

# Relation between grain growth, densification and surface diffusion in solid state sintering—a direct observation

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A direct observation of the grain growth and densification of BaTiO<sub>3</sub> ceramics were made in a TEM equipped with an *in-situ* installed heating platform. Both real two-sphere and three-sphere models for BaTiO<sub>3</sub> ceramics were found and parallel processes of the shrinkage between particles and the grain growth (coarsening) were observed during the heating process. Attempts of relating the grain growth and densification was made which reveals, though roughly, the close relation between the two competing process: they took place simultaneously and in parallel, therefore it is believed that the process took place via the same mass transport mechanism. Surface diffusion on the TiO<sub>2</sub> particle surface was observed directly, which takes place with the co-motion of several lattice layers from a smaller grain onto the surface of an adjacent larger one. The surface diffusion was accompanied by the diminishing of a small grain, i.e., overall grain growth.

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## 1. Introduction

Sintering is a basic process for ceramic preparation. This process is complicated as several parallel processes—densification (compact shrinkage), grain growth and pore growth (coarsening)—take place in parallel.

Great efforts have been made to understand the sintering process, including the sintering thermodynamics and the densification kinetics [1]. However, the densification behavior of ceramic powder compacts was interfered by the coarsening (including grain and pore growth) process and associated with mass transport path. So to understand the sintering process, the following two questions should be answered: (1) the correlation among grain growth, pore growth and shrinkage, and densification; (2) the mass transport path, i.e., by what means the pores can shrink and the compacts can densify. These two questions though have been discussed in literature, but were not thoroughly solved [2].

As for the correlations between grain growth and densification, traditional two sphere models for the initial stage of sintering and the microstructure model for the intermediate stage of sintering shows that smaller

particle size is always favorable for faster densification, therefore grain growth was found to affect densification only by negative ways, i.e., stronger grain growth was always to be unfavorable for densification. More than ten years ago, Lange *et al.*, [3, 4], argued that grain growth, either for the intermediate stage or final stage of sintering, was a necessary precondition for continuous densification during sintering. For the intermediate stage of sintering, the formation of dihedral angle between particles was thought to cease the densification process, and only grain growth could reinitiate the densification process by changing the contact angle from the dihedral angle to a smaller one, thus continuous densification could be achieved during the reformation of the dihedral angle between grown grains [3].

In Coble's early study [5], the pores were assumed to only shrink during sintering, and this was one of the assumptions from which the densification equations were derived. However, extensive pore growth was later identified by several researchers in the sintered bodies mainly for the intermediate and final stages of sintering [6–8]. The explanations given by the researchers were different. Kingery *et al.* [6], found very clear pore growth accompanying grain growth in the final stage

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of sintering of  $\text{UO}_2$ . However the pore growth in the intermediate stage of pressureless sintering of some ceramics like  $\text{ZnO}$ ,  $\text{MgO}$ , though also clearly found to be present [7, 8], was only attributed to the particle rearrangement.

Another key issue is the mass transport mechanism, i.e., mass transport path for coarsening and densification. Coarsening was considered to be accomplished either by diffusional mass transport process, e.g., surface diffusion [9] for the intermediate stage of sintering, or by boundary motion [10, 11] at both intermediate and final stages of sintering; while densification has been unanimously recognized as a diffusion mass transport mechanism [5, 12]. Diffusion paths for densification were clearly limited to boundary diffusion and volume diffusion, other mass transport paths like diffusion via surface was considered to contribute nothing to densification, under an assumption that mass transport mechanisms for densification are from the grain boundaries between particles to the immediately adjacent porosity—initially the surface of neck between adjacent particles, and vacancies diffuse in an opposite way from the pores at the pore-grain surface to the boundaries to balance the mass transport.

About five years ago, the author presented a new view about the two key issues [13, 14]. The theoretical model analysis [13] gave the following main conclusions:

1. Although grain boundary motion is possible for particle arrays as in powder or in compacts if the particle size ratio reaches a certain value, however, it is not the controlling step and boundary motion alone does not contribute to densification process;

2. Mass transport via surface diffusion are found to contribute concurrently both to grain growth and shrinkage of particle array, and the contribution of the mass transport to the shrinkage is much more significant than that by the re-formation of the dihedral angle initiated by grain growth;

3. When pores are thermodynamically stable in a compacts, mass transport contribute only to particle coarsening, and when pores are thermodynamically unstable mass transport contributes to both particle coarsening and pore removal;

4. Pore growth is closely related to grain growth, pores grow at the same rate with grain growth with fixed pore-particle size ratio when the pores cannot shrink on thermodynamics; Pores grow at smaller rate than grain growth with decreasing pore to particle size ratio when pores can shrink. The magnitude of the pore to particle size ratio and its change during densification is a key relating coarsening and densification.

5. In the intermediate stage of sintering, surface diffusion is suggested to be at least one of the main mass transport mechanisms for densification except volume diffusion, where pores form continuous network; while in the final stage of sintering only boundary and volume diffusions are possible.

The above statements have been partially verified with the experimental tests on the pressureless sintering of superfine zirconia powder compacts [14]. The main

experimental conclusions associated with the relation between coarsening and densifications were:

1. Pore growth is driven by both grain growth and densification, the former leads to size proportional pore agglomeration, the later results in pore shrinkage, or the decrease of the size ratio of pores to grains. Pore growth is affected by the properties of powder compacts.

2. Grain growth and densification take place simultaneously with each other and the linear relations between grain size and density exist in the density range from green compacts up to the end of the intermediate stage of sintering, with negligible initial stage of sintering, for the superfine powder compacts. This linear relation can be explained with the identical diffusion mechanism for the grain growth and densification, and the similar time dependence during isothermal holding in the intermediate stage of sintering.

More detailed introductions and discussions on the sintering phenomena and mechanisms can be found in author's previous reports [13–15].

However, no direct evidence was given in the above published literature for the relations between coarsening and densification process and the contributions of surface diffusion to the coarsening and densification. Most recently, a direct observation has been made on the sintering of  $\text{BaTiO}_3$  and  $\text{TiO}_2$  under TEM equipped with an *in-situ* installed heating platform. The observations reveal some clear evidence which is very helpful for us to understand the sintering process, especially the relation between the coarsening (grain growth and pore growth) and shrinkage (densification). Surprisingly the direct evidence of surface diffusion during sintering of  $\text{TiO}_2$  is fortunately obtained accompanying the grain growth. The paper is to show these observations and try to discuss the problems combining the former theoretical analysis.

## 2. Experimental

### 2.1. Sample preparation

$\text{BaTiO}_3$  powder was synthesized by hydrolysis method using the process shown in Table I.  $\text{Ba}(\text{OH})_2$  and Ti alkoxide starting materials were mixed with water at  $80^\circ\text{C}$  for 3 h in a pH 12 solution. After washing and drying, as-prepared  $\text{BaTiO}_3$  powders were obtained. By changing the content of Ba and Ti ions in the solutions, we could vary the initial particle diameter in the range of from 20 nm to 55 nm. Calcination was carried out at  $700^\circ\text{C}$  for 2 h, and the resulting average particle diameter was 70 nm. The purity of  $\text{BaTiO}_3$  was not lower than 99.98%. The  $\text{BaO}/\text{TiO}_2$  ratio was 1.0004.

$\text{TiO}_2$  powder sample (Merck) had particle size from 50 to 150 nm, and the purity was not lower than 99.0%.

### 2.2. TEM observation method

Transmission Electron Microscopy (TEM) (TOPCON; model EM-002B) was used to make the *in-situ* observations of the powder grain growth and shrinkage. The

TABLE I Processing for the hydrolysis fine BaTiO<sub>3</sub> powder

Starting materials	Ba(OH) <sub>2</sub> , 8H <sub>2</sub> O and Ti(Opr <sup>i</sup> ) <sub>4</sub> Pr <sup>i</sup> OH
Hydrolysis	NaOH in 80°C water
Aging	mixed at 80°C for 3 h in the solution pH 12
Washing	in boiling water
Drying	at 100°C
Calcining	1050°C 2 h
Dielectric powder	particle size 150 nm

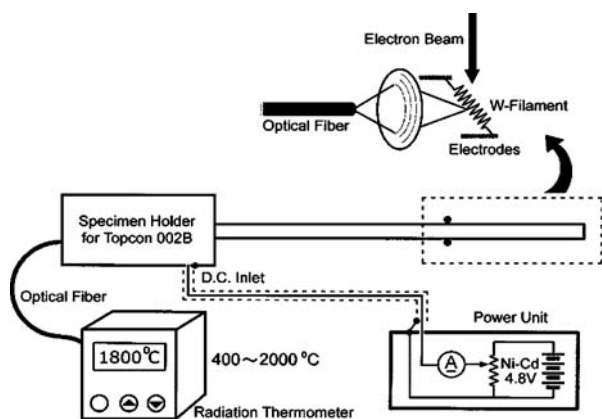


Figure 1 Schematic drawing of the *in-situ* observation set up using hot-stage TEM.

hot-stage installed in the TEM as schematically shown in Fig. 1. The BaTiO<sub>3</sub> powder was placed on a tungsten heater element and the element was then placed on the stage of the TEM. DC current of the heater monitoring with an optical thermometer controlled temperature. Temperature was held for 5 min at every 20 to 30°C temperature interval to stabilize the temperature and observe the particle growth behavior. Pictures were taken by a digital video camera using slow-scan CCD.

### 3. Grain growth in BaTiO<sub>3</sub>

Direct observations regarding the grain growth on the prepared BaTiO<sub>3</sub> powder are shown in Fig. 2. Below 940°C, no obvious change of the configuration were found, however, a small particle on particle 1 in Fig. 2a disappeared when heated up to 950°C in Fig. 2b, together with some, though not serious, pore growth, which was surrounded by particles 1, 2, 3, 4. Particle 1 becomes spheroidized and particle 3 became de-attached with its left neighborhood (Fig. 2c). Particles 1 and 3 apparently become smaller when heated to 960°C, and at the same time, the zone dimension composed of particle 1, 2, 3 and 4 decreased from Fig. 2c to d, which means that the densification (pore removal) takes place simultaneously with the grain growth. During this process one cannot find the apparent evidence for boundary motion during grain growth. Let us focus on the Fig. 2e to h. This is a typical three sphere model with a smaller one (particle 1) being sandwiched between two bigger ones (particles 2 and 4). The middle particle became smaller and smaller which illustrates the mass transport from these particles to the larger adjacent ones. The overall grain size increases along with the

diminishing of the middle particle, and, at the same time, the center distance between the two larger particles decreased gradually. Along with the diminishing of the middle particle, grain growth process becomes faster. At the point of Fig. 2h, the diminishing of the middle particle reached a critical point, it disappeared and the two larger particles became attached with each other, and the distance between them decreased at once.

Usually smaller particles will disappear faster than larger ones. In the configuration of Fig. 2, particle 1 disappears faster than other adjacent particles though at first this particle is not significantly smaller than particles 2 and 4. This is probably because that at first particle 1 is more irregularly shaped than two adjacent particles so it is at higher energy state and would shrink and disappear faster as compared to other particles. Once particle 1 becomes significantly smaller than its adjacent particles, it shrinks at accelerated speed.

Afterwards the remaining issue is just a typical two sphere model (Fig. 2i and the followings). One can see that the size of outer (smaller) particle (particle 2) gradually decreases (from Fig. 1i) and is eventually merged by the particle 4 (Fig. 2o). During the process it is clear that the distance between the two particles also decreases, which demonstrates the densification between the particles. During this process, the particle shape changes along with the diminishing of particle 2, sometimes the particle may become elliptic and then may it spheroidize again (e.g., Fig. 2j and 2k). No “undercutting” configuration [16] was found. Such a spherical—elliptic—re-spherical shape change indirectly shows the effect of surface diffusion.

During the whole process of grain growth (here “particle” is regarded as grain, for the convenience of discussion. This grain growth process implies the diminishing of small particles and the overall growth of the remaining particles), the distance between particles decrease, i.e., densification takes place simultaneously. Boundary motion, even if happened, is not the main or key process for grain growth and do not contribute to densification [13], and the mass transport between the grains should be a diffusion process. This diffusion process can be accomplished by surface, boundary and/or volume diffusion.

A quantity relation between grain growth and the shrinkage between the particles has been attempted. To do this, the particle size was defined as the numerical average value of the largest dimension of a particle and its perpendicular dimension through the line center of the largest dimension. The distance between two particles is the one between two intersection points of two inter-perpendicular lines for the dimension measurements of a particle.

Fig. 3 gives the relation between the sizes of particles 1 and 3 and the distance between particles 1 and 3 in Fig. 2 when particles 1, 2, 3, 4 co-exist; Fig. 4 is a similar relation between the size of particle 1 and the distance between particles 2 and 4 (defined as the sum of the distance between particles 1 and 2 and that between particles 1 and 4) when particle 3 has disappeared (three sphere model); While Fig. 5 is the relation

between the size of particle 2 and the distance between particles 2 and 4 when only particles 2 and 4 are present (two sphere model). The size decreases of particle(s) imply the overall grain growth. The close relation between the grain growth and densification (shrinkage) is clear: no discrete region exists where only grain growth or shrinkage happens.

#### 4. Grain growth and pore growth in BaTiO<sub>3</sub>

Pore growth could be visualized in Fig. 6 with the pores surrounded by several particles. Up to 700°C, an inner small particles as arrowed in Fig. 6b remain almost unchanged to room temperature. However, when heated

to 800°C, the size of this particle apparently decreases leaving more space among other particles. The diminishing of this small particle causes some, but limited, overall grain growth and also accompanied by negligible densification up to Fig. 6d. The densification could be related to the decrease of the size ratio between pores and particles. In the above process, pore and grain growth take place simultaneously. Above 800°C, grain growth continues without apparent pore growth, i.e., the size ratio between pores and grains decrease and densification was obtained at 830°C and above. Note that the observation field has been shifted towards left side due to the densification when heated above 800°C.

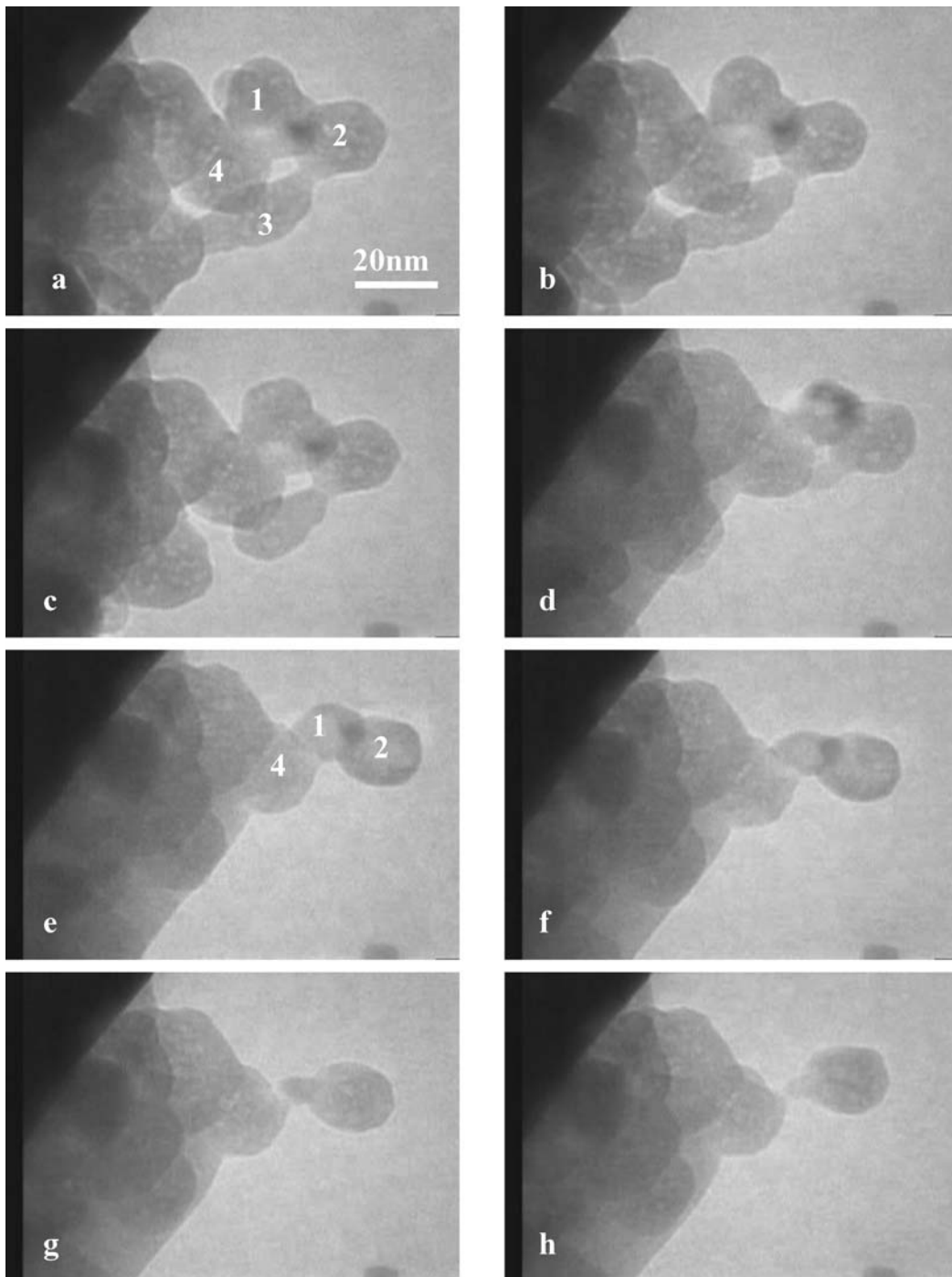


Figure 2 Observations of the grain growth in BaTiO<sub>3</sub> powder at different temperatures from 940°C (a), 950°C ((b), (c)) to 960°C ((d) to (o)). Grains grow by the diminishing of smaller grains and the enlargement of the bigger ones, and the distance between the particle centers decrease simultaneously. (Continued on next page.)



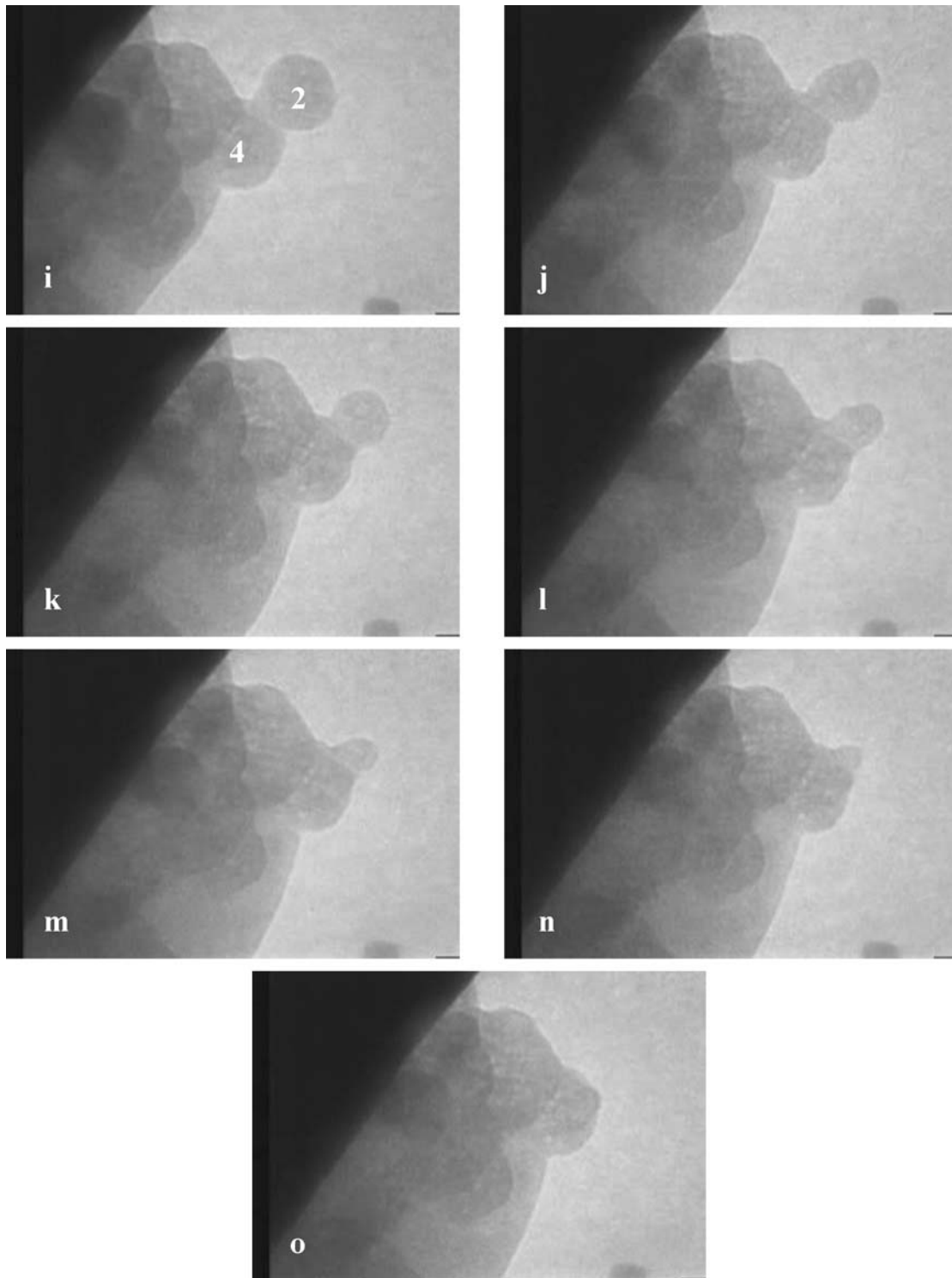


Figure 2 (Continued).

This set of microstructure pictures clearly demonstrate the pore and grain growth. Pores do grow during sintering but is naturally accompanied by the grain growth, or, grain growth resulted in pore growth. The densification process is still related to the grain and pore growth. The pore to grain size ratio became smaller during densification. One cannot distinguish between the densification and coarsening processes during the observation.

It is noted, however, during densification and grain growth at different stages, some pores shrink while some others grow. As has been pointed out by Lange

*et al.* [3], the pore shrinkage and/or growth depends on the thermodynamics of the pores. This matter was also addressed in more details in the author's previous report [15]. Once pores were surrounded by over a critical number of grains, it will be thermodynamically stable and tends to grow. In contrast, pores surrounded by less grains than the critical number, it is unstable and tend to shrink [15].

A quantitative relation between grain growth and densification in the whole field was made by measuring the shrinkage and particles size. Using the method for Fig. 2, the particle at down-right (particle A in Fig. 6h)

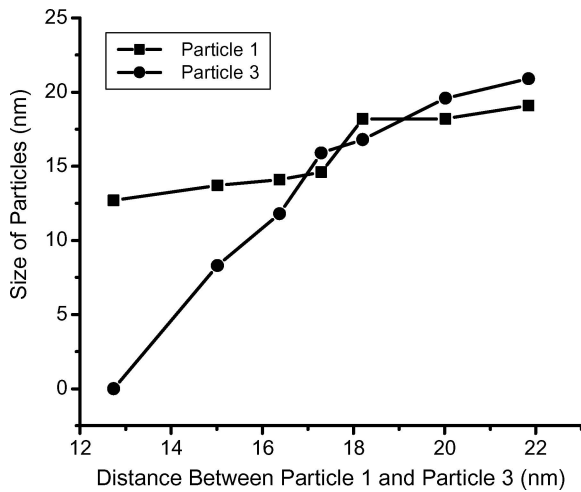


Figure 3 Relations between the sizes of smaller particles (particle 1 and particle 3) and the distance between particle 1 and particle 3 for the configurations in Fig. 2a–d.

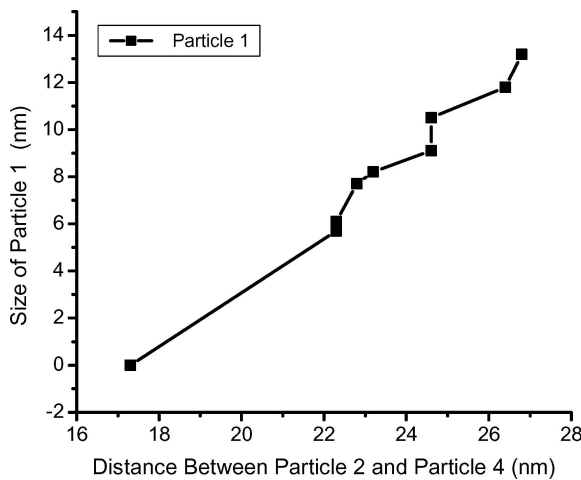


Figure 4 Relation between the size of particle 1 and the distance between particle 2 and particle 4 for the configurations in Fig. 2e to Fig. h.

is calculated to be 228 nm in diameter, then by counting the particle number in other pictures, the average value of the particle size were obtained. The shrinkage was estimated by measuring the distance from the edge of black-solid metal wire, which is used to support the particles, to the edge of the most right particle, on a horizontal line through the center of the pictures. Fig. 7 shows the measured data. Similar to the results by macro-scale measurement [14], an almost linear relation between the relative shrinkage and the average grain size can be obtained. Again, the results show that the shrinkage in a two-dimensional compact is closely related to the grain growth and the processes take place simultaneously and in parallel.

### 5. Role of surface diffusion

As observed in Figs 2 and 6, grain growth can take place along with densification. Experimental test show that there is a rough linear relation between the grain size and density even in the initial stage of sintering. By what means grains grow and powder densifies? Does surface diffusion takes place during grain growth? If the grain growth is accomplished by surface diffusion, will

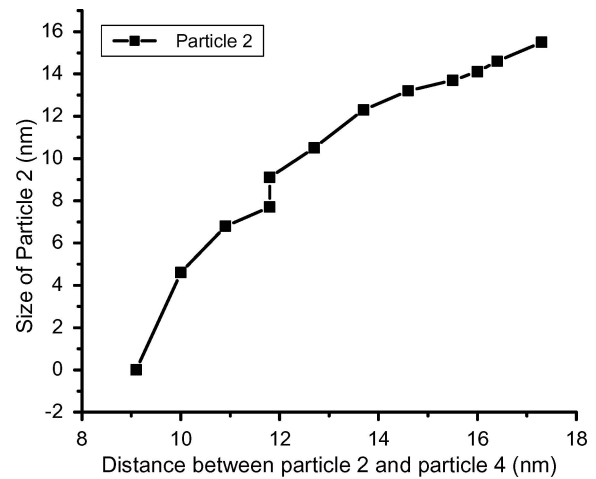


Figure 5 Relation between the size of particle 1 and the distance between particle 2 and particle 4 for the configurations in Fig. 2i and the followings.

densification be reached by the same mass transport path?

A direct observation for TiO<sub>2</sub> ceramic powder illustrates the presence of surface diffusion during grain growth as shown in Fig. 8. Surface diffusion takes place at the contact angle between two particles (Fig. 8a), and the surface diffusion proceeds via the cooperated motion of several lattice layers. Such a diffusion stream of several lattice layers is unexpected before. The mass transport in the diffusion process is from the smaller particle on the up-right, to the much larger one under. Second stream follows the first one (Fig. 8b) shortly after, and totally three streams are observed from Fig. 8d. Along with the stream motion from the up-right smaller particle onto the surface of the underside larger one, more and more mass was transferred between the particles, the up-right particles become smaller and smaller, and the overall grain growth were achieved. At last the up-right particles diminished and the whole grain growth and the surface diffusion processes finished.

The above observations show that surface diffusion does take place during sintering, and the surface diffusion is at least one of the mass transport paths of grain growth. During this process, no boundary motion is observed, but the grain growth does result in the densification between, at least, the two particles. Again, no “under-cutting” configuration [16] is found, and the up-right particles remain spherical during surface diffusion while diminishing.

It has long been believed that there are two paths for the mass transport (or, equivalently, release of vacancies) for densification: by volume diffusion or by boundary diffusion [1]. This concept is based on the traditional assumption that mass transport for densification was from the grain boundaries between particles to the immediately adjacent porosity, and vacancies diffuse in an opposite way from the pores at the pore-grain surface to the boundaries between particles to balance the mass transport [5, 12]. Following this assumption, questions may arise: how the vacancies can be annihilated at boundaries and pores can be removed from the porous compact? And by what means? As a matter of fact, real densification can only happen by compact

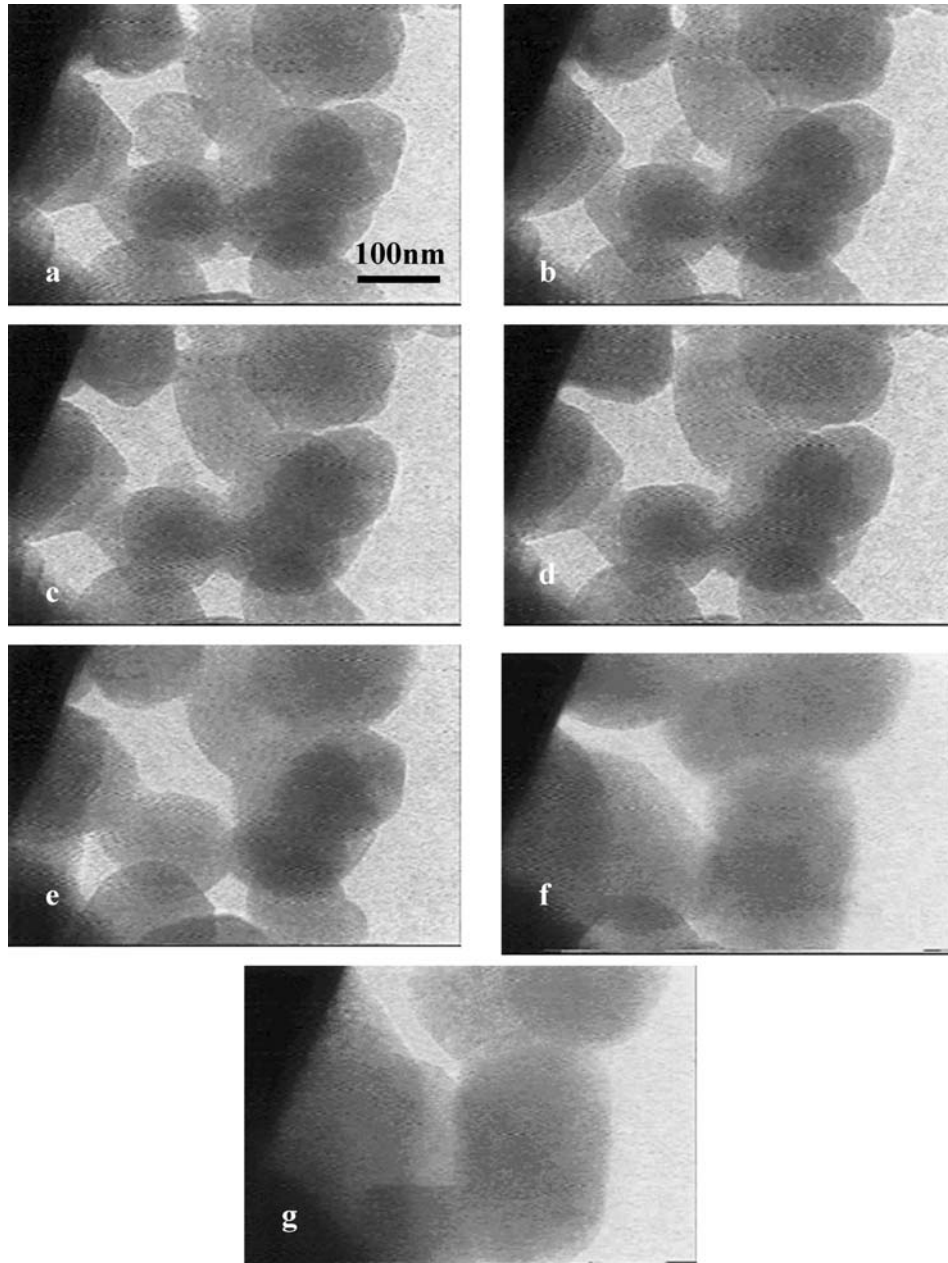


Figure 6 Observations of the grain growth/pore growth and densification: grain growth lead to the pore coarsening, and densification accompany the grain growth with decreased pore to particle size ratio. Temperatures for each image: (a)700°C; (b), (c), (d)800°C, (e)830°C, (f)890°C, (g)920°C.

shrinkage through the pore removal from the interior to the outside on a macro-scale. So we herein assume that densification occurs by pore removal via the vacancy transport of from the interior to the outside of compact.

According to the definition of sintering stages under an ideal condition, as in the intermediate stage of sintering, pores form a continuous network channel [5], boundaries therefore are isolated from each other, and diffusion for the vacancies from interior porosity to the outside of compacts and/or agglomerates cannot be accomplished via boundaries. Based on such an ideal assumption, therefore, the real controlling diffusion mechanism can only be the volume diffusion in spite of the assumed bulk and/or boundary diffusion. By the way of volume diffusion, pores from can be removed by vacancy diffusion outwards to the sample surface, which leads to sample shrinkage. If so, the species diffusion from the interior pore surface outwards to the sample surface can be accomplished by

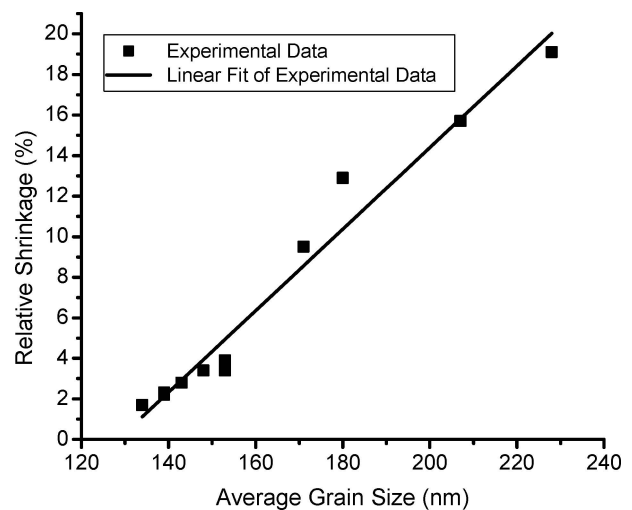
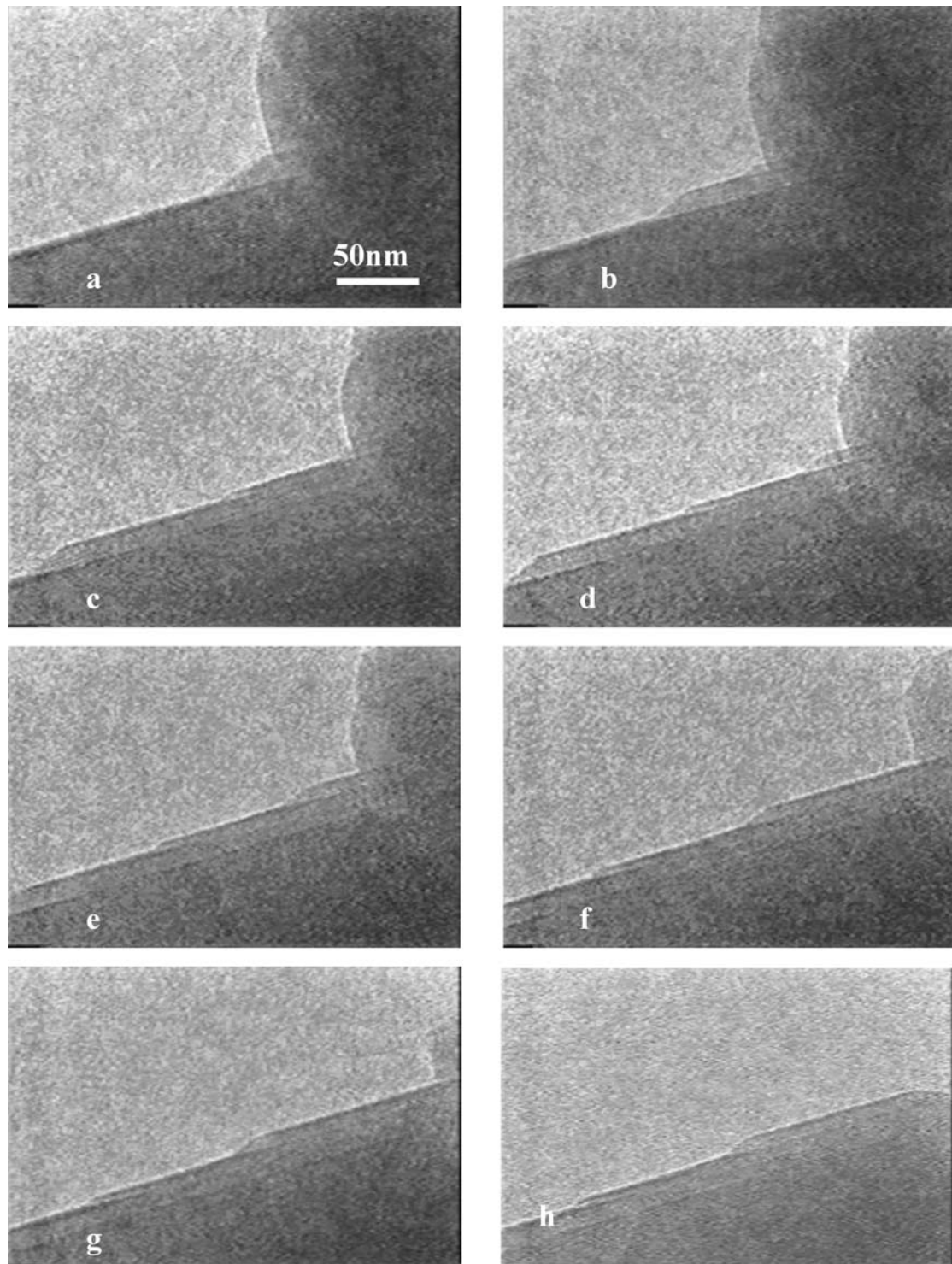


Figure 7 Relation between the linear shrinkage ratio and the average grain size for the configuration shown in Fig. 6.(see text for the detailed data treatment method).





*Figure 8* Direct observation of the surface diffusion on titanium oxide grain surface. Mass transport from a small up-right grain onto the surface of a larger  $\text{TiO}_2$  grain, which is accompanied by the diminishing of the smaller grain and the overall grain growth. The temperature is fixed at  $850^\circ\text{C}$  during the observations.

much easier surface diffusion instead of volume diffusion, because of the much higher activation energy and lower diffusion coefficient of volume diffusion than those of surface diffusion [17], as in the intermediate stage of sintering, pores and pore-particle surfaces, rather than boundaries, form continuous network channels to the sample surface. Partly based on this recognition, it has been stated that surface diffusion could be one of the main mass transport mechanisms for the initial and intermediate stage of sintering [13, 14].

In spite of all the above arguments under ideal conditions and observations, one still cannot exclude the contributions from other diffusion paths, especially boundary diffusion to the grain growth and densification for real powder compacts and/or particle agglomerates. Considering the complexity and non-uniformity of real powder compacts, local boundary network would form, thus boundary diffusion will take place via these local boundary network in the intermediate, or even initial stage of sintering. As a matter of factor, densification



of real compacts should be uneven and non-uniform due to the uniformity throughout the green bodies.

So the mechanism of diffusion mass transport can be by surface diffusion through continuous pore network, and/or by boundary diffusion through continuous boundary network once present, and also by volume diffusion through lattice. The evidence of surface diffusion is clear from the above observation.

## 6. Conclusions

Typical model configurations of two spheres and three spheres and their changes during heating were directly observed under TEM equipped with an *in-situ* installed heating platform. The direct observation of the sintering behavior of the sphere models and two dimensional compact of BaTiO<sub>3</sub> ceramics shows that the grain growth and densification takes place concurrently and in a parallel way, no discrete region exists where only grain growth or shrinkage happens. Surface diffusion on TiO<sub>2</sub> particles were observed directly, which is accompanied by the diminishing of smaller grains, i.e., overall grain growth. One of the main mass transport paths, in addition to boundary and volume diffusions, is believed to be the surface diffusion for both grain growth and densification in the initial and intermediate stages of sintering.

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