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Improving the microstructure of Si_3N_4–TiN composites using various PEIs to disperse raw TiO_2 powder

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Abstract

An in situ synthesis route was developed for the preparation of dense and homogenous Si_3N_4–TiN (5 vol% TiN) composites, with TiN grains formed from TiO_2 and AlN. The dispersion of TiN grains in the Si_3N_4 matrix using various polyethyleneimines (PEIs) as dispersing agents for raw TiO_2 powder was investigated by scanning electron microscopy (SEM). We found that the microstructure of Si_3N_4–TiN composites was improved with the aid of PEI to disperse TiO_2 particles in the mixture. It was critical to disperse original TiO_2 particles with the appropriate dispersant before the sintering process, because the size of TiN grains in the Si_3N_4–TiN composites was strongly dependent on the size of TiO_2 particles. PEI molecules modified the surface of TiO_2 particles and protected the TiO_2 particles in the slurry from aggregations. It was a practical and useful way to obtain the Si_3N_4–TiN composites with homogeneous microstructures without the alteration of the preparation procedure.

Keywords: A. Sintering; B. Composite; B. Microstructure-final; D. Si_3N_4; D. TiO_2

1. Introduction

Silicon nitride (Si_3N_4) ceramics are known for their high heat resistance, hardness, refractoriness, durability, thermal shock resistance, and chemical resistance, which has a high potential in the practical utilization not only as a structural material but also as a functional material [1]. However, they are brittle and have low fracture toughness, which hinders their broad application. Titanium nitride (TiN) exhibits a number of desirable properties, including high hardness, good chemical durability, high electrical conductivity, and good wear-resistance [2], and is a popular second phase additive when sintered in nitrogen to improve the fracture toughness of Si_3N_4 due to its good compatibility with Si_3N_4 [3–5]. Si_3N_4–TiN composites have been investigated extensively [6–8]. An interesting method to obtain these TiN particles is in situ synthesis, which enables the production of composites at low cost, with desirable microstructures and enhanced sinterability [9,10].

In general, most of the ceramic composites containing a dispersed second phase result from a direct addition of the second phase. Such materials can sometimes exhibit poor characteristics, which result from an inadequate dispersion process and the lack of sinterability caused by the large volume fraction of inert dispersion required for conductivity [5]. The addition of dispersants is reported to result in better dispersion and improved electrical and mechanical properties [11]. For the in situ synthesis of Si_3N_4–TiN composites, the TiN grain size in the composite seems to be related to the initial TiO_2 particle size [10]. Thus, it is important to reduce the aggregations of TiO_2 particles in the mixed slurry before the sintering process. Some researchers have discussed the electrostatic repulsion force for the dispersion of TiO_2 and Al_2O_3 particles in the suspensions with alkyl amines in various organic solvents [12,13]. Kakui et al. have reported that the steric repulsion between particles promotes a dominant dipersability and stability in non-aqueous suspension using polymer as the dispersant. In a non-aqueous solvent, an efficient dispersant

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often consists of the functional groups for the adsorption on a particle and the steric repulsive chain, which is long enough to overcome van der Waals attractive forces [14]. Thus, using appropriate molecular structure of the polymer dispersant and its additive conditions to obtain a high dispersion were determined in many systems [15–17].

In the previous work, Si_3N_4–TiN composites were prepared by in situ synthesis method. It was found that the secondary phase TiN grains, which formed from TiO_2 and AlN, distributed in grain-boundary phase throughout the sintered body. Furthermore, the smaller TiN grains in the composite are, the better the wear-resistance is [18,19]. The present work was focused on the investigation of the improvement of the microstructure of Si_3N_4–TiN composites in the presence of PEI dispersant with different molecular weight. PEI molecules coated on the surface of TiO_2 particles and protected the TiO_2 particles in the slurry from aggregations. It would be a practical and useful way to improve the dispersion of TiN grains in the Si_3N_4 matrix in Si_3N_4–TiN composites.

2. Experimental procedure

2.1. Preparation of TiO_2 suspension

Polyethyleneimines (PEI, Nippon Syokubai Co., Ltd.) were used in this study as polymer dispersants with multi-amine functional groups to disperse TiO_2 (P-25, Degussa, BET surface areas: 46 m^2/g, average particles size is 200 nm) in advance. PEIs with molecular weights of 300, 1200 and 10,000 were used in the system. 5.0 g TiO_2 powder was mixed in ethanol containing 0.10 g (or 0.15 g, or 0.20 g) of PEIs with different Mw and then ball-milled for 24 h.

2.2. Preparation of Si_3N_4–TiN sintered bodies

Si_3N_4 (SN-E-10, Ube Industries, Ltd.), Y_2O_3 (RU-P, Shinetsu Chemical Co.), Al_2O_3 (AKP-30, Sumitomo Chemical Co., Ltd.), AlN (F-Grade, Tokuyama Corp.) was added in the TiO_2 dispersion. In the mixed slurry, Si_3N_4, Y_2O_3, Al_2O_3, TiO_2 and AlN powders were weighed at 92:5:3:5:5 (wt%) ratio. The mixture was mixed by ball-milling for another 96 h to get the homogenous dense slurry. After drying and addition of binder, it was molded into Ø 15 × 7 mm by uniaxial pressing and cold isostatic pressing. The green bodies were dewaxed at the temperature of 500 °C in air to remove the organic compounds and PEI dispersant, and then they were subjected to 0.9 MPa at 1800 °C for 2 h in nitrogen atmosphere.

2.3. Characterization of sintered bodies

The densities of the sintered samples were measured according to Archimedes principle. XRD was used to examine the phase composition of Si_3N_4–TiN composite (Rigaku D/MAX rB). The distribution of TiN grains in the Si_3N_4–TiN composite was identified by back-scattered SEM observation (JEOL JXA 8100).

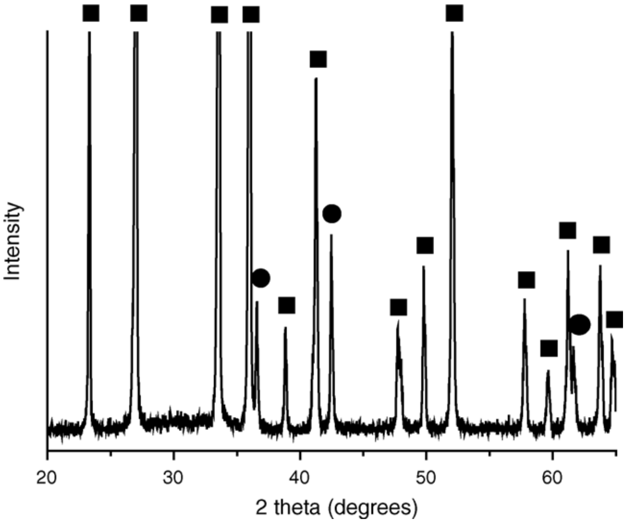


Fig. 1. XRD of Si_3N_4–TiN composite.

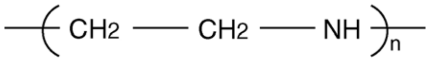
3. Results and discussion

In the Si_3N_4–TiN composites, Ueno et al. surveyed the "in situ" formation of TiN grains in Si_3N_4 matrix from the powder mixture of TiO_2 and AlN [20]. They confirmed that the formation reaction of TiN through the reaction (1) occurred from 1150 to 1450 °C, before the Si_3N_4 matrix sintering. AlN was intended to act as a nitrogen supplier and an oxygen acceptor. Al_2O_3 was one of reaction products, and became one of the sintering agents. It was assumed that the released oxygen to be captured by surrounding carbon mold or Si_3N_4 matrix to form CO or SiO_2.

$$2TiO_2(s) + 2AlN(s) = 2TiN(s) + Al_2O_3 + \tfrac{1}{2}O_2(g) \qquad (1)$$

Fig. 1 showed the X-ray diffraction patterns of Si_3N_4–TiN composite. The distinct peaks assigned to cubic TiN (●) and β-Si_3N_4 (■) could be detected and no peaks of other substance appeared. This indicated that raw TiO_2 particles were completely converted to TiN grains in the sintering procedure.

For the in situ nitridation of TiO_2 to TiN, the size and morphology of TiN grains were significantly influenced by those of original TiO_2 particles [18]. Thus, the size and morphology of TiN grains in Si_3N_4–TiN composite were closely related to those of original TiO_2 particles in the mixed powder before the sintering. On the other hand, mechanical properties of Si_3N_4–TiN composites are strongly dependent on its microstructure. It is important to prepare well-dispersed powder mixtures in the Si_3N_4–TiO_2–AlN–Al_2O_3–Y_2O_3 system, which upon densification would yield dense compacts with homogeneous microstructure. To select the optimum polymer dispersant, the combination between the surface characteristics of the powder materials and organic solvent needs to be



$$-\!\!\left(CH_2 - CH_2 - NH\right)_n\!\!-$$

Fig. 2. The molecular structure of polyethyleneimines (PEI).

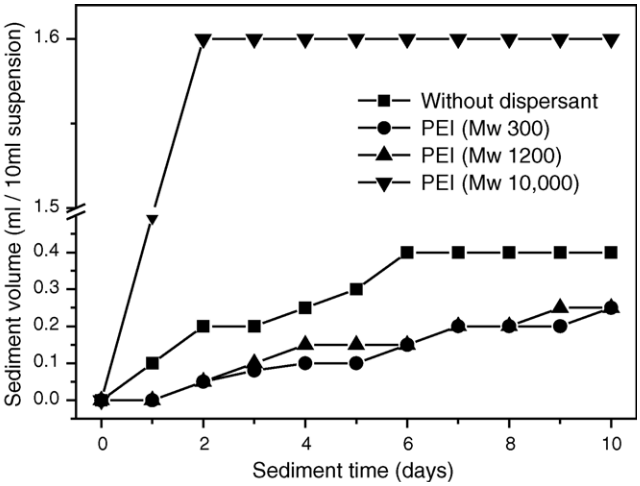


Fig. 3. Sediment of TiO_2 suspensions with 0.15 g PEIs, which ball-milled for 24 h.

considered [14]. Polyethyleneimines (PEIs) with multi-amine functional groups were used as dispersant for TiO_2 powder (P-25) in the Si_3N_4–TiO_2–AlN–Al_2O_3–Y_2O_3 system according to ref. [14]. Fig. 2 illustrated the scheme of molecular structure of PEIs.

Usually the stability of ceramic suspension is determined by measuring the sediment volume versus the sediment time. During the ball-milling process, the ‘‘larger’’ TiO_2 agglomerates fractured into the ‘‘smaller’’ particles. The PEI molecules are coated on the surface of the ‘‘smaller’’ TiO_2 particles, and the steric repulsive chain is long enough to overcome van der Waals attractive forces and prevent them from aggregating again. PEI modified TiO_2 particles repulsed each other in the suspension. From the results of Fig. 3, the particles modified by PEI with Mw 300 or PEI with Mw 1200 were more stable in the suspension. However, the particles modified with PEI with Mw 10,000 precipitated so fast, which maybe caused by the bridging effect between high molecular weight polymers adsorbed TiO_2 particles.

Table 1
Density of the sintered Si_3N_4–TiN composites

Code of samples	PEI’s Mw	Dispersion TiO_2 in advanced (h)	Amount of PEI	Density (%)
0		0	0	98.0
P1-1	1200	24	0.10	98.0
P1-2		24	0.15	97.9
P1-3		24	0.20	98.1
P2-2	10000	24	0.15	98.3
P3-1	300	24	0.10	98.2
P3-2		24	0.15	98.2
P3-3		24	0.20	98.1

The influences of PEI molecular weight and PEI/TiO_2 weight ratio on the relative density of the sintered Si_3N_4–TiN composites with the amount of PEI of TiO_2 in the suspension were summarized in Table 1. As can be seen from Table 1 all composites were close to the theoretical density after sintering.

The back-scattered SEM micrographs of the polished surface of Si_3N_4–TiN composites were presented in Figs. 4–6. Bright TiN grains were homogenously distributed in a darker matrix Si_3N_4, all TiN grains were of a submicron average size.

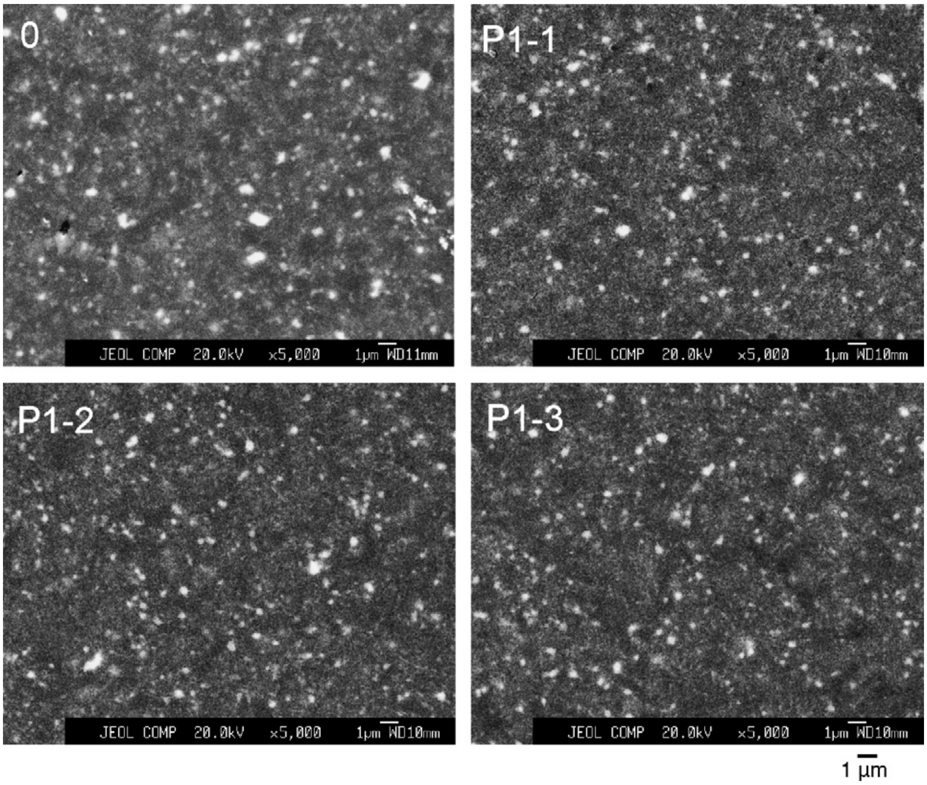


Fig. 4. Back-scattered SEM micrographs of sintered Si_3N_4–TiN composites (0, P1-1, P1-2, P1-3).

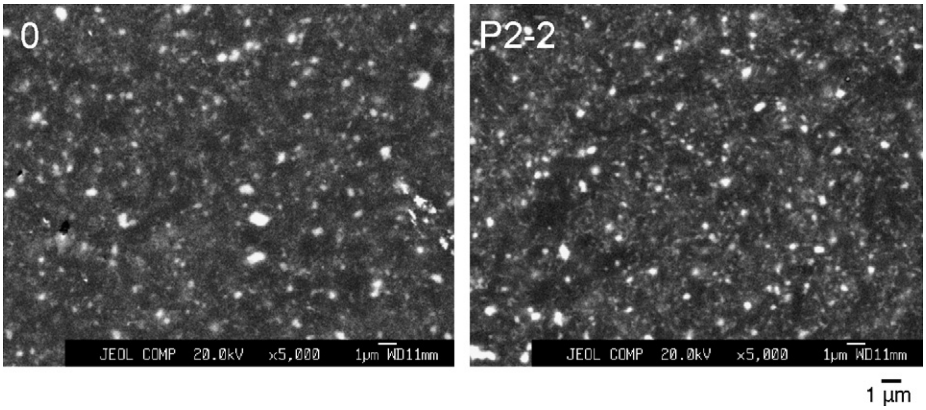


Fig. 5. Back-scattered SEM micrographs of sintered Si_3N_4–TiN composites (0, P2-2).

As shown in detail in previous work, it was found that TiN particles with spherical shape existed at the grain boundary of the sintered body, which seemed to be formed from raw TiO_2 [16]. For in situ synthesis of Si_3N_4–TiN composite, microstructural observations indicated that submicron-size TiO_2 particles yielded TiN with almost the same size [20]. It could also be seen in Figs. 4–6, that, PEI dispersant of TiO_2 (P-25), incorporated in the starting mixture powder, played an important role in the microstructure development. The particle size of original TiO_2 (P-25) was about 200 nm, while it was difficult to break the aggregations of P-25 because of the restricted ball-mill conditions. Clearly, the absence of further aggregations of TiO_2 particles was related to the steric repulsion between TiO_2 particles with adsorbed PEI layers in the suspension. However, with no addition of PEI, the size of TiN grain in the composite 0 was significantly larger than in the other composites grades.

Microstructures of composites (Fig. 4) were very much dependent on the added amount of PEI with Mw 1200 in TiO_2 suspension. As the contents of PEI with Mw 1200 increased in the mixture, it was expected that the microstructure be promoted due to the homogeneous distribution of TiN grains. TiN agglomerate, whose size was about 0.5 μm, could be detected in the microstructure of P1-1. However, their number decreased with increasing amount of PEI with Mw 1200 and at 0.20 g PEI with Mw 1200 addition the microstructure was

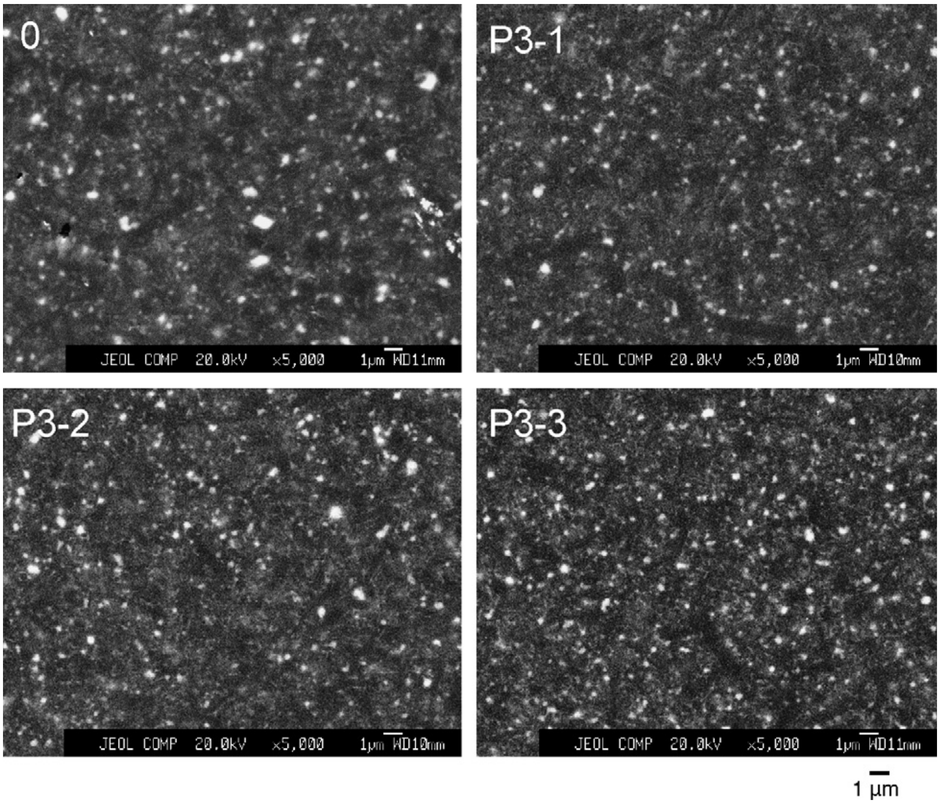


Fig. 6. Back-scattered SEM micrographs of sintered Si_3N_4–TiN composites (0, P3-1, P3-2, P3-3).

homogeneous with almost no agglomerates (P1-3 in Fig. 4), in which the average grain size of TiN was from 0.2 to 0.3 μm.

Although PEI with Mw 10,000 is too large to stabilize TiO_2 particles in the suspension, it could protect TiO_2 from aggregation in the slurry. As can be seen in Fig. 6, with the addition of 0.15 g PEI with Mw 10,000, the resulting microstructure of composite P2-2 improved compared to the composite 0. It was found that TiN grains with size ranging from 0.2 to 0.5 μm distributed throughout the sintered body.

Accordingly, homogeneous and agglomerate-free microstructures of Si_3N_4–TiN composites were obtained with the aid of PEI with Mw 300 (Fig. 5). The amount of PEI with Mw 300 was found to be less critical for microstructure homogeneity of Si_3N_4–TiN composites (P3-1, P3-2 and P3-3). Large TiN agglomerates disappeared compared to composite 0, TiN grains with 0.2–0.3 μm in diameter distributed throughout Si_3N_4 matrix.

Based on these results, it was expected that using PEI with Mw 300 to disperse original TiO_2 particles would result in a homogeneous microstructure with smaller TiN grains in Si_3N_4–TiN composites.

4. Summary

This study has developed a practical route suitable for the preparation of Si_3N_4–TiN composites with homogenous microstructures. Appropriate PEI dispersing raw TiO_2 powder would control the microstructure of Si_3N_4–TiN composites. In all cases, it was possible to obtain well-dispersed secondary TiN phase in the Si_3N_4 matrix phase in the presence of PEIs with different molecular weights and added amount of PEI. It is believed that the uniform distribution of TiN grains with 0.2–0.3 μm in diameter contributes to the improvement of the wear-resistance of Si_3N_4 ceramics.

Acknowledgements

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