

striking velocity is  $3.3 \text{ m sec}^{-1}$ . Analysis of these data using linear elastic fracture mechanics [10] shows that  $G_c \approx 1.39 \text{ kJ m}^{-2}$  (i.e.  $K_c \approx 1.94 \text{ MPa m}^{1/2}$ ) in both air and methanol thus confirming the absence of an environmental effect at these extremely high strain rates. It is however worth mentioning that similar impact experiments performed on a more ductile polymer, ABS, give lower impact energy values ( $\omega$ ) in methanol than in air at equivalent ligament areas,  $B(D-a)$ , as shown in Fig. 3. This suggests that the picture is more complicated than is originally thought and assessment of impact fracture resistance of polymers in liquid environments should be a subject of technological importance which requires further studies in the future.

Table I summarizes our recent experimental results obtained in a series of primary alcohols. It is shown that in general terms both  $\epsilon_c$  and  $K_I$  increase with the Flory-Huggins interaction parameter ( $\chi_H$ ). The instability  $K_c$  values although show a similar trend their magnitudes are determined principally by the relative sizes of the crack tip craze bundles prior to unstable fracture. From methanol to pentanol, the craze size increases as the molar volume increases. It is also noted that in the course of the critical strain measurement experiments [9] we have observed, as Phillips does, that methanol (AR grade) behaves somewhat differently to PMMA than the other alcohols. Compared with say ethanol which produces many fine crazes in PMMA the crazes created in methanol are relatively few in number but larger in size. A full discussion on this subject will be contained in a future publication [11].

#### Note added in proof

Although the cause of "stick-slip" fracture is not fully known, reanalysis of Mai and Atkins' data

[5] shows that for the particular epoxy resin they studied "stick-slip" may be due to an isothermal-adiabatic transition. Using Equations 12 and 13 in [13] the instability crack velocity is calculated to be some  $0.2 \text{ m sec}^{-1}$  when  $T = 298 \text{ K}$  and the crack tip temperature rise is approximately  $8^\circ \text{ C}$ . These calculated results are in good agreement with the experimental data presented in [5].

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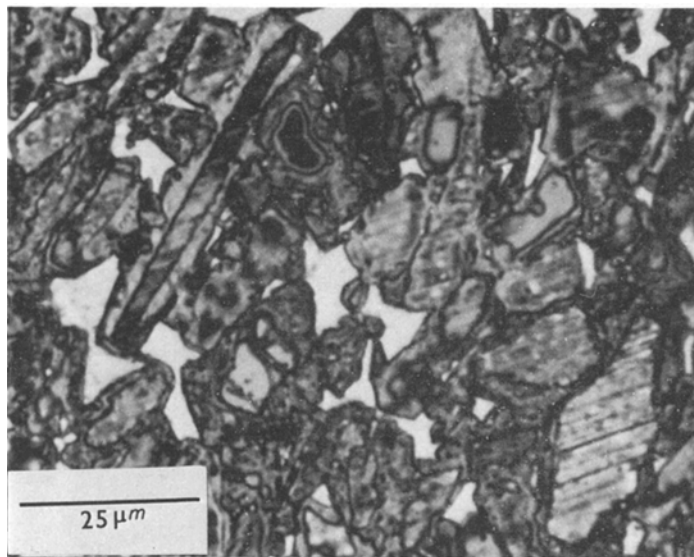
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#### Discussion of "Microstructural characterization of 'REFEL' (reaction-bonded) silicon carbides"

Sawyer and Page [1], in studying the microstructure of "REFEL" reaction-sintered SiC, claim that, "... in contrast to previous descriptions of

the microstructure, it has been found that the newly-formed SiC is deposited from the super-saturated solution of carbon in molten silicon both epitaxially on the original SiC grains, maintaining the same  $\alpha$ -polytypic stacking sequences, and by nucleation of fine cubic  $\beta$ -SiC elsewhere". The main thrust of their argument is that, while the SiC that



*Figure 1* Optical micrograph of "REFEL" SiC. The epitaxial deposits of  $\beta$ -SiC on the  $\alpha$ -SiC seed crystals are revealed by electrolytic etching (electrolytic solution of  $\text{CrO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{COOH}$  in  $\text{H}_2\text{O}$ ; 6 V, 1 A; etching time is a few seconds).

nucleates on the fine particle size graphite present in the original green body is the cubic  $\beta$ -SiC polymorph (in agreement with previous descriptions of the structure), the deposit that forms epitaxially on the  $\alpha$ -SiC seed crystals present in the green body is not  $\beta$ -SiC, as has been claimed in the literature (e.g. [2]), but the same  $\alpha$ -SiC polytype as the seed. Our research on similar reaction-sintered SiC shows that the epitaxial deposit is indeed  $\beta$ -SiC, and is thus at variance with the results of Sawyer and Page; we believe they erred in not recognizing that the  $\beta$ -SiC deposit transforms to the  $\alpha$  polymorph of the seed at some point during processing.

In the course of studies conducted separately at Case Western Reserve University and at Ford Motor Company Research Laboratories on the  $\beta \rightarrow \alpha$  phase transformation in polycrystalline SiC, two different reaction-bonded SiCs have been examined by optical, scanning electron (SEM) and transmission electron microscopy (TEM). The gross morphology of the grains in the two materials, as revealed by optical microscopy (Fig. 1) and SEM, are as described by Sawyer and Page; however, the means by which contrast is obtained in Fig. 1, as well as the secondary electron SEM mode used by Sawyer and Page, does not reveal the polymorphic modification of the epitaxial deposit. TEM examination and electron diffraction, on the other hand, have clearly established that the epitaxial deposit in our samples

is definitely  $\beta$ -SiC, in agreement with prior work, but transforms to  $\alpha$ -SiC upon annealing. While we have no knowledge on the purity of the SiC deposit of the materials we studied, we agree with Sawyer and Page that strings of microvoids and other microstructural defects are formed during reaction sintering and can delineate the boundary between an  $\alpha$ -SiC seed and its epitaxial deposit; this is evident on the TEM micrographs now to be presented. Nevertheless, we wish to emphasize that the epitaxial deposit in an unannealed reaction-sintered SiC is  $\beta$ -SiC, and not  $\alpha$ -SiC.

Our findings are illustrated by micrographs obtained from a single as-received "REFEL" sample and show that  $\beta$  deposits on different  $\alpha$  seeds have undergone various amounts of transformation; identical results were obtained from reaction-sintered SiC fabricated at Ford Motor Co Research Laboratories. Fig. 2 shows an  $\alpha$ -SiC seed crystal (15R polytype) and its epitaxial deposit, which is heavily-microtwinned  $\beta$ -SiC. The  $[11\bar{2}0]_\alpha$  and  $[110]_\beta$  diffraction patterns from seed and deposit are shown as insets; note also that two variants of  $\{111\}_\beta$  twins, formed by reflection across  $(1\bar{1}1)$  and  $(\bar{1}11)$ , are present in the deposit and are revealed in the diffraction pattern. Diffraction spots (arrowed) due to one of these micro-twins occur at reciprocal lattice positions where no  $\alpha$ -SiC polytype can cause diffraction. The complete coherency of the two portions of the grain was readily established by taking a diffraction pattern

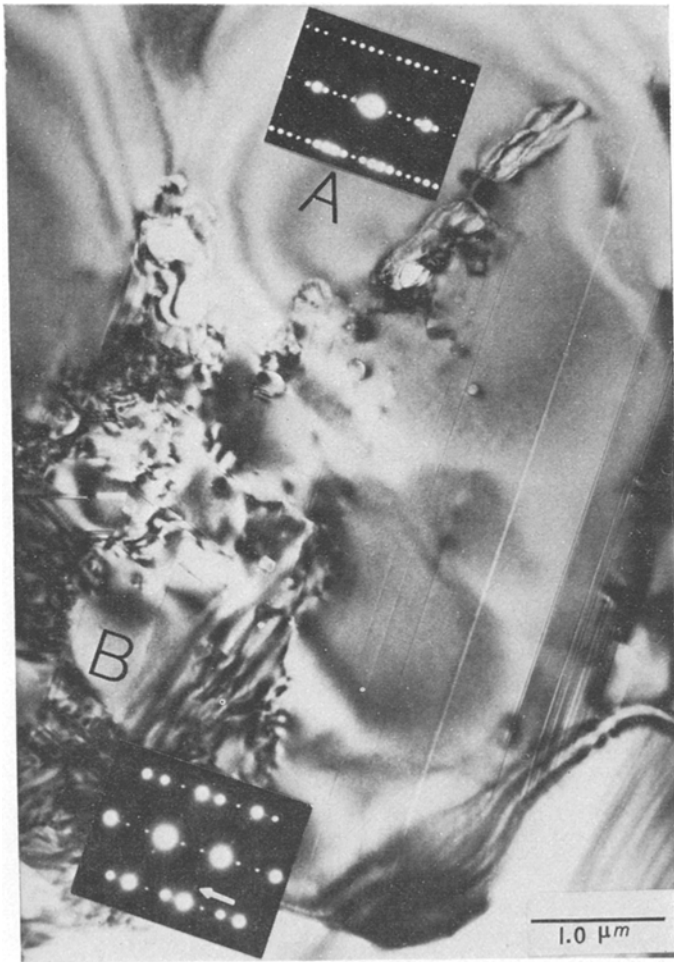


Figure 2 TEM micrograph of a grain in the "REFEL" sample showing the  $\alpha$ -SiC seed crystal (A) (featureless background) and the  $\beta$ -SiC epitaxial deposit (B). The diffraction pattern at the top was obtained from the  $\alpha$ -SiC region, while that at the bottom is from  $\beta$ -SiC.

using a selector aperture large enough to sample both regions.

In view of the well-known propensity of polycrystalline  $\beta$ -SiC to transform to  $\alpha$ -SiC upon annealing [3], it is likely that the samples investigated by Sawyer and Page underwent some transformation during processing, i.e. subsequent to infiltration with molten Si. The possibility that reaction-sintering at temperatures higher than normal gave rise to  $\alpha$ -SiC deposits can be discounted by the presence of some fine  $\beta$ -SiC that did not form epitaxially on the  $\alpha$  seeds and by the assertion of Sawyer and Page that their observed polytype distribution was "... characteristic of material formed from the vapour phase at much higher temperatures ( $>2000^\circ\text{C}$ ) than those attained

during the "REFEL" process", i.e. the distribution was that of the original  $\alpha$ -SiC seeds.

The "REFEL" material is usually fabricated at  $\sim 1700^\circ\text{C}^*$ , and at this temperature,  $\beta$ -SiC will start to transform to the  $\alpha$  polymorph. In fact, the Ford reaction-sintered SiC is usually fabricated at  $\sim 1500^\circ\text{C}$  [2] and, upon subsequent annealing at temperatures as low as  $\sim 1600^\circ\text{C}$ , will undergo appreciable transformation [6]. Reaction sintered samples fabricated at temperatures in excess of  $1700^\circ\text{C}$  but not subjected to subsequent heat-treatment have been observed to have undergone significant  $\beta \rightarrow \alpha$  transformation [7].

That the  $\beta \rightarrow \alpha$  transformation can occur readily in "REFEL" SiC is shown in Fig. 3, in which the  $\beta$  portion of the composite epitaxial  $\beta/\alpha$  grain can be

\*The fabrication procedures for "REFEL" SiC are described by Popper [4] and Forrest *et al.* [5].

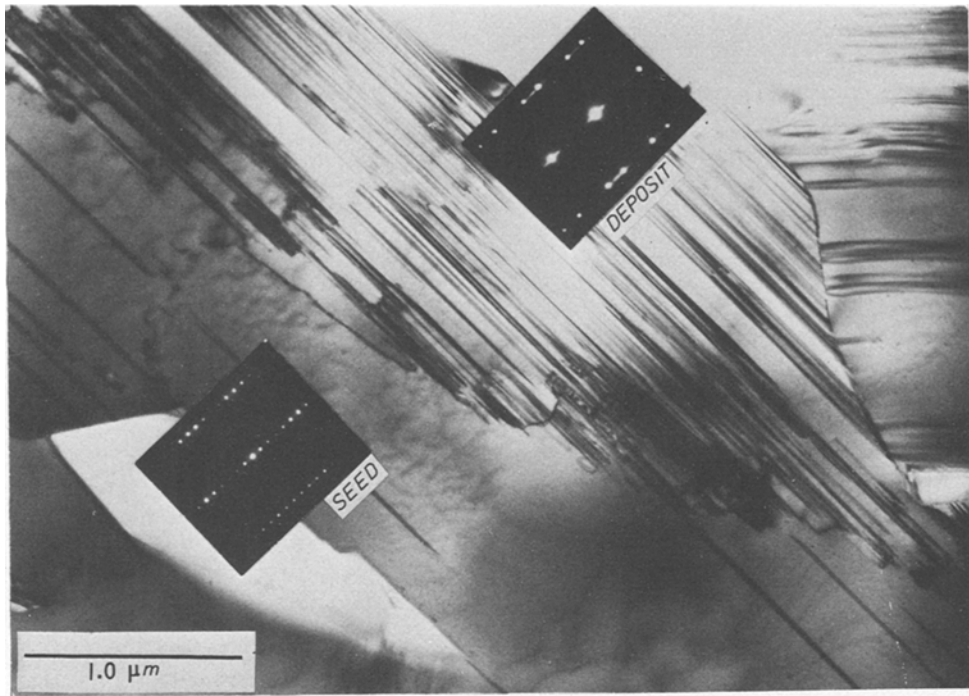


Figure 3 TEM micrograph from "REFEL" showing the onset of the  $\beta \rightarrow \alpha$  phase transformation in the  $\beta$ -SiC deposit, which is evident from the faint  $\alpha$ -SiC (6H) spots in the diffraction pattern from the deposit (top inset).

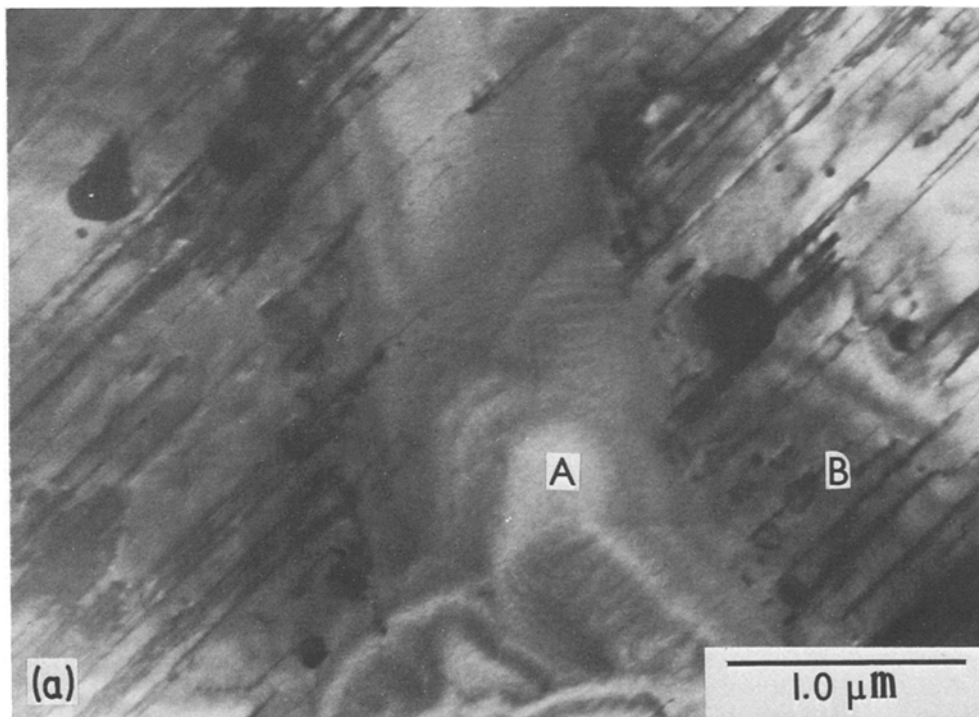


Figure 4 (a) TEM micrograph from "REFEL" showing a grain whose  $\beta$ -SiC deposit (B) has transformed fully to  $\alpha$ -SiC (6H polytype — the same structure as the  $\alpha$ -SiC seed crystal, A).

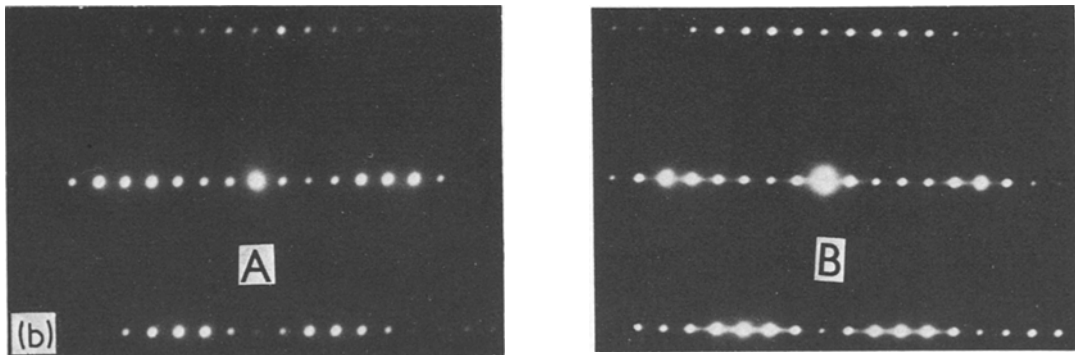


Figure 4 (b) Electron diffraction patterns from the seed (A) and deposit (B) – note the streaking visible in the latter pattern. The diffraction patterns should be rotated so that the rows of spots are perpendicular to the faults in the image in (a).

seen to have started to transform to  $\alpha$ . In the heavily microtwinning  $\beta$  region, the diffraction pattern exhibits faint spots in the 6H positions (the same polytype as the  $\alpha$  region), attesting to the onset of transformation.

Finally, Fig. 4 shows a grain that is fully  $\alpha$ -SiC. That  $\beta \rightarrow \alpha$  transformation of the epitaxial deposit has occurred, and to the same polytype (6H) as the original  $\alpha$  seed, is evident from the microstructural defects present in the deposit (the seed is the central featureless region). It is well known that the newly-formed  $\beta$ -SiC in reaction-bonded samples contains numerous stacking defects. When this material transforms to  $\alpha$ -SiC, the high density of stacking defects is inherited, as can be seen in the bright-field image (Fig. 4a) and as is evident from the streaking visible in the diffraction pattern (Fig. 4b). The demarcation between the  $\alpha$ -SiC seed crystal and the (transformed) epitaxial deposit is very clear.

An important point to note about the  $\beta \rightarrow \alpha$  phase transformation in samples such as "REFEL" is that, once initiated, it goes to completion quite rapidly. The sample studied here is only a short step away from full transformation of its epitaxial  $\beta$ -SiC deposits. It would thus be easy to overlook the transformation step and conclude that  $\alpha$ -SiC forms epitaxially on the  $\alpha$ -SiC seed crystals during reaction-sintering.

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