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**SINTERING OF CERAMIC PARTICULATE COMPOSITES:
EFFECT OF MATRIX DENSITY**

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Abstract

Composites consisting of a fine-grained, polycrystalline zinc oxide matrix and < 10 volume percent coarse, rigid silicon carbide inclusions were prepared by the same mixing procedure and then compacted to produce samples with matrix densities of 0.45 and 0.68. The samples were sintered under identical temperature profiles in separate experiments that employed either a constant rate of heating of 4°C/min or near isothermal heating at 735°C. The densification rate of the composite matrix relative to that for the unreinforced zinc oxide was found to be independent of the initial matrix density at any temperature or time. The processes that may lead to the vastly reduced sinterability in polycrystalline matrix composites are examined.

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* Member, the American Ceramic Society.

L Introduction

Although it has been known for some time that polycrystalline matrix composites are more difficult to sinter compared to glass matrices, it is only within the past five years that the effect has been quantified under controlled conditions. The system that has received most interest is a fine-grained powder matrix containing coarse, inert, rigid inclusions. The work of De Jonghe and coworkers¹ and later work by Bordia and Raj² and by Brook and coworkers³ has shown that the presence of rigid, inert inclusions can drastically reduce the sinterability of polycrystalline matrices. Further work by Rahaman and De Jonghe⁴ demonstrated that the reduction in the sinterability of glass matrices is much smaller for an equivalent inclusion content. For glass matrix composites containing ≤ 12 volume percent (v%) inclusions, the sintering kinetics can be well explained by a theory of Scherer⁵ that assumed a viscous backstress due only to mismatch in shrinkage rates between the matrix and the inclusions. Above this inclusion content, it is believed that network formation of the inclusion phase, which was not incorporated in Scherer's theory, was the main cause for the deviation between theory and experimental data. The sintering data for polycrystalline matrix composites, however, deviate drastically from Scherer's theory, even at quite low inclusion contents (e.g., < 5 v%) when network formation is not a severe impediment. An important problem, therefore, is the definition of the source of the drastically reduced sinterability of polycrystalline matrix composites. Although a number of explanations, based on theoretical models or experimental observations, have been put forward over the past few years, the mechanism remains obscure.

The earliest explanation for the reduced sinterability of polycrystalline matrix composites was in terms of theoretical models^{6,7} that predicted high viscoelastic backstresses due to mismatch in the shrinkage rates between the matrix and the inclusions. Although these models appeared attractive at first and could account for the experimental data through suitable model assumptions⁸, it is now generally recognized^{5,9,10} that these assumptions are unrealistic.

An explanation proposed by Lange¹¹ attributed the reduced sinterability in polycrystalline matrices to the development of "sintering damage" (i.e., crack-like voids) in the matrix due to non-uniform densification. Since these voids may not close, they may limit severely the densification rate and end-point density. While in principle plausible, there is, at present, no direct experimental evidence to support this explanation.

Another explanation put forward by Lange¹² accounted for the reduced sinterability in terms of the formation of a rigid, contiguous network of touching or near-touching inclusion particles. The earliest version of the model employed a fitting parameter that depended on the proximity of the inclusions and could not clearly distinguish between polycrystalline and glass matrices. Recently, Lange¹³ has proposed a microstructural explanation to account for the difference in sinterability

between polycrystalline and glass matrices. According to Lange, network shrinkage caused by powder densification leads to the development of a denser interconnected matrix material surrounding less dense regions. Densification of the lower density regions requires the creep deformation of the denser interconnected region. Grain growth causes this denser region to become more resistant to creep while coarsening within the less dense regions causes desintering and the dissipation of sintering stresses. These processes would not occur in glasses due to the lack of discrete grains and grain boundaries. Although some initial mercury porosimetry data¹⁴ for the sintering of Al₂O₃ containing SiC platelet inclusions have been reported, much work still needs to be done to provide convincing support for this explanation. However, it is improbable that the inclusion would form a contiguous network for inclusion contents of < 10 v% where the drastically reduced sinterability is also very evident.

Grain growth can be a factor in causing the drastic reduction in densification rate when it is present in the matrix. This explanation appears attractive because it might justify the difference in densification rates between polycrystalline and glass matrix composites. However, experiments¹ performed so far at a fixed (isothermal) sintering temperature have not revealed a large enough grain growth rate difference to account for the drastic deviation in the densification rate from theory.

It has been suggested^{15,16} that non-uniform or random distribution of the inclusion particles within the matrix can also account for the reduced sinterability of polycrystalline matrix composites. The random distribution of the inclusions introduces spatial variations in the matrix green density which results in increased differential densification; this in turn leads to a decrease in the overall densification rate. Since this mechanism is also present in glass matrices, it was argued¹⁶ that the difference in stress relaxation was the key issue in accounting for the marked difference in sintering of polycrystalline and glass matrices. Differential stresses in glasses can be relaxed by bulk viscous flow while the mechanism of stress relaxation in polycrystals is by directionally-specific diffusion processes in which only a small fraction of the atoms takes part.

Rahaman and De Jonghe¹⁷ recently used the technique of loading dilatometry^{18,19} to measure simultaneously the densification and shear deformation (i.e., creep) rates of composites consisting of a fine-grained ZnO matrix containing < 10 v% coarse SiC inclusions. The data showed that the time-dependence of the matrix shear viscosity was unaffected by the inclusion phase. Model considerations as well as experiments^{5,9} indicate that the shear viscosity and the bulk viscosity are intimately related. It was therefore argued that the relative decrease in the observed matrix densification rate resided in the decrease in the sintering stress rather than in an increase in the bulk viscosity. It was also shown that the factors that caused the reduced sinterability were present from the beginning of sintering and must therefore originate in the compacted matrix microstructure. Since the matrix shear viscosity was unaffected by the inclusions,

the data also supported the view that network formation between the inclusion phase is unimportant at these relatively low inclusion contents.

For inclusion contents where network formation and grain growth are unimportant, it appears therefore that either sintering damage or non-uniform inclusion dispersion is the most likely factor causing the reduced sinterability of polycrystalline matrix composites. The aim of the present paper is to determine the relative importance of these two mechanisms.

A composite powder consisting of fine-grained ZnO and 10 v% SiC (based on the fully dense matrix) was prepared by the same mixing process and then compacted to produce samples with different matrix densities. The effect of the matrix density on the densification rate was then measured by dilatometry.

II. Experimental Procedure

A fine-grained ZnO powder[#] with an average grain size of $\approx 0.4 \mu\text{m}$ and SiC powder^{*}, classified to a narrow size range about an average of $\approx 12 \mu\text{m}$, were used as the matrix and inclusions, respectively. The amount of SiC was chosen to give an inclusion volume fraction of 10% based on the fully dense composite. The powders were mixed in chloroform and stir-dried, and then disrupted using a mortar and pestle. For comparison, the unreinforced ZnO powder was also given the same mixing treatment. The unreinforced and composite powders were pressed in a uniaxial die to form green compacts (6 mm in diameter by 6 mm) with the same matrix density of 0.45 ± 0.01 of the theoretical. Some of these die-pressed samples were further compacted in a cold isostatic press to produce samples with a matrix density of 0.68 ± 0.01 .

The compacted samples were sintered in separate experiments that utilized different heating schedules. In one set of experiments, the samples were sintered at a constant heating rate of $4^\circ\text{C}/\text{min}$ up to 1000°C ; in the other set of experiments the samples were sintered under near isothermal conditions at 735°C for 2 hours. All experiments were performed in air in a dilatometer that allowed continuous monitoring of the axial shrinkage. The sample density was measured from the shrinkage data and the initial density.

III. Results and Discussion

Figure 1 shows the density of the unreinforced and composite samples as a function of temperature for the constant heating rate sintering experiments. The

[#] Reagent Grade, Mallinckrodt Inc., Paris, KY.

^{*} Union Carbide Corp., New York, NY.

data for each curve are the average of two runs under identical conditions. The volumetric strain of the matrix per unit temperature, $(1/\rho_m) d\rho_m/dt$, can be easily obtained in units of min^{-1} by multiplying the data for $(1/\rho_m) d\rho_m/dT$ by 4.

The corresponding data for the samples sintered isothermally at 735°C are shown in Figs. 3 and 4. In figure 3, the density of the samples as a function of time, t , is shown; $t=0$ represents the beginning of shrinkage and the sintering temperature was reached after $t=5$ min. The data for each curve are the average of two runs under identical conditions. The volumetric strain rate of the matrix is plotted as a function of time in Fig. 4. An interesting feature of Fig. 4 is that for both initial matrix densities, the curve for the composite matrix is nearly parallel to that for the unreinforced ZnO. This means that the volumetric strain rate of the matrix relative to the unreinforced ZnO is nearly independent of time.

In figure 5, the volumetric strain rate of the composite matrix relative to the unreinforced ZnO, i.e. $\dot{\epsilon}_{mr}/\dot{\epsilon}_u$ is plotted as a function of temperature for the constant heating rate experiments, and against time for the isothermal heating experiments. The estimated errors are in the range of $\pm 5\%$ at early and intermediate times or temperatures to $\pm 10\%$ at later times or temperatures; the error bars have been omitted from the figure in order to maintain clarity. For the constant heating rate data, $\dot{\epsilon}_{mr}/\dot{\epsilon}_u$ at any temperature is independent of the initial matrix density. For the isothermal sintering experiments, the ratio is independent not only of initial density but also of sintering time. Another remarkable feature of Fig. 5 is that the isothermal data intersect the constant heating rate data almost at the isothermal sintering temperature.

The data of Fig. 5 show that the matrix densification rate of the composite at any temperature or time is related to that for the unreinforced sample by the expression

$$\dot{\epsilon}_{mr} = \dot{\epsilon}_u F \quad (1)$$

where F is dependent on temperature but independent of the initial density of the sample. This expression has important consequences for understanding the mechanisms that impede the sintering of polycrystalline matrix composites. As outlined earlier, sintering damage and random distribution of the inclusions appear to be the most likely mechanisms when network formation and grain growth are insignificant. The extent of sintering damage would be expected to be different for the sample die-compacted to different initial densities. The initial volumetric density differential between the matrix and the inclusion increases from 0.32 for the higher density sample to 0.55 for the lower density sample.

As seen in Fig. 2 for the constant heating rate experiments, this results in almost a two-fold increase in the matrix densification rate for the lower initial density composites compared to the higher density ones. Sintering damage produced in the compaction of the green body should be expected to depend on the compaction stress, since this determines the accommodation strains between the undeformable inclusion particles and the compacting matrix. The insensitivity of the factor F in Eqn. (1) to the initial matrix density and to the large change in densification rate differential is difficult to reconcile with sintering damage being the dominant impediment to composite densification.

The random inclusion distribution in the matrix therefore emerges as the most likely cause of the reduced sinterability. Indeed, the relative spatial distribution of the inclusion phase in the lower density, die-pressed samples is maintained through the isostatic pressing process used for forming the higher density samples. Thus it is the single, constant factor which is present in both the low density and high density samples. In terms of a mechanism for explaining the reduced sinterability, it can be appreciated that the random distribution of the inclusions will introduce spatial variations in the matrix green density which, in turn will result in increased differential densification and a decrease in the matrix densification rate.

The densification rate of the unreinforced ZnO can be expressed as

$$\dot{\epsilon}_u = \Sigma / \eta_p \quad (2)$$

where Σ is the sintering stress and η_p is the bulk viscosity. It has been shown in earlier work^{16,17} on ZnO containing < 10 v% SiC inclusions that the reduced sinterability due to the presence of the inclusions can be attributed to a decrease in Σ rather than an increase in η_p . This is the way in which the proposed mechanism of differential densification produced by random inclusion distribution would indeed be expected to alter Eqn. (2). It would also be present from the earliest stages of sintering as observed earlier.¹⁷

Figure 5 shows that F [Eqn. (1)] increases with increasing temperature, approaching 1.0 at high temperatures. This indicates that improved processing conditions for particulate composites should prevail at increased sintering temperatures. The temperature dependence of F does not follow from a treatment of the viscous backstress in a concentric sphere model for a densifying composite. Instead it indicates that an additional mechanism is involved that is dependent on temperature only and is increasingly effective with increasing temperature. Such an additional mechanism might be the alteration of grain growth in the composite matrix.

Figure 6 shows scanning electron micrographs of the fracture surfaces of (a) the unreinforced ZnO and (b) the composite after isothermal sintering (i.e., 2 h at 735°C); the initial matrix density of the samples was 0.45. It is seen that the grain size of the unreinforced ZnO is ≈ 2 times that for the composite. Thus the inclusions provide a mechanism for grain growth limitation in the composite. The scanning electron micrographs of the fracture surfaces of the unreinforced ZnO and the composite after constant heating rate sintering (4°C/min to 1100°C) are shown in Figs. 7(a) and (b), respectively; the initial matrix density of the samples was again 0.45. The difference in grain size after high temperature densification is much more striking compared to the samples sintered isothermally at 735°C. The grain size of the composite matrix is significantly smaller than for the unreinforced one, offsetting the intrinsic retarding effects of the dispersed phase. This is equivalent to an increasingly effective suppression of the matrix grain growth by the inclusions with increasing temperature. The mechanism by which this process acts, is at present, not clear but it is evident that the effect of the inclusions on the grain growth and microstructure development of the composite matrix requires careful consideration.

As outlined earlier, the data of Rahaman and De Jonghe⁴ showed that glass matrix composites prepared by a similar mixing process are much easier to densify. In the light of the present discussion, the explanation for the difference in matrix sinterability between glass and polycrystalline ceramic matrices should be primarily in terms of the difference in relaxation of the transient stresses produced by differential shrinkage. Glasses relax stresses through viscous flow in a much larger fraction of the bulk material compared to directional diffusion processes in polycrystalline systems. Grain growth in polycrystalline matrix composites can lead to additional differences but cannot by itself account for the drastic reduction in the densification rate, as is evident from the isothermal experiments at 735°C.

Finally, the present work would indicate that solid state sintering of polycrystalline matrices can be improved through remedies that seek to maximize the packing uniformity of both the inclusion phase and the matrix, or maximize the extent of the stress relaxation processes such as through the use of ultra-fine powders. Such work is currently being carried out by the authors.

IV. Conclusions

For composites consisting of polycrystalline ZnO powder matrices and < 10 v% SiC inclusions that were prepared by the same mixing procedure, the matrix densification rate at any temperature or time is equal to that for the unreinforced ZnO times a factor which increases with temperature but is independent of the initial matrix density.

The data support a mechanism of differential densification due to random or non-uniform inclusion distribution within the matrix as the primary cause of the reduced sinterability of polycrystalline matrix composites.

Grain growth and microstructural development are important additional considerations in polycrystalline matrix composites. Observations show that the inclusions produced a reduction in the grain growth rate of the composite matrix compared to the unreinforced matrix which was increasingly significant at increasing temperatures.

Improved packing uniformity of both the inclusion phase and the matrix, increased sintering temperatures, and the use of ultra-fine grain matrix powders would lead to improved sintering of particulate composites.

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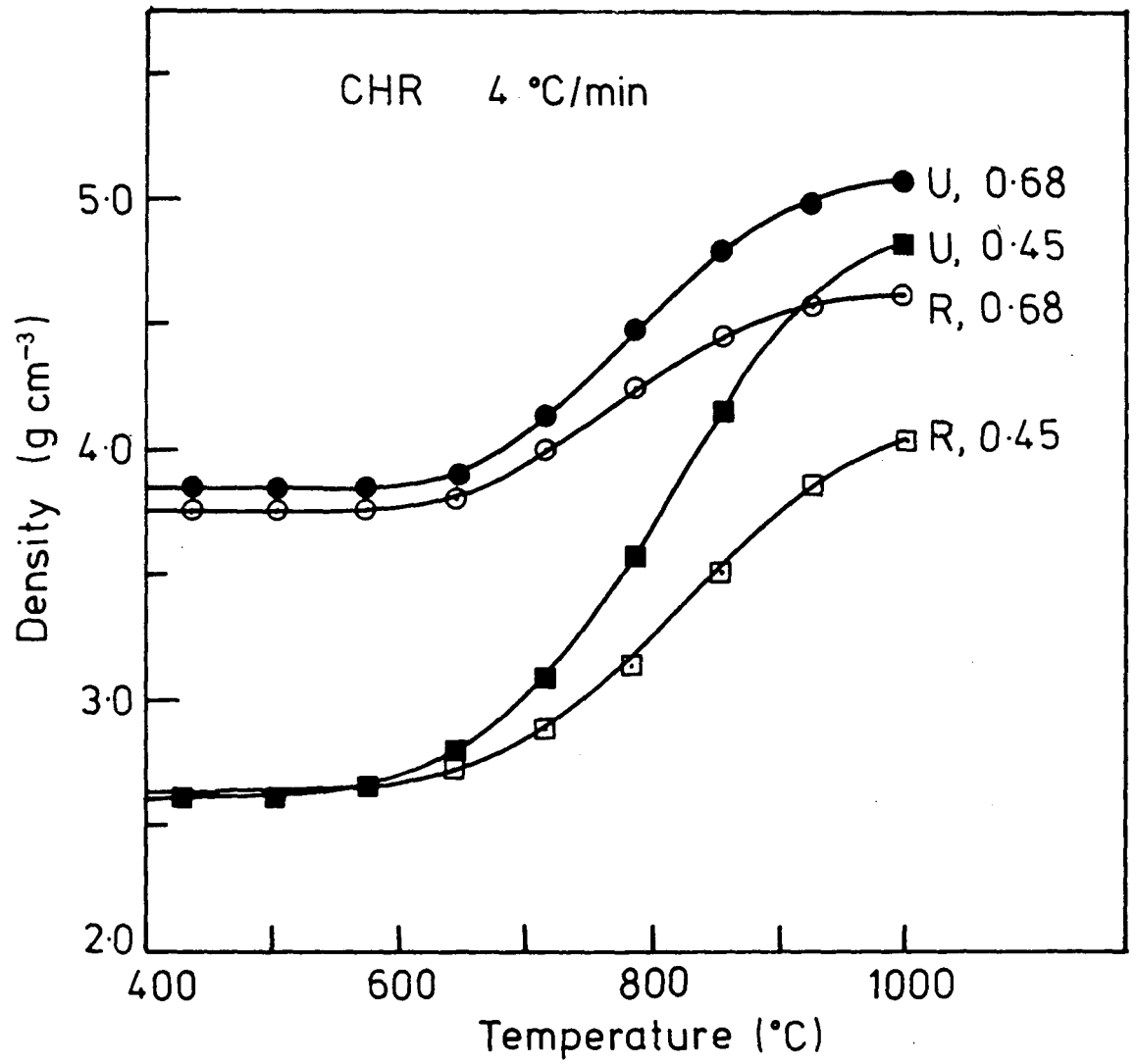
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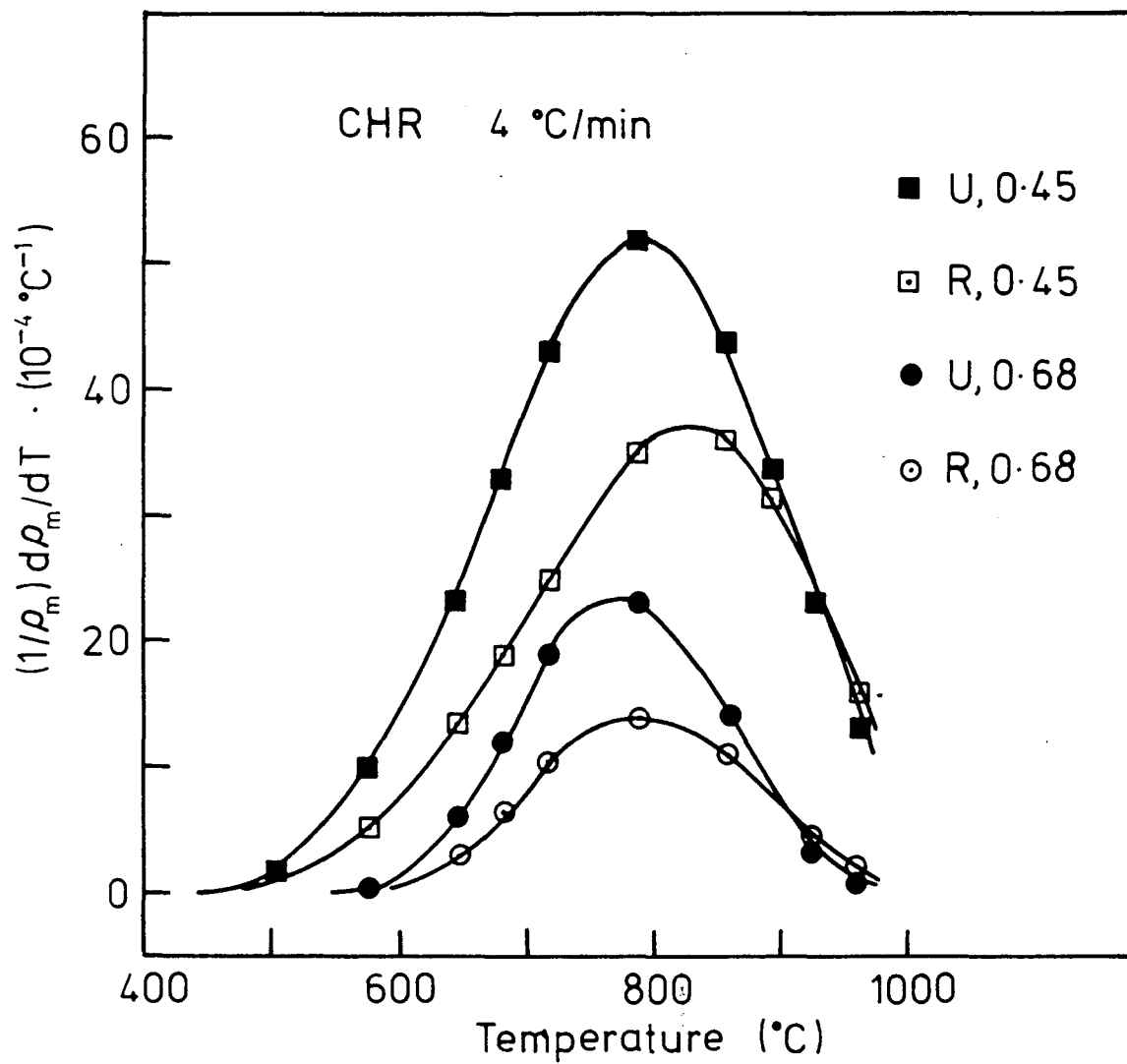
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Figure Captions

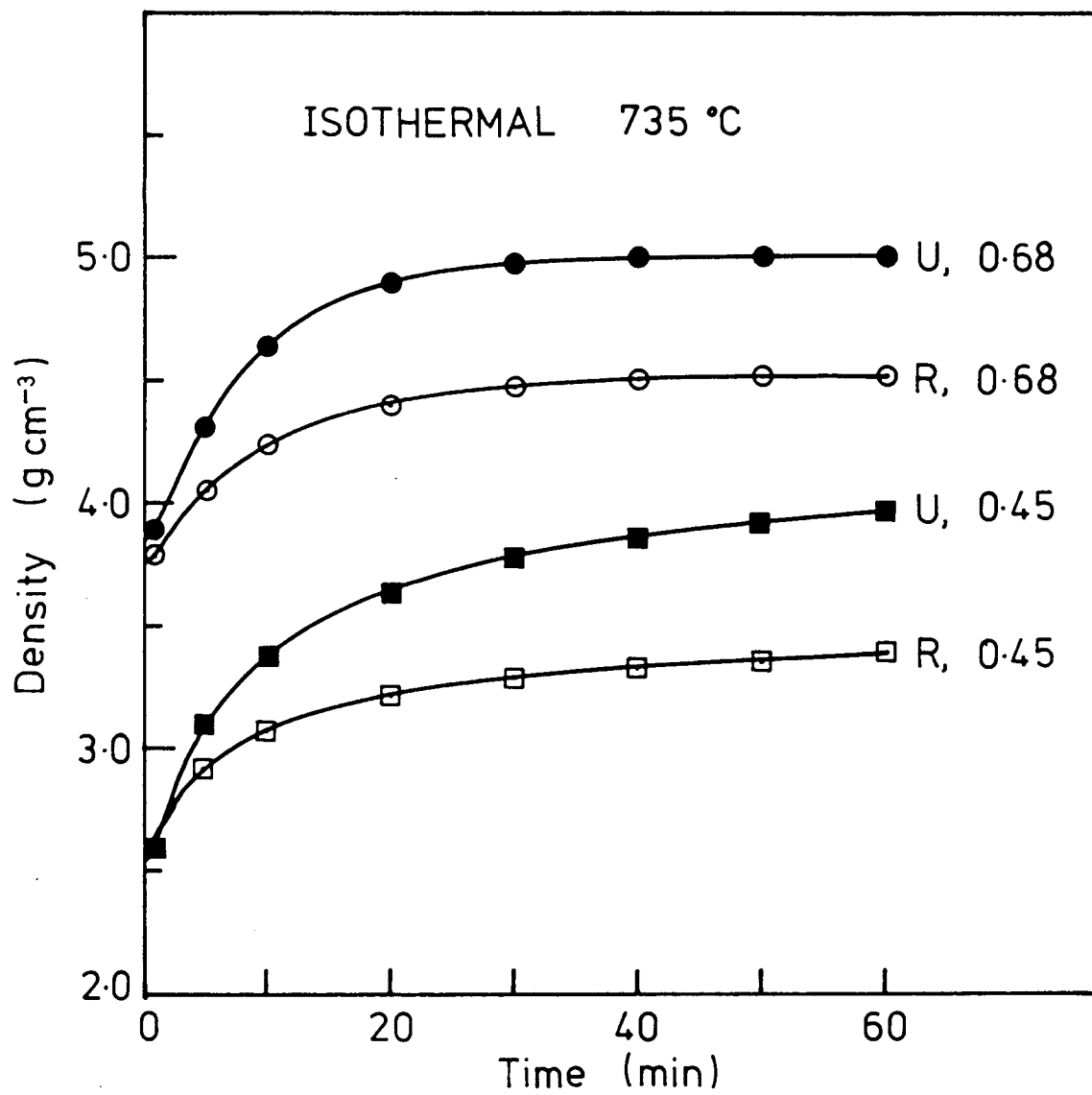
- Fig. 1. Density as a function of temperature for the samples sintered at a constant heating rate of $4^{\circ}\text{C}/\text{min}$. The data are shown for the unreinforced ZnO, (U), and ZnO containing $< 10 \text{ v}\%$ SiC, (R), compacted to matrix densities of 0.45 and 0.68.
- Fig. 2. Volumetric matrix strain per unit temperature as a function of temperature for the experiments described in Fig. 1.
- Fig. 3. Density as a function of time for the samples sintered isothermally at 735°C . See Fig. 1 for the sample descriptions.
- Fig. 4. Densification rate as a function of time for the experiments described in Fig. 3.
- Fig. 5. The matrix densification rate of the composite relative to that for the unreinforced ZnO as a function of temperature for the constant heating rate experiments ($4^{\circ}\text{C}/\text{min}$), and as a function of time for the isothermal sintering experiments (735°C).
- Fig. 6. Scanning electron micrographs of the fracture surfaces of (a) the unreinforced ZnO and (b) the composite after (isothermal) sintering for 2 h at 735°C . Matrix initial density = 0.45.
- Fig. 7. Scanning electron micrographs of the fracture surfaces of (a) The unreinforced ZnO and (b) the composite after constant heating rate sintering at $4^{\circ}\text{C}/\text{min}$ to 1100°C . Matrix initial density = 0.45.



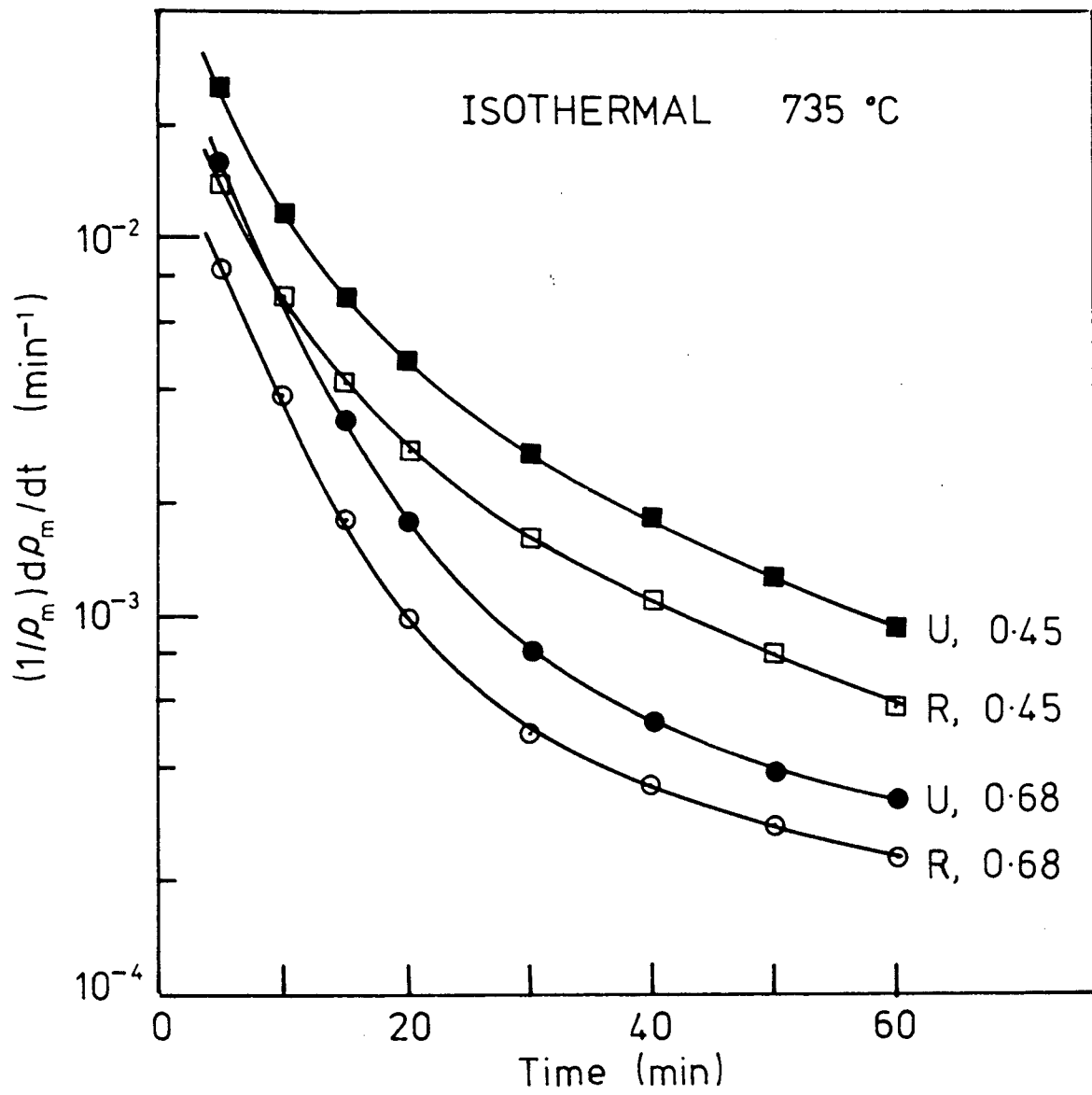
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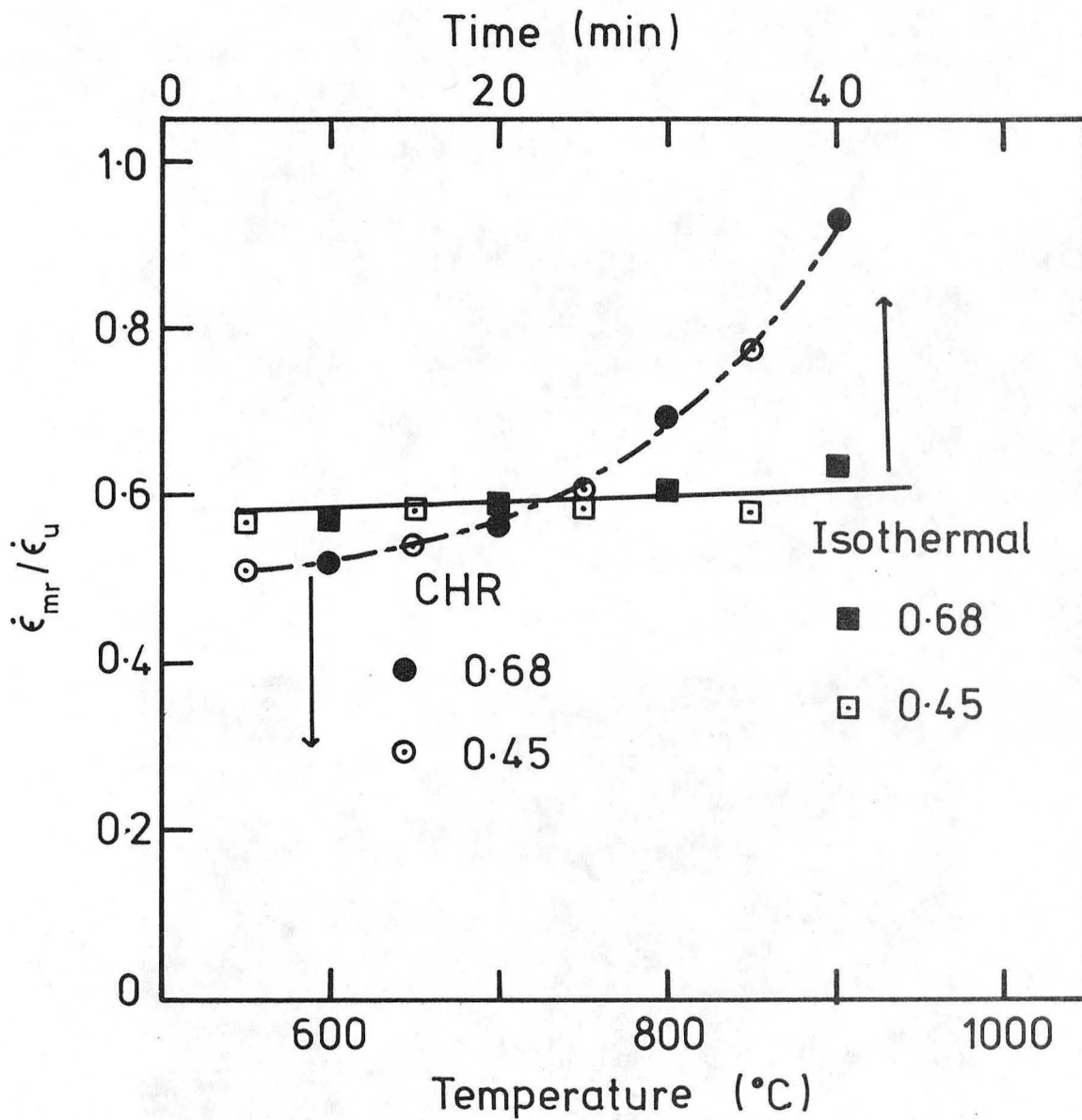
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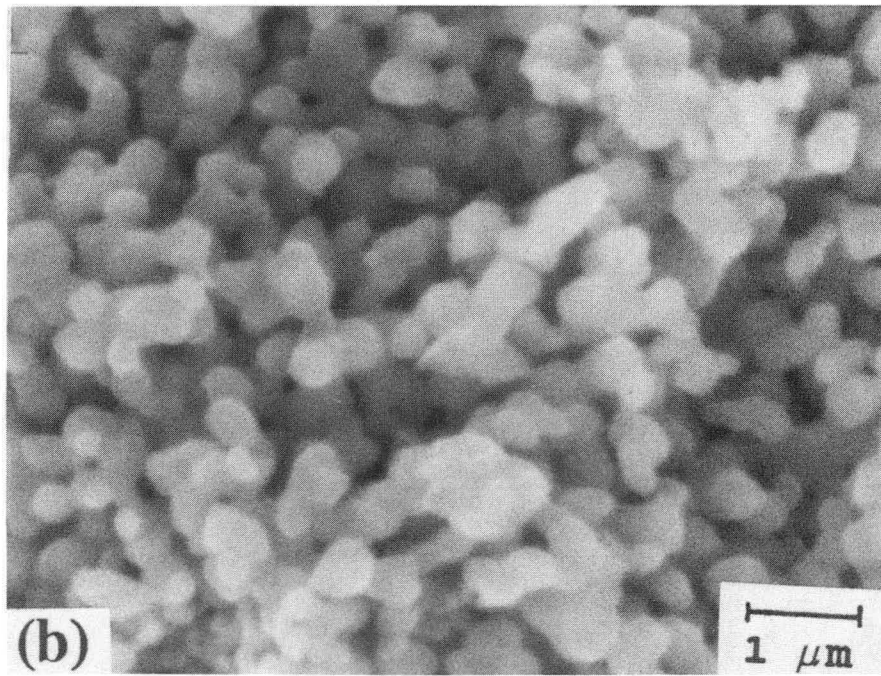
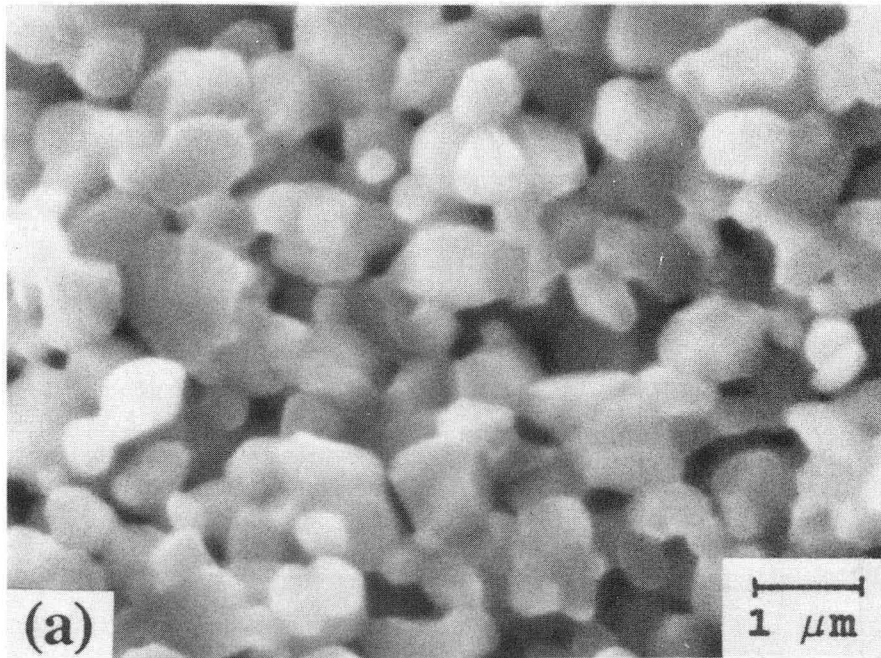
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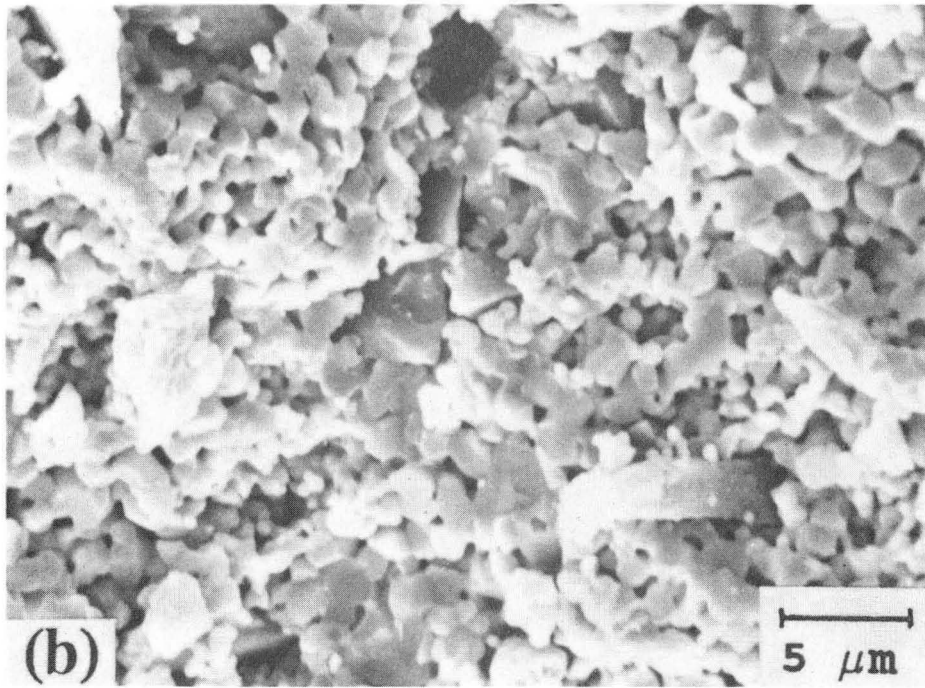
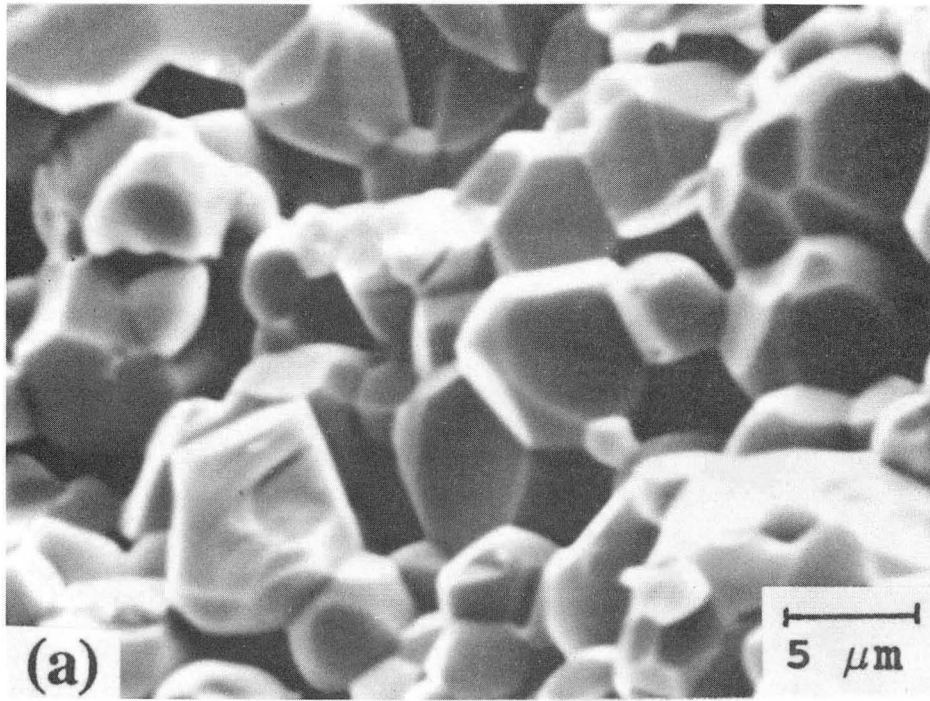


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