Fabrication of silicon nitride from a slurry containing cellulose nanofibers

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1. Introduction

Cellulose nanofibers (CNFs) are isolated wood-based fibers that are several nanometers in diameter and few micrometers in length. They exhibit extremely high strengths of a few GPa, as well as good dispersibility in water. Recently, CNFs have been commercialized, and their application areas continue to expand. However, only a few examples of their use have been reported thus far in the field of ceramic processing. CNFs seem to be useful in slurry or wet processes such as slip casting, tape casting, extrusion, and injection molding, where the above-mentioned properties of CNFs are advantageous. We expected the addition of CNFs into a ceramic slurry to yield benefits such as reducing the amount of organic binder, preventing sedimentation of the powders, increasing the viscosity, avoiding cracking of the consolidated body during drying, reinforcing the green body, etc. On the other hand, the addition of CNFs might have disadvantageous effects such as preventing densification, reducing the strength of the sintered body, etc. Therefore, any disadvantages must be evaluated prior to investigating the advantages.

In this study, the authors intended to examine the influence of adding CNFs into a slurry. In this regard, a silicon nitride sintered body was fabricated from a slurry containing CNFs. The viscosity of the slurry, its consolidation and densification behavior, as well as the microstructure and strength of the sintered body were examined.

2. Experimental procedures

The silicon nitride slurry was prepared based on a water-based slurry for tape-casting, and the CNFs were added to it. The CNFs used were "Rheocrysta", manufactured by DKS (Daichi Kogyo Seiyaku) Co. Ltd., Japan, and were purchased in the form of a suspension in water. The silicon nitride powder used here was SN-9S (Denka Co. Ltd., Japan), and had average and maximum particle sizes of 1.1 and 20 μm, respectively. The dispersant and organic binder were ammonium polyacrylate (A6114, Toagosei Co. Ltd. Japan) and urethane emulsion (DB21, Yukan Industry Co. Ltd., Japan), respectively. The slurry contained ~20 ppm sodium, which was from aqueous solution of CNFs. The amounts of the dispersant, binder, and CNFs given above reflect the solid contents in the liquid, whereas any water contributed by these components are included in the total water content. The volume fraction of the raw powders in the slurry was 35.0%. The slurry was mixed using a planetary centrifugal vacuum mixer without mixing media for 3 min. The mixing conditions were as follows; revolution rate: 2000 rpm, rotation rate: 1000 rpm, vacuum: 30 kPa. A slurry without CNFs, with a water content that was the same as in the slurry with CNFs, was also made for comparison. The viscosity of the slurry was measured by using a rotational viscometer.

The slurry with CNFs was poured into a non-water absorbptive silicone mold. After natural drying, a green body with approximate dimensions of 45 × 45 × 6 mm was obtained. It was subjected to a de-binder treatment at 500°C for 2 h in air, and subsequently sintered at 1800°C for 6 h in 0.5 MPa N₂ to form a sintered silicon nitride body. A similar silicon nitride body was also obtained following the same procedures from the slurry without CNFs.

The microstructures of the sintered bodies were observed by scanning electron microscopy (SEM). In addition, the crystalline phases present were investigated via X-ray diffraction (XRD) analysis. Flexural strength measurements were conducted in the 3-point bending condition with a 30 mm span, using a 3.5 × 2.5 × 40 mm rectangular shaped specimen.

3. Results and discussion

The viscosities of the slurries are depicted in Fig. 1. The slurry with CNFs showed a higher viscosity than the one without CNFs. It has been reported that the addition of CNFs into water, even at small levels of only 0.1%, increases viscosity. The silicon nitride slurry with CNFs showed a similar behavior. The viscosity...
Ities of both slurries (with and without CNFs) decreased at higher shear rates, i.e., they showed a shear rate dependence similar to that exhibited by a pseudo-plastic fluid. The viscosity of the slurry with 0.2 outer mass% of CNFs appeared to be the upper limit in terms of being able to pour the slurry into the mold. In other words, further addition of CNFs makes it difficult to pour the slurry.

The relative densities of the dried green bodies with and without CNFs were 47.1 and 49.2%, respectively. These values were calculated based on the shrinkage during sintering and the density of the sintered body. Thus, the relative densities above correspond to the raw powders. The volume due to the binder and CNFs was considered as belonging to the volume of the pores. The sintered bodies fabricated from the slurries with and without CNFs (hereafter called 'with CNFs' and 'without CNFs'), possessed absolute densities of $3.142 \times 10^3$ and $3.193 \times 10^3$ kg m$^{-3}$, respectively. Their relative densities were 95.2 and 96.8%, respectively, if the full density of the sintered body was taken to be $3.30 \times 10^3$ kg m$^{-3}$. These relative densities are summarized in Fig. 2. As can be seen from the above data, the addition of CNFs slightly reduced the densities of the green and sintered bodies.

The microstructures of the sintered bodies with and without CNF are shown in Fig. 3. They exhibit rod-like grains and glassy grain boundary phases similar to those observed in typical sintered silicon nitride. No carbide phase, which might have formed after sintering due to carbon from the CNFs or organic binder remaining after the de-binder treatment, was found. A number of pores, with sizes less than 20 µm, were found in both sintered bodies. The existence of the pores caused a slight decrease in the density of the sintered bodies relative to the full density. Since the pores were found in both sintered bodies, the addition of CNFs was not the reason for the pore formation.

The most probable reason for the formation of the pores is considered to be large particles in the raw silicon nitride powder. The maximum particle size was \(~20\) µm, and is therefore comparable to the pore size in the sintered bodies. The existence of large particles with sizes approximately more than 10 µm leads to the formation of pores of comparable size. When the slurry was
mixed by the planetary centrifugal vacuum mixer without mixing media, the large particles remained intact after mixing due to insufficient pulverization, causing the formation of pores. Moreover, the slightly lower density of the sintered body with CNF might be due to the higher viscosity of the slurry, which impedes pulverization.

The results of the XRD analysis is shown in **Fig. 4**. Only $\beta$-silicon nitride was detected as a crystalline phase in both sintered bodies. No carbide phase was detected. From the results of the SEM observations and XRD analysis, it can be concluded that both the CNFs and organic binder were well removed by the de-binder treatment.

The flexural strengths of the sintered bodies with and without CNF were 595 ± 27 and 598 ± 44 MPa, respectively. They are virtually identical, and are comparable to values observed in commercially available moderate grade silicon nitride. Therefore, the addition of ~0.2 mass% CNFs did not reduce the strength.

### 4. Conclusions

The effects of adding CNFs into a silicon nitride slurry were evaluated. The addition of only 0.2 mass% of CNFs drastically increased the viscosity of the silicon nitride slurry. Nevertheless, the slurry with CNFs could be poured into a mold. The sintered silicon nitride was successfully fabricated from the above slurry via drying, de-binder treatment, and sintering. For comparison, silicon nitride was also fabricated from a slurry without CNFs.

The microstructures of the sintered bodies were similar to that typically seen in silicon nitride. No crystalline phases except for silicon nitride were found. The densities of the sintered bodies with and without CNFs were $3.142 \times 10^3$ and $3.193 \times 10^3$ kg m$^{-3}$, respectively. While the densities were slightly lower than the full density, this was not due to the addition of CNFs, but rather due to the creation of pores from residual large particles in the raw silicon nitride powder. The flexural strengths of the sintered bodies with and without CNFs were 595 ± 27 and 598 ± 44 MPa, respectively. These were similar to that of moderate grade silicon nitride.

In conclusion, the addition of CNFs into the slurry drastically increased its viscosity. However, the CNFs were well removed by the de-binder treatment. Therefore, effects of adding CNFs on the microstructure, density, and strength of the sintered body were negligible. A silicon nitride body with properties similar to those of a typical moderate grade sample could be obtained.

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