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RELATION BETWEEN MICROSTRUCTURAL HETEROGENEOUS SURFACE LAYER
AND NITROGEN PRESSURE DURING SINTERING
IN $\text{Si}_3\text{N}_4\text{-MgO-Al}_2\text{O}_3$ CERAMICS

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16. Abstract effects of N ₂ pressure (0.1 to 50 MPa) during sintering on the thickness of the microstructurally heterogeneous layer (MHL) formed near the surface of the compact, transverse-rupture strength, etc., were investigated for Si ₃ N ₄ -(10 to 20) mol% MgO-5.5 mol% Al ₂ O ₃ ceramics. The sintering temperature and time were 1973K and 3.6 ks, respectively. The N ₂ gas was introduced into the furnace at about 1273 K. When the compacts were sintered under a certain N ₂ pressure, for example, about 20 and 7 MPa for 10 and 15 mol% MgO, respectively, the evolutions of N and Si were suppressed, the thickness of the MHL became very small and at the same time the strength of the surface layer of the compact (which was normally less than that of the inside in the case of 0.1 MPa) became nearly the same value as that of the inside. At the higher pressure, the strength of both surface layer and the inside decreased considerably. Some discussion was made on these results.					
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I. Introduction

According to the results of the investigation of $\text{Si}_3\text{N}_4\text{-MgO-Al}_2\text{O}_3$ ceramics manufactured through sintering in 1 atmosphere nitrogen gas (N_2) by these authors [1], a microstructurally heterogeneous layer (maximum thickness of 1 mm) generally developed in the surface of the sintered body based on the degassification (denitrification, desilicidation) during sintering, generally markedly reducing the strength of the surface of the sintered body compact to less than that of its interior. Consequently, when an attempt is made to utilize this type of compact, it becomes necessary to remove a great deal of the compact's surface through grinding, etc.

Since it is believed that the above-mentioned degassification can be controlled by increasing the pressure of the N_2 during sintering [2], it is anticipated that the development of a microstructurally heterogeneous layer could be controlled, and the strength of the surface of the compact could be made equal to the that of its interior by sintering in high pressure N_2 . A basic investigation of these points was conducted in this research.

* Numbers in the margin indicate pagination in the foreign text.

II. Preparation of Samples and Methodology of Testing

Si_3N_4 (Starck H1, 0.7 μm particle size, ratio of alpha- Si_3N_4 = 94%), MgO (0.2 μm), and Al_2O_3 (0.5 μm) similar to that of a previous report [1] were combined using a wet-process bowl mill and used as the base powder, then, after drying, a lubricant (camphor, to 3% of the powder) was added to the mixture, after which, the powder was molded using a metal mold. Si_3N_4 - (10,15,20) mol% MgO-5.5 mol% Al_2O_3 (Si_3N_4 -(3.1 to 6.8) mass% MgO-(4.4 to 4.7) mass% Al_2O_3) compacts (dimensions = (4.2 to 5.2) x + 10 x 25 mm³) were then manufactured using HIP equipment (manufactured by Kōbe Seikōjo Co., Inc.) under conditions of 0.1 to 50 MPa N_2 , 1973 K x 3.6 ks. These compacts were placed into a graphite crucible during sintering, but the surfaces of the samples were coated with a powder mixture of BN+ Si_3N_4 +MgO as a means to control reaction between the samples and the graphite. The interior of the furnace was maintained as a vacuum up to 1273 K, at which point, and as the temperature rose above that, N_2 was introduced at a constant pressure into the interior of the furnace and that pressure maintained until sintering was completed. The heating and cooling rates were 0.17 and 0.25 Ks⁻¹, respectively.

First, the microstructure of the cross-sectioned surfaces of the resultant compacts were observed under an optical microscope, their composition analyzed by XMA and their apparent phase determined through X-ray diffraction. After these analyses were completed, the transverse-rupture strength (representative grinding amounts were 0.05 mm and 1.0 mm. The dimensions of the

finished samples in both cases were approximately $4 \times 8 \times 25 \text{ mm}^3$, with a span of 20 mm) and Vickers hardness of the compacts was measured. After transverse-rupture fracturing, the defects in the samples which caused their fracturing were investigated [1,3-5]. Particular attention was paid to differences between the surface region and the interior of the compacts during all of these observations, analyses and measurements.

III. Test Results and Considerations

The effects of N_2 pressure inside the sintering furnace on the percentage of shrinkage in the compacts is shown in Figure 1. /29

Shrinkage in each of the compositions generally increased initially accompanying increases in N_2 pressure, reaching maximum values at certain N_2 pressures (approximately 20 or 7 MPa for 10 and 15 mol%, and less than 5 MPa for 20 mol%). It was

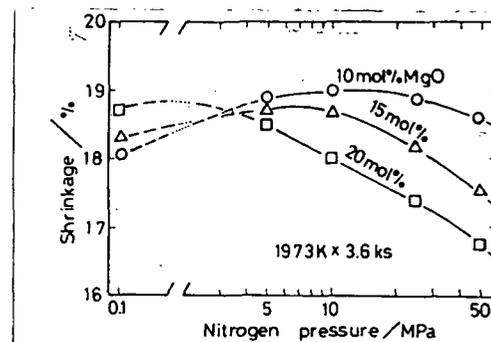
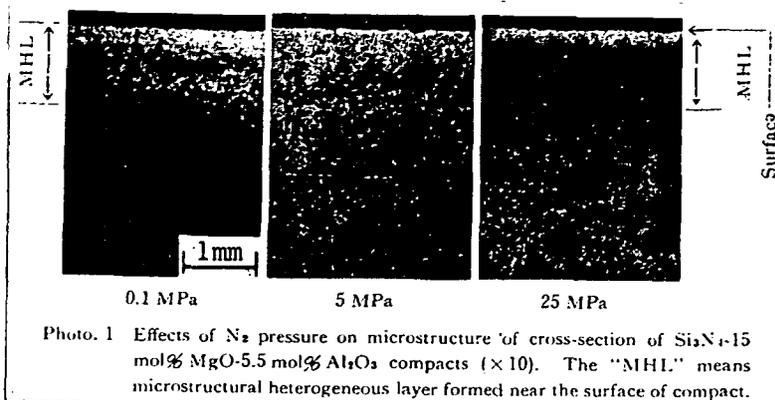


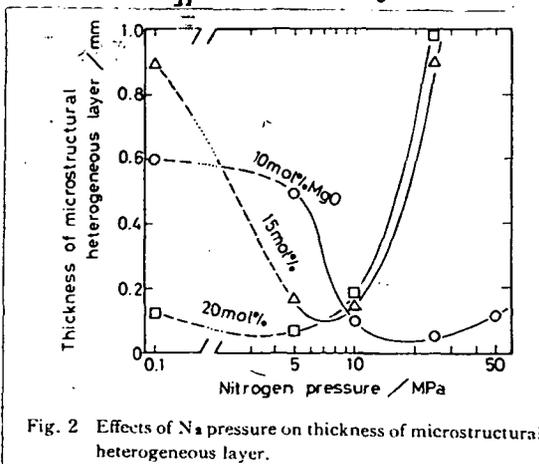
Fig. 1 Effects of nitrogen (N_2) pressure during sintering on shrinkage of Si_3N_4 -(10~20) mol% MgO-5.5 mol% Al_2O_3 compacts.

discovered that this shrinkage then decreased accompanying further increases in gas pressure beyond these points.

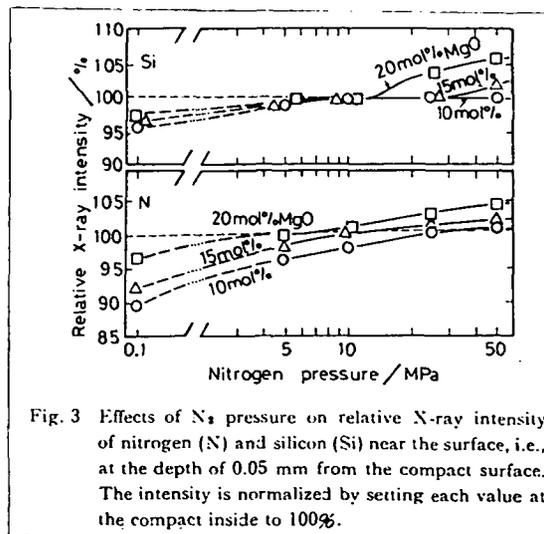
Examples of the effects of N_2 pressure on the microstructure of the cross-sections (X10) of 15 mol% MgO compacts are shown in Photograph 1 (next page). It can be seen from these that the condition of the microstructurally heterogeneous layer (MHL) is changed by N_2 pressure. The effects of N_2 pressure on the thickness (d_L) of the microstructurally



heterogeneous layer in each of the compacts are shown in Figure 2. In the 10 and 15 mol% MgO compacts, d_L initially decreased accompanying increases in the N_2 pressure, and then increased again after reaching minimum values at approximately 20 and 7 MPa, respectively. Meanwhile, the d_L for the 20 mol% MgO small at low N_2 pressure, but grew rapidly at pressures greater than approximately 10 MPa.



Results of the XMA analysis of compact cross-sections are shown in Figure 3. Values along the vertical axis were arrived at by dividing the characteristic X-ray intensity of nitrogen and silicon near the surface (at a depth 0.05 mm from the surface) of the compacts by the respective X-ray intensities



at the center of the compacts. From this, it was discovered that, while there was considerable denitrification and desilicidation near the surface of the compacts at low N_2 pressures [1], the amount of that denitrification and desilicidation decreased as the N_2 pressure was increased, and that the amount of nitrogen and silicon at the surface of the compact became nearly equal to the amounts in the interior under a certain N_2 pressure, nitrification and silicidation actually occurring in the surface of the compacts as the N_2 pressure reached higher levels.

From the results in Figure 2 and Figure 3, above, it can be seen that the development of microstructurally heterogeneous layers in sintered compacts is controlled under N_2 pressures at which the amounts of nitrogen and silicon in the surface and those amounts in the interior of the compacts become equal. This type of N_2 pressure is considered to be the equilibrium dissociation N_2 pressure (expressed as P_e) of the sintered body at the sintering temperature (1973 K). In other words, the progress of the reaction which causes denitrification and desilicidation during sintering in 0.1 MPa (normal pressure) N_2 , believed to be the reaction, for example, $Si_3N_4 + 3SiO_2 \longrightarrow 6SiO + 2N_2$ [6], is suppressed by increasing the N_2 pressure towards P_e , causing denitrification and desilicidation to become more difficult, consequently, suppressing the development of a microstructurally heterogeneous layer. Then, it is believed that as the pressure is increased to above this point (P_e), the reaction opposite from the above formula evolves and

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nitrification and silicidation occur, developing a microstructurally heterogeneous layer which is essentially different than that developed in low N_2 pressure situations. In this instance, the source of silicon for silicidation is believed to be the Si_3N_4 in the coating powder mixture on the surface of the test material.

Photograph 2 shows the microstructure of the interiors of the compacts at high magnification than in Photograph 1. It can

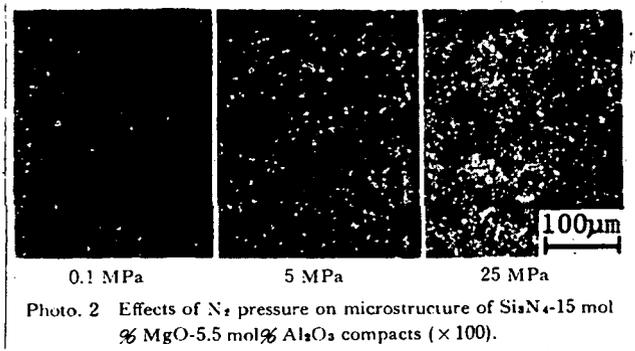


Photo. 2 Effects of N_2 pressure on microstructure of Si_3N_4 -15 mol % MgO -5.5 mol % Al_2O_3 compacts ($\times 100$).

be seen from these that a white phase (this is $MgAl_2O_4$ spinel at 0.1 MPa [1]) has developed in the compacts, which white phase increases accompanying increased N_2 pressure. These photographs are abridged, but the microstructures of the surfaces were nearly the same as those of the interiors at N_2 pressures of 0.1 to 5 MPa, the amount of this white phase becoming considerably great on the surfaces at pressures of 25 MPa and greater. Meanwhile, the Si_3N_4 granulation was slightly rougher in the surfaces of the compacts than in their interiors at low N_2 pressures [1], but at N_2 pressures where microstructurally heterogeneous layers began to disappear and higher, localized differences in granulation also became practically non-existent. In addition, Si_3N_4 granu-

ation [1] inside the compacts was virtually unchanged by the N_2 pressure (approximately 1.5 to 2.5 μm in the 10 and 20 mol% MgO compacts, respectively). The bound-phase domain (the region in which Mg_2SiO_4 forsterite displays unified crystal orientation [5]) was equally unclear in the 10 mol% MgO at both high pressures and at 0.1 MPa [1], but it was determined that its dimensions in the 15 and 20 mol% MgO compacts tended to become slightly rougher as the pressure increased.

Besides β' - Si_3N_4 (β - Si_3N_4 in solid solution with aluminum and oxygen) and α - Si_3N_4 being detected through X-ray diffraction as apparent phases, regardless of the N_2 pressure, traces of Mg_2SiO_4 and $MgAl_2O_4$ were also detected. The relations between the amount of $MgAl_2O_4$ found among these phases and the N_2

pressure are as shown in Figure 4. In the case of 10 mol% MgO, there was virtually no visible difference in the amounts of $MgAl_2O_3$ in the surface and the interior of the compact at any N_2 pressure, but at 15 and 20

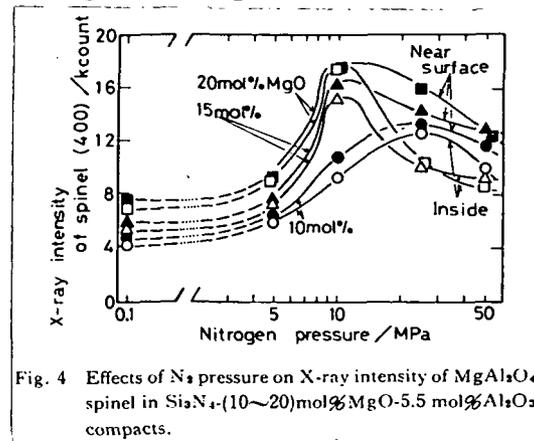


Fig. 4 Effects of N_2 pressure on X-ray intensity of $MgAl_2O_4$ spinel in Si_3N_4 -(10~20)mol% MgO -5.5 mol% Al_2O_3 compacts.

mol%, as the pressure reached approximately 10 MPa and higher, the surface developed greater amounts. Also, these amounts increased in all of the compositions, regardless of place, up to 10 to 25 MPa, and then decreased at pressures greater than that. Through this, it was assumed that the white phase in the above-mentioned microstructure would have to have been $MgAl_2O_4$, regardless of the N_2 pressure. Incidentally, there is not

necessarily a good correlation between the effects of N_2 pressure on the amount of $MgAl_2O_4$ and the effects of N_2 pressure on the above-mentioned microstructurally heterogeneous layer or on denitrification and desilicidation, but this point was not fully understood. In addition, the amount of Mg_2SiO_4 was virtually unchanged by the N_2 pressure, while the amount of β' - Si_3N_4 decreased ($\beta'/(\alpha + \beta')$ went from approx. 100% to 50 to 70%) with increases in N_2 pressure from 0.1 MPa up to 10 to 25 MPa and then increased (up to 90%) at pressures over these levels.

The effects of N_2 pressure on transverse-rupture strength are shown in Figure 5. In this testing, compacts were used in which the amounts ground from the compact surface (t_1) were either 0.05 mm or 1.0 mm. The transverse-rupture strength when $t_1 = 0.05$ mm (namely, the surface transverse-rupture strength) was remarkably low at lower N_2 pressures, compared to when $t_1 = 1.0$ mm (namely, the interior transverse-rupture strength), but it was discovered that as the N_2 pressure was increased, the difference between the two strengths decreased, becoming practically non-existent when the N_2 pressure reached P_e (namely, the value at which virtually no MHL develops, see Figure 2). Meanwhile, the transverse-rupture strength when $t_1 = 1.0$ mm was virtually unchanged, or was increased only slightly, by

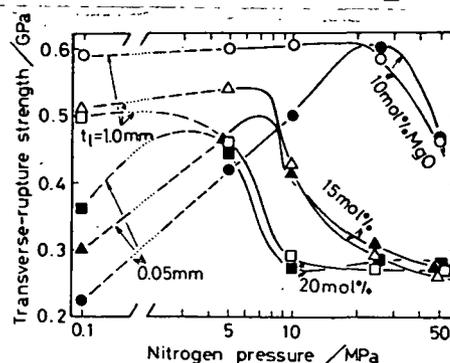


Fig. 5 Effects of N_2 pressure and t_1 on transverse-rupture strength of compacts. The " t_1 " is the thickness of the surface layer removed by grinding with diamond wheel (#150).

strength), but it was discovered that as the N_2 pressure was increased, the difference between the two strengths decreased, becoming practically non-existent when the N_2 pressure reached P_e (namely, the value at which virtually no MHL develops, see Figure 2). Meanwhile, the transverse-rupture strength when $t_1 = 1.0$ mm was virtually unchanged, or was increased only slightly, by

increases in the N_2 pressure, as long as the N_2 pressure remained in the range below P_e . In other words, it is clear that compacts of both homogeneous microstructure and uniform strength can be obtained by performing sintering in N_2 of somewhat higher pressure than generally used, thus yielding nearly the anticipated results.

In the case of high N_2 pressure, as well as 0.1 MPa N_2 [1,5] and most other cases, the defects which became the source of fracturing in the compacts were pores (regions in which Si_3N_4 grains were present, but only the binding phases were missing [5]). The effects of N_2 pressure on the average size (diameter) of the defects which became fracture sources are shown in Figure

6. In comparing the sizes of defects in the $t_1 = 0.05$ mm and 1.0 mm compacts, the sizes were larger in the $t_1 = 0.05$ mm at low N_2 pressure [1], but as the N_2 pressure was increased, the difference in sizes decreased

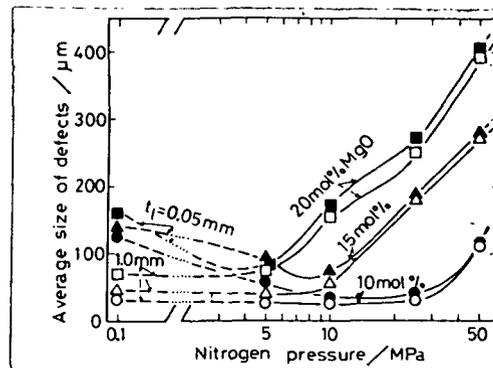


Fig. 6 Effects of N_2 pressure on the average size of defects (pore) acting as fracture source.

until they became nearly equal at around P_e . Then, as the N_2 pressure was increased further, the defect dimensions increased rapidly, regardless of the value of t_1 . Thus, from Figures 5 and 6, it can be seen that transverse-rupture strength increases relative to decreases in the size of the defects, showing highly correlative changes in the two measurements.

Though the reasons for the changes in the size of the pores which became the causes of fracturing, as explained above, are

not necessarily clear, the thoughts of the authors on this subject are as follows. First, the fact that the size of the pores in the surface or MHL of the compacts was greater than in the interior when N_2 pressure inside the sintering furnace (P_a)' is lower than P_e was believed to be due to the following: namely, that these micropores increase in size since the pressure of the gasses (P_e) which developed based on the above-mentioned reaction and are confined within these pores, which pores are found in the micron order between the Si_3N_4 grains, is greater than the compression strength of the micropores ($P_a = 2\gamma/r$; wherein $2\gamma/r$ is the so-called surface stress, γ being the surface tension of the liquid phase and r being the radius of the pore)[8] when P_a is low. It is also believed that these micropores grow into macropores through the exchange of gasses between pores (one type of Ostwald growth [9]) and/or growth based upon a merging mechanism among the pores [8], resulting in a decrease in the number of pores together with an increase in the dimensions of the pores, which accompany this gas pressure-based growth. At this point, liquid phase must be forced toward the surface of the compact because of the increased volume of the pores in gas pressure-based growth. Since the distance of the flow (and, consequently, the viscous drag) of the liquid phase at this time is less at the surface than in the interior, it is easier for this pore growth to occur at the surface than in the interior. Consequently, the size of the enlarged pores is greater at the surface than in the interior. It is further believed that the liquid phase condenses while it also coagulates

during the cooling process after sintering, and that the above-mentioned pores grow further due to this coagulation/condensation. Supposing that there is no difference in the amount of coagulation/condensation at the surface and in the interior at this time, the final size of the pores (and, consequently, the size of the pores which will be the cause of fracturing) will be larger at the surface, which was where they were larger during sintering.

When $P_a = P_e$, the above-mentioned kind of gas production does not occur, for the most part, and, consequently, the micropores are compressed and eliminated through the operation of surface stress. Namely, the micropores are no more than the product of coagulation/condensation, therefore, when $P_a = P_e$, the dimensions of the micropores become nearly equal in the interior and at the surface of the compact and are made smaller than when $P_a < P_e$.

When $P_a > P_e$, high pressure N_2 inside the compact is trapped inside micropores. In this case, since the mass of the gas inside the pores is great, due to the higher value for P_a , it is believed that a portion of the gas is dissolved/absorbed into the liquid phase [8], while a great deal of the gas remains, unabsorbed, inside the pores. During sintering, these kinds of pores become coarse by exchanging gasses or merging with other pores, similar to when $P_a < P_e$, so that, consequently, the dimensions of the pores when P_a is high are believed to be greater than when $P_a = P_e$. It was also believed that little difference in the sizes of the pores in the interior and those at

the surface of the compacts develops since gas production does not occur when $P_a > P_e$, either. These beliefs do not seem to contradict the compact shrinkage results shown in Figure 1, but more in depth investigation is required in the future. Besides this, N_2 was introduced at specific pressure levels at a temperature over approximately 1273 K in this research, but, in the future, we would also like to investigate what kind results would be obtained by introducing N_2 at normal pressure up to the appearance of liquid phase (approximately 1700 K), and at specified pressure levels beyond the appearance of liquid phase.

The results of the measurement of hardness are shown in Figure 7. It was discovered that there was virtually no difference in the hardness at the surface and the hardness in the interior at N_2 pressures at which virtually no MHL developed (see Figure 2). In addition, the surface became harder than

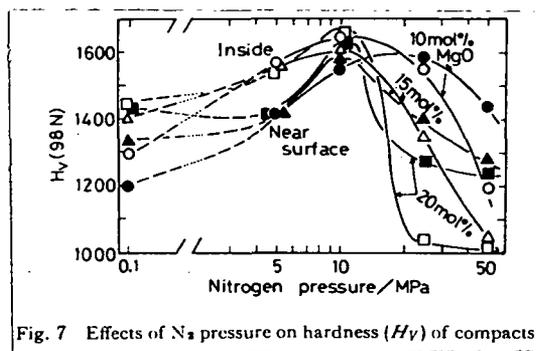


Fig. 7 Effects of N_2 pressure on hardness (H_v) of compacts.

the interior on the higher N_2 pressure side, and the hardness of the compacts showed maximum values at 10 to 25 MPa, regardless of the position in the compact. Referring to Figure 4, it can be seen that the hardness of these types of ceramics is strongly affected by the amount of $MgAl_2O_4$, there being a general tendency that the higher the amount of $MgAl_2O_4$, the harder the compact becomes. A similar relation was seen in a previous report [1] in which the relation between hardness and microstructure in normal pressure-sintered compacts was

investigated.

It should also be added that while reports [10][11] in which MHL (surface layers [10]) was seen in normal pressure-sintered (sintering temperature = 2073 K) Si_3N_4 -5 mass% MgO compacts, and in which MHL (surface anisotropic layers [11]) similarly developed when hot pressed Si_3N_4 - Al_2O_3 - Y_2O_3 compacts were HIP treated (at 1973 to 2173 K in 100 MPa argon and nitrogen gas) have already been seen, this research is the first to indicate the knowledge that the development of microstructurally heterogeneous surface layers in sintered compacts can be controlled, and that the differences in mechanical properties between the surface and interior regions in sintered compacts can be virtually eliminated [1] through sintering such compacts under a certain appropriate N_2 pressure.

IV. Summary

The following results were obtained in the investigation the room temperature microstructural properties of Si_3N_4 -(10 to 20) mol% MgO-5.5 mol% Al_2O_3 sintered compacts which were prepared in nitrogen gas (N_2) at 0.1 to 50 MPa, at 1973K for 3.6 ks, paying primary attention to microstructurally heterogeneous surface layers.

(1) Microstructurally heterogeneous layers became thinner as the N_2 pressure was increased and virtually stopped developing under a certain N_2 pressure (P_e ; approx. 20 MPa for 10 mol% MgO, the higher the mol% of MgO, the lower the pressure level). Then, as the pressure was increased higher, MHL again

began to develop. Corresponding with this, the amounts of nitrogen and silicon near the surface of the compacts were less than those in the interior of the compacts at N_2 pressures below P_e , equal at P_e , and greater than those in the interior at N_2 pressures greater than P_e . In this case, P_e was viewed as the equilibrium dissociation N_2 pressure.

(2) In compacts in which virtually no MHL was developed, there was practically no difference in the amounts of $MgAl_2O_4$ spinel, or in Si_3N_4 granulation at the surface and in the interior of the compacts, but the Si_3N_4 granulation was slightly coarser at the surface at pressures below P_e , while the amount of $MgAl_2O_4$ increased at the surface at pressures greater than P_e .

(3) The transverse-rupture strength near the surface of the compacts was lower than in the interior when the N_2 pressure was below P_e , but this difference virtually disappeared when the the N_2 pressure reached P_e , at which point practically no MHL could be detected. Also, the transverse-rupture strength in the interior of the compacts was either virtually unaffected by the N_2 pressure or showed a slight increase with increased pressure. Then, as the N_2 pressure increased over P_e , the transverse-rupture strengths at the surface and the in the interior showed equal values, both decreasing markedly, regardless of the development of MHL. This kind of transverse-rupture strength fluctuation showed an excellent correlation with the changes in size of pores in the compacts which became the source and cause of fracturing therein.

(4) In addition, the hardness at the surface of the compacts became nearly equal to that in the interior when there was no MHL development. There was generally also a tendency for the hardness to increase as the amount of $MgAl_2O_4$ increased.

In closing, we would like to express our thanks to Mr. Y. Mitsuda, a graduate research student (presently at Tōkai Kōnetsu Kōgyō Co., Ltd.), for his cooperation in this research.

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