Phase field simulation of grain growth in Al$_2$O$_3$-based composite ceramic cutting tool materials containing second phase nanoparticles and pores

Youxin Zhou and Bin Peng

College of Mechanical and Electrical Engineering, Lanzhou University of Technology, Lanzhou City, Gansu Province, People’s Republic of China

E-mail: zhouyx_lut@163.com

Keywords: grain growth, phase field model, second phase nanoparticle, pore, Al$_2$O$_3$ composite ceramic cutting tool materials

Abstract

A phase field model was established to simulate the grain growth of Al$_2$O$_3$-based composite ceramic tool materials containing second phase nanoparticles and pores. The free energy parameters of the model are directly related to the surface and grain boundary energies of Al$_2$O$_3$ such that the grain growth process can be quantitatively analysed. The model was used to investigate the effects of the volume fraction and size of second phase particles on grain growth in Al$_2$O$_3$ with a certain initial pore volume fraction. Findings show that pores and second phase particles jointly hinder grain growth. When the radii of second phase nanoparticles are the same, as the number of particles increase, most of the grain boundaries occur as straight lines in the microstructure, and grain size decreases. It is beneficial to obtain fine and uniform microstructure. However, when the particles content reaches a certain level, the second phase particles tend to agglomerate at the grain boundary of matrix grains, which will result in a decrease in the properties of nanocomposite ceramic tool materials.

The study also found that, at a constant volume fraction of particles, with the decrease of particle radius, the grain size decreases. When the second phase particle size is reduced to 50 nm, relatively more intragranular microstructure was observed, which is considered to be the main reason for increasing the toughness of nano composite ceramic tool materials. Through analyzing the simulation results, the optimal combination of the content and size of the second phase particles can provide theoretical guidance for Al$_2$O$_3$ nano composite ceramic tool materials design and preparation.

1. Introduction

Ceramic tool materials have many more advantages than cemented carbide tools (including coated tools, especially at high temperature), such as high wear resistance, relatively low chemical reactivity with steel and many other materials, and high hardness [1]. However, ceramic tool material has the critical weakness of brittleness, and it lacks adequate fracture toughness as cutting tool. The major method used to increase fracture toughness is adding nanoparticles, which strengthen and toughen the ceramic matrix material to generate the composite ceramic tool material. Since Niihara [2] first proposed the concept of nanocomposite ceramic in the early 1980s and successfully prepared Al$_2$O$_3$/SiC nanocomposite ceramic with room temperature strength up to 1500 MPa, this concept has attracted the attention of many scholars. Due to the complexity of microstructure and preparation technology, it is difficult to trace the process of grain growth for composite ceramics in reality, especially at the nanoscale. Using computer simulation with the coupling effects of various factors, the microstructure evolution of materials has become a promising and feasible research direction. Phase field method considers the influence of complex factors, such as physical field and grain boundary geometry, on grain growth without directly tracking the complex dynamic interface, and the simulation has a higher efficiency and explicit physical meaning.
Inclusions, pores and bubbles in polycrystalline solids affect the overall grain growth rate and grain size of ceramic materials [3, 4]. Here, we focus on the effect of particles and pores on grain growth. Phase field methods have been established to investigate the effect of second phase particles on microstructure evolution [5, 6]. Vedantam and Mallick [7] formulated a phase field model to study the interaction between mobile particles and the migration boundary. K Ahmed first established a phase field method model for grain growth in the presence of mobile particles [8, 9].

In addition to particles, pores also affect grain growth. The presence of pores (mobile or immobile) significantly inhibits grain growth in porous materials, regardless of the temperature, and when the porosity is high enough, the grain growth process stops completely [8]. A phase field that accounts for the interaction between the pore and grain boundary kinetics model has been developed to investigate grain growth in porous polycrystalline UO₂ [10]. Recently, a large-scale 3D phase field model was established to study grain growth in porous microstructures during the final stage of sintering. The effect of different porosities and pore sizes on grain growth was analysed with statistical relevance comparable to real microstructure [11].

To describe the microstructure of a specific material, the material properties have also been introduced into the phase field models that simulate grain growth. In these models phase field model parameters are found in terms of measurable material properties [10, 12]. A phase field model was established to investigate grain growth in porous polycrystalline UO₂ by introducing the material properties into the model parameters [10]. The grain growth of a nanostructured AZ31 magnesium alloy, which considered material properties under realistic spatial and temporal scales, has been simulated [12].

In this study, we present a phase field model for grain growth of Al₂O₃-based composite ceramic tool material coupled with pores and second phase nanoparticles. By introducing second phase particles, the existing local free energy function expression is improved. The parameters of the model are directly related to the thermodynamic and kinetic properties of the ceramic tool material, and the simulation is more accordant with practical material. The effects of particle size and volume fraction on the grain growth of Al₂O₃ nanocomposite ceramics with a certain initial pore volume fraction were analysed in detail. The findings can provide proposed theoretical guidance for composite ceramic tool material design.

2. Model descriptions

A combination of non-conserved \( \eta_r (r, t) \) and conserved order parameters \( \rho_r (r) \) is used to fully represent the microstructure of a solid containing second phase particles and pores. The long-range orientation parameter \( \eta_r (r, t) \) (with \( p = 1, 2, ..., n \)) represents different grains with different crystallographic orientations in the solid phase. Fan [13] showed that the difference was not significant when \( p \) was considered a very large number, so it is possible to describe real materials with a limited \( p \). In the paper, \( p \) was set to 36. The conserved field \( \rho_r (r) \) is used to represent the fractional density of the solid. This value is 1 in the solid phase and 0 in pores. According to the Cahn and Hilliard equation, the free energy function of the material system is written in the form of all orientation field variables and their gradient functions:

\[
F = \int \left\{ f_0(\rho_r); \eta_{1r}, ..., \eta_{nr} \right\} + \frac{\kappa_1}{2} \sum_{i=1}^{p} (\Delta \eta_i(r))^2 + \frac{\kappa_2}{2} (\Delta \rho(r))^2 \right\} dV
\]  

Where \( \kappa_p \) and \( \kappa_r \) are the gradient coefficients.

The first term in equation (1) represents the bulk free energy density. When simulating the grain growth of ceramics with only porosity, such as single phase Al₂O₃, the following form that was suggested by Wang [14] can be adopted:

\[
f_0(\rho_r, \eta_r) = B \rho^2 (1 - \rho)^2 + C \left[ \rho^2 + 6(1 - \rho) \sum_{i=1}^{p} \eta_i^2 + 4(2 - \rho) \sum_{i=1}^{p} \eta_i^3 \right.
\]

\[
+ \left. 3 \left( \sum_{i=1}^{p} \eta_i \right)^2 \right]
\]  

Where \( B \) and \( C \) are constants. The bulk free energy form given in equation (2) is a Lyapunov (positive definite) function with \( p + 1 \) minima, corresponding to the different equilibrium phases represented, i.e., pores and all grains in the solid. The model is able to capture different stages of sintering including grain growth. Based on the model, K Ahmed [8] established a direct relationship between the model parameters and the material properties, which will be helpful for quantitative analysis of grain growth.

When the particle matrix interfaces are incoherent and the particle is immobile, the local free energy density produced by the second phase particles is expressed as \( f_0^p = \Phi \sum_{\beta=1}^{n} \eta_\beta \), \( \beta = 1, ..., n \) [5], where \( \Phi \) is used to describe the particle distribution. When \( \Phi \) equals 1, there is a particle, while there are no particles when \( \Phi \) equals 0. In this study, we set \( \Phi \) as a constant factor to account for the particle effect.
It is considered to be constant over time. The free energy density function of the system can be constructed as follows:

\[
F = B \rho^2 (1 - \rho)^2 + C \left[ \rho^2 + 6(1 - \rho) \sum_{i=1}^{p} \eta_i^2 - 4(2 - \rho) \sum_{i=1}^{p} \eta_i^3 \right] + \Phi \sum_{i=1}^{p} \eta_i^2
\]

(3)

For \( \Phi = 0 \), the bulk free energy has \( p + 1 \) minima in the pore and in each grain of the solid phase. For \( \Phi = 1 \), the bulk free energy has one minimum at all \( \eta_i \) equal to 0. The free energy parameters are related to the material properties as follows [8]:

\[
\gamma^B = \frac{2}{\sqrt{3}} \sqrt{G \kappa_i}
\]

(4)

\[
\gamma^f = \frac{\sqrt{2}}{6} \sqrt{(\kappa_i + \kappa_p)(B + 7C)}
\]

(5)

\[
l = \frac{4 \kappa_i}{3C} = \delta
\]

(6)

\[
6C \frac{\kappa_i}{\kappa_p} = \frac{B + C}{\kappa_p}
\]

(7)

Where \( \gamma^B \) is the grain boundary energy, \( \gamma^f \) is the surface energy, \( \delta \) is the grain boundary width, and \( l \) is the diffuse interface width. The above equations completely fix the free energy functional parameters for any ceramic tool material of interest.

The non-conserved order parameter evolves according to the Allen Cahn equation [15], and the conserved density field evolves according to the Cahn Hilliard equation [16]. They are written in the following forms:

\[
\frac{\partial \eta_i}{\partial t} = -L \frac{\delta F}{\Delta \eta_i(r, t)} = -L \left( \frac{\partial \Phi_0}{\partial \eta_i} - \kappa_i \nabla^2 \eta_i \right)
\]

(8)

\[
\frac{\partial \rho}{\partial t} = \nabla \cdot \left[ M \nabla \frac{\delta F}{\delta \rho(r, t)} \right] = \nabla \cdot \left[ M \nabla \left( \frac{\partial \Phi_0}{\partial \rho} - \kappa_p \nabla^2 \rho \right) \right]
\]

(9)

Where \( L \) and \( M \) are the material properties related to the physical grain boundary mobility and the chemical mobility tensor, respectively.

The micron Al2O3 matrix addition of nanoparticles is discussed in the model. The reason we do not choose the nanomatrix is that the nanoparticles are small and have high surface energy, which can cause agglomeration and nucleated growth in the sintering process, so the performance of the composite ceramic tool material is reduced [17, 18]. The combination of a micron matrix and nanoparticles can increase the bulk density and affect the density and properties of the sintered body [19].

### 3. Model implementation

For convenient numerical implementation, we define \( \varepsilon = B \) as a reference energy density, \( \tau = 1/L \varepsilon \) as a reference time scale, and \( l^* = \sqrt{4K_i/3C} \) as a reference length scale [8]. Then all the physical parameters are transformed to non-dimensional form. \( B \) is replaced by non-dimensional coefficient \( B^* = B/\varepsilon \) and the other physical parameters should be treated accordingly. The spatial coordinates \( x_i \) are replaced by \( x^* = x/l^* \) and the time coordinate \( t \) is replaced by \( t^* = t/\tau \).

The dynamic equations are discretized and then treated by the Euler formula. The dynamic equations can be discretized as follows:

\[
\varphi(t + \Delta t) = \varphi(t) + \frac{d\varphi}{dt} \times \Delta t
\]

(10)

Where \( \Delta t \) is the time step. The Laplace operator \( \nabla^2 \) in the dynamic equations can be discretized by the following equation [13]:

\[
\nabla^2 \varphi_i = \frac{1}{(\Delta x)^2} \left[ \frac{1}{2} \sum_j (\varphi_j^n - \varphi_i^n) + \frac{1}{4} \sum_c (\varphi_c^n - \varphi_i^n) \right] \quad i = 1, 2, \ldots, m
\]

(11)
In the above equation, \( \varphi \) represents an arbitrary variable, \( m \) is the number of variables, \( \Delta x \) is the grid size, \( j \) represents the nearest neighbour grid of \( i \), \( c \) represents the next nearest neighbour of \( i \), and \( n \) is the \( n \)th time step. Here, we set \( \Delta t^* \) to 0.25 and \( \Delta x^* \) to 1.

In applying our model to Al\(_2\)O\(_3\) nanocomposite ceramics, a domain size of 300 \( \times \) 300 grid points, which corresponds to a physical system size of 100 \( \times \) 100 \( \mu \)m\(^2\) was used. For Al\(_2\)O\(_3\) with a surface energy of 1 J m\(^{-2}\), a grain boundary energy of 0.4 J m\(^{-2}\) [20], and assuming a grain-boundary width of 1 nm, the free energy parameters in reference to equations (4)–(7) take on the values \( B = 9.2 \times 10^9 \) J m\(^{-3}\), \( C = 4 \times 10^8 \) J m\(^{-3}\), \( K_1 = 3 \times 10^{-10} \) J m\(^{-1}\) and \( K_2 = 1.2 \times 10^{-9} \) J m\(^{-1}\). The grain-boundary mobility, \( L \), of Al\(_2\)O\(_3\) was obtained from [21]. Periodic boundary conditions were applied to minimize the boundary effect on the grain growth kinetics.

4. Results and discussion

4.1. Comparison of grain growth in fully dense Al\(_2\)O\(_3\) and Al\(_2\)O\(_3\) with pores

According to Coble’s sintering model [22, 23], there are a lot of connected pores in the sintered body in the initial stage of sintering, so we assume that the initial pore volume fraction is 10 vol\%. For comparative analysis, grain growth in fully dense Al\(_2\)O\(_3\) is also simulated. As shown in figure 1(d), the adjacent pore lattices fuse together to form a pore over time, and some pores are connected with each other, which is similar to the distribution state of pores in the actual sintered ceramic body.

From figure 2, we can see that the average grain radius of fully dense Al\(_2\)O\(_3\) is larger than that of Al\(_2\)O\(_3\) with pores. Compared with the grain growth rate of the fully dense body, the residual porosity obviously delays the grain growth rate and prevents abnormal grain growth. After 3000 time steps, the grain growth rate of the material containing initial pores increased significantly. This is because after 3000 time steps, the density of Al\(_2\)O\(_3\) with pores is greater than 95\%, and the effect of pore on grain growth is decreased.
4.2. The effect of the second phase particle volume fraction on the grain growth of Al₂O₃

Second phase particles with different volume fractions and sizes were introduced into Al₂O₃ with 10% initial pore volume fraction. First, particles with different volume fractions but the same radius were investigated. The volume fractions were 0, 5%, 10% and 15%, with the size of the second phase particles was 50 nm and the initial pore volume fraction was 10%. In figure 3, the blue area indicates the second phase particles, and the red area indicates pores.

As shown in figures 3(a)–(c), a simulation time of 3000 steps is equivalent to entering the intermediate and final stages of sintering. The grain boundary drives the pores to move together. In the process of migration, pores always remain on the grain boundary, and pores are transported by grain boundaries as vacancies to achieve either convergence or disappearance. Moreover, with the increase of particles, the average grain size decreases, and the grain size tends to be uniform. The grain distribution is close to the ideal trigeminal grain. Most of the grain boundaries occur as straight lines in the microstructure after 6000 steps. When the curvature of the grain boundary is reduced, the driving force for grain growth will be decreased, and grains grow more slowly. As the number of second phase particles increases, this trend is more obvious. After 6000 steps, most of the pores had disappeared, as shown in figures 3(d)–(f). Most of the second phase particles are distributed on the grain boundary, and only a small amount of the second phase particles are distributed inside the grains. It is worth noting that when the second phase content is 15%, the second phase particles agglomerate at the grain boundary, as shown in figure 3(f), which will result in a decrease in the properties of the composites ceramic tool materials.

As shown in figure 4, when there are neither particles nor pores in the microstructure, the grain size increases rapidly with increasing time. When the second phase volume fraction is between 5% and 15%, the grain growth rates are almost the same before 3000 steps and increase after 3000 steps, while the higher the second phase volume fraction, the slower the growth rate. The reason for this phenomenon is that before 3000 steps, the kinetics of grain growth in Al₂O₃ is mainly controlled by pores. After 3000 steps, the kinetics of grain growth in Al₂O₃ change gradually from pore-controlled to grain-boundary-controlled kinetics with the disappearance of pores, and the pinning effect on the grain boundary increases with increasing particle content.

4.3. The effect of the second phase particle size on the grain growth of Al₂O₃

The effects of three different sizes of second phase particles on grain growth in Al₂O₃ are captured in figure 5. The particle sizes were 50 nm, 70 nm and 100 nm with both the second phase particle volume fraction and the initial pore volume fraction at 10 vol%. As shown in figures 5(a) and (d), when the second phase particle size is 50 nm, most of the second phase particles tend to be located at the junction of fine grains, and a small number of particles are encapsulated with matrix grains, forming an intragranular structure. Many researches have indicated that nanoparticles exist not only on the grain boundary, but also inside the matrix grains, i.e. ‘intergranular’ and ‘intragranular’ coexist in nanocomposite structure [24–27]. There are two explanations for intragranular structure at present. Pan et al [28] considered that the ‘intragranular’ structure was the result of grain boundary migration and encapsulation of the second phase during liquid phase sintering. Niihara [29] proposed that nanoparticles were the core of crystallization and that the matrix grew up with them to form the internal crystalline phase. In our study we didn’t find core particles. We considered that the pinning effect of
single small grain is weak, and the second phase particles are more easily separated from the grain boundary and encapsulated inside grains.

As shown in figures 5(b), (e) and (c), (f), when the second phase particle sizes are 70 nm and 100 nm, almost all the second phase particles are located at the grain boundary. Niihara et al [2] first proposed that the ‘intragranular’ nano phase is the main reason for the toughening of composite ceramics materials. However, it is difficult to control and prepare the composite ceramics mainly composed of the ‘intragranular’ structure.
Therefore, most of the second phases of composite ceramics obtained at present exist in the ‘intergranular’ structure.

Figure 6 shows the evolution of the average grain size for Al₂O₃ with different second phase particle sizes. As the second phase particle size decreases, grain growth slows. The grain growth rate of Al₂O₃ with both pores and second phase particles increased significantly at 3000 steps, which is similar to Al₂O₃ containing only pores. There are no statistically significant differences in the grain radii and growth rates between second phase particle sizes of 70 nm and 100 nm. Grain growth is obviously delayed when the second phase particle size is 50 nm. This is because, although the pinning effect of single, small second phase particles is not obvious, the pinning effect of multiple small particles was strengthened, and the grain boundary is pinned by the particles. It makes the resistance of grain boundary migration greater and grain merging slower.

Therefore, considering both the content and size of particles, when the content is 10% and size is 50 nm, the grains are fine and uniform, and ‘intragranular’ exist in nanocomposite structure, which is perfect microstructure for ceramics cutting tool materials.

5. Concluding remarks

A phase field model was implemented to study the effect of different particle content and size on the grain growth in Al₂O₃ with 10 vol% initial porosity content. Based on this model, the grain morphology and size in each stage of sintering can be observed. The free energy parameters of the model are directly related to the surface and grain boundary energies of Al₂O₃ such that the grain growth process can be quantitatively analysed.

It was found that pores and second phase particles jointly hinder grain growth. A simulation time of 3000 steps is equivalent to entering the intermediate and final stages of sintering. In the process of migration, pores always remain on the grain boundary. After 6000 steps, grain growth tends to be stable, most of the pores disappear, and second phase particles are distributed on the grain boundary.

The simulation results show that when the second phase particle sizes are the same, the grain size decreases with the increase of particles. It is beneficial to obtain fine and uniform microstructure. However, when the volume fraction of particles increases from 10 vol% to 15 vol%, the grain growth rate and the grain radius are less...

---

Figure 5. Microstructures evolution of Al₂O₃ containing different particle sizes: The particle radius of (a) and (d) is 50 nm, when the simulation time is 3000 steps and 6000 steps, respectively. The particle radius of (b) and (e) is 70 nm. The particle radius of (c) and (f) is 100 nm. The second phase particle and the initial pores volume fraction are 10 vol%.
differentiating, and the second phase particles tend to assemble on the boundary of the matrix grains at 15 vol%, which will result in a decrease in the properties of the composites.

The study also found that for a constant volume fraction of particles, as the particle size decreases, the grain size decreases. When the second phase particle size is 50 nm, a small number of second phase particles are distributed inside the grains, forming an intragranular structure. The reason is that the smaller the size of the second phase particles, the weaker the pinning effect of single particle, and the second phase particles are more easily separated from the grain boundary and encapsulated inside grains. This intragranular structure is beneficial to increase the toughness of ceramic tools. Thus, when the particle content is 10% and size is 50 nm, the ideal microstructure can be obtained. These results are valuable for the study of the effects of second phase particles and pores on grain growth and for the design of nanocomposite ceramic tool materials.

Acknowledgments

This research was supported by the National Key Research And Development Project—“Science and technology help economy 2020” Key projects (No.SQ2020YFF0420989).

ORCID iDs

Youxin Zhou https://orcid.org/0000-0003-1231-9812

References

[1] Aruna M, Dhanalakshmi V and Mohan S 2010 Wear analysis of ceramic cutting tools in finish turning of Inconel 718 Inter. J. Eng. Sci. Tech. 2 4253–62
[2] Niihara K 1991 New design concept of structural ceramics ceramic nanocomposites J. Ceram. Soc. Jpn. 99 974–82
[3] Rahaman M N 1995 Ceramic Processing and Sintering (New York: Marcel Dekker)
[4] Petrishcheva E and Renner J 2005 Two-dimensional analysis of pore drag and drop Acta Mater. 53 2793–803
[5] Moelans N, Wollants P and Blanpain B 2005 A phase field model for the simulation of grain growth in materials containing finely dispersed incoherent second-phase particles Acta Mater. 53 1771–81
[6] Zhou G Z, Wang Y X and Chen Z 2012 Phase-field method simulation of the effect of hard particles with different shapes on two-phase grain growth Acta Metall. Sin. 48 227–34
[7] Mallick A and Vedantam S 2010 Phase-field theory of grain growth in the presence of mobile second-phase particles Acta Mater. 58 272–81
[8] Ahmed K, Yablinsky C, Schulte A, Allen T and EL-Azab A 2013 Phase field modeling of the effect of porosity on grain growth kinetics in polycrystalline ceramics (Article) Modell. Simul. Mater. Sci. Eng. 21 065005–28
[9] Ahmed K, Allen T and EL-Azab A 2016 Phase field modeling for grain growth in porous solids J. Mater. Sci. 51 1261–77
[10] Ahmed K, Pakarinen J, Allen T and EL-Azab A 2014 Phase field simulation of grain growth in porous uranium dioxide J. Nucl. Mater. 446 90–9

Figure 6. Effect of second phase particle size on grain growth in Al₂O₃. The second phase particles and the initial pore volume fraction are 10 vol%, and d is the particle radius.
Veronika R, Hötzer J, Rheinheimer W, Seiz M, Christopher S and Nestler B 2019 Phase-field study of grain growth in porous polycrystals Acta Mater. 174 439–49

Wu Y, Zong Y P and Jian F J 2016 Grain growth in a nanostructured AZ31 Mg alloy containing second phase particles studied by phase field simulations Sci. China Mater. 59 355–62

Fan D 1996 Computer Simulation of Microstructural Evolution in Multiphase Materials using a Diffuse-Interface Field Model The Pennsylvania State University

Wang Y U 2006 Computer modelling and simulation of solid-state sintering: a phase field approach Acta Mater. 54 953–61

Allen S M and Cahn J W 1979 A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening Acta Metall. 27 1085–95

Cahn J W 1961 On spinodal decomposition Acta Metall. 9 795–801

Liu N, Xu Y D, Li H, Li G H and Zhang L D 2002 Effect of nano-micro TiN addition on the microstructure and mechanical properties of TiC-based cermet J. Eur. Ceram. Soc. 22 2409–14

Sternitzke M 1997 Review: structural ceramic nanocomposite J. Eur. Ceram. Soc. 17 1061–82

Li J, Yuan W J, Deng C J and Zhu H X 2012 Effect of SiC particle size distribution on SiC-Si3N4/SiC composite ceramics China Ceramic Industry 19 9–13

Tsoga A, Sotiriopoulos D and Nikolopoulos P 1996 grain boundary grooving in polycrystalline oxides and surface diffusion coefficient in polycrystalline alumina Mater. Sci. Forum 207–209 565–8

Coble R L 1961 Sintering crystalline solids I intermediate and final state diffusion models J. Appl. Phys. 32 787–92

Coble R L 1961 Sintering crystalline solids II experimental test of diffusion models in powder compacts J. Appl. Phys. 32 793–9

Wang K and Sacks M D 1996 Mullite formation by endothermic reaction of α-alumina/silica microcomposite grains J. Am. Ceram. Soc. 79 12–6

Nagashima M, Maki K and Hayakawa M 2001 Fabrication of Al2O3/ZrO2 micro/nano-composite prepared by high energy ball milling Mater. Trans. 42 1119–23

Sakka Y, Bidlinger D D and Aksay I A 1995 Processing of silicon carbide–mullite–alumina nanocomposites J. Am. Ceram. Soc. 78 497–486

Wang C M, Mitomo M and Emoto H 1998 Nucleation and growth of silicon oxynitride grains in a fine-grained silicon nitride matrix J. Am. Ceram. Soc. 70 2036–40

Pan X Q, Mayer J and Ruhle M 1996 Silico nitride based ceramic nanocomposites J. Am. Ceram. Soc. 79 585–90

Niihara K, Nakahira A and Sekino T 1993 Recent technology of control of fine particle preparation Funtai Kogaku Kaishi 30 870–7