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Crystallite Growth Characteristics in Superfine Zirconia Powders and Compacts

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Abstract

Crystallite growth characteristics of coprecipitated superfine zirconia powders have been investigated. It was found that the crystallite growth in powders follows a cubic law at 800 and 1000°C; however, the crystallite size data for compacts of both Y-TZP and YSZ cannot be fitted with a traditional parabolic or cubic law, but with a linear relation between crystallite size and the logarithm of time. In addition, it was also found that the degree of agglomeration of the powders can affect the crystallite growth.

Das Kristallitwachstum von extrafeinen, durch gemeinsame Ausscheidung hergestellten Zirkoniumoxidpulvern wurde untersucht. Die Untersuchungen ergaben, daß das Kristallitwachstum in Pulvern zwischen 800 und 1000°C einem kubischen Gesetz folgt. Die Kristallitgröße in Y-TZP- und YSZ-Preßlingen jedoch folgt weder dem herkömmlichen parabolischen noch einem kubischen Gesetz, sondern einer linearen Beziehung zwischen der Kristallitgröße und dem Logarithmus der Zeit. Desweiteren ergab sich, daß die Agglomeration des Pulvers das Kristallitwachstum beeinflussen kann.

On a étudié la croissance de cristaux dans des mélanges de poudres de zircone coprécipitées et ultrafines. La croissance cristalline suit une loi cubique à 800 et 1000°C; cependant, pour Y-TZP comme pour YSZ, l'évolution des cristallites avec le temps ne suit pas la loi parabolique ou cubique habituelle, mais plutôt une loi logarithmique. De plus, on a constaté que le degré d'agglomération préalable des poudres peut affecter la croissance.

1 Introduction

Zirconia ceramics are some of the most promising materials for advanced technologies.[1–3] They can be fabricated by sintering superfine zirconia powders processed via chemical routes, for example, by the hydroxide coprecipitation method.[4,5] The zirconium hydroxide precipitates and zirconia powder obtained by calcining the coprecipitates below 400°C are amorphous. At elevated temperatures, zirconia crystallizes out and the crystallites grow substantially as the temperature increases.[6] Crystallite growth is also significant in powder compacts.[7,8] However, crystallite growth can be unfavourable for the properties in both powders and compacts; therefore it should be controlled.[9] The present work is an investigation of crystallite growth both in powders and in compacts.

In dense ceramics, grain growth commonly follows the equation:[10,11]

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

where t is the time at a given temperature, G_0 and G are the grain sizes at $t = 0$ and $t = t$, and K is a constant at a fixed temperature. Equation (1) has been proposed also for powder systems or for very porous powder compacts.[7] The value of K is proportional to the diffusion coefficient and the surface (or interface) tension and is dependent on the mechanisms by which crystallite (or grain) growth proceeds.

2 Experimental Procedure

Superfine yttria-doped zirconia powders were prepared by the coprecipitation method which may be described briefly as follows: (1) preparation of a mixed solution of yttrium chloride and zirconium oxychloride with an appropriate ratio of Y^{3+}/Zr^{4+}; (2) adding the mixed solutions to ammonia solution which resulted in the formation of coprecipitates; (3) washing the coprecipitates with distilled water repeatedly to remove Cl^- (to <10 ppm in filtrate); (4) washing the cake with

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ethanol more than six times to replace water (up to a water content in the filtrate of less than 4 vol.%); and finally (5) calcining at various temperatures (from 400 to 1200°C) for various time periods (from 0 to 360 min). This procedure results in powders of very soft agglomerates.

For investigating the effect of agglomeration on crystallite size, powders containing different kinds of agglomerate were prepared. In addition to the one already mentioned (powder I), differently agglomerated powders could be prepared by different washing and drying processes: powders of mid-hardness agglomerates were prepared by dispersing the coprecipitates with ultrasonic treatment for 10 min and by eliminating the ethanol washing (powder II); powders of hard agglomerates were prepared by washing with water only (powder III), or by such washing followed by spray-drying of the dilute hydroxide suspensions made from the coprecipitates (powder IV).[12,13]

Powders calcined at 600°C or 750°C were compacted at 250 MPa uniaxally and sintered by heating to various temperatures at a constant rate (5°C/min) and/or isothermal holding. The powder micrographs were observed with TEM (transmission electron microscopy, JEM-200CX, JEOL) and the crystallite size of the powders or compacts was determined by the XRD-LB (X-ray diffraction line broadening) technique.[6] The crystallite size was calculated from the equation:

$$D = 0{\cdot}89\lambda/\cos\theta B \qquad (2)$$

where λ is the wavelength of the X-rays used ($\mathrm{Cu}K_\alpha$), θ is the Bragg angle of the selected diffraction peak (the 111 peak of Y-TZP and YSZ was used in this study) and B is a calibrated peak breadth found by subtracting the instrumental broadening from the total peak breadth.

3 Results and Discussion

3.1 Grain growth in powders

Figure 1 shows photomicrographs of YSZ (7 mol% yttria-stabilized zirconia) powders calcined at different temperatures for 25 min. The crystallite size increases rapidly with the increase of temperature. Crystallite growth during isothermal holding was also observed, as illustrated in Fig. 2. Results of systematic measurement of the crystallite size for both YSZ and Y-TZP (yttria-tetragonal zirconia polycrystals) powders by the XRD-LB method are

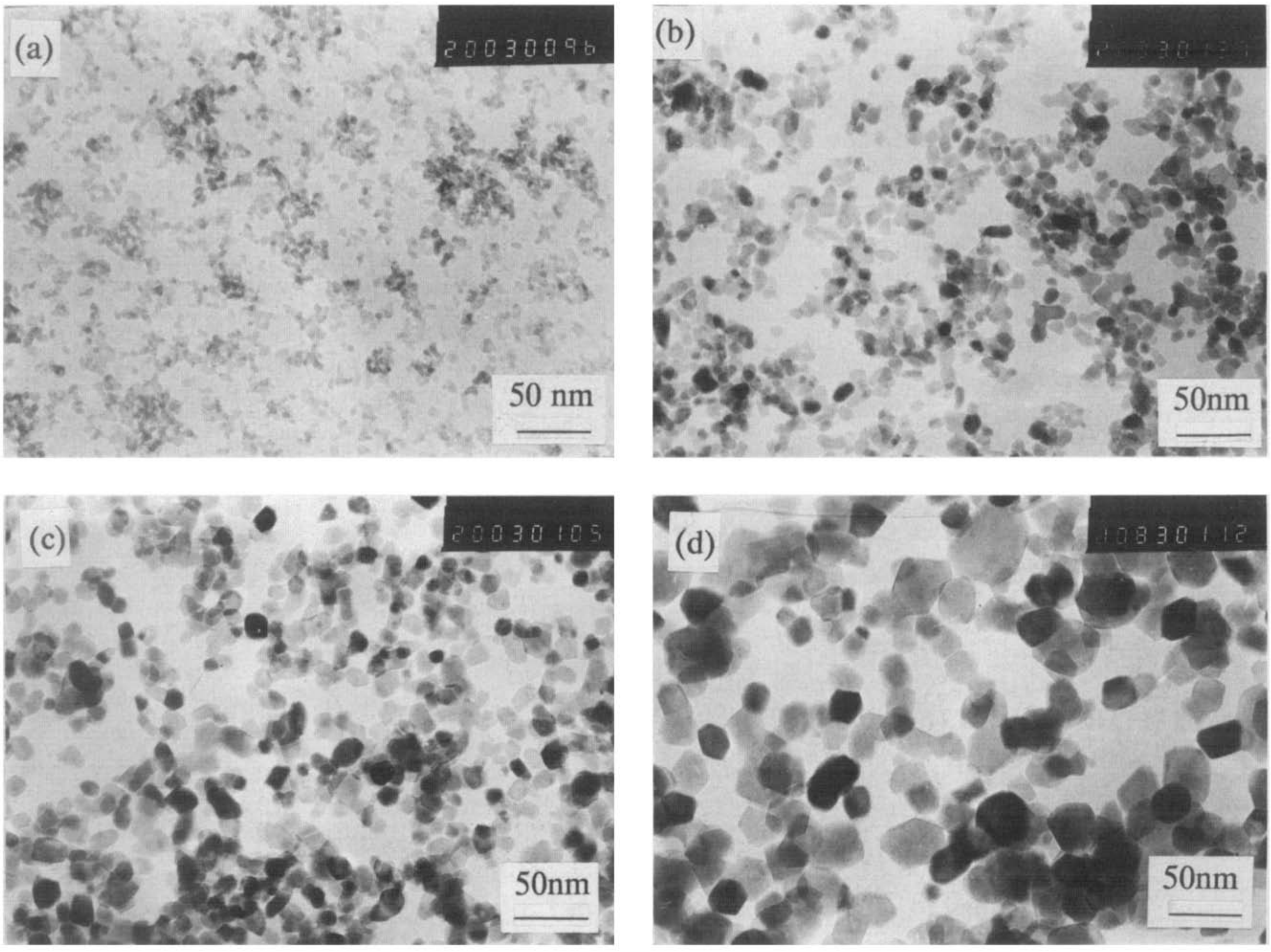

Fig. 1. Photomicrographs (TEM) of YSZ powders calcined for 25 min at different temperatures: (a) 420, (b) 600, (c) 800 and (d) 1000°C.

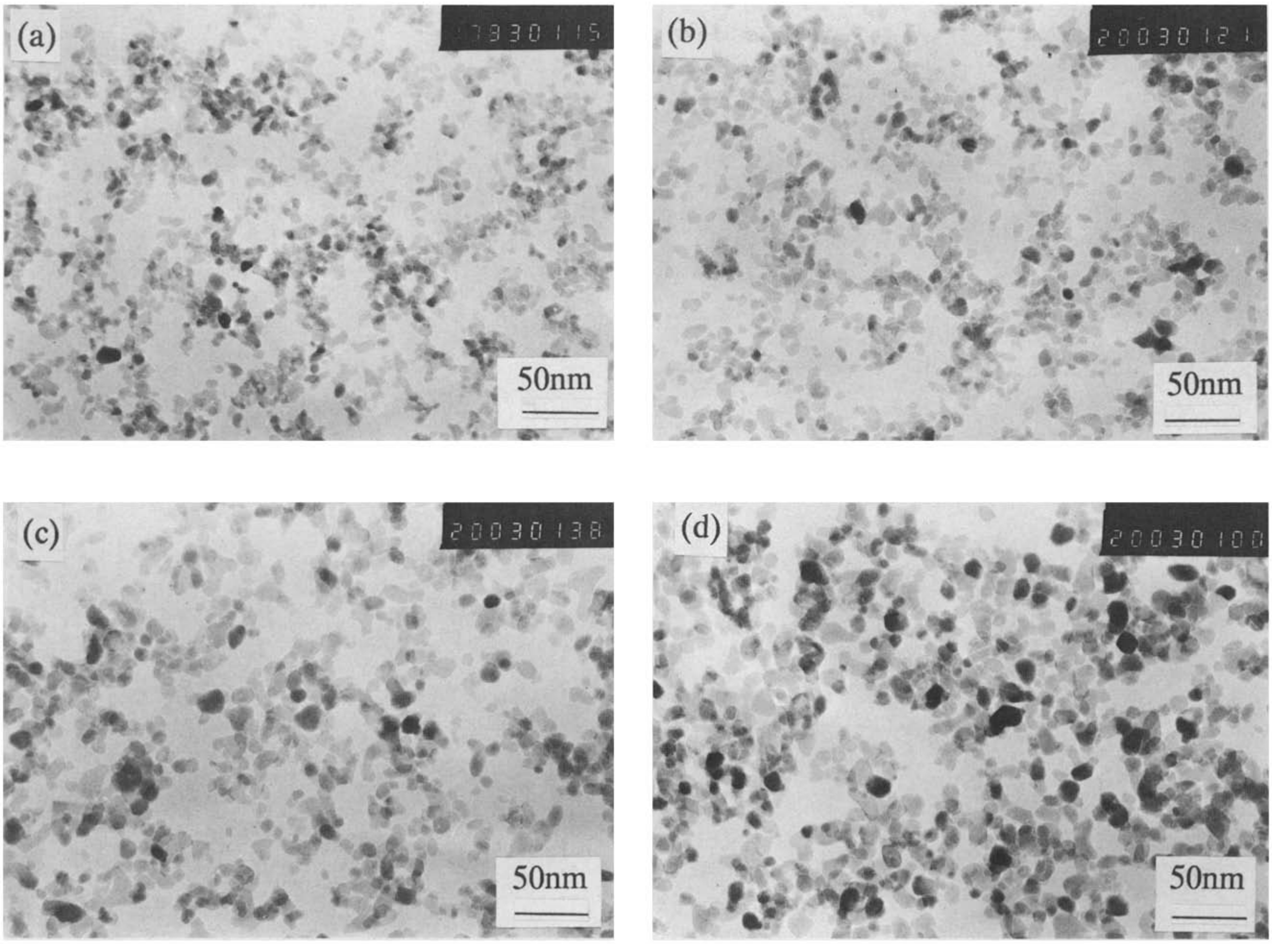

Fig. 2. Photomicrographs (TEM) of YSZ powder at 600°C for different holding times: (a) 0, (b) 55, (c) 110 and (d) 240min.

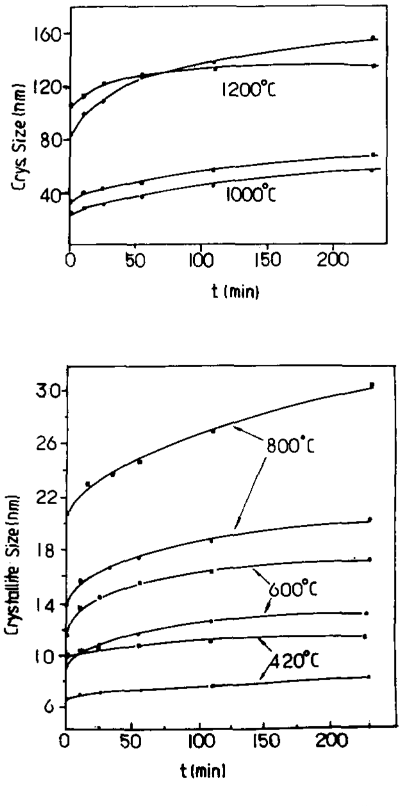

Fig. 3. Calculated crystallite size of Y-TZP (■) and YSZ (●) powders as a function of calcination temperature and holding time.

shown in Fig. 3. The crystallite size data at 800 and 1000°C are found to fit eqn (1) with $n = 3$, as shown in Fig. 4, while at other temperatures the data cannot be fitted with the equation.

Although a number of diffusion mechanisms have been distinguished for grain growth in dense

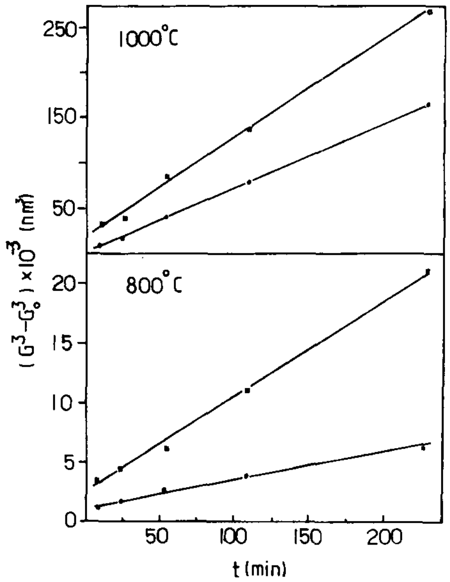

Fig. 4. Linear relations between G^3–G_0^3 and holding time of Y-TZP (■) and YSZ (●) powders at 800 and 1000°C.

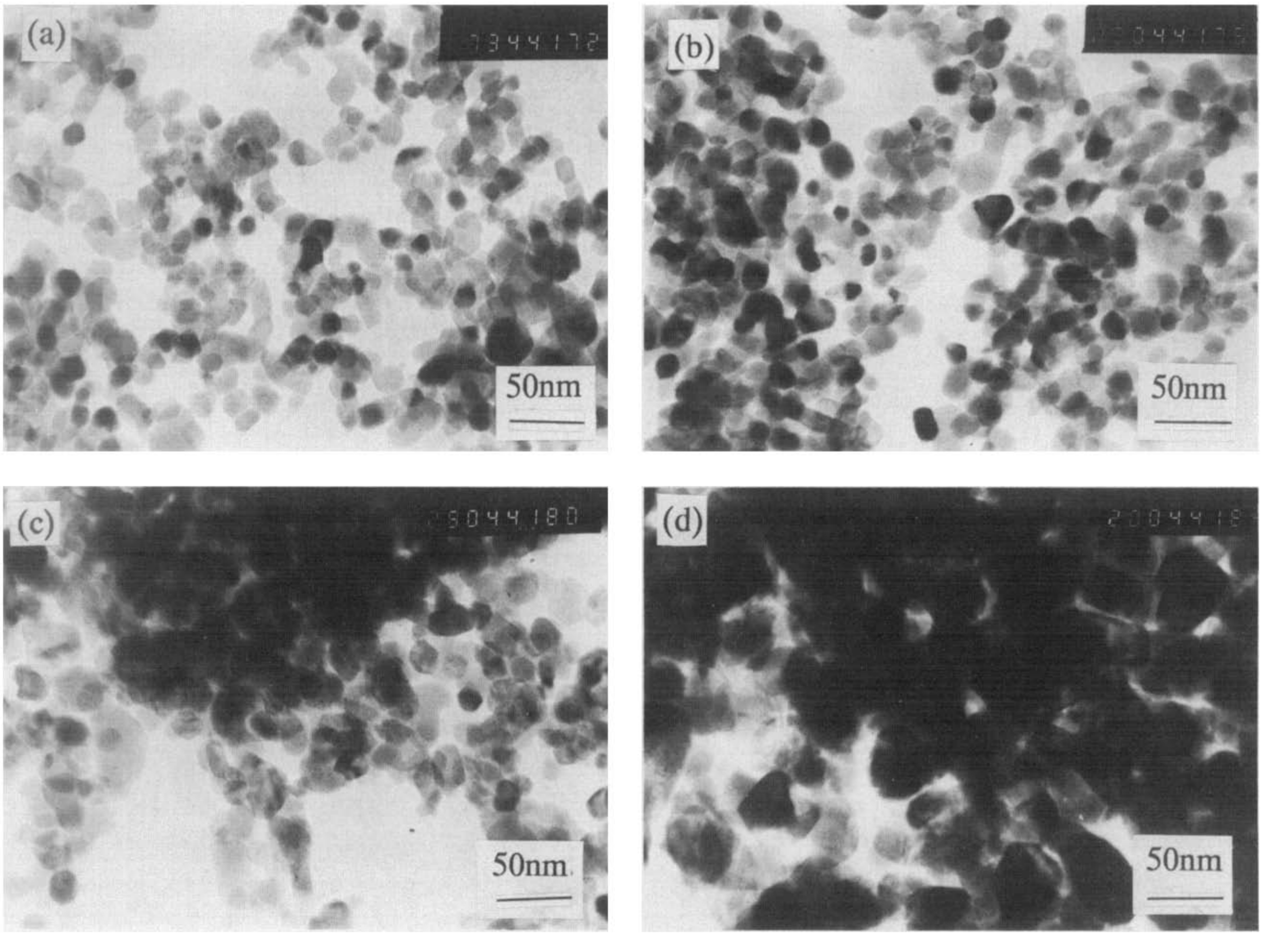

Fig. 5. Photomicrographs (TEM) of differently agglomerated Y-TZP powders (for details see text).

materials,[11] the crystallite growth phenomena in powders received less attention. In very loose and weakly agglomerated powders, the possibility for the occurrence of volume and/or boundary diffusion is believed to be too small to account for the substantial crystallite growth at the low temperatures used, and the very limited contacts between the particles in the powders would also impede diffusion via the volume or boundaries. Surface diffusion may be responsible for the crystallite growth; however, the exponent 3 in Fig. 4 does not agree well with surface diffusion where the scaling law predicts an exponent of 4, as indicated by Herring.[14] As a variety of mechanisms can be fitted by the exponent 3,[11] further results are needed to distinguish between the possible diffusion mechanisms.

3.2 Effect of agglomeration state on crystallite size

In addition to the temperature and time dependence, crystallite size was also affected by the powder processing history. Figure 5 shows photomicrographs of differently agglomerated Y-TZP powders prepared by the previously mentioned processing routes. Corresponding to the photomicrographs, Fig. 6 shows the pore size distributions of the compacts of powders I to IV. It is clear that the residual agglomerate content (reflected by the presence of inter-agglomerate pores larger than 0·05 μm) in the powder compacts (and therefore the agglomerate strength) increased from powder I to IV. The detailed characterization of the agglomerate strength in the powders has been presented elsewhere.[15] In fact, the agglomerates in powder I are very soft and can be fragmented at as low as 100 MPa.[12] Figure 5 reveals that under the same calcination conditions (750°C for 120 min), the crystallite sizes in the more strongly agglomerated powders are larger than those in the more

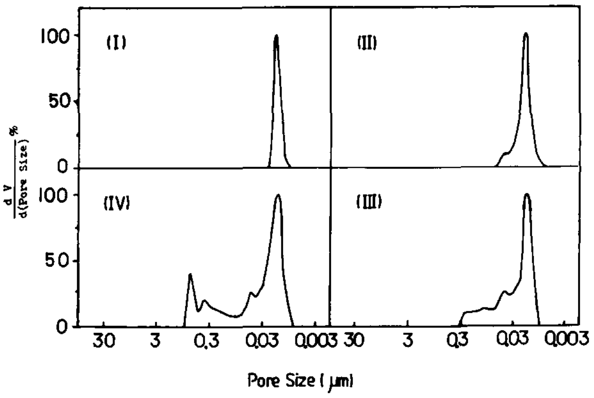

Fig. 6. Pore size distributions of differently agglomerated Y-TZP powder compacts I–IV at 250 MPa.

Table 1. Crystallite sizes of differently agglomerated Y-TZP powders (750°C, 120min)

	Powders			
	I	*II*	*III*	*IV*
Crystallite size (nm)	19·2	22·0	25·0	36·2

weakly agglomerated powders. Table 1 gives the calculated crystallite size using the XRD-LB method. It can be concluded that the agglomeration of powder particles acts to promote crystallite growth.

The promoted crystallite growth of strongly agglomerated powders, as compared to weakly agglomerated ones, may be attributed to the larger contact area and the shorter diffusion path between particles.

3.3 Crystallite growth in powder compacts

Figure 7 shows the crystallite size in powder compacts as a function of heating temperature and isothermal holding time. Although it is believed[7] that grain growth in porous compacts, in addition to that in dense materials, follows eqn (1), the data shown in Fig. 7 do not fit the equation either for $n = 2$ or $n = 3$. Alternatively, it was found that the data can be fitted with a linear relation of crystallite size versus logarithm of time for this study with only one exception at 1100°C for Y-TZP, as shown in Fig. 8.

The diffusion phenomena in porous compacts are complicated because of the possibility of the coexistence of several different mechanisms. The grain growth in the compacts is further affected by the presence of pores around the grains and the rapid densification accompanying and therefore interfering with the grain growth process, which tends to make a more detailed kinetic analysis of the results inappropriate.

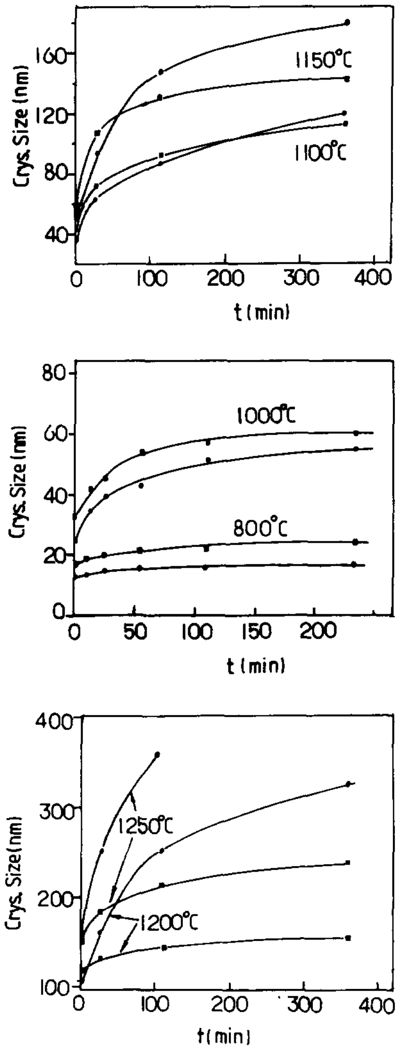

Fig. 7. Calculated crystallite size of Y-TZP (■) and YSZ (●) in powder compacts (250 MPa) as a function of firing temperature and holding time.

4 Conclusion

Crystallite growth characteristics in superfine zirconia powders and porous powder compacts are

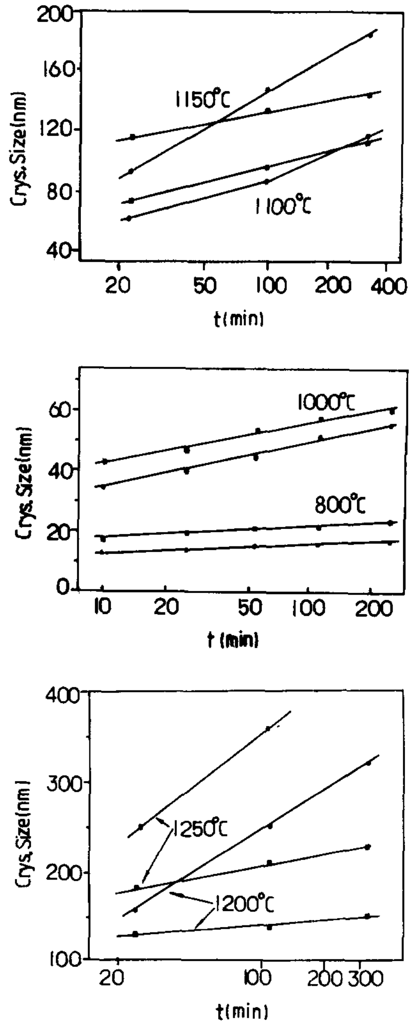

Fig. 8. Relations between crystallite size and logarithm holding time for Y-TZP (■) and YSZ (●) powder compacts.

different. The crystallite growth in powders can be fitted by the common relation: $G^n - G_0^n = At$ over a certain temperature range, but the relation is not applicable for the crystallite growth data for compacts. The crystallite growth rate can be affected by agglomeration state between the crystallites, probably by changing the species diffusion distances and contact area between them.

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