Slow the drying rate of the "green" coating and control the drying geometry. Slowing the drying rate was successful in preventing cracking in EPD coatings up to about 1 E-003 m thick (when the coating was only constrained by adhering to a substrate on one side with the other side free).

Fabrication of large structures (such as the SiC composite tube joined to the Hexoloy SiC "header") illustrated the need for better placement and control of the volume of molten silicon available to the joint during the high temperature reaction bonding process. The use of tape-cast strips of powdered silicon might be a good solution to this problem.

5. Conclusions

The Electrophoretic Deposition (EPD) technique was successfully applied to fabricate reaction-bonded joints using a variety of silicon carbide and silicon nitride ceramic compositions and shapes as demonstration parts. Extremely thin metal coatings were used to make the surface of non-conductive ceramic compositions suffi-

ciently conductive to utilize them as electrodes in the EPD process. The EPD slurry consisted of silicon carbide or silicon nitride particles mixed with graphite and carbon black particles. This slurry was sufficiently optimized to result in low (7–11 vol %) residual "free" silicon content in joints after the reaction bonding process. This low level of residual silicon favorably compares with the lowest levels found in experimental versions of bulk siliconized-silicon carbide manufactured using conventional techniques. Resulting joints retained the residual silicon over a large number of high temperature thermal cycles (cycling from below to above the melting point of silicon). This implies the majority of the residual silicon was retained in closed porosity and that parts made with these joints might be successfully utilized at very high temperatures.

It was demonstrated that the EPD technique can be applied to butt, lap, and scarf type joining geometries. A particularly attractive feature of using EPD to form joints is the capability to fill in large gaps and coat around corners or undercut sections. This should allow the fabrication of large complex structures of silicon carbide or silicon nitride.

Acknowledgement

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