Experimental and Computational Study of Grain Growth and Microstructures in AlN Composite Ceramics

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実験及び計算機による窒化アルミニウム複合焼結体での粒成長と微構造についての検討

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Grain growth of AlN-TiN composite ceramics was studied under conditions where the AlN/Al₂O₃/Y₂O₃ grain boundary phase is presumed to be liquid. It was found that the growth of AlN grains was strongly inhibited as the level of TiN additions increased. Compared to AlN, TiN particles showed very little grain growth under the conditions studied. AlN grain growth in both monolithic and composite systems proceeded at a rate of one-third the sintering time, and it was postulated that AlN grain growth proceeded by the "solution-reprecipitation" mechanism. Microstructure observation showed that TiN particles were present at grain boundaries and within AlN grains. Heat treatment of the composite resulted in a severe microstructural change in which the grain boundary phase was isolated at triple points of AlN grains. Computational studies of grain growth in the presence of both, a liquid phase and dispersoids, similar to the AlN-TiN composite system, were undertaken using Monte Carlo simulation based on the Potts model. The simulation effectively expressed the dependency of grain growth on the size and amount of dispersoid as well as predicting the inclusion of dispersoid particles into matrix grains. Adjusting the γ_{sl}/γ_{ss} value from 0.5 to 1.0 yielded microstructural changes that were similar to those observed upon annealing experiments.

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1. Introduction

In previous computational studies,^{1,2)} grain growth behavior in the presence of a liquid phase was examined using the Monte Carlo method. These simulations were generally effective in expressing the grain growth behavior of AlN within the yttrium-aluminate system. The simulation technique was considered a helpful method in enhancing the understanding of microstructural development in AlN and other liquid phase sintered ceramics.

AlN has several desirable physical properties that make it an important commercial material. Particularly valued is its high thermal conductivity that can approach its theoretical value of 320 W/mK.³⁾ Understanding the influence of compositional and processing variations on thermal conductivity has been the primary focus of previous AlN studies.⁴⁻⁸⁾ There have been relatively few investigations on the mechanical properties of AlN ceramics.^{9,10)} AlN has been considered as the ceramic substrate for high power semiconductor devices.¹¹⁾ However, better mechanical properties are being demanded for this application. AlN composites have the potential of offering the enhanced physical properties while maintaining its desirable thermal conductivity. While several combinations with AlN can be considered, TiN may be a good addition considering its high modulus

and strength. AlN-TiN composites therefore may offer the desired combination of properties.

The purpose of this study was to understand grain growth behavior and microstructural development in AlN-TiN composites and to generate basic information concerning the effectiveness of Monte Carlo based simulations in predicting grain growth behavior of more complex composite structures.

2. Experiment

2.1 Preparation of AlN-TiN composite ceramics

In these experiments, a commercial AlN powder (XUS35560, The Dow Chemical Company), produced by the carbothermic reduction method, was used. Oxygen and carbon contents of the AlN powder were 0.85 and 0.03%, respectively. Metallic impurities were relatively low, being 32, 111 and 44 ppm, respectively, of Fe, Ca and Si. The TiN powder used in the preparation of the AlN-TiN composites was also a commercial product (Japan New Metals Co., Ltd.). In addition to the 1.05% oxygen and 0.43% carbon, the major impurity for this TiN powder was 0.1% Fe. The AlN powder has a narrow particle size distribution with an average size of about 0.5 μ m, while TiN powder was somewhat coarser with an average size of 0.8 μ m. These powders were mixed by ball milling in ethanol with urethane coated steel balls. The TiN powder levels studied were 0, 5 and 10 vol%. Y₂O₃ powder was added to these powders as a sintering aid. The amount of Y₂O₃ was 5 mass% for AlN powder. The ball milling was done for 20 h and the slurry was vacuum dried in a vibration drier. After that, the mixed powder was uniaxially pressed at 24.5 MPa to disks having a diameter of 20 mm and thickness of about 5 mm. Then, the disks were isostatically pressed at 294 MPa. The obtained

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green compacts were placed on BN powder in a BN crucible. The BN crucible was next set into a carbon crucible whose inside was spray coated with a BN slurry. The compacts were heated at 10°C/min in a carbon furnace (FVPHP-R-10, Fujidempa Kogyo Co., Ltd.) to 1850°C and held at this sintering temperature for 1 to 20 h in a flowing nitrogen atmosphere. Some of the sintered samples were also heat-treated at 1800°C for 50 h. The setting and furnace conditions used in the heat treatment step were similar to the initial sintering operation.

2.2 Analysis of microstructures of AlN-TiN composite

The microstructures of sintered AlN-TiN composite were observed with a scanning electron microscope (SEM; S-800, Hitachi). SEM observation was done on polished cross sections of the samples. Grain size was defined as the maximum diameter of a given grain. After counting more than three hundred grains, the average grain size was obtained from the following equation:

$$\bar{x} = \sum(x_i) / n$$

where $\bar{x}$ is the average grain size, x_i is the grain size of i th grain, and n indicates the number of grain counted.

3. Simulation

3.1 Algorithm in the simulation

Previous papers^{1),2)} described the results of computational studies of grain growth and microstructural development in solid-liquid systems. For the current experiments, mass transfer between solid and solid was based on the Potts model developed by Anderson et al.,¹²⁾ while a random walk process was used to describe the diffusion through the liquid phase. The dispersoid particles were incorporated into the composite structure as part within the solid lattice and liquid phase. The initial particle size of the dispersoids was homogenous consisting of one of three specific diameters shown in Fig. 1. It was also defined that these dispersoid particles did not move during simulation.

3.2 Simulation conditions

In this simulation additional parameters, γ_{sp} , γ_{pl} , d_p and f_p , were needed to define this more complex multiple solid-liquid system. Values γ_{sp} and γ_{pl} are the mean interfacial energy between solid-dispersoid particle and between dispersoid particle-liquid, respectively. In the actual simulation, the interfacial energy ratios, γ_{sp}/γ_{ss} and γ_{pl}/γ_{ss} were the input parameters used. The dispersoid particle diameter, d_p , was one of three different diameters. Depending on the simulation, d_p consisted of either one, three or five cell diameters that corresponded to particles that consisted of either one, seven and nineteen cells, respectively. The fraction of dispersoid particles in the lattice, f_p , used in the simulations was 1, 5, or 10%. Also, the lattice size used was 200 × 200 cells and included 64 crystal orientations. These were the same conditions as used in the previous study.¹⁾ By assuming that the solid phases consisted of uniform and round

particles, the grain size of each phase in the simulated microstructures could be determined by counting the solid phase cell number.

4. Results and discussion

4.1 Grain growth behavior and microstructures in AlN-TiN composite

Figure 2 shows the microstructures of AlN-TiN composites containing 10 vol% of TiN that were sintered for 1 to 20 h at 1850°C. Comparing of the microstructures of AlN-TiN composite system with those of the system in the previous study,²⁾ TiN particles and grain boundary phase were found to be round and angular, respectively. The three components, AlN grains, TiN particles, and the yttrium-aluminate grain boundary phase are distinguished in these high contrast photomicrographs. AlN grains grew isotropically with the increase in sintering time, while TiN particles were essentially unchanged under these conditions. Large TiN particles, whose particle size was more than about 2 μm, were primarily present at the grain boundaries although small particles were included in AlN grains. Figure 3(a) shows the relationship of average grain size of AlN with sintering time and the corresponding growth rates for the three TiN levels studied. From the log/log plot in Fig. 3(b), it is observed that the cube of AlN grain size is proportional to the sintering time in each of the compositions. Based on these observations, it is estimated that AlN grain growth in the AlN-TiN composite system may also proceed by a "solution-precipitation" mechanism.^{7),13),14)}

The microstructure of the AlN-TiN composite heat-treated at 1800°C for 50 h is shown in Fig. 4. Grain boundary phases are isolated at the triple points of AlN grains after this heat treatment. As in earlier observations of monolithic AlN ceramics,²⁾ this dramatic microstructural change in the composite is considered to be caused by a shift in the γ_{sl}/γ_{ss} value under the employed heat treatment conditions. The γ_{ss} value, which means the grain boundary energy between AlN grains, is considered essentially same before and after heat treatment. Meanwhile, the γ_{sl} value, which means the interfacial energy between AlN grain and grain boundary phase, is considered to vary with the change of phase composition caused by, for example, the solution of AlN into the grain boundary phase or the precipitation from it. Min and Mitomo reported that the heat treatment of α-SiAlON brought the composition change of grain boundary phase and that the microstructures showed the isolation of grain boundary phase at triple points of matrix grains as observed in heat-treated AlN-TiN composite.¹⁵⁾ Further analysis of grain boundary phase will be helpful for verifying the change of γ_{sl}/γ_{ss} value during heat treatment.

4.2 Simulation

4.2.1 Effect of dispersoid size and amount on grain growth

In the computational study, the effect of dispersoid size on grain growth was examined. In these simulations, the amount of dispersoid particles was fixed at 5% and the diameter was changed from one to five cells. The parameters of γ_{sl}/γ_{ss} , γ_{ps}/γ_{ss} and γ_{pl}/γ_{ss} were set at 0.5, 1.0 and 2.0, respectively. The results of these simulations are shown in Fig. 5. In general, the presence of dispersoids inhibited grain growth of the matrix grains and as expected, the grain size increased with increasing number of MCS. However, as the size of the dispersoid particles increased, their effectiveness in inhibiting grain growth decreased dramatically. The average grain size for the simulation with 5 cell diameter dispersoids was essentially equivalent to the value generated for the baseline simulation. These simulation results showed that grain growth was effectively inhibited by the increase of the amount of dispersoid or/and the decrease of

Fig. 1. Dispersoid particles with different diameters of (a) one, (b) three and (c) five cell.

Fig. 2. SEM photomicrographs of microstructures of AlN-TiN composites sintered at 1850°C for 1–20 h.

Fig. 3. Grain growth of AlN and TiN in AlN-TiN composite.
(a) Relationship of AlN and TiN grain size with sintering time,
(b) Log-log plot of AlN grain size vs. sintering time.

dispersoid size and that especially the size of dispersoid had a large effect for the inhibition of grain growth.

Figure 6 shows the simulated microstructures after 1000 MCS for the baseline case and the three dispersoid sizes studied. In addition to obvious grain size differences discussed earlier, the dispersoid location for these microstructures are also different. While all three simulations contain examples of intragranular particles, their frequency is greatly influenced by the dispersoid cell diameter. The number of dispersoid particles contained within the matrix grains was in-

versely proportional to the size of the particles.

Figure 7 shows the effect of the amount of dispersoid particle on the average matrix size for the intermediate sized dispersoid simulations. Grain growth in these simulations decreased substantially with increasing dispersoid levels. Figure 8 shows the simulated microstructures with the three simulations. These results may suggest that it is the number of dispersoid particles rather than their size which has the greatest impact on the average matrix grain size.

Fig. 4. SEM photomicrograph of microstructure of heat-treated AlN-TiN composite.

Fig. 5. Grain growth of solid phase in simulated microstructures with different dispersoid size.

Fig. 6. Simulated microstructures with different dispersoid size (dispersoid amount: 5%, 1000 MCS).

Fig. 7. Grain growth of solid phase in simulated microstructures with different amount of dispersoid.

Fig. 8. Simulated microstructures with different amount of dispersoid (dispersoid diameter: 3 cell, 800 MCS).

4.2.2 Relationship of grain size with MCS

Figure 9 shows the simulated microstructures for the intermediate dispersoid at 5%, after four different MCS. As indicated earlier (Fig. 5), the grain size of the matrix increased with increasing MCS number. A log/log plot of grain size vs. MCS number is shown in Fig. 10. While there is some deviation from linearity that increases with dispersoid amount, the calculated slope was nearly one third, consistent with a "solution-reprecipitation" transport mechanism in a solid-liquid system. These observations were all consistent with the experimental results described earlier for the sintered AlN/TiN system.

4.2.3 Microstructural change with varying γ_{sl}/γ_{ss} value

In order to simulate the heat treatment experiments for the AlN-TiN composite and verify the influence of γ_{sl}/γ_{ss} on microstructural development, the γ_{sl}/γ_{ss} value was changed

Fig. 9. Simulated microstructures with the diameter and amount of dispersoid being 3 cell and 5%, respectively.

Fig. 10. Relationship of grain size with MCS number.

from 0.5 to 1.0. This value change was previously shown to have a dramatic influence on microstructural development in both the simulation and experimental results for monolithic AlN ceramics.²⁾ In the paper experimental results showed the increase of γ_{sl}/γ_{ss} value in heat-treated AlN ceramics from the measurement of dihedral angle between AlN grain and grain boundary phase. Moreover, in the previous computational study, the microstructural changes similar to observed upon heat-treated AlN ceramics were shown by varying γ_{sl}/γ_{ss} value from 0.1 to 1.0. So, the similar set up to γ_{sl}/γ_{ss} value in this study is considered suitable for simulation of the microstructural change in heat-treated AlN-TiN composite. The γ_{sl} and γ_{ss} values of AlN-TiN composite system are considered similar to those of the previous system²⁾ because these systems basically consisted of AlN grain and yttrium aluminate grain boundary phase.

Figure 11 shows that the microstructural change that resulted from this parameter modification for the 3 cell diameter, 5% dispersoid composition. While there was only a modest effect on the average grain size for this simulation, the liquid phase became more isolated at the solid grain tri-

Fig. 11. Simulated microstructures with changing γ_{sl}/γ_{ss} value 0.5 to 1.0.

ple points as the MCS number increased. This simulation was able to generally confirm the microstructural change observed in the AlN-TiN ceramic composite that was heat-treated at 1800°C for 50 h.

5. Conclusions

An experimental and computational study was done on grain growth and microstructural development in AlN-TiN composites. For the AlN-TiN composites, it was found that AlN grains grew isotropically and that the cube of grain size was proportional to the sintering time. TiN grain growth was very slow and changed little under the processing conditions studied. Large TiN particles more than about 2 μm were observed at grain boundaries and small ones within AlN grain. It was confirmed that TiN particles inhibited the grain growth of AlN and this effect increased as the amount of TiN increased. Heat treatment of sintered composite resulted in the isolation of the grain boundary phase at the AlN grain triple points.

The physical experiments were duplicated computationally by studying the effect of the amount and size of dispersoid particles on grain growth of the matrix phase in the solid-liquid-dispersoid system. The simulations effectively replicated the AlN-TiN experimental results. Grain growth of the solid phase was inhibited by the amount increase and size decrease of the dispersoid particles. Changing the γ_{sl}/γ_{ss} value in the simulation resulted in the isolation of the grain boundary phase at the grain triple points, which was also consistent with the performed experiments.

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