LBL-36451
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Submitted to Journal of the American Ceramic Society

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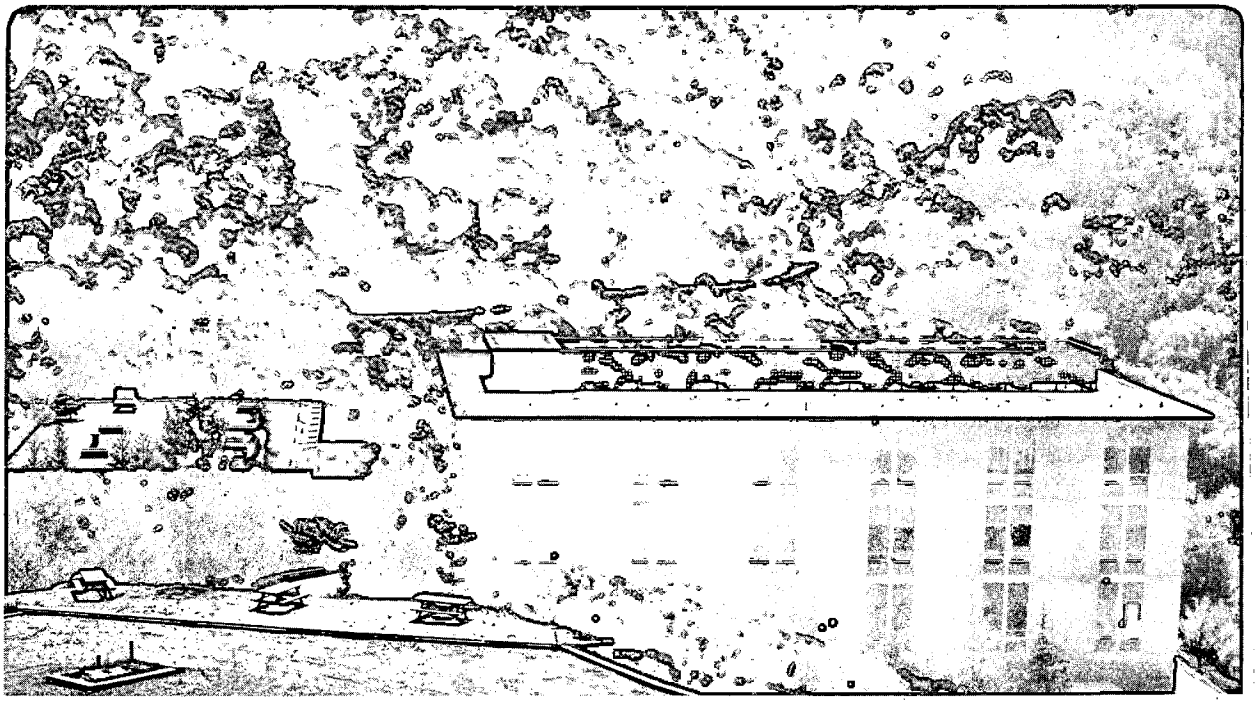
W.-S. Hong, L.C. De Jonghe, X. Yang, and M.N. Rahaman

October 1994



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Wan-Shick Hong and Lutgard C. De Jonghe

Department of Materials Science and Mineral Engineering
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Xi Yang and Mohamed N. Rahaman

Department of Ceramic Engineering
University of Missouri
Rolla, Missouri 65401

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Reaction Sintering of ZnO-Al_2O_3

Wan-Shick Hong and Lutgard C. De Jonghe*
Lawrence Berkeley Laboratory, Materials Sciences Division, and Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720

Xi Yang and Mohamed N. Rahaman*
University of Missouri, Department of Ceramic Engineering, Rolla, MO 65401

Abstract

The reaction sintering of equi-molar mixtures of ZnO and Al_2O_3 powders was investigated as a function of primary processing parameters such as the temperature, heating rate, green density and particle size. The powder mixtures were prepared by two different methods. In one method, the ZnO and Al_2O_3 powders were ball-milled. In the other method, the ZnO powder was chemically precipitated onto the Al_2O_3 particles dispersed in a solution of zinc chloride. The sintering characteristics of the compacted powders prepared by each method were compared with those for a pre-reacted, single phase powder of zinc aluminate, $ZnAl_2O_4$. The chemical reaction between ZnO and Al_2O_3 occurred prior to densification of the powder compact and was accompanied by fairly large expansion. The mixing procedure had a significant effect on the densification rate during reaction sintering. The densification rate of the compact formed from the ball-milled powder was strongly inhibited compared to that for the single phase $ZnAl_2O_4$ powder. However, the densification rate of the compact formed from the chemically precipitated mixture was almost identical to that for the $ZnAl_2O_4$ powder. The difference in sintering between the ball-milled mixture and the chemically precipitated mixture is interpreted in terms of the different microstructures of the intital powder compacts resulting from the different preparation procedures.

*Member, The American Ceramic Society

Supported by the Division of Materials Science, Office of Basic Energy Research, U.S. Department of Energy, under Contract No. DE-AC0376SF00098.

I. Introduction

Reaction sintering refers to a process in which the chemical reaction of the starting powders and the densification of the powder compact are both achieved in the same heating cycle [1-3]. The general principles of reaction sintering have been outlined by Yangyun and Brook [2]. Briefly, depending on the material and processing variables such as powder particle size, sintering temperature and applied pressure, reaction and densification can occur in sequence, or concurrently, or in some combination. It is important to understand how these process variables influence the rate of reaction and densification to achieve adequate control of the fabricated microstructure. Rahaman and De Jonghe [3] have shown that the heating rate during sintering is also an effective variable for manipulating the rates of densification and reaction.

Generally, it has been found that reaction sintering is difficult to control, especially when a chemically homogeneous, single phase product with high density and uniform microstructure is desired. This difficulty led Yangyun and Brook [2] to suggest that the process might better be applied to the fabrication of composites, i.e., materials which require inhomogeneity as a microstructural characteristic. Provided that there is no significant volume change during the reaction, Yangyun and Brook further proposed that densification should occur prior to the reaction if high density and controlled microstructure are to be achieved.

Recently, Rahaman and De Jonghe [3] investigated the reaction sintering of equi-molar mixtures of ZnO and Fe_2O_3 powders. They found that while the reaction occurred prior to densification, the densification rate of the reaction sintered sample was approximately the same as that for a sample formed from a pre-reacted, single phase $ZnFe_2O_4$ powder. Under almost identical sintering conditions, both the reaction sintered mixture and the single phase $ZnFe_2O_4$ powder reached densities greater than 95% of the theoretical and had roughly similar microstructure. The results of the ZnO-Fe_2O_3 investigation led Rahaman and De Jonghe to suggest that a key issue in the reaction sintering process is the degree to which the microstructure is disrupted as a result of the chemical reaction. For systems in which the reaction

does not cause severe microstructural disruption, e.g., the ZnO-Fe_2O_3 system, the achievement of high density and controlled grain size in the fabricated article is not dependent on whether the reaction occurred prior to, or after, the densification process.

The present work, concerned with the reaction sintering of equi-molar mixtures of ZnO and Al_2O_3, forms an attempt to follow up the results of Rahaman and De Jonghe for the ZnO-Fe_2O_3 system. The two systems have important similarities and differences. In both systems, two simple oxides react to form an alloy oxide such that the molar volume of the two reactants and of the product are almost the same. For the present work, the molar volumes of a $ZnO+Al_2O_3$ mixture and the compound $ZnAl_2O_4$ are 39.47 and 40.03 cm^3, respectively. Both systems have seen considerable use as model materials for investigations into the kinetics and mechanism of solid state reactions. At temperatures normally used in their sintering (less than ≈1300 °C), the reaction between ZnO and Fe_2O_3 occurs by a Wagner counter-diffusion mechanism in which cations migrate in opposite directions and the oxygen ions remain essentially stationary [4,5]. In comparison, the reaction mechanism in the ZnO-Al_2O_3 system is not as clear. The work of Branson [6] indicates that the reaction occurs by a solid state mechanism in which the diffusion of Zn ions through the $ZnAl_2O_4$ spinel layer is rate controlling. However, Schmalzried [7] reported that the rate constant for the gas-solid reaction between ZnO vapor and Al_2O_3 is in excellent agreement with the measured reaction rate. Another significant difference between the two systems is the observed magnitude of the expansion which accompanies the reaction between physical mixtures of the two simple oxides. For the ZnO-Fe_2O_3 system [3], the expansion is typically less than ≈3 vol% while for the ZnO-Al_2O_3 system [8], it is typically greater than 20 vol%.

In the present work, the densification, chemical reaction and microstructural evolution of equi-molar mixtures of ZnO and Al_2O_3 powders were investigated. To assess the effects of microstructural uniformity on the reaction sintering, two different methods were used to prepare the mixtures. One was a conventional ball milling procedure for powders of the two simple oxides. The other involved dispersing the Al_2O_3 powder in a solution of zinc chloride followed by

chemically precipitating ZnO on the Al_2O_3 powder surfaces. This precipitation process has been used by De Jonghe and coworkers [9,10], Hu and Rahaman [11, 12] , and others [13-15] to prepare coated powders in which the inclusion particles are uniformly coated with layer of powder. When compared to the mixing of similar powder compositions prepared by ball milling, the homogeneity of mixing achieved by the coating process is considerably better. The sinterability of the compacted powder mixtures was compared with that for a pre-reacted, single phase $ZnAl_2O_4$ powder.

II. Experimental Procedure

(i) Powder Mixtures Prepared by Ball Milling

ZnO powder (Reagent grade; purity 99.1%; J. T. Baker Chemical Co., Phillipsburg, NJ) and Al_2O_3 powder (A16SG, Alcoa, Pittsburg, PA) were classified by sedimentation and centrifuging to produce powders with a fairly narrow size distribution and with roughly the same average size ($\approx$0.3 μm). Equi-molar quantities of the two powders were dispersed in hexane containing 0.5 wt% Oloa 1200, which was used as a dispersant. The slurry was mixed for 10 minutes in a shear mixer running at 8000 rpm and then dried under an infra-red lamp. The dried powder was hand-ground lightly in an agate mortar and pestle and passed through a 150 mesh sieve to eliminate any large agglomerates.

Powder mixtures containing different particle sizes of the Al_2O_3 powder were also prepared by the same procedure to study the effect of varying the ZnO/Al_2O_3 particle size ratio. For these mixtures, Al_2O_3 powder (A152 SG; Alcoa, Pittsburg, PA) was classified to produce powders with average particle sizes of 1 and 1.5 μm.

Pre-reacted, single phase $ZnAl_2O_4$ powder was prepared by calcining the ball milled mixture for 3 h at 1300 °C in a ZrO_2 crucible. X-ray analysis showed that the calcined powder was single phase to within the detection limit of the instrument ($\approx$1%). To break up the agglomerates produced as a result of the calcination step, the powder was ground for 3 h in a planetary mill, in

ethanol, using ZrO_2 balls as the milling medium. After drying, the powder was treated in the same way as the mixed powders. It was dispersed in hexane containing 0.5 wt% Oloa-1200, dried under an infra-red lamp, hand-ground, and finally passed through a 150 mesh sieve.

(ii) Powder Mixtures Prepared by Chemical Precipitation

Powder mixtures consisting of nearly equi-molar quantities of ZnO and Al_2O_3 were prepared by a procedure similar to that described by Hu and Rahaman [11] for the coating of ZrO_2 particles with ZnO. The starting materials used were Al_2O_3 (particle size 0.6-0.8 μm; AKP 50, Sumitomo Chemical Co., Japan), zinc chloride and urea (both reagent grade; Aldrich Chemical Co., Milwaukee, WI). Briefly, an aqueous suspension containing 2.5 g/L Al_2O_3, 0.2 mol/L zinc chloride and 0.7 mol/L urea was prepared and aged at 75 °C with constant stirring for up to 20 h to produce powder mixtures with ZnO/Al_2O_3 molar ratios near to 1. After aging, the suspension was cooled and the solids were recovered by centrifuging. The solids were washed with distilled water to remove excess solute and dried at 200 °C for 24 h. The amount of ZnO and Al_2O_3 in the mixture was determined from the initial mass of the Al_2O_3 powder used and the mass of the dried mixture. From a plot of ZnO to Al_2O_3 molar ratio versus aging time, the time ($\approx$15 h) required to produce a molar ratio equal to 1 was determined. This aging time was used in the preparation of the mixtures used in the sintering experiments.

In a separate experiment, pure ZnO powder (i.e., containing no Al_2O_3 powder) was precipitated from a solution of zinc chloride under the identical conditions used for the mixed powders. The pure ZnO powder was heated at 200 °C for 24 h and used in the preparation of a single phase $ZnAl_2O_3$ powder as follows. Equi-molar quantities of ZnO and Al_2O_3 (i.e., the Sumitomo powder used above) were mixed by ball milling while dispersed in distilled waster with ZrO_2 balls as the milling medium. After drying, the mixture was hand-ground in an agate mortar and pestle and calcined for 3 h at 1200 °C in a ZrO_2 crucible. X-Ray analysis showed the powder

to be single phase to within the detection limits of the instrument. The calcined powder was balled milled again under the conditions used for the mixture, dried and hand-ground.

(iii) Compaction, Sintering and Characterization

Cylindrical compacts (6 mm in diameter by 6 mm) were prepared by die pressing or a combination of die pressing and cold isostatic pressing. Green densities in the range of 0.52 to 0.69 of theoretical were produced to study the effects of green density on the densification rate. However, most experiments were performed with compacts having a green density of 0.60-0.65. Prior to sintering, the compacts prepared from powders with Oloa 1200 were heated at 2 °C/min to 450 °C to burn off the dispersant.

Sintering was carried out in air, at constant heating rates of 1, 2, 4 and 10 °C/min to ≈1400 °C, in a dilatometer that allowed continuous monitoring of the shrinkage kinetics. The density of the compacts at any temperature was determined from the green density and the measured shrinkage.

In separate experiments, sintering runs with reaction sintered samples were terminated at intervals of 100 °C between 700 and 1400 °C and the samples were cooled rapidly. A different sample was used for each run. The phase composition of the quenched samples was determined by x-ray analysis. Microstructural observations were made by scanning electron microscopy (SEM) of fracture surfaces and of polished and thermally etched surfaces. Thermal etching was accomplished by heating for 2 h at 1200 °C, in air.

III. Results

To investigate how the reaction sintering characteristics of the ZnO-Al_2O_3 system depended on the primary variables such as temperature, heating rate, green density and particle size, the first set of experiments was done with powder mixtures prepared by the ball milling process. The

results obtained with these samples will be described before considering those for the chemically precipitated mixtures.

(i) Powder Mixtures Prepared by Ball Milling

Figure 1 shows data for the relative density, ρ, versus temperature, T, for the reaction-sintered $ZnO-Al_2O_3$ mixture (Al_2O_3 particle size ≈0.3 μm) and for the single phase $ZnAl_2O_4$ powder, during constant heating rate sintering of 4 °C/min. The single phase powder starts to show measurable shrinkage at ≈1000 °C and, starting from a green density of 0.68, reaches a density of 0.81 at 1400 °C. In comparison, the reaction sintered mixture with the same green density shows an expansion starting at ≈800 °C and the relative density falls to 0.54 of theoretical at ≈1000 °C. After remaining nearly constant up to ≈1200 °C, the relative density increases slowly to reach a value of 0.60 at 1400 °C. Figure 1 also shows data for the single phase powder compacts with a relative green density of 0.55, i.e., a value close to the minimum reached by the reaction sintered sample during its expansion. Even for this lower green density, the single phase powder starts to sinter at a much lower temperature and has a much higher sintering rate when compared to the reaction sintered mixture.

The temperature derivative of the densification strain, defined as $(1/\rho)d\rho/dT$, was calculated from Fig. 1 by fitting smooth curves to the data and differentiating (Fig. 2). The single phase $ZnAl_2O_4$ powder shows trends similar to those found in earlier work [16] with simple oxides (e.g., ZnO). For the reaction sintered mixture, the regions of expansion and densification are clearly distinguished.

The expansion of the reaction sintered mixture is clearly correlated with the occurrence of the reaction between the ZnO and Al_2O_3. Figure 3 shows the X-ray diffraction patterns for the reaction sintered mixtures which were heated at 4 °C/min and quenched at 800, 900 and 1000 °C. The data show that the reaction starts above 800 °C and is essentially completed by 1000 °C. This temperature region corresponds to that of the expansion in Fig.1.

The effect of heating rate (1, 2, 4 and 10 °C/min) on the densification of the single phase powder and the reaction sintered mixture is shown in Fig. 4. In this case also, the data for the single phase powder show trends similar to those obtained for earlier simple oxides [17]; the density curves fall within a fairly narrow band with the density at any temperature decreasing slightly with increasing heating rate. For the reaction sintered mixture, both the expansion and the densification shift to higher temperature.

Fig. 5 shows the effect of green density on the densification of the reaction sintered mixture at a heating rate of 4 °C/min. For the range of 0.56 to 0.69 investigated, the green density has little effect : the curves are nearly parallel and the magnitude of the expansion in each case is ≈20-25 vol%.

Figures 6(a)-(c) show scanning electron micrographs of polished surfaces of the single phase $ZnAl_2O_4$ samples after sintering to 1000, 1200 and 1400 °C, respectively. The sample sintered to 1000 °C has nearly the same density as the green compact (0.64). At 1200 °C, considerable necking has occurred with a small amount of densification. Above 1200 °C, densification and coarsening accelerate, with the sample reaching a density of 0.81 at 1400 °C. The corresponding micrographs for the reaction sintered mixture are shown in Fig. 6(d)-(f). The main feature is coarsening of the microstructure with very little densification. By 1400 °C, coarsening has led to the development of particle strings with large necks.

The effect of Al_2O_3 particle size on the densification of the reaction sintered mixture is shown in Fig. 7. For these mixtures, the ZnO powder was the same (average particle size of 0.3 μm) while the average particle sizes of the Al_2O_3 powders were 1.5 μm (referred to as "coarse"), 1.0 μm (medium) and 0.3 μm (fine). The data show a systematic trend: with decreasing Al_2O_3 particle size, the region of expansion shifts to lower temperature and the magnitude of the expansion decreases slightly.

(ii) Powder Mixtures Prepared by Chemical Precipitation

Figure 8(a) shows an SEM of the Sumitomo Al_2O_3 powder used in the preparation of the mixtures by the chemical precipitation process. The ZnO-Al_2O_3 mixtures prepared by precipitating the ZnO on to the Al_2O_3 particles by the coating process are shown in Fig 8(b). The process did not produce coating of the individual Al_2O_3 particles. Instead, under the conditions required for heterogeneous precipitation of the ZnO, the Al_2O_3 particles tended to agglomerate. Each coated agglomerate produced in the process, with a size in the range of 3 to 5 μm, contained a few Al_2O_3 particles which were fairly uniformly distributed within the agglomerate. Figure 8(c) shows the powder mixture prepared from the pure ZnO (precipitated from the zinc chloride solution) and the Sumitomo Al_2O_3 powder by ball milling. The ZnO (lighter phase) appears to be distributed rather non-uniformly.

Figure 9 shows the data for ρ versus T, during constant heating rate sintering at 4°C/min, for the reaction sintered mixtures prepared by the coating process and by ball milling. Both samples undergo an expansion starting at ≈800 °C and the magnitude of the expansion is roughly the same. However, following the expansion, the densification of the sample prepared from the coated powders is significantly higher than that for the sample prepared from the ball-milled powders. After sintering to 1450 °C, the density of the sample prepared from the coated powders is ≈0.78 compared with a value of 0.57 for the ball-milled mixture.

In Fig. 10, the densification of the reaction sintered mixture prepared from the coated powders is compared with that for the single phase $ZnAl_2O_4$ powder during constant heating rate sintering at 4 °C/min. The densification curve for the $ZnAl_2O_4$ powder compact with a green density of ≈0.53 (i.e., a value corresponding to the minimum reached by the reaction sintered sample during its expansion) is almost identical to that for the reaction sintered mixture. Furthermore, above ≈1250 °C, the density of the reaction sintered sample is fairly close to that for the $ZnAl_2O_4$ powder compact with a green density of ≈0.60 (i.e., a value corresponding to the green density of the reaction sintered sample).

The microstructures of the powder compacts sintered under almost identical conditions (4 °C/min to 1600 °C) are shown in Fig. 11. The difference between the reaction sintered mixtures prepared by ball milling (Fig. 11a) and by the coating process (Fig. 11b) is quite pronounced. The sample prepared by the coating process has a higher density and a larger grain size. In comparison, the sample prepared from the single phase $ZnAl_2O_4$ has a microstructure (Fig. 11c) which is fairly similar to that for the reaction sintered sample prepared from the coating powder.

IV. Discussion

The data show that for the powders used in the present investigation, the reaction between ZnO and Al_2O_3 to form $ZnAl_2O_4$ spinel occurs prior to any significant sintering and is accompanied by a fairly large volumetric expansion. We must first examine the origins of the expansion and its consequences for the densification and microstructural evolution of the reaction sintered powder mixtures.

As outlined earlier, the expansion cannot be explained simply in terms of a difference in molar volumes because the theoretical density of $ZnAl_2O_4$ spinel (4.58 g/cm^3) is nearly the same as that for an equi-molar mixture of ZnO and Al_2O_3 (4.65 g/cm^3). In the literature, two mechanisms have been invoked to account for an expansion during the solid state reaction of powder mixtures. In one mechanism, the particles are pushed apart by the reaction product. This mechanism has been modeled by Leblud *et al* [8] who used it to account for the expansion observed in their experiments for ZnO-Al_2O_3 powder compacts at 900-1000 °C. For particles of the same size, Leblud *et al* assumed uniform packing in which each Al_2O_3 particle is in contact with six ZnO particles in a cubic array. They assumed further that the reaction product is formed on the Al_2O_3 particles at each point of contact within an angle of aperture 2θ. Leblud *et al* found that their data can be fitted by the model predictions when $2\theta \approx 49°$. The packing in real powder compacts is random. Furthermore, the regular packing model of Leblud *et al* cannot generate an expansion for a solid state reaction mechanism.

The other mechanism put forward to account for an expansion during a solid state reaction is the development of Kirkendall porosity [18,19]. The expansion observed during the reaction sintering of PZT [20] and $ZnFe_2O_4$ [21] has been explained in terms of the Kirkendall effect. In the reaction ZnO-Al_2O_3 system, a possible mechanism is the precipitation of excess vacancies produced by the one-way diffusion of Zn ions across the $ZnAl_2O_4$ reaction layer, leaving porosity at the $ZnO/ZnAl_2O_4$ interface. A problem with this mechanism is that while the Kirkendall effect has been well demonstrated in metallic systems, its occurrence in oxides is controversial. Pore formation must necessarily also involve the oxygen sublattice, and pores can therefore not form if cation diffusion is the only active mass transport mechanism. The expansion as a result of reaction in the ZnO-Al_2O_3 system is likley to have another origin.

For the mixtures prepared by ball milling, the microstructure of the sample sintered to 1450 °C (Fig. 11a) appears to be simply a slightly coarsened version of the original Al_2O_3 particles used in the mixture (Fig. 8c). An argument for the observed magnitude of the volume expansion may be construcuted as follows. The alumina will react with ZnO to form $ZnAl_2O_4$, increasing its molar volume from 25.7 cm^3/mol to 40.03 cm^3/mol, thus giving as expansion of 14.33 cm^3 per mol of alumina. If we assume that the specimen dimensions are determined by a percolative network of alumina paricles, then the ratio of densities before and after reaction would be $25.7/40.03 \approx 0.64$. This is a larger density ratio than the typical experimentally observed one here of about 0.8. The differences in molar volumes of the alumina and the zinc oxide makes the alumina volume fraction in the equimolar mixture approximately 65 vol%. In a random mixture this is well above the percolation treshold [22]. It can be safely assumed that expansion of the individual particles in the percolative network will be reflected macroscopicly by an equal volume expansion. Based on the increase in the molar volume upon reaction of Al_2O_3 to $ZnAl_2O_4$ spinel, a volume ratio ΔV_r of $V_{spinel}/V_{alumina} = 1.54$ should be expected. The experimental value ΔV_e, however, is only about 1.2 to 1.3. A reaction mechanism whereby only Zn ions are mobile therefore would lead to a significantly larger volume expansion than what is observed. The lower

expansion of the percolative alumina network can only be accounted for is it is assumed that during reaction, a fraction of the alumina, equal to 15-20 vol% [i.e., $1-(\Delta V_e/\Delta V_r)$] leaves the percolative network. This will be the case if the mechanism of reaction involves a mutual counter-diffusion of Zn and Al ions. Schematically, the concept is illustrated in Fig. 12. The approximate ratio of the Zn and Al ion fluxes through a spinel product layer, J_{Al}/J_{Zn}, commensurate with the observed volume changes can then readily be calculated to be about 0.5. While it is likley that the bulk diffusion rate of oxygen within the spinel phase is insignificant, oxygen must be transported to accommodate the necessary particle shape changes. However, transfer of oxygen can occur through the vapor phase, by interface transport, and by interface movement.

The proposed mechanism for volume expansion upon reaction does not involve the details of the particle distribution, as long as a dominant percolative network is established, and is consistent with the absence of significant influences of particle size ratios and green compact structure. While the argument provides a plausible mechanism for the observed volume expansion during reaction, it does not address the significant depression in the sintering rate for the ball milled mixture.

A comparison of the densification of the reaction sintered mixtures prepared by ball milling and by the coating process (Fig. 9) indicates that both samples undergo approximately the same amount of expansion during the reaction. However, following the reaction, the densification of the mixture prepared by ball milling is considerably lower than that of the coated powder. This lower densification of the ball milled mixture cannot therefore be accounted for simply in terms of the expansion. The origins of the reduced densification must lie in microstructural differences produced by the reaction. The importance of the microstructure is supported by the data of Fig. 10 which shows that the reaction sintered mixture, while also undergoing an expansion during the reaction, sinters in roughly the same manner as the single phase $ZnAl_2O_4$ powder.

The influence of the microstructure on the densification of the reaction sintered mixtures is sketched in Fig. 13. For the mixture prepared by ball milling (Fig. 13a), the reaction leads to the formation of particle networks based on the original Al_2O_3 particle structure. Following the reaction, the structure is difficult to densify because of the large pores and the fairly rigid network of grains. The mixture prepared by the coating process forms a structure which is better able to support densification and grain growth (Fig. 13b). This structure is expected to be fairly close to that of the single phase $ZnAl_2O_4$ powder compact formed by pressing in a die (Fig. 13c). The sinterability of the coated powder would therefore be expected to be roughly similar to that for the single phase powder, as is observed (Fig. 10).

The experiments described here then indicate that the difference in the densification behavior of the various mixtures resides in the differences of the microstructures generated as a result of reaction. Indeed, in a random mixture, as is (poorly) approximated with ball milling, it must be expected that the percolative network expands non-uniformly because of its intrinsic spatial irregularity. This will cause effects on the microstructure and packing that are similar in nature to differential densification. Microstructural reaction damage will result on the scale of the network irregularities. Qualitatively, it can thus be expected that while the coating of the alumina agglomerates does not eliminate reaction expansion, it will limit the resulting reaction damage to the scale of the coated agglomerate.

The results for the present system are consistent with the earlier work of Rahaman and De Jonghe [3] for the ZnO-Fe_2O_3 system. For the ZnO-Fe_2O_3 system, densification of the reaction sintered mixtures was similar to that of a single phase $ZnFe_2O_4$ powder. While the powder mixtures were prepared by ball milling, the reaction (which occurred prior to densification) caused no significant disruption of the microstructure which evolved in roughly the same way as the single phase powder. For the present ZnO-Al_2O_3 system, the reaction produces undesirable microstructural features in the mixtures prepared by ball milling, which drastically impede subsequent densification. However, if the undesirable microstructural features are significantly

reduced (as in the case of the coated powders), then the reaction sintered mixtures densify in roughly the same way as the single phase $ZnAl_2O_4$ powder.

V. Conclusions

In the reaction sintering of ZnO-Al_2O_3 powder mixtures, the reaction occurs prior to any significant densification and is accompanied by a fairly large expansion. The sinterability of the reaction sintered mixtures is influenced strongly by the homogeneity of mixing in the starting powder compact. The densification of a reaction sintered mixture prepared by ball milling is significantly lower than that of a pre-reacted, single phase $ZnAl_2O_4$ powder. Coated powders prepared by a chemical precipitation process undergo about the same initial reaction expansion as the ball milled mixture but, following the reaction, show a substantially higher densification rate. The densification of the coated powders is roughly similar to that of a single phase $ZnAl_2O_4$ powder.

The reaction and the associated expansion are, by themselves, not the dominant factors in the subsequent densification process. Instead, the microstructural change produced by the reaction in the dominant percolative network is a major factor in controlling the subsequent densification. The changes in the percolative network are, in turn, affected by the reaction transport mechanisms.

Finally, the results for the ZnO-Al_2O_3 system and comparison the ZnO-Fe_2O_3 system show that when reaction disrupts the microstructure, the occurrence of a reaction prior to densification can inhibit densification, but that this inhibition can be relieved by modification of the initial powder packing as achieved by use of coated powders.

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Figure Captions

Fig. 1. Relative density versus temperature for the single phase $ZnAl_2O_4$ powder and the reaction sintered mixture prepared by ball milling during heating at 4 °C/min to 1400 °C.

Fig. 2. Temperature derivative of the densification strain versus temperature for the samples described in Fig. 1.

Fig. 3. X-ray diffraction patterns for the reaction sintered mixture prepared by ball milling after heating at 4 °C/min to (a) 800 °C, (b) 900 °C and (c) 1000 °C. (The letters A, Z and ZA refer to peaks associated with alumina, zinc oxide and zinc aluminate, respectively.)

Fig. 4. Relative density versus temperature for (a) the single phase $ZnAl_2O_4$ powder and (b) the reaction sintered mixture prepared by ball milling for heating rates of 1, 2, 4 and 10 °C/min.

Fig. 5. Effect of green density on the densification of the reaction sintered mixture prepared by ball milling for a heating rate of 4 °C/min.

Fig. 6. Scanning electron micrographs of the polished surfaces of the single phase $ZnAl_2O_4$ powder (a)-(c), and the reaction sintered mixture prepared by ball milling (d)-(f), after heating at 4 °C/min to 1000, 1200 and 1400 °C.

Fig. 7. Effect of the Al_2O_3 particle size on the densification of the reaction sintered mixture prepared by ball milling for a heating rate of 4 °C/min.

Fig. 8. Scanning electron micrographs of (a) the Al_2O_3 powder used in the chemical precipitated mixture, (b) the coated powder prepared by chemical precipitation and (c) the mixed powder prepared by ball milling.

Fig. 9. Relative density versus temperature for the coated powder prepared by chemical precipitation and the mixed powder prepared by ball milling during reaction sintering at 4 °C/min to 1450 °C.

Fig. 10. Relative density versus temperature for the coated powder prepared by chemical precipitation and the single phase $ZnAl_2O_4$ powder during heating at 4 °C/min to 1450 °C.

Fig. 11. Scanning electron micrographs of the fracture surfaces of (a) the reaction sintered mixture prepared by ball milling, (b) the reaction sintered mixture prepared from the coated powders and (c) the single phase $ZnAl_2O_4$ powder. The samples were heated at 4 °C/min to 1450 °C.

Fig. 12 Schematic illustration of the ZnO/Al_2O_3 reaction mechanism. The dotted outline gives the volume change expected on the basis of Zn transport only, with particle shape change accomodated.

Fig. 13. Sketch illustrating the microstructural evolution, during the reaction stage of the sintering process, of (a) the mixture prepared by ball milling and (b) the coated powder prepared by chemical precipitation. The microstructure of the green compact of the single phase $ZnAl_2O_4$ powder formed by die pressing is illustrated in (c).

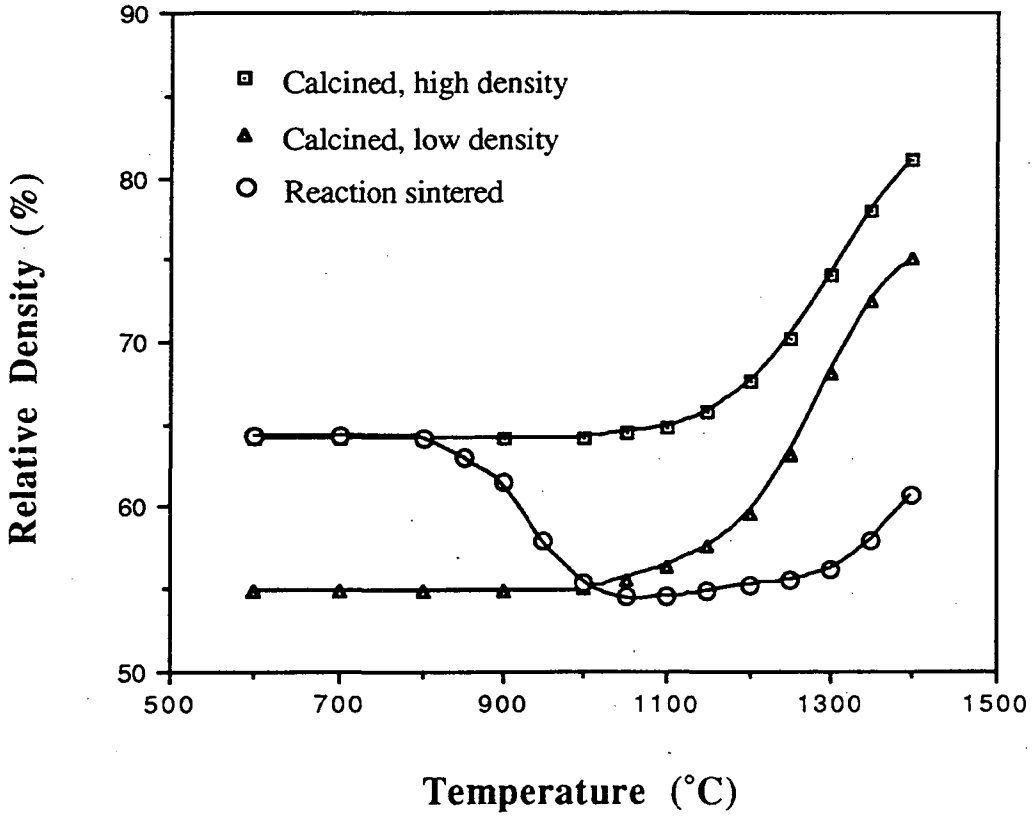

Calcined, high density
Calcined, low density
Reaction sintered
Relative Density (%)
90
80
70
60
50
500
700
900
1100
1300
1500
Temperature (°C)

Fig. 1

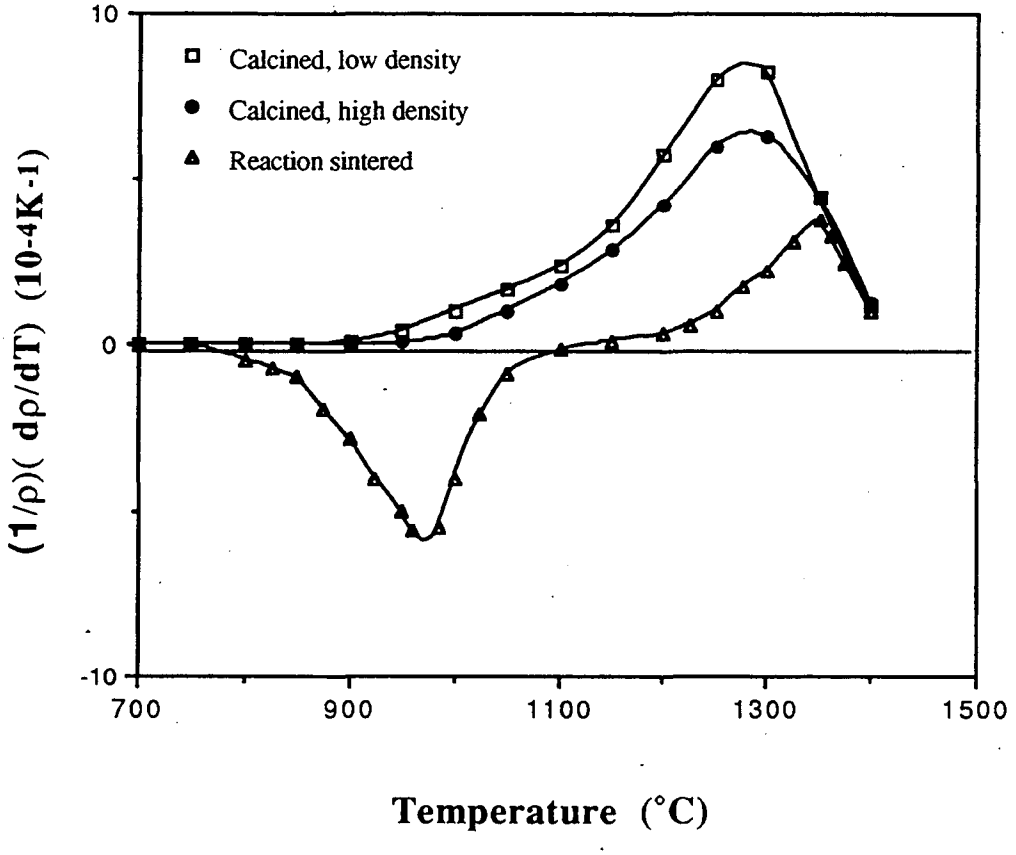

10
0
-10
700
900
1100
1300
1500
Calcined, low density
Calcined, high density
Reaction sintered
(1/ρ)(dρ/dT) (10-4K-1)
Temperature (°C)

Fig. 2

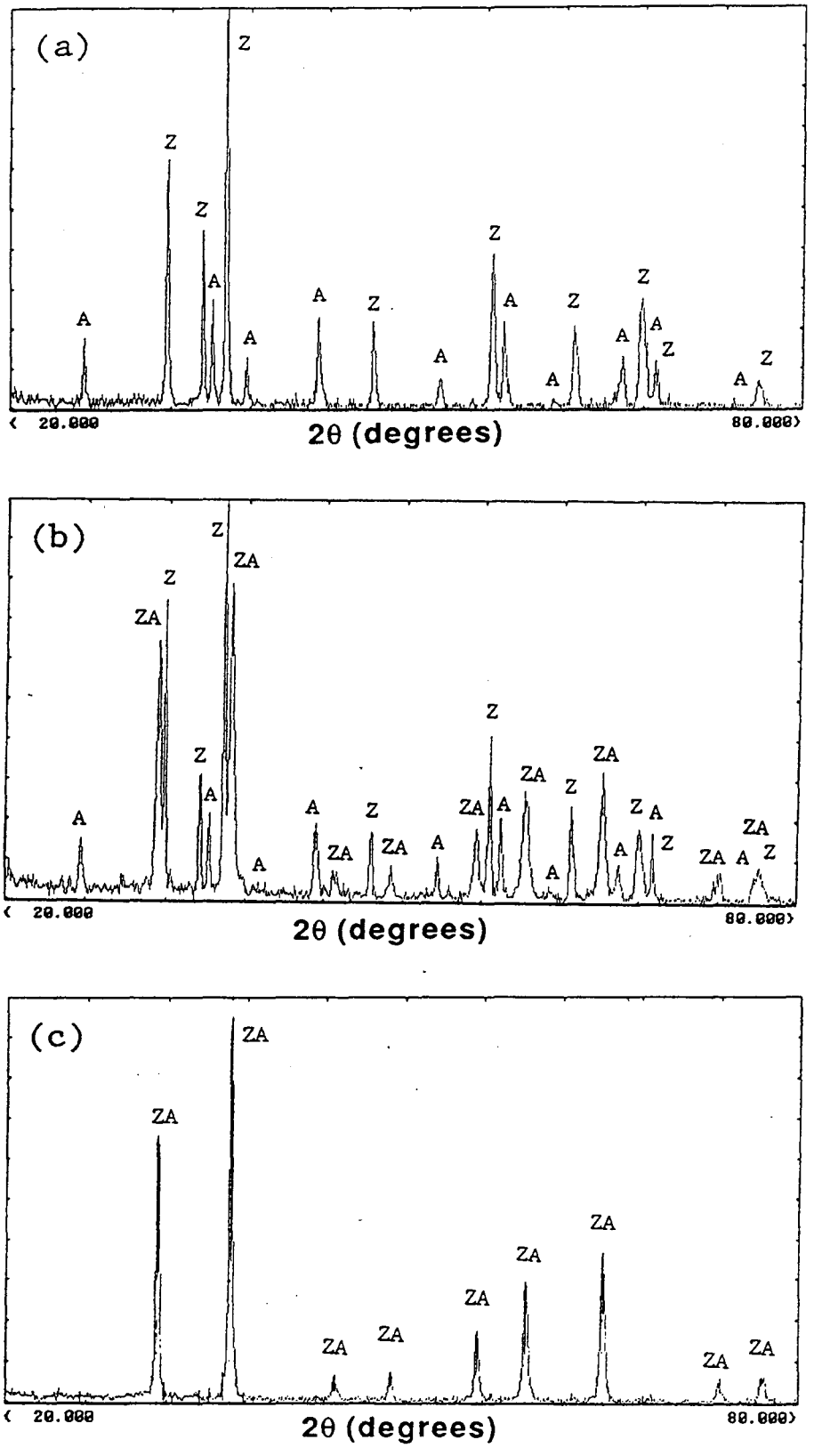

(a)
Z
Z
Z
A
A
A
A
Z
Z
A
A
Z
A
Z
A
A
Z
A
Z
20.000
2θ (degrees)
80.000
(b)
Z
ZA
Z
ZA
Z
A
A
A
ZA
Z
ZA
A
ZA
A
Z
ZA
Z
ZA
A
Z
A
Z
ZA
A
Z
20.000
2θ (degrees)
80.000
(c)
ZA
ZA
ZA
ZA
ZA
ZA
ZA
ZA
ZA
20.000
2θ (degrees)
80.000

Figure 3

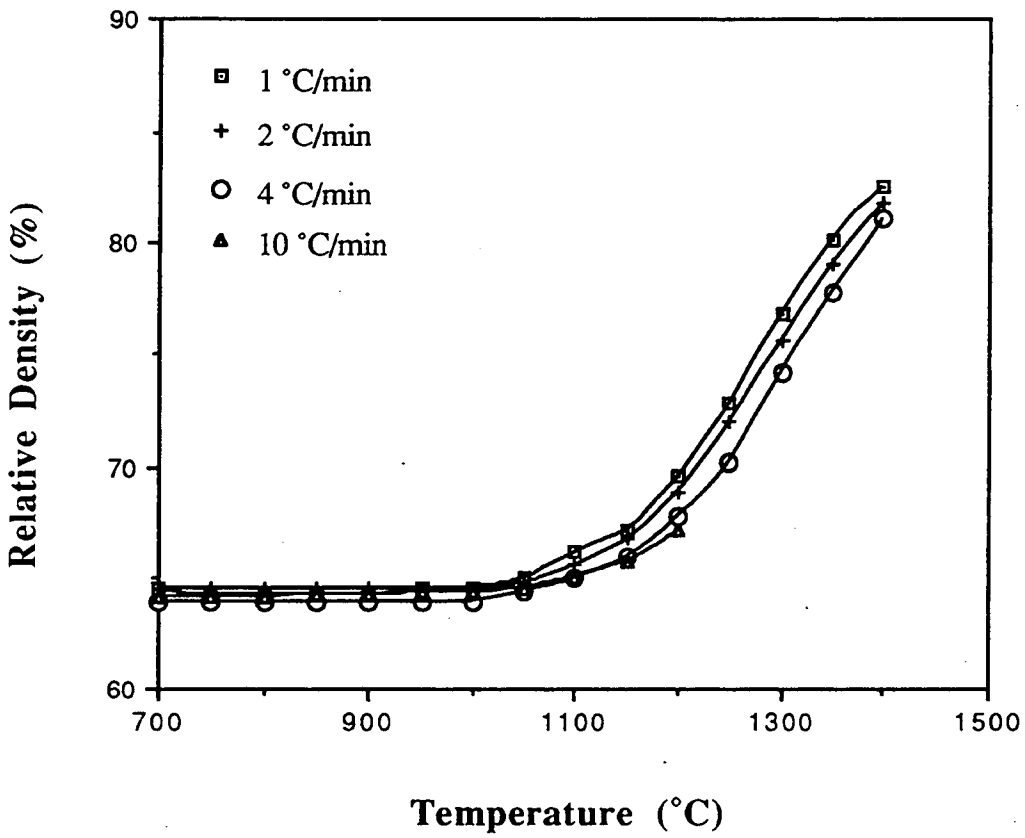

90
80
70
60
700
900
1100
1300
1500
1 °C/min
2 °C/min
4 °C/min
10 °C/min
Relative Density (%)
Temperature (°C)

Fig. 4a

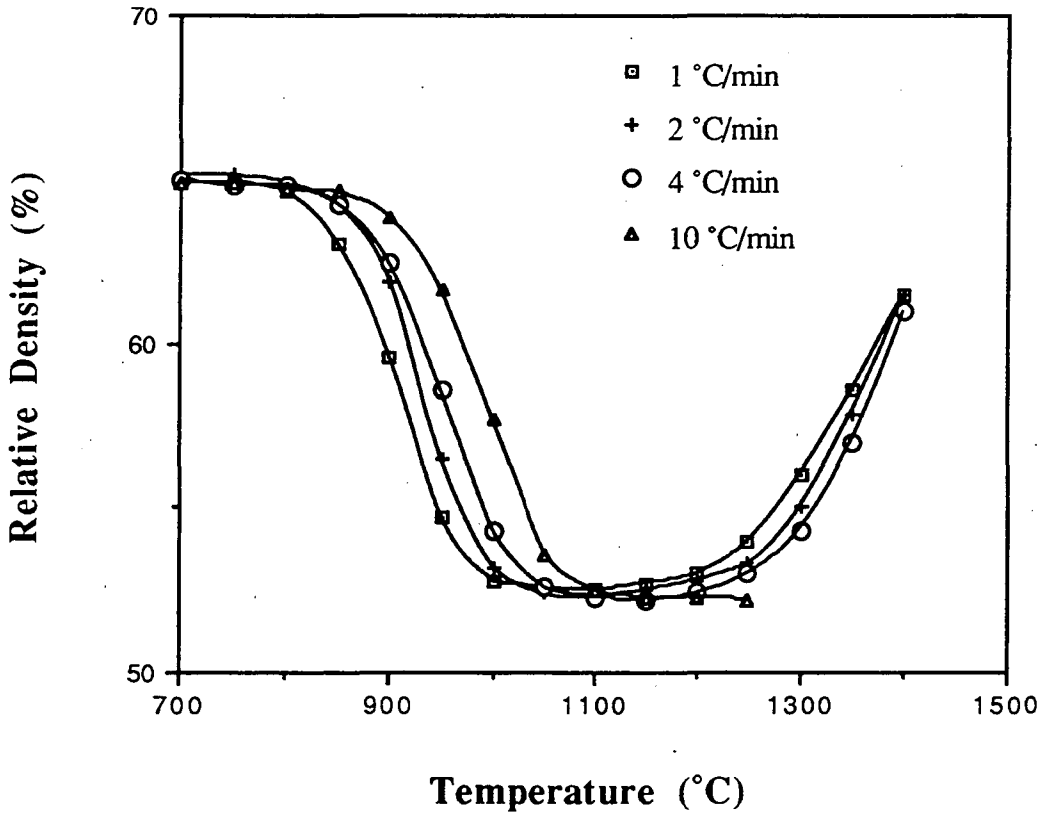

70
60
50
700
900
1100
1300
1500
1 °C/min
2 °C/min
4 °C/min
10 °C/min
Relative Density (%)
Temperature (°C)

Fig. 4b

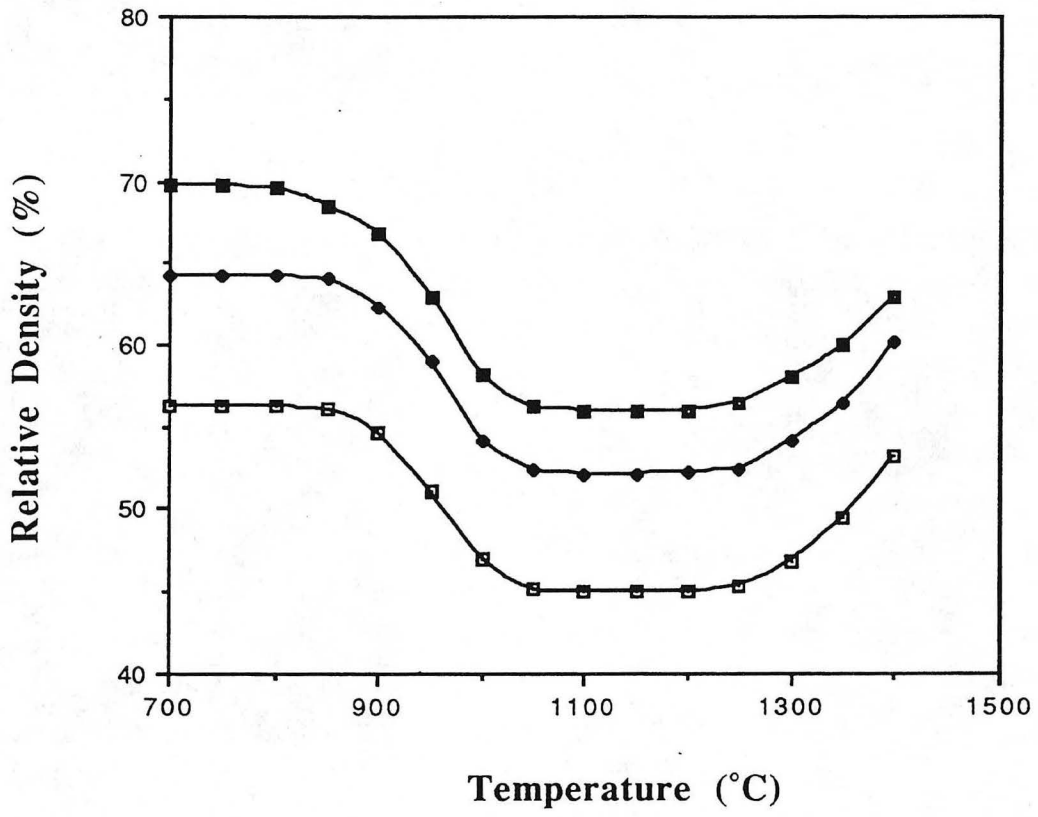
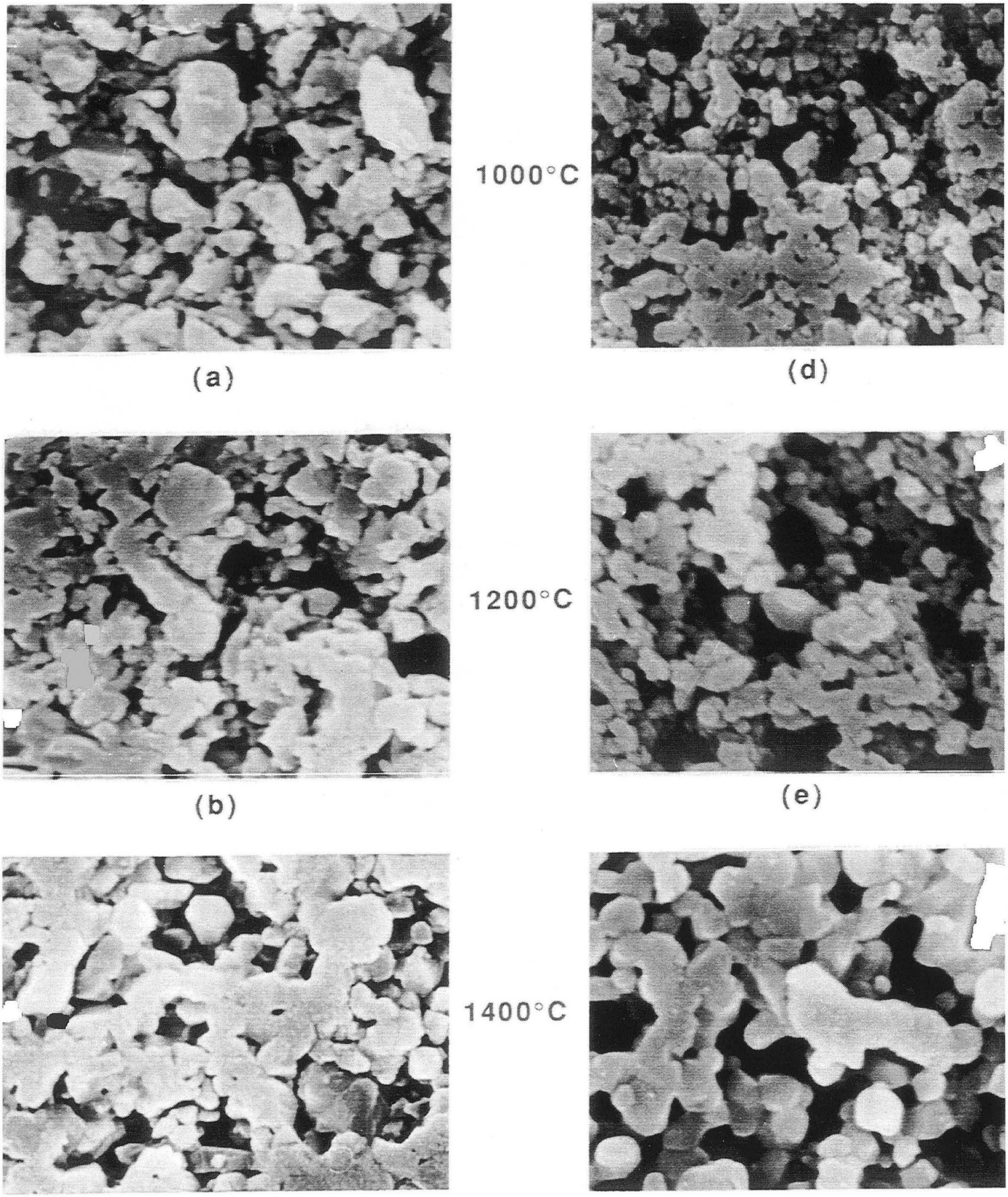

80
70
60
50
40
700
900
1100
1300
1500
Relative Density (%)
Temperature (°C)

Fig. 5


1000°C
(a)
(d)
1200°C
(b)
(e)
1400°C
(c)
(f)
1 μm

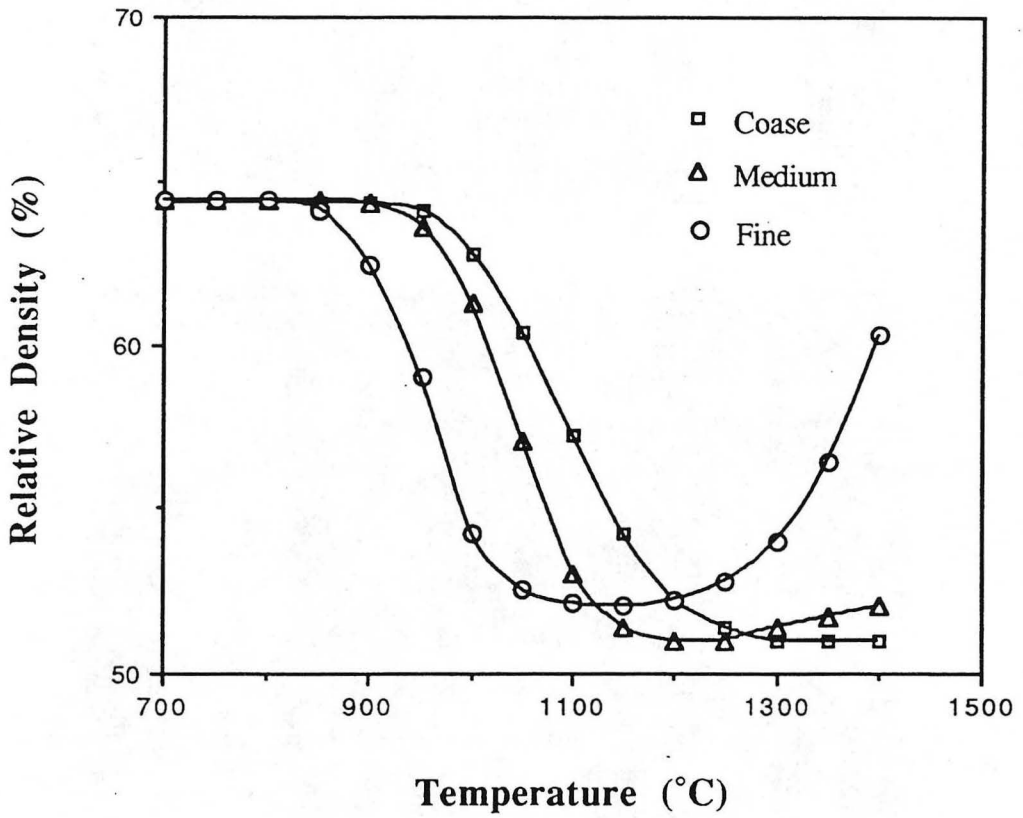
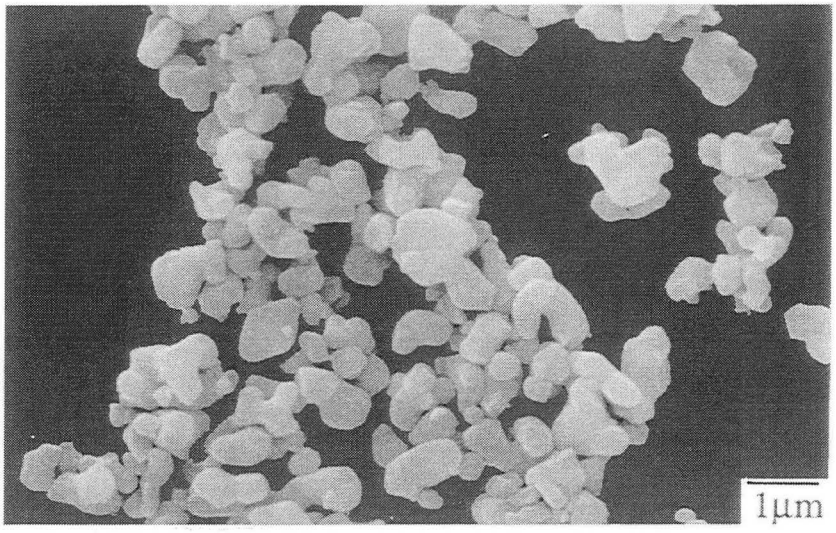
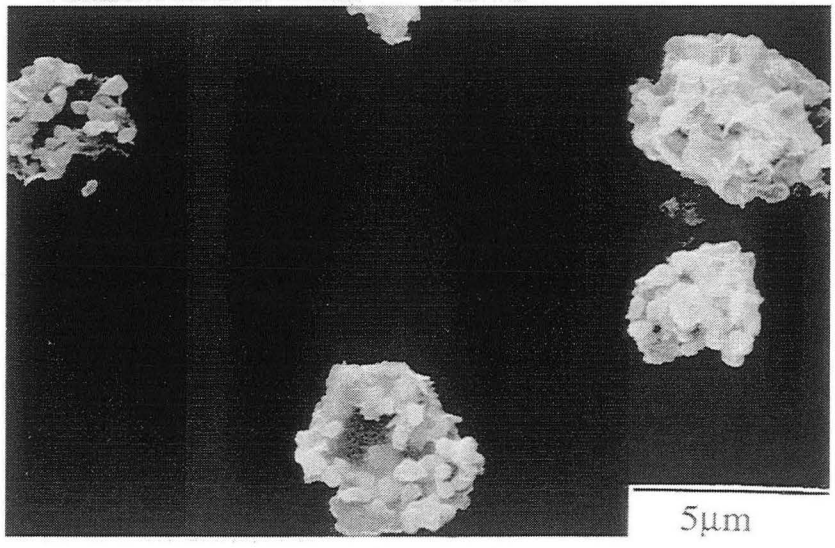

70
60
50
700
900
1100
1300
1500
Relative Density (%)
Temperature (°C)
Coase
Medium
Fine

Fig. 7


1μm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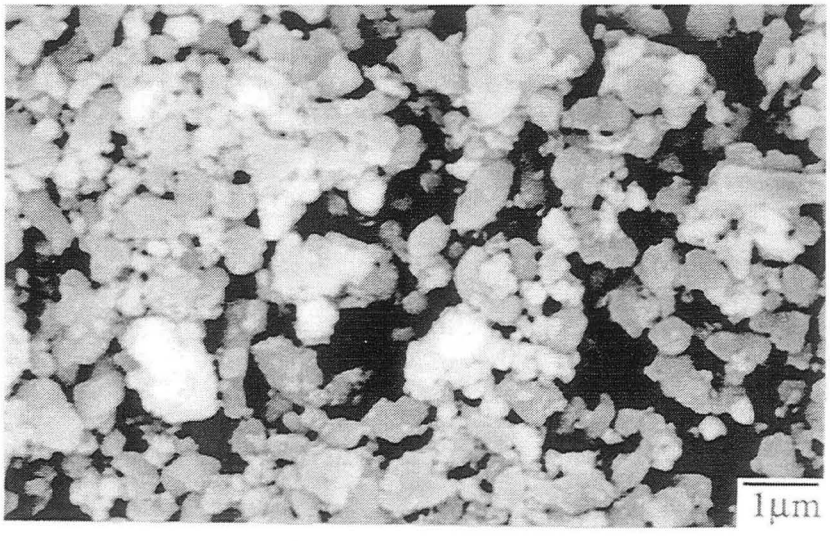

1μm

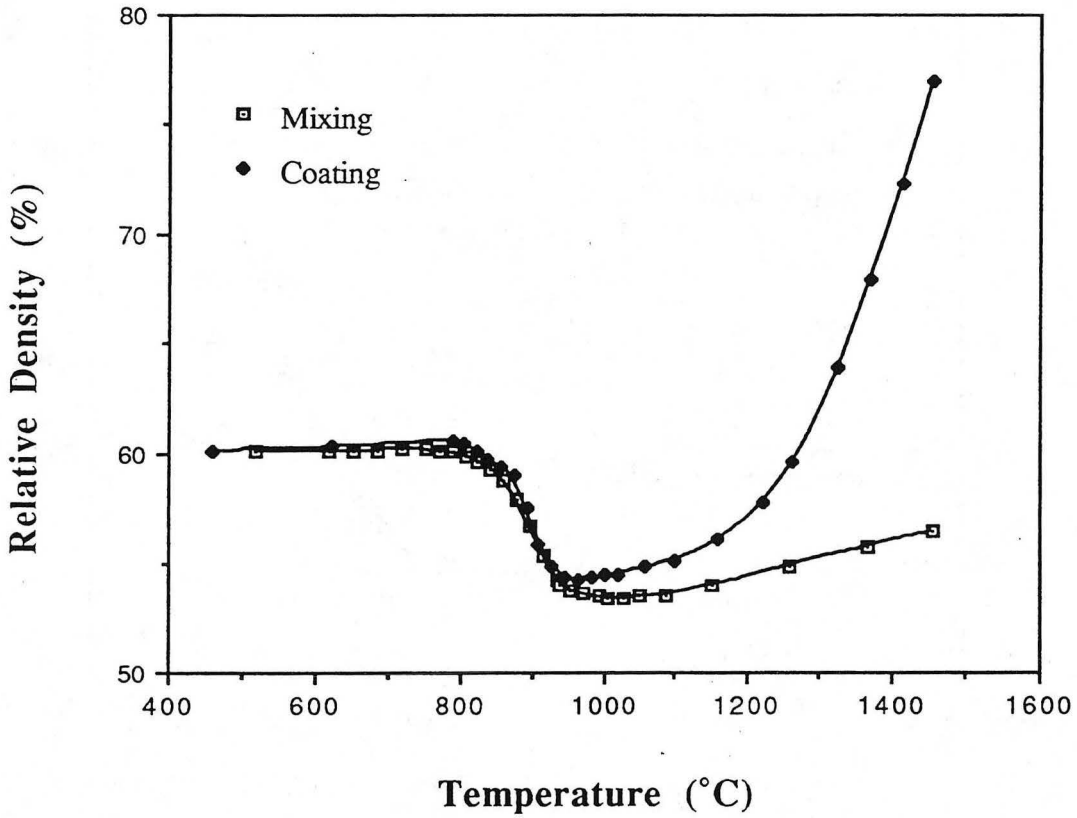

Mixing
Coating
Relative Density (%)
Temperature (°C)
80
70
60
50
400
600
800
1000
1200
1400
1600

Fig. 9

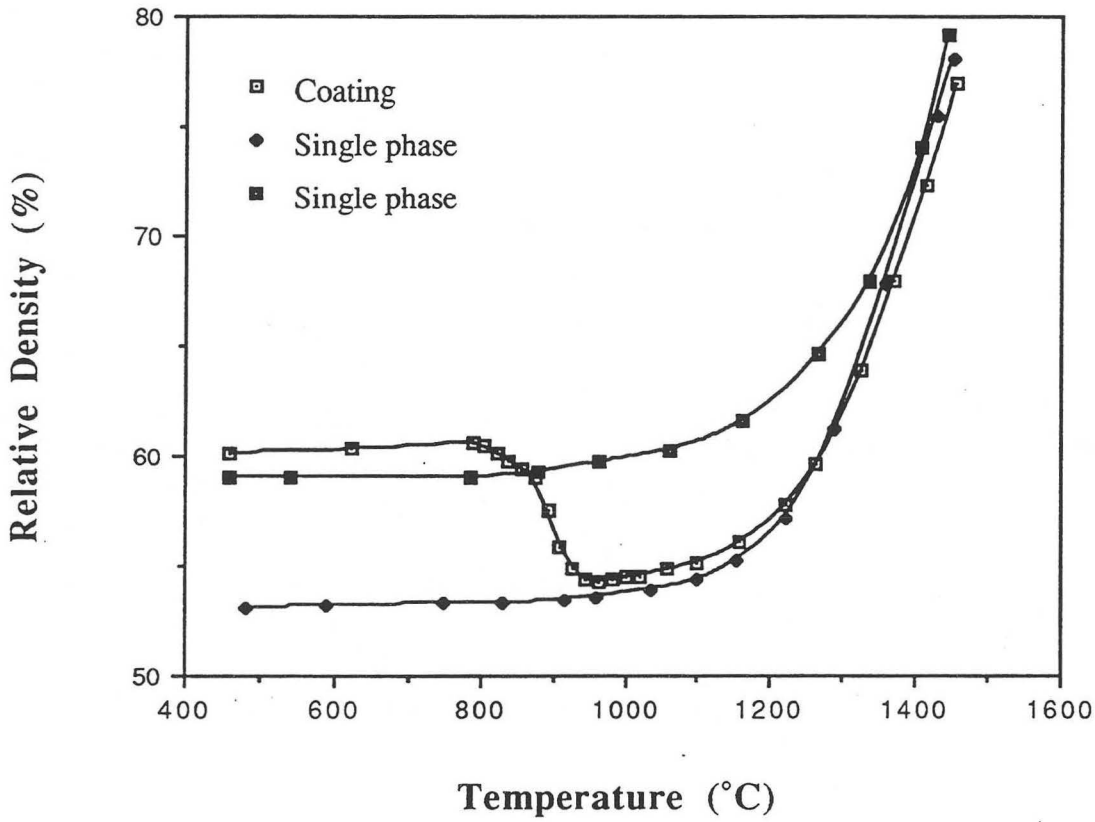
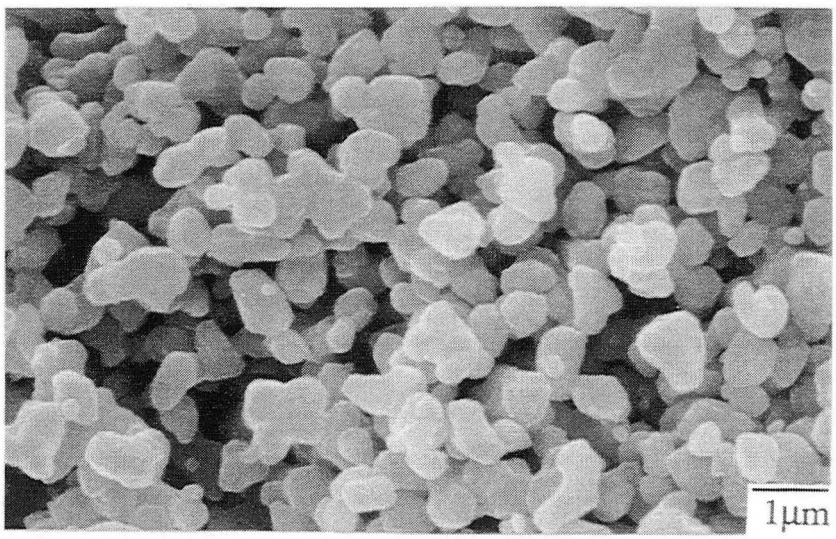

Coating
Single phase
Single phase
Relative Density (%)
Temperature (°C)
80
70
60
50
400
600
800
1000
1200
1400
1600

Fig. 10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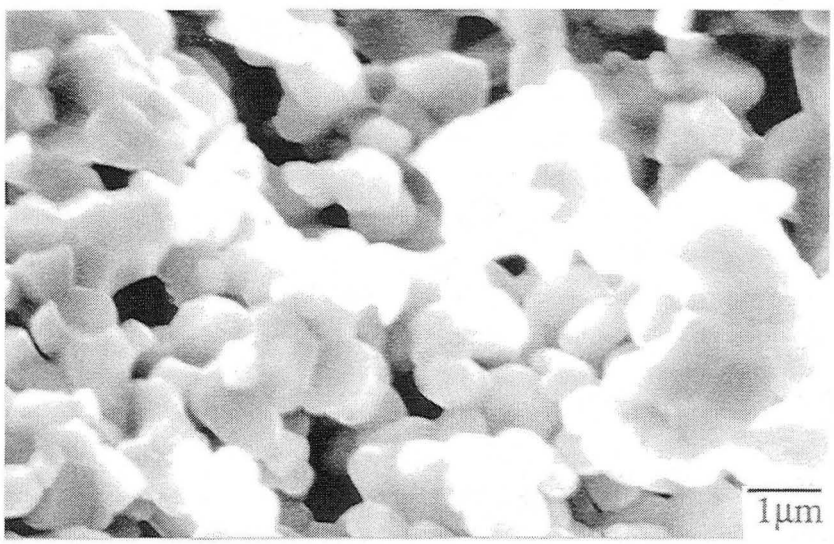
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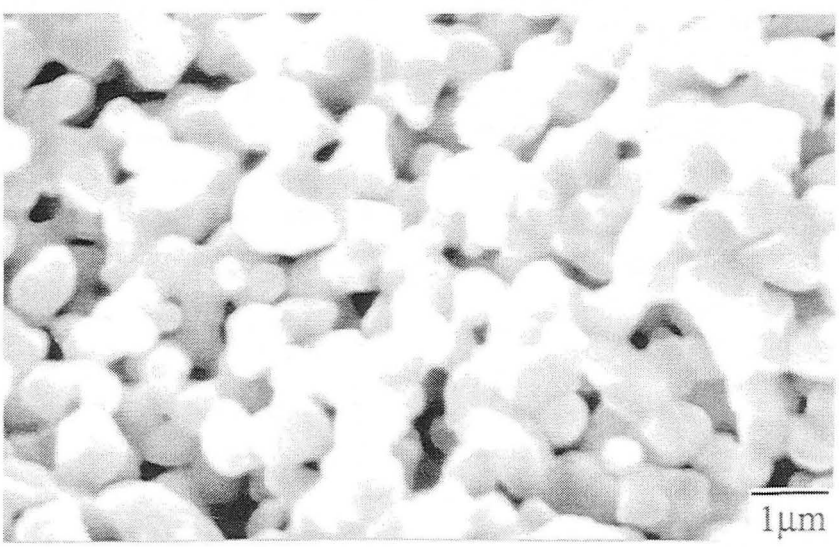
1μm

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720