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Grain growth in $(Ca_{1-x},Mg_x)Zr_4(PO_4)_6$ ceramics

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Grain growth in $(Ca_{1-x},Mg_x)Zr_4(PO_4)_6$ (CMZP) ceramics in the final stage of sintering has been investigated. The grain growth in CMZP ceramics obeys the isothermal grain-growth kinetics with time exponent, n, lying between 1.8 and 2.4 which depends on magnesium content, indicative of a change in grain-growth rate. The time exponent for the grain growth of CMZP can be taken as 2.0 which implies that a normal grain growth develops in the CMZP ceramics. The apparent activation energy for grain growth demonstrates a maximum at $x = 0.0$ and a minimum at $x = 0.1$, with 103.2 and 39.4 kcal mol^{-1}, respectively, indicating that a small amount of magnesium promotes grain-boundary migration. The critical grain size for initiating microcracks in the CMZP increases with increasing magnesium and reaches 9–12 μm when $x = 0.4$.

1. Introduction

$(Ca_{1-x},Mg_x)Zr_4(PO_4)_6$ (CMZP) ceramics with $x = 0.0$–0.4, which were synthesized by incorporating magnesium into the $CaZr_4(PO_4)_6$, possess a framework structure resembling that of the well-known $NaZr_2(PO_4)_3$ ceramic (NZP) [1–3] and exhibit an ultra-low coefficient of thermal expansion (CTE) [4, 5]. However, owing to the existence of opposite axial displacement in NZP [3], an anisotropic characteristic in the thermal expansion results, and always initiates microcracking in the matrix while the grain size of the material is larger than a certain critical size [6]. For $CaZr_4(PO_4)_6$ [3], Van Aken [5] has reported that the thermal expansion anisotropy (TEA) of the CMZP can be minimized by introducing 40% magnesium for calcium, i.e. $x = 0.4$. With the minimization in TEA, the critical grain size for the CMZP accordingly is allowed to reach a sufficient size without initiating the microcracks and thus it subsequently extends the service life of the materials during application in severe environments.

In this study, the grain growth of the CMZP ceramics in terms of compositions and possible service temperatures has been monitored during the late stage of sintering [8]. The critical grain size of CMZP was empirically determined because of the difficulty in finding the exact grain size at which microcracking occurs. In determining the isothermal grain-growth kinetics of CMZP, a well-developed formula was used to evaluate its grain-growth parameters [9]

$$G^n - G_0^n = Kt \qquad (1)$$

where G is the average grain size at time t, G_0 the average grain size at $t = 0$, n the time exponent, and K is proportional to the rate constant for grain-boundary migration. The rate constant, K, which varies with temperature can be written as

$$K = K_0 \exp(-E/RT) \qquad (2)$$

where E represents the apparent activation energy for grain-boundary migration, T the absolute temperature, and R the gas constant. Equation 1 can be simplified as [10]

$$G^n = Kt \qquad (3)$$

when the initial grain size is negligible. In the present study, Equation 3 was employed. In addition, it was one of the purposes of this investigation to show that CMZP ceramics follow the aforementioned grain-growth equations.

2. Experimental procedure

2.1. CMZP powder preparation

Single-phase CMZP powders were synthesized by a sol–gel process. Reagent-grade $Ca(NO_3)_2 \cdot 4H_2O$ (98.5%, Hanawa Inc.), $Mg(NO_3)_2 \cdot 6H_2O$ (98.5%, Hanawa Inc.), $ZrO(NO_3)_2 \cdot xH_2O$ (99.0%, Hanawa Inc.), and H_3PO_4 (85%, Merck), which were used as starting materials, were prepared to form 1.0 M aqueous solutions. The zirconium nitrate and a nitrate solution containing calcium and magnesium ions with the desired molar ratios were mixed first. The phosphate solution was adjusted to pH 9 by ammonium water prior to adding to the nitrate solution, which was stirred vigorously. The pH value of the solution was kept at 9–10 by adding ammonium hydroxide until the solution became a gel. The gel was dried at 40 °C for 24 h, and then calcined at 900–1000 °C for 24 h to drive off the nitrates and resulted in fine single-phase powders having an average particle size of 45–50 nm.

2.2. Sintering

The CMZP powders were compacted into a cake with a diameter of 5 cm in a stainless steel die under a 100 MPa hydraulic pressure followed by hot pressing at 30 MPa at 1350 °C for 20 min, resulting in an initial

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grain size smaller than about 0.3 μm. The densities of the as-sintered solid were determined to be 96.7% –98.6% theoretical density using Archimedes' method with water as the immersion medium.

2.3. Grain-size measurement

The specimens used for grain-growth observation were prepared by cutting the as-sintered specimen into pieces, then annealing at various temperatures from 1150–1300 °C at 50 °C intervals. Observations of grain growth were made on polished specimens prepared by wet grinding with 600 grit silicon carbide paper followed by polishing on a cloth-covered lap with the aid of 1 μm alpha alumina, then etching in 1.5 N HCl solution. The average grain size, *G*, of the annealed CMZP was determined by examining the polished surface using scanning electron microscopy (Cambridge Instruments, S-360 system) using a linear-intercept technique [11], and approximately 50 grains were counted for each sample.

3. Results and discussion

Fig. 1a–d illustrate the logarithmic relation of grain size with annealing time of the CMZP with compositions of $x = 0.0$, 0.1, 0.2, and 0.4 at various temperatures. The various grain-growth dependencies on the composition indicate a variation in grain-growth rate.

Isothermal grain-growth variables were derived from the slopes ($1/n$) and the intercept (a product of $1/n$ and rate constant) in Fig. 1. Table I lists the grain-growth exponents in terms of the annealing temperature and composition, and the mean values (denoted as $\boldsymbol{n}$) with a standard deviation are shown in the last column. The $\boldsymbol{n}$ values tend to decline with increasing temperature, which was also observed in Coble's study of grain growth in Al_2O_3 [12]. From these data the time dependence of grain growth can be taken as simply the second-power kinetics, i.e. $n = 2$, which is different from that observed at the intermediate stage sintering where $n = 3$ [13]. This difference in time exponent is believed to be a result of the porosity effect between these two stages of sintering [12]. The occurrence of a simple time-dependence of grain growth suggests a normal grain growth [14, 15] develops at the late stage sintering of CMZP. Fig. 2, as an example with $x = 0.4$ in which the materials were annealed at 1300 °C for various durations, substantiates that the CMZP obeys the normal grain-growth kinetics.

TABLE I Time exponents of the CMZP in terms of various compositions and annealing temperatures

	T				
x	1150 °C	1200 °C	1250 °C	1300 °C	***n***
0.0	1.93	1.86	1.81	1.83	1.86 ± 0.14
0.1	2.98	2.21	2.47	2.18	2.44 ± 0.37
0.2	2.90	2.29	2.15	1.97	2.33 ± 0.40
0.4	2.36	2.05	1.96	1.80	2.04 ± 0.34

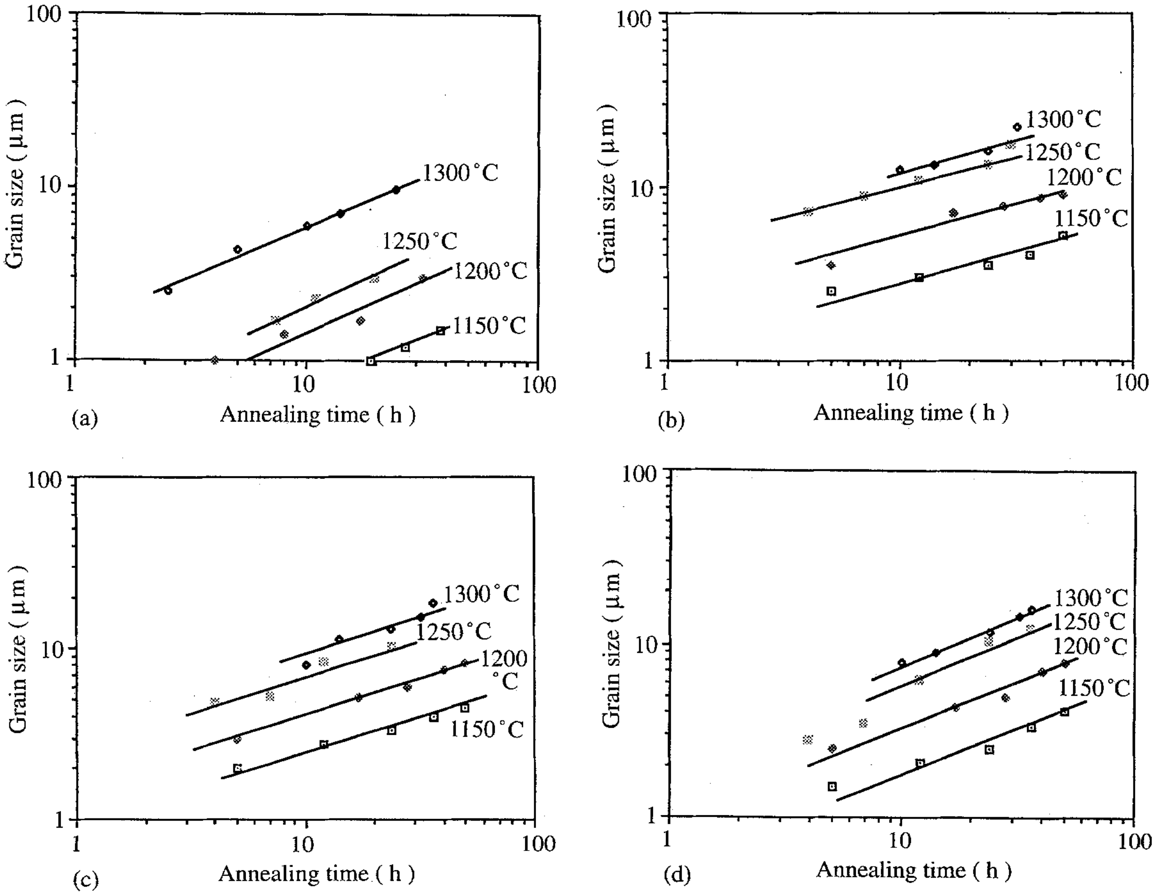

Figure 1 Logarithmic relations between grain size and annealing time at various temperatures in the CMZP with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, and (d) $x = 0.4$.

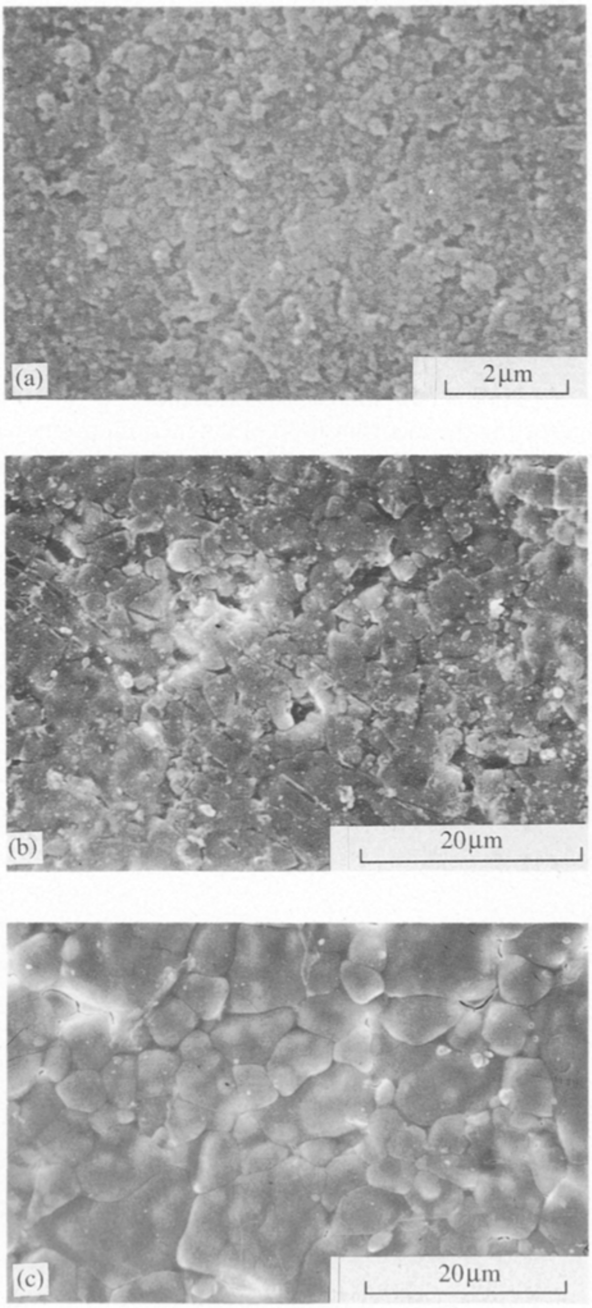

Figure 2 The grain growth in the CMZP (with $x = 0.4$) showing a normal grain-growth behaviour. The sample was annealed at 1300 °C for periods of (a) 30 min, (b) 120 min, and (c) 300 min.

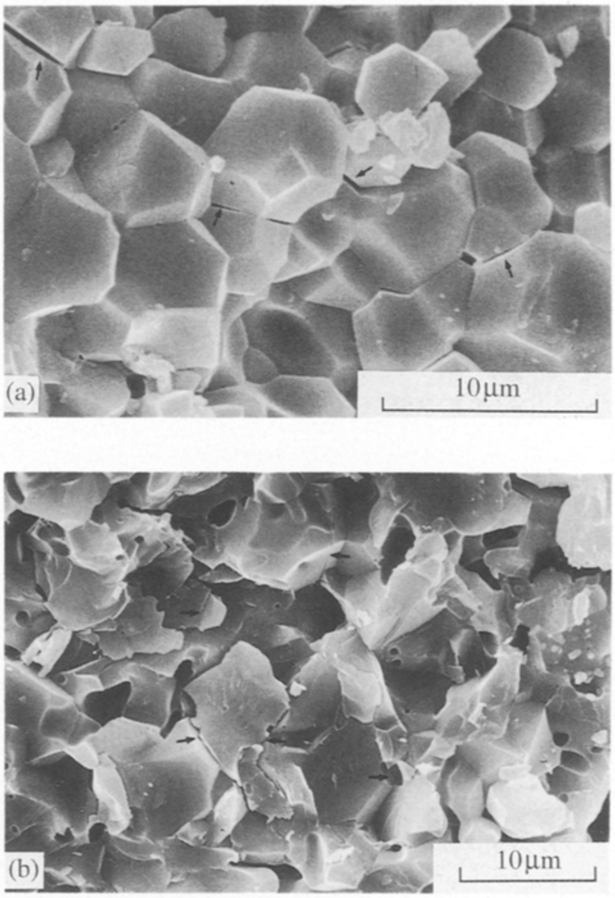

Figure 3 Microcracks present in the CMZP matrix while the grain size of the ceramics is larger than a certain critical size. (a) $x = 0.2$ and (b) $x = 0.4$.

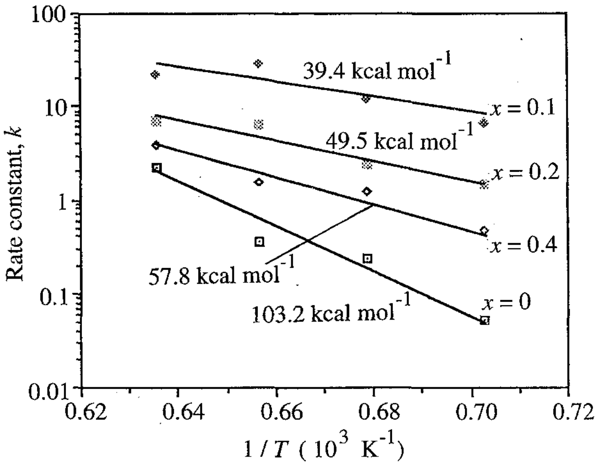

Figure 4 Rate constant as a function of reciprocal absolute temperature for different compositions.

The grain size at which the microcracking occurs within the ceramic matrix was empirically determined to be 1–2, 2–4, 3–5, and 9–12 μm for compositions of 0.0, 0.1, 0.2, and 0.4, respectively, using a scanning electron microscope. Fig. 3a and b illustrate the fractured surface of $x = 0.2$ and 0.4, respectively, in which cracks (arrowed) appear in the matrix. The critical grain size which varies with the magnesium content, is consistent with the results reported by Van Aken [5], who indicated that the TEA decreased on the addition of magnesium, and this is also coincident with the observation in the study of CTE of CMZP by Liu *et al.* [4].

The activation energy for grain growth is determined in an Arrhenius sense using Equation 2 by plotting the rate constant, K, against reciprocal absolute temperature using the least squares method. In Fig. 4, the straight lines with different slopes indicate a variation in the rate of grain-growth migration due to composition changes. In the relation of the activation energy and composition, Fig. 5 shows that the activation energy for CMZP grain growth reaches a maximum of 103.2 kcal mol^{-1} at $x = 0.0$, but remarkably decreases to a minimum of 39.4 kcal mol^{-1} on introducing 10% magnesium for calcium. The activation energy, however, increases again with further increase of magnesium.

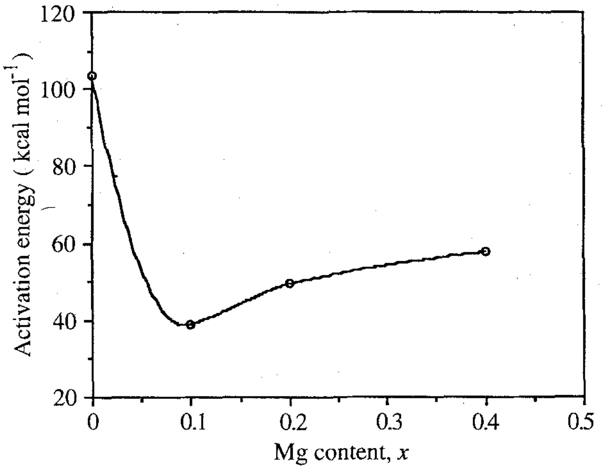

Figure 5 Activation energy for the grain growth of CMZP in terms of magnesium content.

The compositional dependence of grain growth in CMZP ceramics strongly suggests that grain-boundary migration is accelerated by incorporation of a small amount of Mg^{2+} ions. Because it is not possible to determine the grain-growth mechanism in CMZP at present, a tentative description for the effect of magnesium addition on the rate of grain-boundary migration, however, is described.

The temperature dependence of grain growth for $x = 0.0$ (103.2 kcal mol^{-1}) was found to be somewhat lower than the value from lattice diffusion-controlled sintering data (i.e. about 120 kcal mol^{-1}) [13]. It is normally assumed to be due to grain-boundary diffusion because it usually exhibits a lower activation energy than that for lattice diffusion [9]. However, to a first approximation, the roughly equivalent energy may suggest that the grain-boundary migration in the late stage of sintering is partially attributable to lattice diffusion, although it may be more realized by assuming the mechanism is a result of a combination effect [9, 15]. The grain-growth enhancement resulting from magnesium incorporation can thus be regarded as due to enhanced ionic diffusion (or inversely, vacancy diffusion), through the framework structure, especially along the positions with larger "holes" or "vacancies" [2] or grain boundaries. Further, the diffusion rate is significantly increased at temperatures above 1250 °C, which gives rise to a higher grain-growth rate and is associated with a decreased time exponent, n, as given in Table I. However, no obviously enhanced grain-growth rate is observed in the ceramics without magnesium content, as indicated by its near-constant time exponent values in Table I. The grain-growth rate decreases as more than 20% calcium is substituted by magnesium which results in apparent activation energies of 49.5 and 57.8 kcal mol^{-1} for $x = 0.2$ and 0.3, respectively. This decrease in activation energy may be explained as the decrease in lattice volume [5] which limits the diffusion path and results in a suppression of grain-boundary migration.

4. Conclusion

The grain growth in the CMZP ceramics in the final stage of sintering obeys the normal grain-growth kinetics with a time exponent, n, of approximately 2.0 in the temperatures range 1150–1300 °C. Activation energies show a maximum of 103.4 kcal mol^{-1} at $x = 0.0$ and a minimum of 39.4 kcal mol^{-1} at $x = 0.1$, suggesting the incorporation of magnesium promotes the rate of grain-boundary migration. The mechanism for grain growth in the CMZP has not been determined at present. However, the effect of magnesium on grain growth suggests that the lattice diffusion may make a contribution. The critical grain size increased with increasing magnesium content suggesting prospective application of the CMZP ceramics with appropriate magnesium content in severe environments.

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