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AMMONIA FORMATION CAUSED BY THE PRESENCE OF WATER IN THE WET GRINDING OF SILICON NITRIDE POWDER

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Translation of "Si_3N_4 no shisshiki Funsai ni Okesu Suikuanc Kango to NH_3 Seisei", Yogyo Kyokaishi, Vol. 91, No. 8, 1983, pp. 386-388.

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16. Abstract

Si_3N_4 powder (amorphous, α-, and β-Si_3N_4) was mixed with MeOH containing 8.87 mol. % H_2O and ground. The NH_3 generation rapidly increased after a grinding time of 100 hours.

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AMMONIA FORMATION CAUSED BY THE PRESENCE OF WATER IN THE WET GRINDING OF SILICON NITRIDE POWDER**

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Silicon Nitride (Si_3N_4) sintered material was chosen as one of the high-temperature, high-strength structural materials, and studies of the control of the raw material powder [1], preparation of the sintered body (finding the proper assistant [2], hot press [3], high pressure sintering [4], fracture toughness and oxidation at high temperature have been performed. In order to obtain highly efficient ceramics as a structural material, it is generally necessary to use a raw material powder which is highly purified and controlled. Among the ceramic manufacturing processes, a method of grinding or pulverizing raw material powder and improving its powder characteristics and improving the characteristics of the sintered body is often used. The writers -are going to report here that a mechanochemical reaction of Si_3N_4 raw material powder from a grinding process was investigated and some new information was obtained.

α-Si_3N_4 and β-Si_3N_4, and amorphous (Am)-Si_3N_4, which have three crystal structures, were used for the Si_3N_4 raw material powder. The concentrations of metallic impurities (Al, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Ti, V, Zn) by ICP (inductive coupling plasma) emission analysis and atomic absorption analysis were almost all less than 10 ppm, except for 100 ppm of Fe. Furthermore, the α molecular ratio of α-Si_3N_4 sample was measured as 86% by using a α-β molecular ratio assay curve [6] from the integral strength ratio of powder X-ray analysis.

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*Numbers in margin indicate foreign pagination.

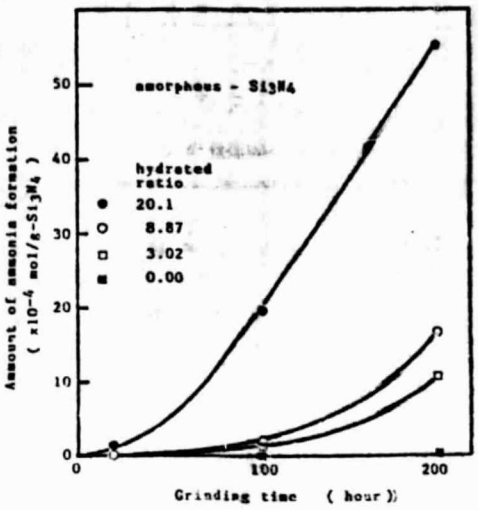
**Presented May 30, 1983.

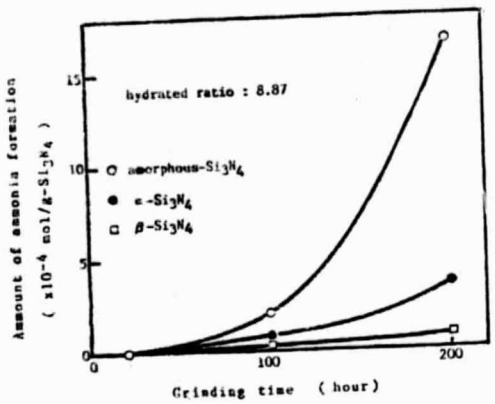
A glass container was filled with Si_3N_4 powder for preprocessing under an atmosphere of nitrogen in a glove box (P.A.C.E. chamber) manufactured by Lab-Line Company) and the air was removed by vacuum for an entire day and night at 400°C. After that 15 g of the powder, which was vacuum processed, was weighed in a glove box and combined with methanol of various moisture contents (212 g) in the chamber of a vibrating ball mill under an atmosphere of nitrogen, and wet grinding was performed. The materials for the chamber and ball which were used was Si_3N_4. 5 µl solvent was withdrawn with a microsyringe from the small hole (sealed by silicon rubber) which was made in the chamber before every scheduled grinding time (20 hours, 100 hours and 200 hours) and analyzed by gas chromatography. The gas chromatographic analysis was performed with He carrier gas by using a chromosorb 103 and PEG 1000 column at 110°C. Furthermore, the measurement of the specific surface area of Si_3N_4 was performed by the BET method with nitrogen gas adsorption and the sample before grinding (original) and 200 hours after grinding was measured. The results of this are shown in Table 1.

sample	original (m^2/g)	200 hour grinding (m^2/g)
amorphous-Si_3N_4	318.4	282.0
α-Si_3N_4	13.8	99.0
β-Si_3N_4	2.35	79.3

According to Table 1, it is assumed that the specific surface area of Am-Si_3N_4 is very large, and active. Furthermore, the specific surface area after 200 hours of grinding decreases for Am-Si_3N_4, but a remarkable increase was recognized for α-Si_3N_4, and β-Si_3N_4.

Figure 1 exhibits the relationship between the degree of ammonia formation and grinding time in the case of various amounts of included moisture.





It is understood that there is a tendency for the degree of ammonia formation to increase nearly proportional to the moisture content. Therefore, it is assumed that the ammonia formation reaction in Si_3N_4 has a close relation with the water concentration. Furthermore, ammonia was not detected during grinding by purified methanol, and this shows that ammonia formation is not from a reaction which is related to methanol but from the small amount of water which is included.

Figure 2 exhibits the relationship between ammonia formation amount per unit mass of Si_3N_4 and grinding time for three kinds of Si_3N_4 in the case when methanol of a moisture content of 8.86 mol % ($H_2O/(H_2O + CH_3OH)$ x 100 (mol/mol) was made as a solvent.

According to Figure 2, there is a tendency for the amount of ammonia formation to increase from a grinding time of 100 hours and it is considered that a delay phenomenon exists in a surface reaction. And also it is considered that the surface reaction proceeds when a sufficient amount of water has been adsorbed by the active sites on the new surfaces which have appeared from grinding and which have a high specific area, and ammonia was formed. If the ammonia formation amount per Si_3N_4 unit surface area is found with Table 1 and Figure 2, Am->α->β-Si_3N_4 . This shows that as Si_3N_4 has a higher and steadier temperature, activity toward ammonia formation reaction is lower.

Processing powder by sintering gives a large influence toward the characteristics of the final products and especially in the case when an amorphous powder is processed, great attention is required. Ammonia formation suggests that the surface of the Si_3N_4 powder is being changed to heterogeneous material. Because of that, sufficient attention must be paid toward water in the ceramic manufacturing process. Furthermore, also in the high temperature stable type β-Si_3N_4 if it is considered that ammonia is formed by grinding, service condition of Si_3N_4 as a structural material must be chosen carefully, especially for heat resistance and corrosion resistance.

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