

Effect of Crystal Shape on the Grain Growth during Liquid Phase Sintering of Ceramics

Wook Jo, Nong-Moon Hwang*[†] and Doh-Yeon Kim

Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

**National Research Laboratory of Charged Nanoparticles, Seoul National University, Seoul 151-744, Korea*

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ABSTRACT

The equilibrium or growth shape of ceramic materials is classified largely into two categories according to the thermodynamic conditions imposed. One is a polyhedral shape where the surface free energy is anisotropic, and the other a spherical shape where the surface free energy is isotropic. In the case of grains with a polyhedral shape of anisotropic surface free energy, so-called abnormal grain growth usually takes place due to a significant energy barrier for a growth unit to be attached to the crystal surface. In the case of grains with a spherical shape of isotropic surface free energy, however, normal grain growth with a uniform size distribution takes place. In this contribution, the state-of-the-art of our current understanding of the relationship between the crystal shape and the microstructure evolution during the sintering of ceramic materials in the presence of a liquid phase was discussed.

Key words: *Liquid phase sintering, Grain growth, Crystal shape, Surface free energy, Interface structure*

1. Introduction

When ceramic solid grains are dispersed in a liquid medium, the overall interfacial excess free energy is minimized by grain growth of individual grains. The grain growth, which is normally called the grain coarsening, takes place in two different ways. One is the normal grain growth (NGG) and the other the abnormal grain growth (AGG). In the case of NGG, the average grain size of the system increases continuously so that the resulting normalized size distribution is unimodal and nearly time-independent. In the case of AGG, on the other hand, several large grains appear suddenly out of fine matrix grains and grow so rapidly at the expense of the fine matrix grains that a bimodal size distribution results.¹⁻³⁾

A number of experimental observations on the coarsening behavior of the ceramic materials in the presence of a liquid medium have revealed that the two drastically different modes of the grain growth are closely related to the crystal or grain shape.⁴⁻⁷⁾ That is, when the grain is polyhedral, the coarsening behavior of the entire system often results in AGG. On the other hand, when the grain is spherical, the coarsening behavior results in NGG without exception.

When spherical grains with an atomically rough interface are dispersed in a liquid medium, the overall coarsening process is controlled by the diffusion process. This is because there is no energy barrier for the atomic attach-

ment at the interface. For the polyhedral shaped grains, however, the interface atomic structure is atomically smooth so that the attachment of an individual atom to the interface always produces excess broken bonds. Therefore, an advance of the atomically smooth interface cannot be initiated without the presence of ledge-generating sources like 2-dimensional (2D) nuclei. It means that only the grains, which are large enough to induce 2D nucleation, can grow exclusively at the expense of the fine matrix grains. Based on this logic, it was proposed that the 2D nucleation-assisted growth is the mechanism of AGG.^{8,9)}

This approach based on the interface atomic structure could explain many well-known puzzling problems in the sintering community, which had not been clearly understood till quite recently. Typical examples are the role of MgO in suppressing AGG during the sintering of alumina ceramics¹⁰⁻¹⁷⁾ and the role of VC in inhibiting the overall growth rate of WC grains.^{18,19)}

This presentation will begin by discussing how the macroscopic entity, the grain shape, can be related to the microscopic entity, the interface atomic structure. Then, it will be followed by the discussion on the step free energy, which is a key parameter in predicting whether the microstructure of a system will evolve via NGG or AGG. The final section of this presentation will be devoted to comparison between this theory and the experimental results.

2. Interface Atomic Structure

At low temperatures, all the crystal surfaces are either atomically smooth or stepped according to its crystallo-

[†]Corresponding author : Nong-Moon Hwang
E-mail : nmhwang@snu.ac.kr
Tel : +82-2-880-8922 Fax : +82-2-883-8197

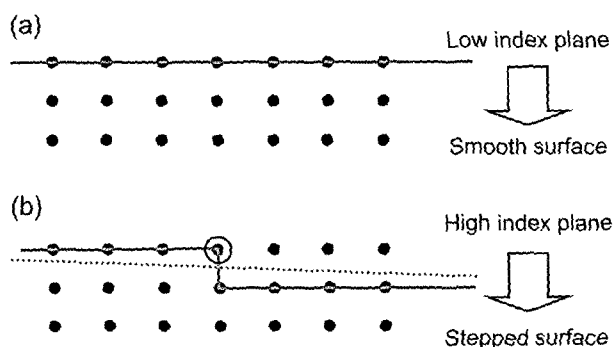


Fig. 1. Schematic illustration showing why crystal surfaces tend to be atomically (a) smooth or (b) stepped.

graphic orientation as shown schematically in Fig. 1.^{20,21} Therefore, the equilibrium shape of crystals should be a polyhedron composed of several low energy surfaces.^{22,24} Note that the presence of steps also creates an excess free energy.

In 1951, Burton, Cabrera, and Frank (BCF)²⁵ predicted by the application of statistical thermodynamics that atomically smooth crystal surfaces can become atomically rough at sufficiently high temperatures, and the atomically rough surface is featured by a complete disruption of crystallinity only at the surface level. They attributed the origin of the transition to the entropic contribution. It means that when the crystal surface becomes rough, atoms at the surface level can possess any position that is forbidden by the bulk symmetry. In other words, steps lose their identity and the difference between a low energy surface and its vicinal ones disappears. As a consequence, the equilibrium crystal shape changes from a polyhedron to a sphere as the surface structure changes from an atomically smooth to an atomically rough. The experimental evidences and recent progresses of this roughening transition concept are well documented in the review papers.²⁶⁻³¹

3. Step Free Energy

As was discussed in the previous section, crystal surfaces can be either atomically smooth or rough, and those surface states change reversibly at a roughening temperature. The roughening transition temperature is featured by the disappearance of the anisotropy in the surface free energy of a crystal, which changes the equilibrium crystal shape from a polyhedron to a sphere.

The anisotropy in the surface free energy is not suitable as a criterion to identify between the rough and the smooth interfaces from a practical point of view. Precise measurement on the surface free energy of various crystal surfaces only for the purpose of checking a possible presence of anisotropy is a time-consuming and painstaking job in most cases.³²⁻³⁹ Therefore, another criterion, which is not only intuitively recognizable but also represents the anisotropy, needs to be developed.

The parameter that satisfies all the requirements is the

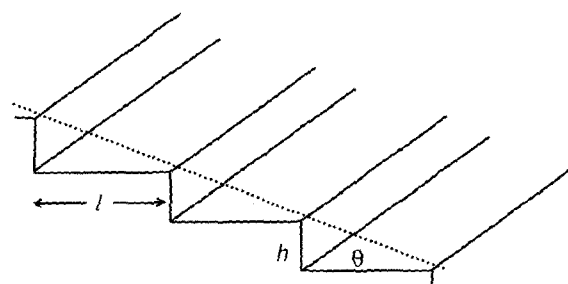


Fig. 2. Schematic illustration of a stepped vicinal surface.

step free energy, because the step free energy can be easily estimated by the shape of crystals. The step free energy is the free energy which is required to create a single atomic step on an atomically smooth surface. Thus, the step free energy should be positive at all times except the roughening transition temperature where it vanishes to zero.²⁶⁻³¹ The crystal shape is related to the step free energy as explained below.

Let us suppose there is a surface tilted away from a low energy surface with the angle of θ , as shown in Fig. 2. Due to the periodicity imposed by the bulk crystal, this surface will be readily corrugated with steps of the height h and their average interval l . Then, since the step density is $1/l$, the energy of the stepped surface is given

$$\chi(\theta) = \left(\gamma_0 + \frac{\varepsilon}{l} \right) \cos \theta = \gamma_0 \cos \theta + \frac{\varepsilon}{h} \sin \theta, \quad (1.1)$$

where γ_0 and ε refer to the surface free energy of the low energy surface and the step free energy, respectively. By differentiating Eq. 1.1 and approaching θ to zero, we get

$$\left(\frac{\partial \chi}{\partial \theta} \right)_{\theta \rightarrow 0} = \frac{\varepsilon}{h}. \quad (1.2)$$

That is, the step free energy can be estimated simply by measuring the tangent value of the surface free energy near the low energy surface. Although this mathematical relation is still more or less abstract from a practical point of view, an additional geometrical consideration yields a very useful result.

Fig. 3 shows a simple geometrical consideration showing how the step free energy is related to a crystal shape. Since the step free energy is, by definition (see Eq. 1.2), the tangent value at A, it can also be represented by comparing the crystal dimensions, say $\frac{AB}{OA}$. That is, the step free energy corresponds to the ratio of the facet dimension to the crystal size. Typical examples showing the relationship between frequently-observed crystal shapes during the liquid phase sintering of ceramic materials and the related step free energy value are presented in Fig. 4.

4. Coarsening Behavior of Polyhedral Grains during Liquid Phase Sintering

When solid grains with a size distribution are dispersed in

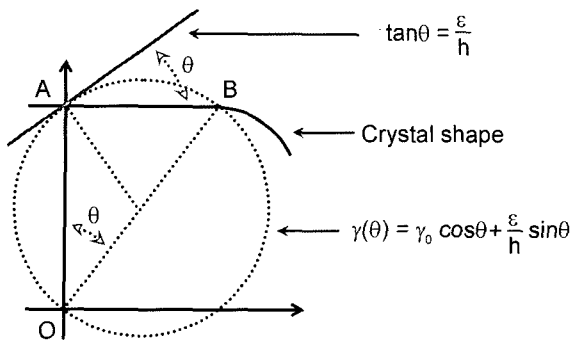


Fig. 3. Geometrical consideration showing how the step free energy is related to the size of the surface facet of a crystal.

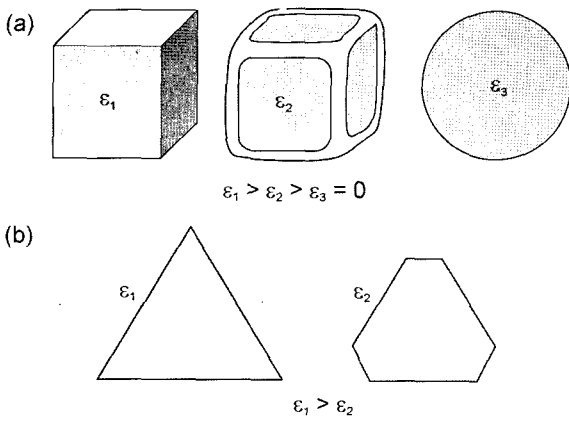


Fig. 4. Schematic illustrations showing how the step free energy is related to the size of the surface facet of a crystal in the case of (a) cubic and (b) hexagonal crystals.

a liquid medium, large grains grow at the expense of small grains by the atomic transfer through liquid. This process, which is called Ostwald ripening, can be broken down into three steps: detachment of atoms from smaller grains, diffusion of the atoms through the liquid medium, and attachment of the atoms onto the surfaces of large grains. Among these, the final step is critically dependent upon the interface atomic structure.

When the interface is atomically smooth, the atomic attachment is possible only in the presence of ledge-generating sources such as screw dislocation or 2D nucleus. The analysis will be focused on coarsening by 2-D nucleation controlled kinetics because coarsening by screw dislocation controlled kinetics does not lead to AGG. The size of the stable 2D nucleus and the energy barrier for the 2D nucleation can be calculated simply by the free energy change associated with the formation of a 2D nucleus as follows.

When a disc-shaped 2D nucleus of size r is formed on an atomically smooth interface, the associated free energy change is expressed as

$$\Delta G_r = -\pi r^2 h \cdot \Delta G_V + 2\pi r \epsilon, \tag{1.3}$$

where h and ΔG_V are the step height and the bulk free

energy change due to phase transformation of solutes from liquid to solid, respectively. Since the nucleus is stable only when the chemical potential of the nucleus is the same or less than zero, the critical size and energy barrier are expressed, respectively, as

$$r^* = \frac{\epsilon}{h \Delta G_V} \tag{1.4}$$

$$\Delta G_r^* = \frac{\pi \epsilon^2}{h \Delta G_V} \tag{1.5}$$

According to Eqs. 1.4 and 1.5, both the critical size and energy barrier approach zero, when the step free energy does. It means that there exists no barrier for the atomic attachment to the growing surface and the growth process is controlled by diffusion. In this case, the size distribution of the final microstructure will be uniform and time-independent, as well established in the LSW theory, because the linear growth rate of individual grains should decrease as they grow.^{39,40)}

Eqs. 1.4 and 1.5 also indicate that the critical grain size, which can induce the supersaturation high enough to initiate 2-D nucleation, decreases quickly as the step free energy decreases. In other words, the smaller the step free energy, the greater the number of growing grains. Note that the energy barrier for 2D nucleation is proportional to the square of the step free energy. Therefore, we can expect that AGG tendency is critically dependent on the change in the step free energy of the system, i.e. a high and low step free energy will lead to strong and weak AGG, respectively.

An experimental result demonstrating the relationship between the grain shape and the microstructure evolution is presented in Fig. 6.⁴¹⁾ The scanning electron microscope (SEM) images of a 3D shape of $Nb_{1-x}Ti_xC$ grains and the related microstructure of $Nb_{1-x}Ti_xC-Co$ system are displayed, respectively, from (a) to (c) and from (d) to (f) as the content of TiC increases. The step free energy is shown to increase with the content of TiC as can be deduced from the

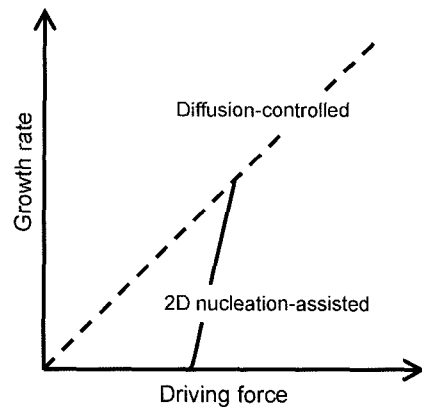


Fig. 5. Schematic diagram showing the dependence of the growth rate on the driving force for the crystals with a different interface structure.

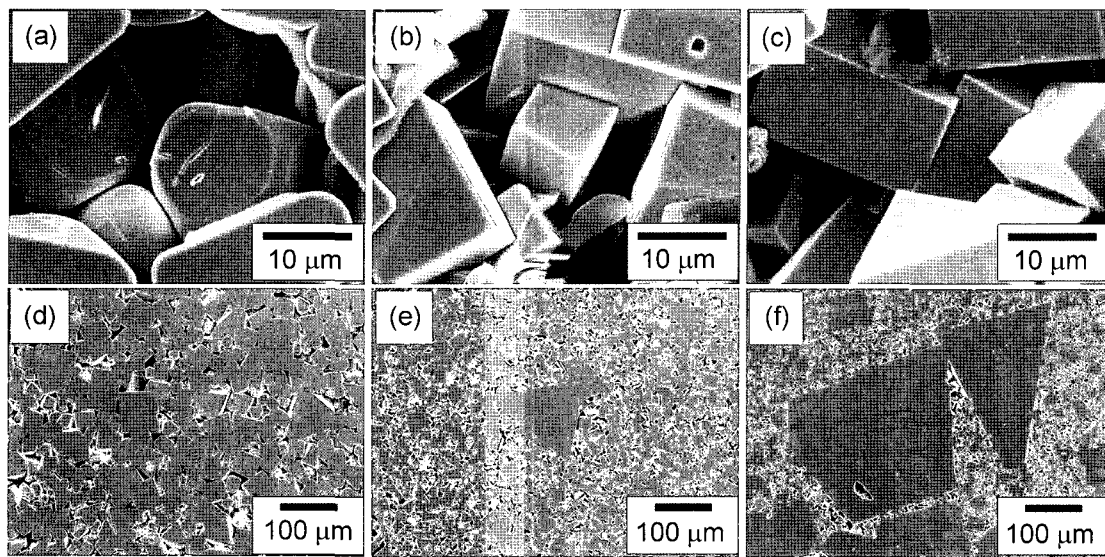


Fig. 6. SEM images of 3D shape of $Nb_{1-x}Ti_xC$ grains and the related microstructure of $Nb_{1-x}Ti_xC-Co$ system: (a) & (d): $x=0$, (b) & (e): $x=0.1$, and (c) & (f): $x=0.25$.⁽⁴¹⁾

3D shapes of $Nb_{1-x}Ti_xC$ grains. Besides, the increase in the step free energy is shown to increase the AGG tendency.

In the mean time, the role of VC addition in inhibiting the grain growth during sintering of the WC-Co system has long been an unsolved puzzle among the sintering community. This problem can be approached by the effect of VC on the step free energy. The 2-D nucleation barrier in Eq. 1.5 is proportional to the square of the step free energy, indicating that the 2-D nucleation rate is sensitively affected by the step free energy (See Fig. 4). Fig. 7⁽¹⁹⁾ shows that in the absence of VC, the WC grain has a

shape of truncated prism whereas the addition of VC changes the shape to the prism without truncation, indicating that VC increases the step free energy. The increase in the step free energy will increase the 2-D nucleation barrier and thereby markedly inhibit the growth by 2-D nucleation. However, the increase in the step free energy will increase the AGG tendency as shown in Fig. 7.

Although only a few examples of grain coarsening problem are treated in this paper, the approach based on the interface atomic structure can be generally applicable to

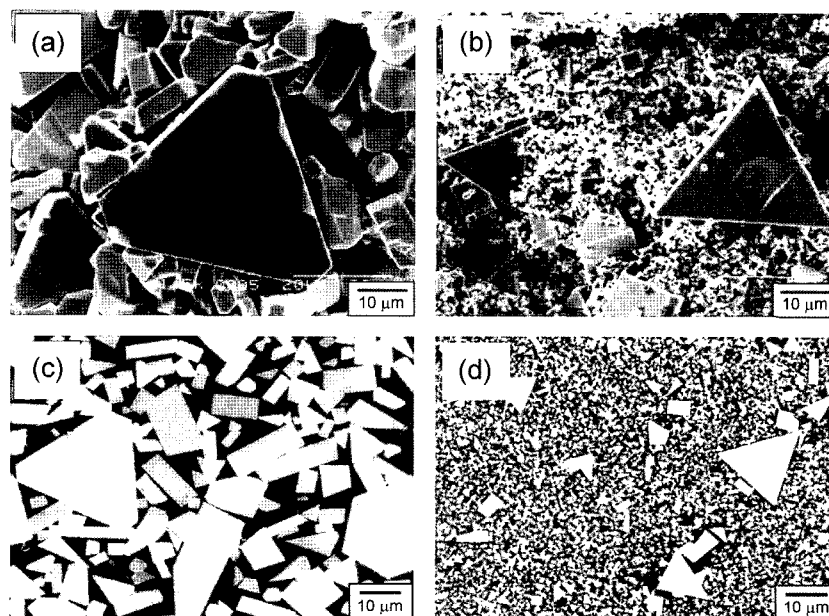


Fig. 7. SEM images of 3D shape of WC grains and the related microstructures of WC-30Co-xVC system: (a) & (c): $x=0$ and (b) & (d): $x=1$.⁽¹⁹⁾

grain coarsening of angular grains in the presence of liquid. It is also applicable to the case where the liquid phase exists as a thin intergranular film. Besides, the approach based on the interface structure is applicable to the densification behavior during sintering.⁸⁾

4. Conclusion

The relationship between the crystal shape and the coarsening behavior during the liquid phase sintering of ceramic materials was discussed in detail. It was shown that the microstructure evolution is closely related to the interface atomic structure, which can be monitored by the shape of individual grains. The step free energy plays a critical role in the growth behavior such as the AGG tendency and the grain growth inhibition.

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