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Inclusion Size and Sintering of Composite Powders

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Abstract

Ceramic powders containing dispersed inert particulates often exhibit dramatically lower densification rates than the pure powder. This decrease results from the shrinkage incompatibilities of the matrix and the inclusion during densification. The analyses of this phenomenon all predict that the shrinkage rate is only dependent on the overall volume fraction of the inert second phase, and not on the particle size. Experiments on ZnO containing dispersed SiC particles of different size showed that the retarding effect of the second phase increases significantly with decreasing particle size, at constant SiC volume fraction.

1. Introduction

Recent investigations have addressed the effect of structural heterogeneities on the densification of ceramic powders both theoretically as well as experimentally [1-9]. The interest in the behavior of heterogeneous powder systems during densification arises from the considerable improvements in various properties that may be obtained for particulate ceramic matrix composites.

In most cases, densification of ceramic powders becomes much more difficult if they contain dispersion of an inert second phase, and often hot pressing or hot isostatic pressing is necessary to achieve densification. The investigation of the free densification behavior of ceramic powders containing dispersed phases is important to improve our understanding of the densification process. A clear understanding of the relevant processing parameters may allow for production of particulate composites without resorting to thermo-mechanical treatments or incorporation of significant amounts of liquid-phase forming additives.

The current analyses of densification of particulate, ceramic matrix composites indicates that the mismatch in shrinkage rates between the powder matrix and the inert dispersed phase leads to an effective hydrostatic backstress that opposes densification. The magnitude of the backstress that can be calculated from the decrease in the densification rate is significantly larger than would be expected on the basis of a viscoelastic analysis of a homogeneously dispersed system [4-9]. The hydrostatic stress inside the dispersed particulates, σ_i, must be related to the hydrostatic backstress in the matrix, σ_h, by the volume fraction relation:

$$\sigma_i = - \sigma_h \, f \, / \, (\, 1 \, - \, f \,)$$

where f is the volume fraction of the dispersed, inert particulate phase. This relationship follows from the necessity of having a zero net stress on the entire free sintering body. It implies that the effect should only depend on the volume fraction of the dispersed inert second phase, and not on its particle size, so long as a continuum visco-elastic analysis remains applicable. Such an analysis is likely to be inappropriate if the second phase particles become much smaller than the matrix grain size, so that many particles are present per grain facet.

The present work examines the dependence of the densification of a ZnO matrix/SiC particulate composite powder as a function of SiC particle size. It tests the validity of the models that assert that volume fraction of the second phase is the only relevant variable.

2. Experimental

A model particulate composite, consisting of a ZnO powder* matrix with an average grain size of 0.25 μm was prepared, containing 2.5 to 20 vol% of silicon carbide inclusions. The silicon carbide particles had been classified to narrow size distribution fractions ranging from 0.5 to 75 μm. The powders were mixed in the appropriate amounts adding 2.5 vol% of Carbowax† as a binder. The mixtures were ultrasonically dispersed in an excess of acetone, and stir-dried.

The power was subsequently hand-ground in an alumina mortar, and passed through a 32 mesh sieve, to break up any large agglomerates. The powder was pressed in a die, to obtain a matrix green density of 0.5±0.025 of the full theoretical one. The compacts were densified in a dilatometer, at 1000K in dry air, after binder burnout at 650K for 30 min. During this treatment a reproducible shrinkage of 0.25% was observed. After the burnout the sample was moved rapidly into the hot zone of the dilatometer furnace, and thermal equilibrium was reached within 3 to 4 min. The volumetric densification was calculated from the recorded shrinkage, and data from three to six identical runs were averaged for each combination of volume fraction and particulate size of the SiC. After densification, some samples were prepared for scanning electron microscope examination of the microstructure.

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* Mallinckrodt Inc., Paris, KY 40361
† Polyethylene glycol 3350, Union Carbide Corporation, New York, NY 10017

3. Results

Figure 1 shows the matrix density versus time for ZnO containing the indicated volume percent of 75 μm SiC inclusions. A significant decrease in the densification is observed with increasing volume fraction of inclusions. This is in general agreement with the earlier observations of De Jonghe and Rahaman [8,9], although the effect is not as strong as in that earlier work. Possible differences may result from differences in matrix grain size, the SiC inclusion size, and the sample preparation method. After an initial transient of about 5 minutes, the density is approximately proportional to the log of time.

Figure 2 shows the matrix densities versus time for various SiC inclusion sizes at a constant volume fraction of of 0.0476. A significant decrease in densification is evident with decreasing particle size. For the largest inclusion sizes, 45 and 75 μm, the densification is not significantly affected, but strong decreases are found for the smaller inclusion sizes. Grain growth in ZnO at the sintering temperature is quite slow [10,11], and thus the inclusions remain larger than the matrix grain size, except for the longest sintering times and smallest inclusions.

Careful examination of the matrix at the matrix/inclusion interface revealed that a thin layer of matrix around the particle exhibited minimal grain growth and densification. This is particularly evident in the scanning electron micrographs of Figure 3, showing the ZnO/SiC interface where SiC particles had pulled out during the fracturing of the samples.

4. Discussion.

The concept of an effective volume fraction may be introduced to characterize

the effect of the particle size on the densification. The effective volume fraction is defined here as the volume fraction of 75 μm inclusions that gives an equivalent effect on densification as the given inclusion size and volume fraction. The data used to determine the effective volume fractions are shown in Figure 4. Thus, the ratio of the effective particle radius over the actual one, R_e/R, can be determined. R_e/R has been plotted versus the log of the inclusion radius, R, in Figure 5. A clear correlation is evident, showing that the effective inclusion radius increases with decreasing inclusion size.

The microstructural investigation indicates the presence of an nearly invariant matrix shell adjacent to the inert SiC inclusions. The effective volume fraction of SiC calculated from the densification behavior was significantly larger than would be derived assuming that the effective particle radius was equal to that of the actual volume fraction plus the non-sintering matrix shell.

A mechanism that rationalizes the dependence of the effective particle size on the actual one has not been formulated at the present time. It is very likely that the degree of clustering of the dispersed phase has a significant effect upon the densification behavior. This aspect is currently being investigated in our laboratory.

In conclusion, the experiments have clearly demonstrated that a strong particle size dependence can be present in the sintering of particulate composites. The mechanism by which this effect operates remains to be determined.

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Figure Captions

1. Matrix density versus sintering time for various volume fractions of 75 μm SiC inclusions.

2. Matrix density versus sintering time for compacts containing 4.76 volume percent of 0.5 to 75 μm SiC inclusions.

3. Scanning electron micrographs of the fracture surface showing the ZnO/SiC interface.

4. Matrix density at 320 minutes versus volume fraction of 75 μm SiC inclusions illustrating the determination of the effective volume fraction for SiC inclusions of other sizes.

5. The ratio of the effective to the actual volume radius versus the log of the inclusion radius.
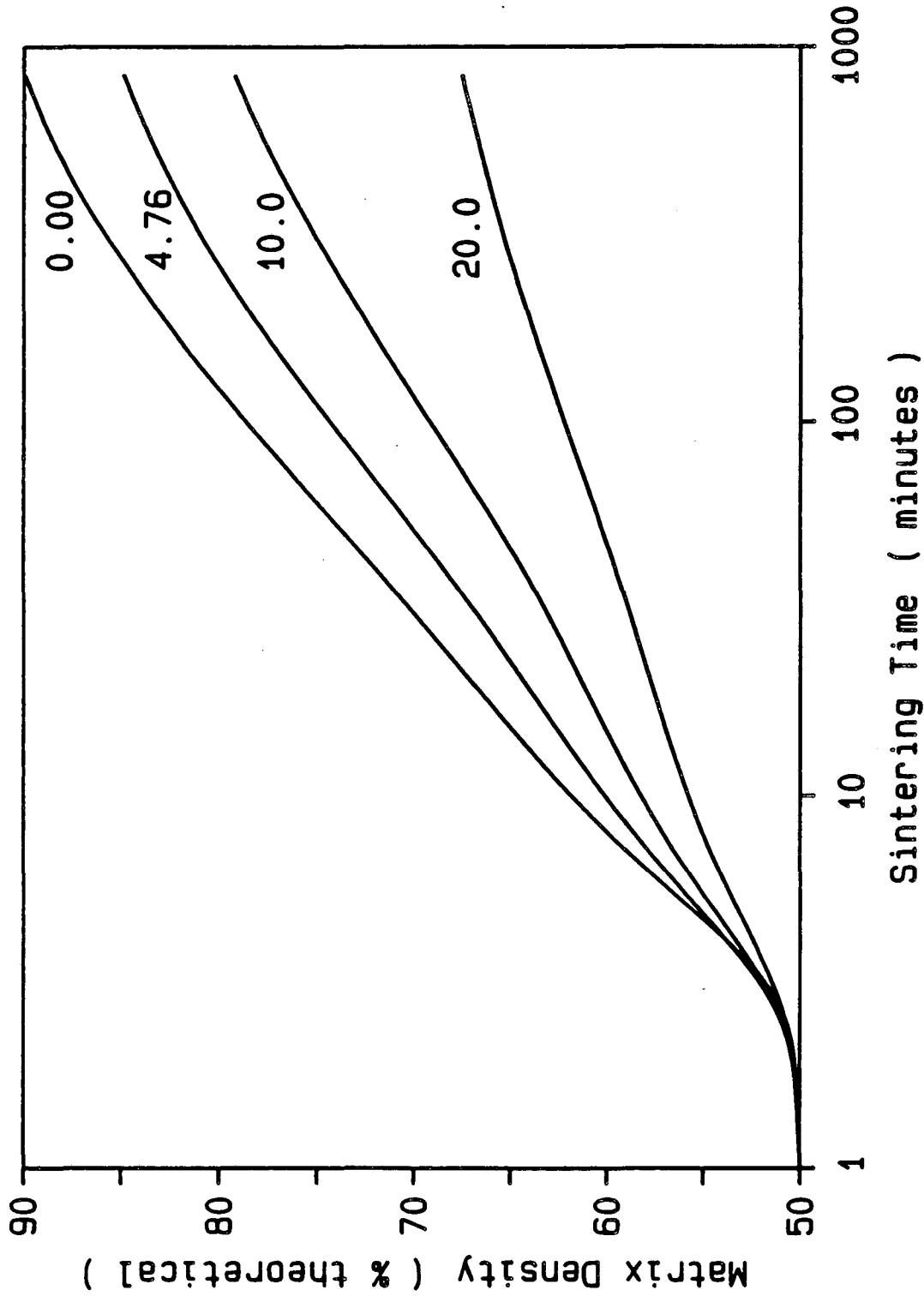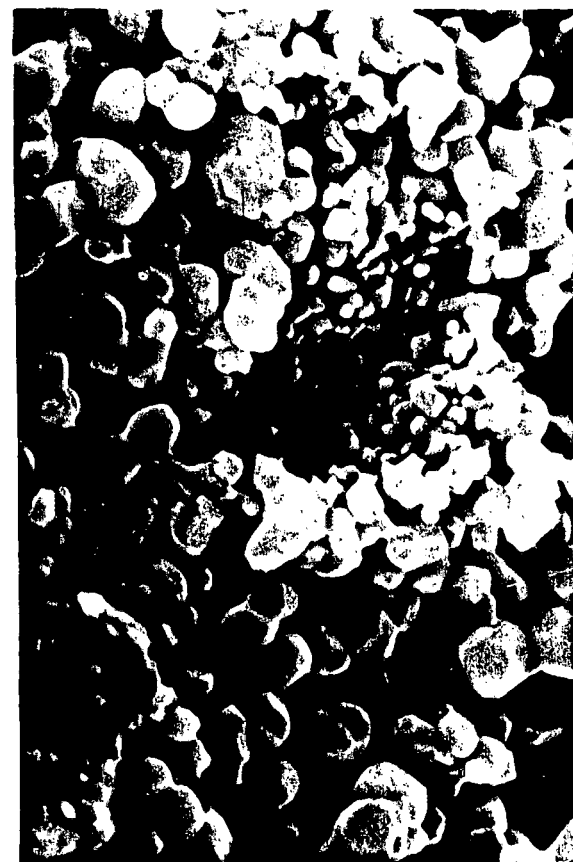
Fig. 1

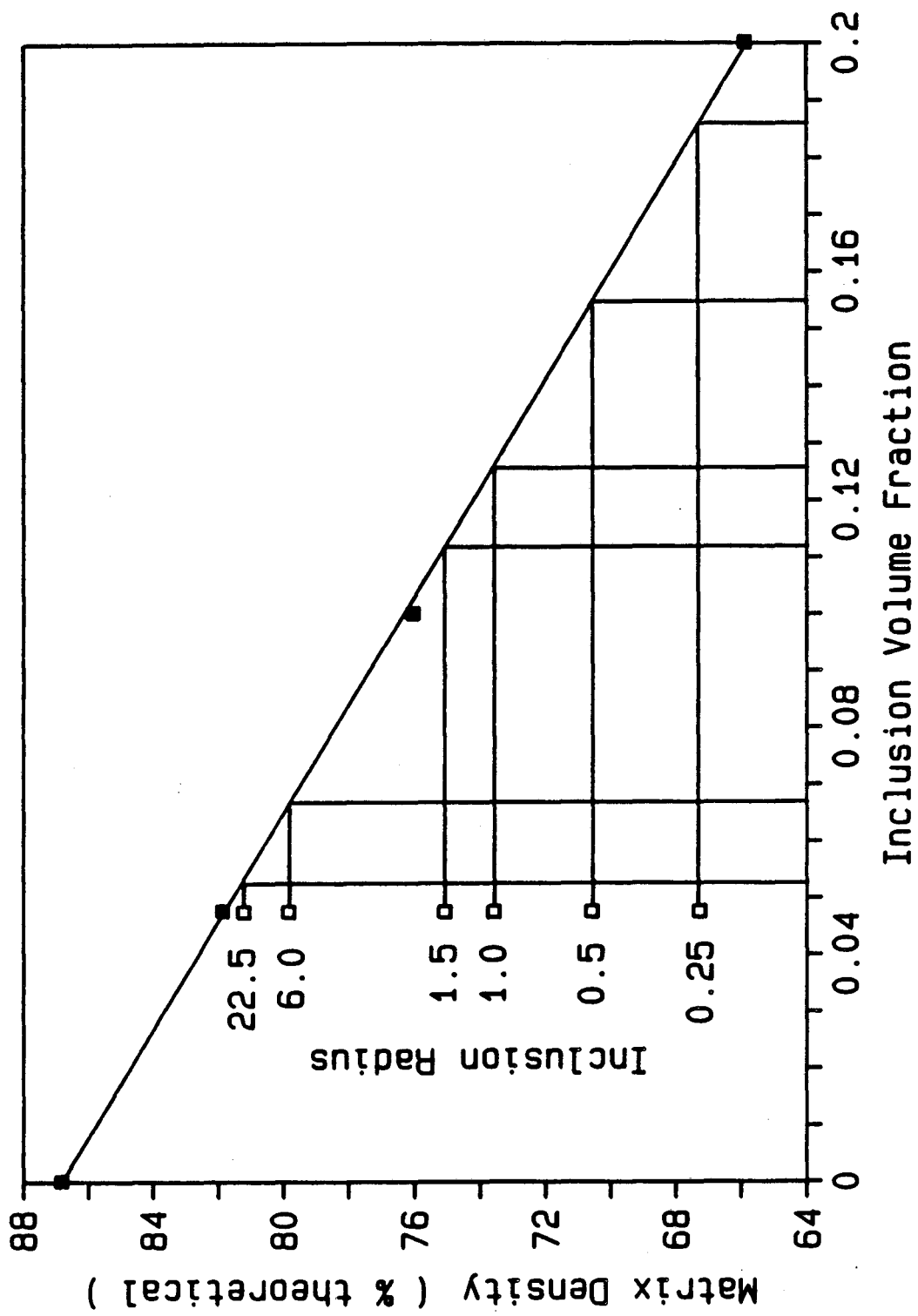XBL 876-2596
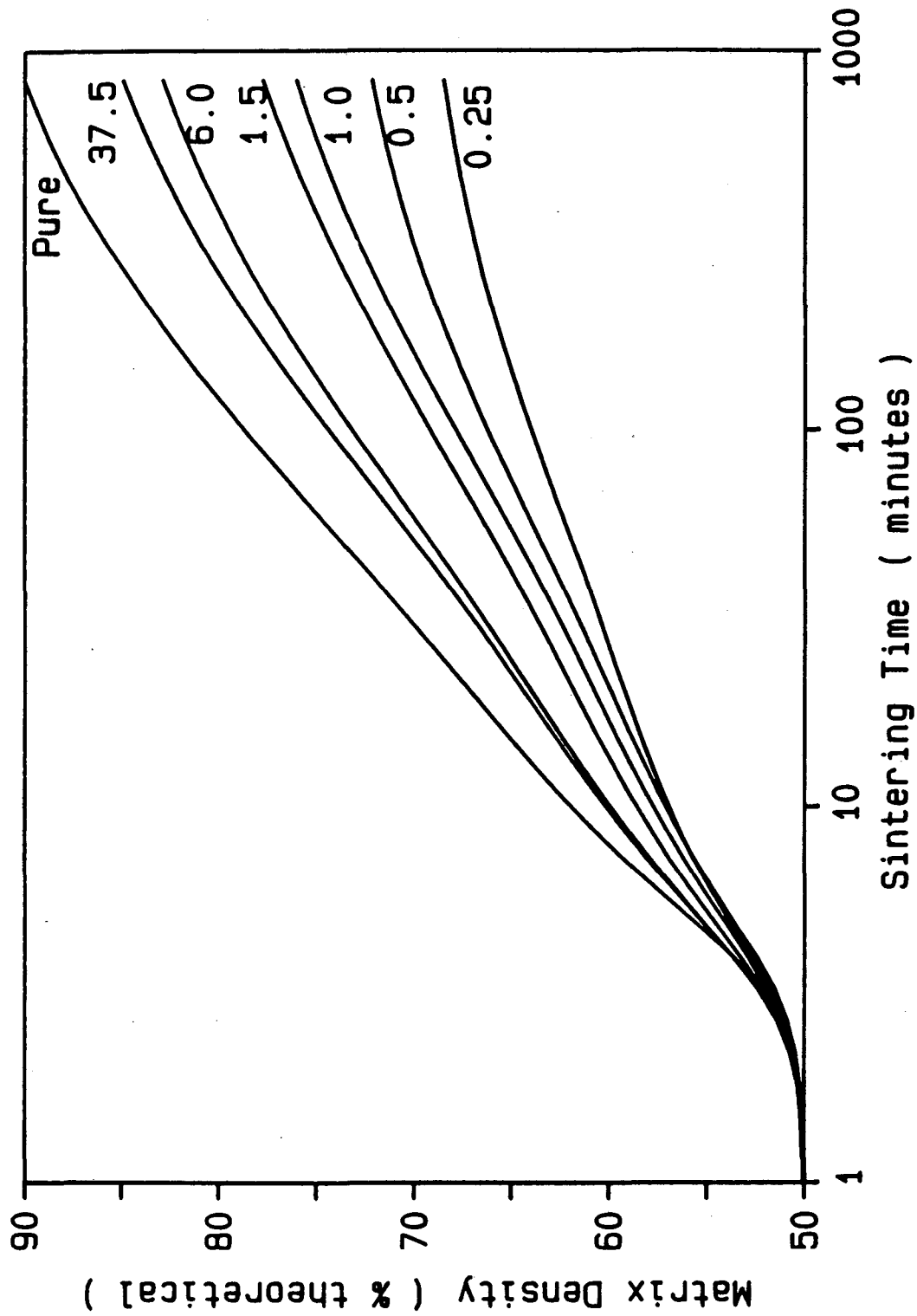
Fig. 2

XBL 876-2595
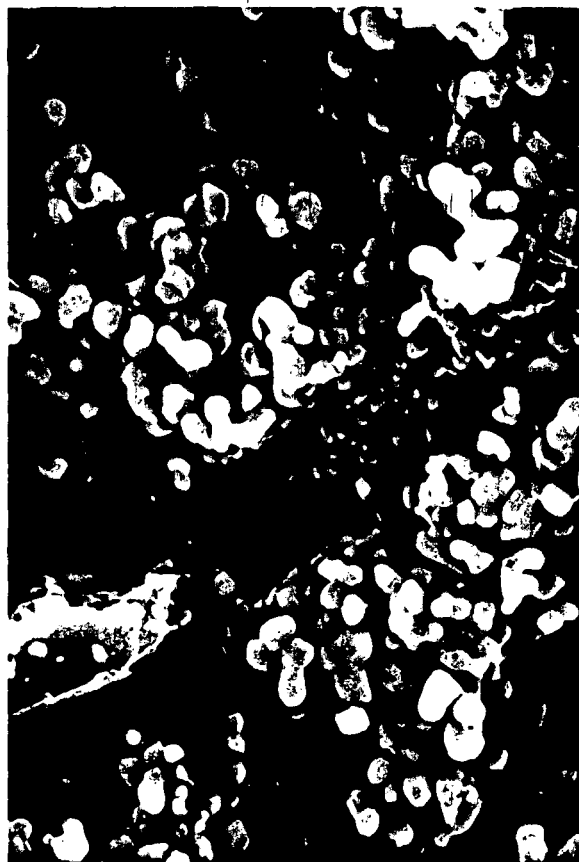
5 minutes   30 minutes   944 minutes

1 μm

ZnO matrix containing 4.76 volume percent 3.0 μm SiC
inclusions and sintered at 950 K for the times indicated.

Fig. 3

Fig. 4

XBL 876-2594

11

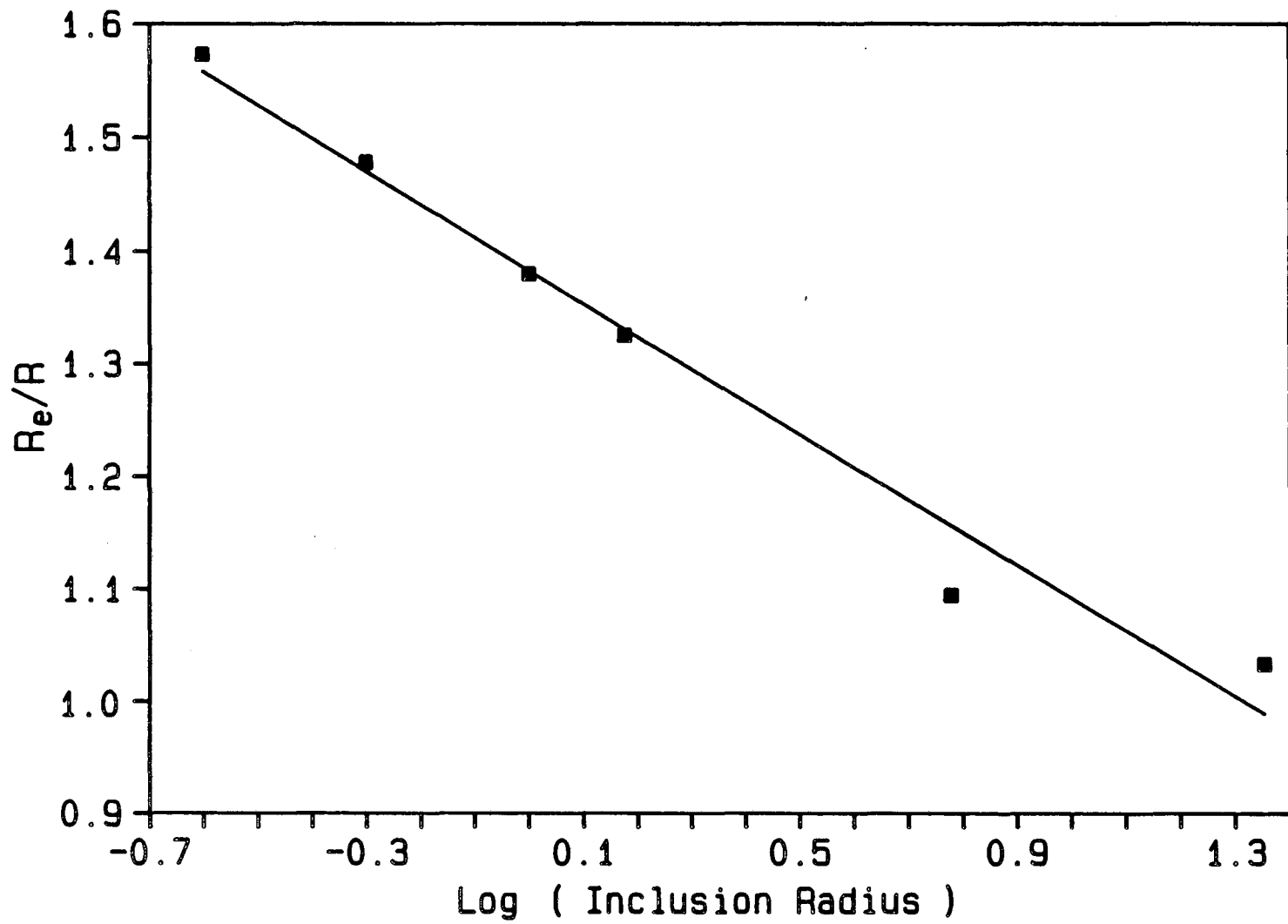Fig. 5