

IMPROVEMENT OF THE THERMAL CONDUCTIVITY OF SiC_f/SiC COMPOSITE - G. E. Youngblood (Pacific Northwest Laboratory)* and W. Kowbel (MER Corporation, Tucson AZ)

OBJECTIVE

The objective of this work is to examine SiC composites fabricated by various processing methods designed to improve their thermal conductivity. Specifically, it is desired to increase the thermal conductivity of these composites to meet requirements for potential fusion reactor applications.

SUMMARY

Two methods, high temperature annealing and doping, were examined for improving the thermal conductivity of simulated CVI/B-SiC matrix material. For instance, a two hour 1500°C anneal led to the increase of the room temperature (RT) thermal conductivity from 38 to 59 W/mK. Be-doping was even more effective in causing the thermal conductivity to increase with RT conductivity values up to 160 W/mK attained. To further optimize the thermal conductivity, hot-pressed SiC materials with carefully controlled amounts of Be- and B₄C-doping were investigated. Although a small improvement (\approx 8%) was achieved with 2.0 wt% Be-doping, the effort to refine the amount of doping needed was largely unsuccessful. Apparently, hot-pressing SiC introduced numerous substructural stacking faults which effectively scattered phonons in the intermediate temperature range and nullified the benefits of doping. Nevertheless, Be- and B₄C-doping and/or thermal treatments appear to be promising strategies to achieve the goal of eventually improving the thermal conductivity of SiC_f/SiC composite.

PROGRESS AND STATUS

Introduction

Silicon carbide (SiC) has been considered as a structural material for fusion applications because of its low neutron activation and after heat and its stability at high temperature during irradiation as well as its outstanding mechanical properties.¹⁻³ To provide improved strength and toughness, continuous fiber reinforced SiC composites (SiC_f/SiC), being developed primarily for advanced aerospace applications, also are now being examined for fusion reactor applications.⁴⁻⁷ Such composites typically are fabricated with about 40% by volume fiber reinforcement, while the matrix can be fabricated by either chemical vapor infiltration (CVI) or polymer infiltration and pyrolysis (PIP). The higher strengths as well as the improvement in toughness and strain-to-failure originate from a somewhat "weaker" interphase, generally either pyrolytic carbon or porous SiC, that is applied as a thin coating to the fiber bundles or fabric layups prior to the matrix infiltration. Under load the weak interphase (or a weak interface) deflects matrix cracks and the fibers tend to debond from the matrix, thus allowing transfer of the load to the inherently stronger fiber bundles.⁸

Unfortunately, while the thermomechanical properties of SiC_f/SiC can be improved over that of monolithic SiC, the thermal conductivity is significantly reduced. For instance, a high density, high purity SiC made by chemical vapor deposition (CVD) generally will have a RT thermal conductivity value >300 W/mK,⁹ while through-the-thickness conductivities of SiC_f/SiC(CVI) have been observed to be <10 W/mK.⁷ Generally, the thermal conductivity of SiC_f/SiC(PIP) has been observed to be even less

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with values of 2-4 W/mK typical. Although porosity in the composite can account for some of this observed reduction in thermal conductivity, reasonable porosity correction factors cannot account for the observed factor of 30 or greater reduction. Moreover, upon neutron irradiation to doses above a few dpa, the composite's thermal conductivity is substantially reduced even further due to accumulation of point defects.⁷

In a conceptual design study of the thermal performance of a fusion reactor with a SiC_f/SiC first wall of thickness 3 mm, efficient steady operation could be maintained if the thermal conductivity of the SiC_f/SiC exceeded 7 W/mK.¹⁰ For the high thermal efficiency required for a fusion reactor diverter, the thermal conductivity would have to exceed 70 W/mK.¹⁰ Obviously SiC_f/SiC with a thermal conductivity much below 10 W/mK will greatly limit potential applications of these materials.

Recent studies have shown that in the direction perpendicular to the fiber planes in 2D plane weave SiC_f/SiC, the SiC fibers themselves contribute very little to the thermal conductivity of the composite.¹¹ The weakly bonded fiber structures, necessary for optimized mechanical properties in SiC_f/SiC, apparently act as an insulating phase, while heat transport takes place primarily through the matrix phase. Thus, differences in thermal conductivity between types of SiC_f/SiC will depend upon the morphology and substructure of the matrix as well as the degree of crystallinity and purity of the matrix, but probably will depend little on the type of SiC fiber used. **Importantly, significant improvement in the matrix conductivity does appear to be attainable by optimizing processing parameters to control purity and structure of the matrix.**

Takeda showed that SiC hot-pressed to full density while using 1-2% BeO or other Be-compounds as sintering aids exhibited RT thermal conductivities up to 270 W/mK.¹² While examining the effect of thermal treatments, Collins *et al.* showed that the thermal conductivity of high purity CVD/SiC could be improved by increasing the deposition temperature from 1300 to 1350°C.¹³ They attributed this improvement to an increase in the grain size attained by use of a higher processing temperature. Using these concepts, researchers at MER Corporation (Tucson AZ), under an SBIR grant from DOE/Fusion Energy, currently are examining the potential for improving the thermal conductivity of β-SiC matrix material by doping and by thermal treatments.¹⁴

MER researchers have simulated CVI/β-SiC matrix material by vapor depositing a thick layer of β-SiC (no fiber preform) onto a graphite substrate while utilizing deposition conditions typical for CVI, i.e., they used a gas mixture of methyltrichlorosilane (MTS) and hydrogen and a deposition temperature of 1150°C. Kinetic constraints for the CVI process with a fiber preform limit deposition temperatures to 1150°C, much below the 1300 to 1450°C range normally used for fabricating dense, high purity β-SiC by CVD. MER also has fabricated simulated Be-doped CVI/β-SiC matrix material by mixing a very low level of BeBr₂ vapor with the MTS/hydrogen mixture to codeposit the Be simultaneously with the SiC, a process amenable to scale up.

Without the Be-doping, a CVI/β-SiC sample deposited at 1150°C had a density of 2.6 g/cc (81% T.D.) and a RT thermal conductivity of 38 W/mK. By annealing the undoped CVI/β-SiC deposit for two hours at 1500°C in helium, a 50% increase in the thermal conductivity was induced.¹⁴ Until recently, SiC_f/SiC composites have been limited to exposure temperatures below about 1200°C due to thermal instability of available first generation SiC fibers (such as Nicalon CG). Therefore, heat treatments to improve the thermal conductivity of SiC_f/SiC were not feasible. Advanced fibers now becoming available, like Hi-Nicalon or MER CVR/SiC, are thermally stable up to 1500°C, so 1500°C now represents a practical high

temperature limit for SiC_f/SiC containing these advanced fibers. Finally, a CVI/β-SiC deposit fabricated with Be-doping exhibited an even greater enhancement of the thermal conductivity; a very promising RT value of 160 W/mK was attained!¹⁴

To optimize the thermal conductivity of CVI/β-SiC even further, MER researchers set about fabricating SiC with precisely controlled levels of Be- or B₄C-doping. Since it was difficult to control the exact amount of Be additive by the vapor codeposition process, conventional hot-pressing was employed to more precisely control the doping levels. The measurement and analysis of the thermal transport properties of these materials, i.e., hot-pressed Be- and B₄C-doped SiC fabricated by MER, are the subjects of this report.

Experimental Procedure

Therefore, dense (>97% TD) SiC plates were fabricated by hot-pressing at 2050°C. Appropriate amounts of SiC powders were mixed with Be or B₄C powders to attain precise doping levels of 0, 0.25, 0.50, 1.0 and 2.0 wt% Be-doping or 0, 1.0 and 2.0 wt% B₄C-doping.

The thermal transport properties of these materials were characterized by measuring the thermal diffusivity by the laser flash technique over a 300 to 1200°C temperature range. In this technique, described else-where,¹¹ four or more separate shots were made at each temperature to give an average thermal diffusivity value with a typical uncertainty of ± 5%. For comparison, diffusivity measurements also were made on six different fully dense, high purity CVD/β-SiC samples (obtained from Morton International) and on a commercially available SiC_f/SiC(CVI) composite (obtained from Dupont) with a two-dimensional (2D) plain weave fiber architecture. Microstructural and phase details currently are being analyzed by TEM (and HRTEM), optical and XRD methods.

Results and Discussion

In Figure 1(a-b), the measured thermal diffusivity values as a function of temperature for the hot-pressed SiC doped with (1a) 0-2 wt% Be or (1b) B₄C are shown together with similar data for the reference material, monolithic CVD/β-SiC, and for the 2D SiC_f/SiC(CVI) composite. For analysis, the data are shown replotted as the reciprocal thermal diffusivity in Figure 2(a-b). In this figure the straight lines through the data points for each composition were determined by least squares regression. The curved lines shown in Figure 1(a-b) are included for guidance only.

The thermal diffusivity (α) is a derived quantity given by $\alpha = k/\rho C_p$, where k is the thermal conductivity, ρ is the bulk density and C_p is the specific heat at constant pressure. A useful expression relating the lattice thermal conductivity to an effective phonon mean free path (l_{eff}) is $k = (1/3)Cvl_{eff}$ where now C is the specific heat per unit volume and v is the lattice wave velocity (usually taken as the sound velocity).¹⁵ If the expressions for thermal diffusivity and conductivity are combined, and noting that $\rho C_p = C$, one gets:

$$\alpha = (1/3)v l_{eff} \quad (1).$$

Since v is only slightly dependent on temperature, the temperature dependence of α directly reflects the temperature dependence of l_{eff} . For analysis purposes, the reciprocal diffusivity ($1/\alpha$) provides a convenient way to separate the contributions of various phonon scattering processes. The reciprocal of Eq. (1) becomes:

$$1/\alpha = (3/v)\Sigma_i (1/l_i) \quad (2),$$

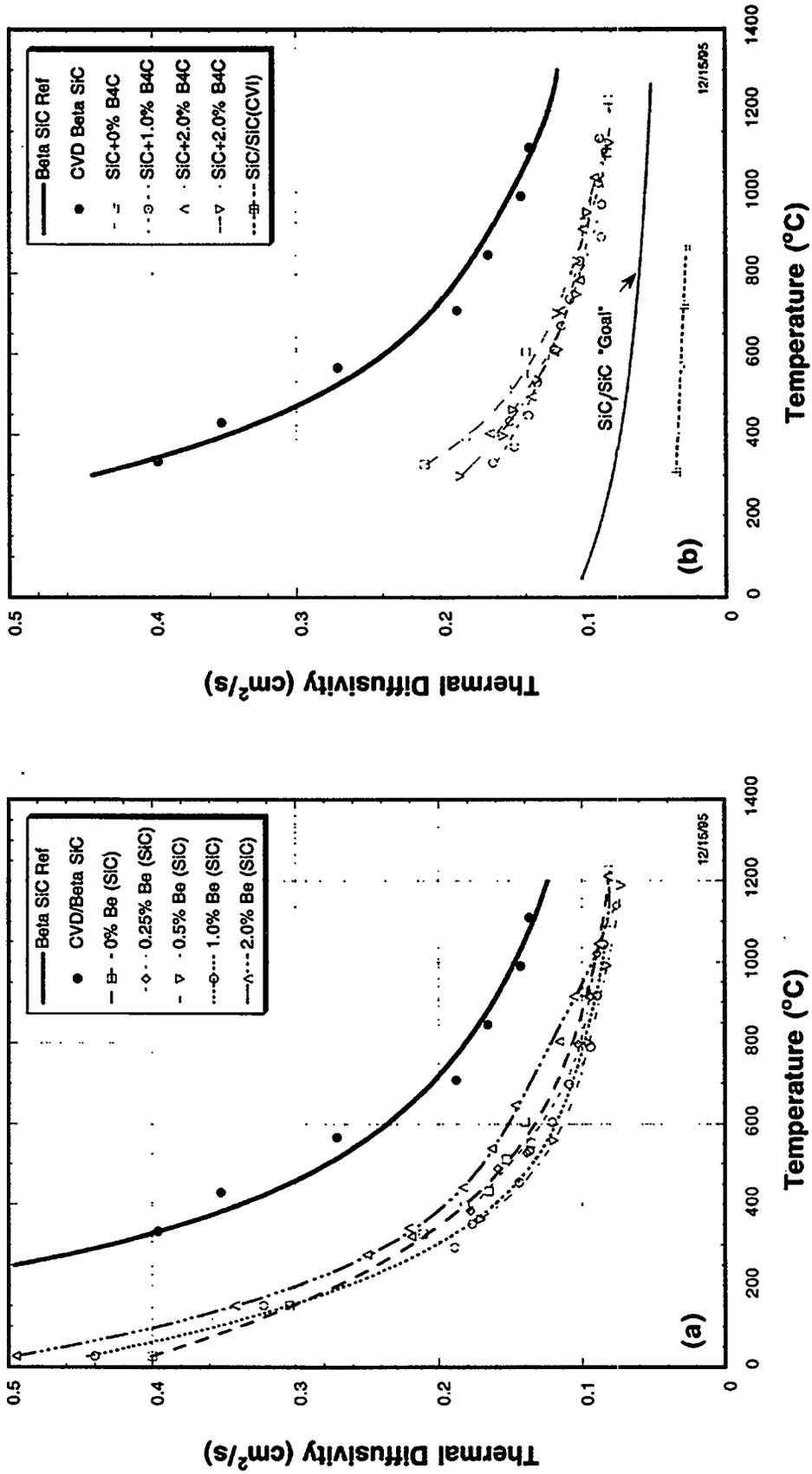


Figure 1(a-b) Comparison of the measured thermal diffusivity of CVD/ β -SiC and hot-pressed SiC doped with 0-2 wt%. **(a)** Be or **(b)** B₄C. Also shown in **(b)** are measured values for a commercial 2D SiC/SiC (CVI) composite and calculated "goal" values for potential fusion reactor applications of this type composite.

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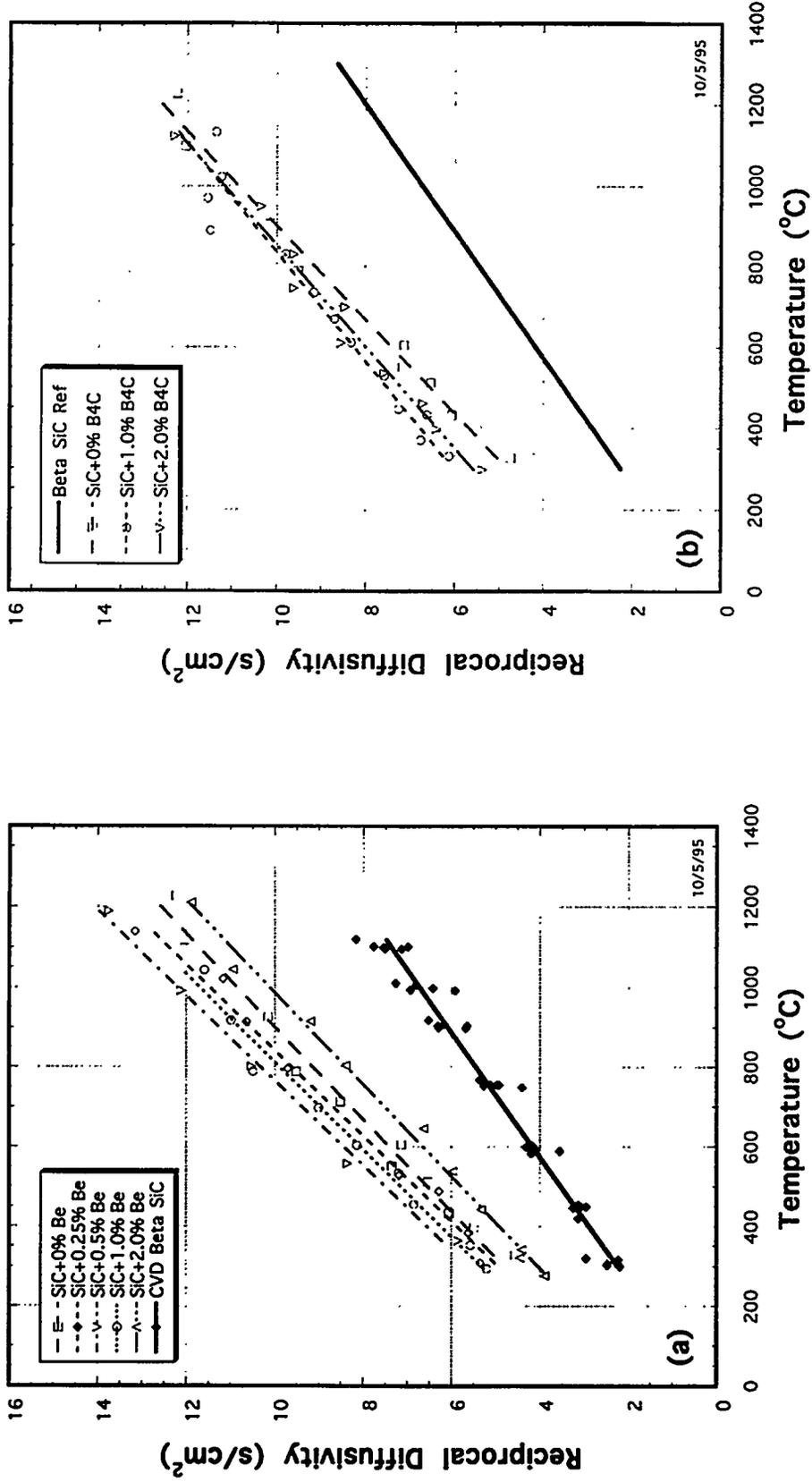


Figure 2(a-b) Reciprocal thermal diffusivity as a function of temperature for hot-pressed SiC doped with 0-2 wt% Be or (b) B₄C. The corresponding plot for the CVD/ β -SiC reference material also is given.

where $1/l_{\text{eff}}$ is composed additively of contributions from each process type (i), i.e., scattering by intrinsic phonon-phonon interactions and by extrinsic impurity, irradiation produced point defects, dislocations, substructural faults, etc. Equation (2) assumes that the scattering processes are independent of each other.

In Figures 2(a-b), the $1/\alpha$ data are fit approximately by a linear relation of the form $a + bT$ over the 300 to 1200°C temperature range for the hot-pressed Be- and B_4C -doped SiC as well as for the Morton CVD/ β -SiC. The effect of a very small amount of Be-doping is to lower α (raise $1/\alpha$) initially by 13% for 0.5 wt% Be, after which α increases for additional doping up to +8% for 2.0 wt% Be. Apparently, in the Be-doped samples some small amount of Be goes into solution and scatters phonons as impurity point defects. Further Be-doping, however, reduces the phonon scattering. The RT $\alpha(k)$ value for the 2 wt% Be-doped SiC, the hot-pressed material exhibiting the highest α , was $0.50 \text{ cm}^2/\text{s}$ (102 W/mK). The latter value is somewhat below the 160 W/mK achieved for CVI/ β -SiC. The calculated mean free path at RT, using a value of $1.26 \times 10^4 \text{ m/s}$ for v in Eq. (1), would be about 12 nm.

In Figure 3, a TEM micrograph of the hot-pressed SiC with 2 wt% Be-doping shows numerous stacking faults within the SiC grains of size $\approx 5 \mu\text{m}$. The stacking faults appear to have a mean spacing of from 10 to 100 nm, which is of the order of the calculated mean free path in this material. The close agreement between the calculated l_{eff} and the observed fault spacing suggests that in β -SiC substructural faults may effectively scatter phonons even up into the intermediate temperature range and, therefore, they may have a significant influence on the magnitude of the thermal conductivity in the range of interest to fusion energy.

It is also observed in Figure 2(a) that the slopes for the hot-pressed Be-doped (and undoped) SiC are similar (the straight lines are approximately parallel), but are somewhat steeper than the slope for the CVD/ β -SiC. Again, this is probably caused by the different temperature dependence of phonon scattering from substructural faults which are likely to be more prevalent in the hot-pressed SiC than in the CVD/ β -SiC.

CONCLUSIONS

In general, the dramatic improvement expected in k for Be- or B_4C -doped SiC was not achieved in these hot-pressed specimens. Even though the doping contents could be controlled and the porosity removed by hot-pressing, this type fabrication did not provide the desired improvement in the thermal conductivity. Apparently, hot-pressing introduces numerous faults into the SiC microstructure so that this process does not simulate the relatively stress-free fabrication of CVI/ β -SiC material. Nevertheless, Be-doping and thermal treatments appear to be promising strategies to achieve the goal of eventually improving the thermal conductivity of SiC_f/SiC.

FUTURE WORK

Further efforts to optimize and control the Be-doping in simulated CVI/ β -SiC matrix will be carried out. However, future fabrication will preferably utilize the lower temperature, CVD-type deposition process. Also, examination of simulated β -SiC matrix material made using PIP-type processing with doping and thermal treatments will be initiated. MER will continue to carry out the fabrication development and structural analysis, while PNNL will carry out the thermal transport analysis.

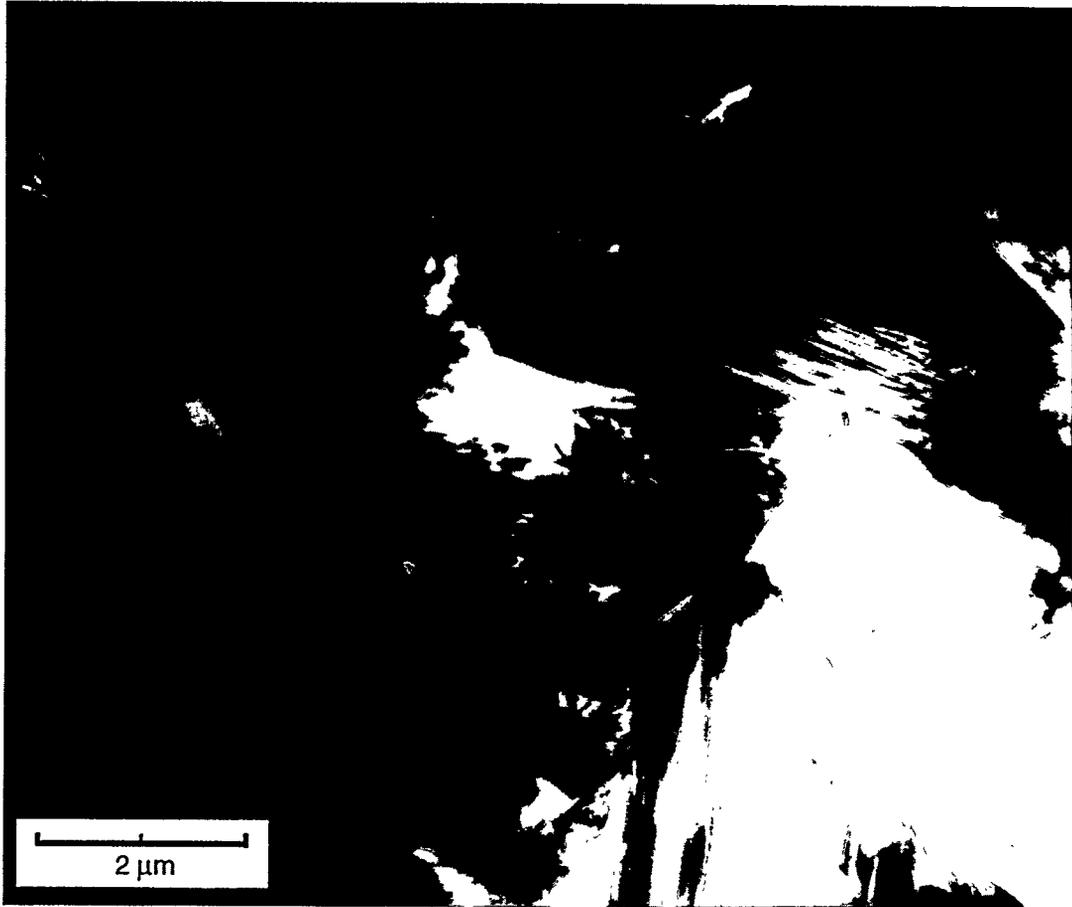


Figure 3 TEM micrograph of hot-pressed SiC with 2.0 wt% Be-doping showing numerous stacking faults.

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