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Preparation of Porous Al_2O_3-AlN-Mullite and Al_2O_3-AlN-SiC

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Porous composite of Al_2O_3 and AlN based mullite and SiC can be prepared by alumium reaction synthesis and atmosphere controllied sintering in order to improve the durability of a gas filter body. The porous Al_2O_3-AlN-mullite, which has a strength of 168 kg/cm^2 and porosity of 51.59%, could be obtained by atmospheric firing at 1600°C and the porous Al_2O_3-AlN-SiC with a porosity of 33% and strength of 977 kg/cm^2, could also be prepared The average pore size has been changed from 0.2 μm to 0.5 μm in a reduction atmosphere and to 2 μm in an air atmosphere, respectively.

Key words : Porous, Al_2O_3-AlN-mullite, Al_2O_3-AlN-SiC, Reaction synthesis

I. Introduction

AlN ceramics are widely used in a radiant heat plate material such as IC substrate due to their good electrical insulation and excellent thermal conductivity up to 8 times higher them that of Al_2O_3 ceramics.[1,2]

They are also used as a starting material for synthesis of SIALON, a casting nozzle for steel and non-ferrous metals and refractories for gas injection and laser tubes, etc., because of their good chemical durability to molten metal.[3] They has also been studied for a use of abrasive materials.[4]

AlN ceramics were firstly obtained by Geuther in 1862. He got AlN powder by firing alumina and coke powder mix near 1750°C in nitrogen atmosphere ($Al_2O_3+3C+N_2 \rightarrow 2AlN+3CO$). Nonoxide ceramics like AlN are usually fabricated by hot pressing, gas pressure sintering, hot isostatic pressing, recrystallization and reaction sintering. Nonoxide ceramics have an advantage in chemical durability.[5]

The purpose of this study is to fabricate and to characterize porous composites of Al_2O_3-AlN-mullite and Al_2O_3-AlN-SiC systems based on the reaction sintering of aluminum.

II. Experimental Procedure

A composite of Al_2O_3-AlN was prepared by oxidation, and nitridation of aluminum. Particle size distribution of aluminum (99% Al) as a starting material is shown in Fig. 1. Overall experimental procedure is shown schematically in Fig. 2. Mixture of SiO_2 sol and Al powder in a weight ratio of 45 : 55 was dried with stirring in order to prevent separation of Al and SiO_2 sol. Then the mixture was milled with a small amount of organic binder in an attritor and isostatically pressed into bars at 500 kg/cm^2. Physical properties were measured in oil instead of water in order to prevent hydrolysis of AlN.

X-ray diffraction analysis (Rigaku) was carried out to examine an existance of mineral phases gained by reaction sintering process. Microstructure observation and chemical micro analysis were performed by scanning electron microscopy (SEM, JSM-840A) and energy dispersive X-ray analysis (EDXA, AN-10000), respectively.

Pore size distribution analysis was performed by the mercury porosimetry (Quantachrome) and mechanical strength was measured by the 3 point bending method.

III. Results and Disscussion

Figures 3 and 4 were the results of X-ray diffraction analysis to examine mineral synthesis of reaction sintering process in various sintering temperatures and controlled atmospheres, respectively.

In Fig. 3, the specimen was sintered in air and the content of metal silicon decreased as the sintering temperature was increased. Mullite synthesis occurred at 1600°C and corundum was formed by oxidation at 1350°C remaining silicon. It is considered that these phenomena did not take place by the reaction (1) but were done by the reaction (2) at 1200°C and 1350°C.

$$4Al + 3O_2 = 2Al_2O_3(s) \quad (1)$$

$$SiO_2(s) = Si(s) + O_2(g) \quad (2)$$

Especially, it seems to be related to the reaction (2) at 1350°C.

AlN formation was decreased by the reaction (3) under higher oxygen partial pressure.

$$2AlN(s) + 3/2O_2(g) = Al_2O_3(s) + N_2(g) \quad (3)$$

It was reported that the value of log Po_2 was below -20.867 from the relationship with equilibrium partial pressure and phase diagram.[6] Reduction and the 2nd reduction phenomena ($SiO_2 \rightarrow Si$, $Al_2O_3 \rightarrow Al(g)+3/4O_2$) were more predominent at 1350°C than at 1200°C.

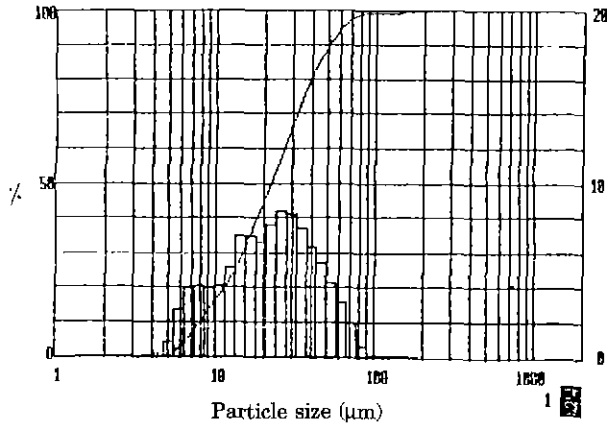

Fig. 1. Particle size distribution of aluminum powder.

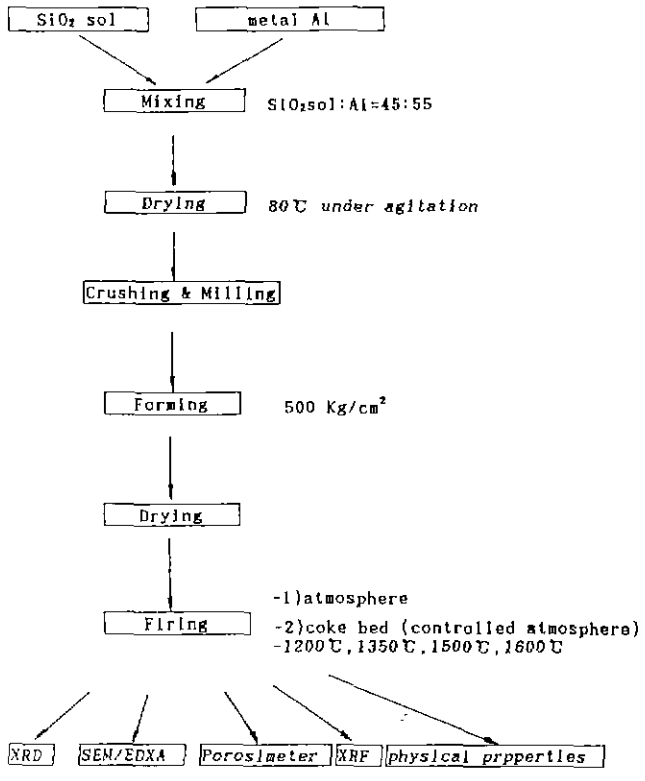

Fig. 2. Experimental procedure.

It is clear that a small amount of corundum was obtained at 1350°C. Synthesis of mullite took place at 1600°C and contents of silicon decreased under reduction. This reaction can be represented as follow:

$$3Al_2O_3(s) + 2Si(s) + 2O_2(g) = 3Al_2O_3 \cdot 2SiO_2(s)$$

Meanwhile, silicon carbide was formed in a cokes bed without any formation of Al_4C_3, AlON and sialon. Since the reaction, $SiO_2(s) + Si(s) + 2CO(g) = 2SiC(s) + 2CO_2$, proceeded by higher Pco partial pressure at 1600°C, synthesis of silicon carbide increased with increasing temperature but a small amount of silicon was remained.

It can be concluded that Al_2O_3-AlN-mullite or SiC

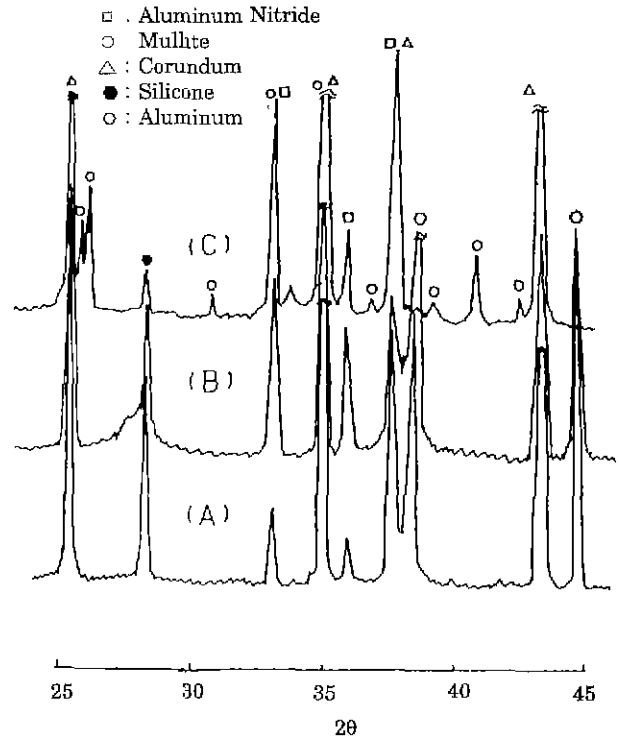

Fig. 3. XRD patterns after atmospheric firing at (A) 1200°C, (B) 1350°C and (C) 1600°C.

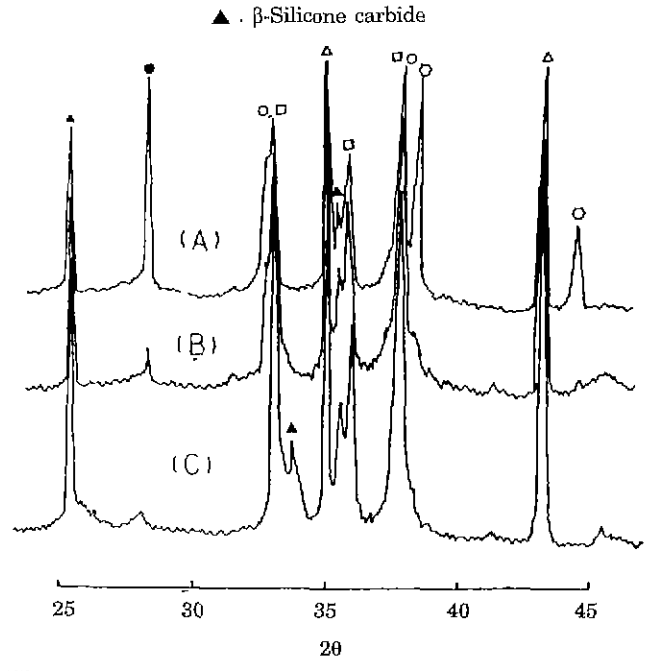

Fig. 4. XRD patterns under controlled atmosphere after firing at (A) 1200°C, (B) 1350°C and (C) 1600°C.

ceramic composites can be prepared by controlling atmosphere. Also aluminum was not found at 1600°C. In Figs. 5 and 6, microstructure was shown with change of sintering temperature and atmosphere. As the temperature increased, whisker formation decreased and

whisker shape changed into a rod shape. The grain growth of each phases occurred not under a reduction atmosphere but an oxidation atmosphere.

It is not clear whether whiskers were formed from Al,

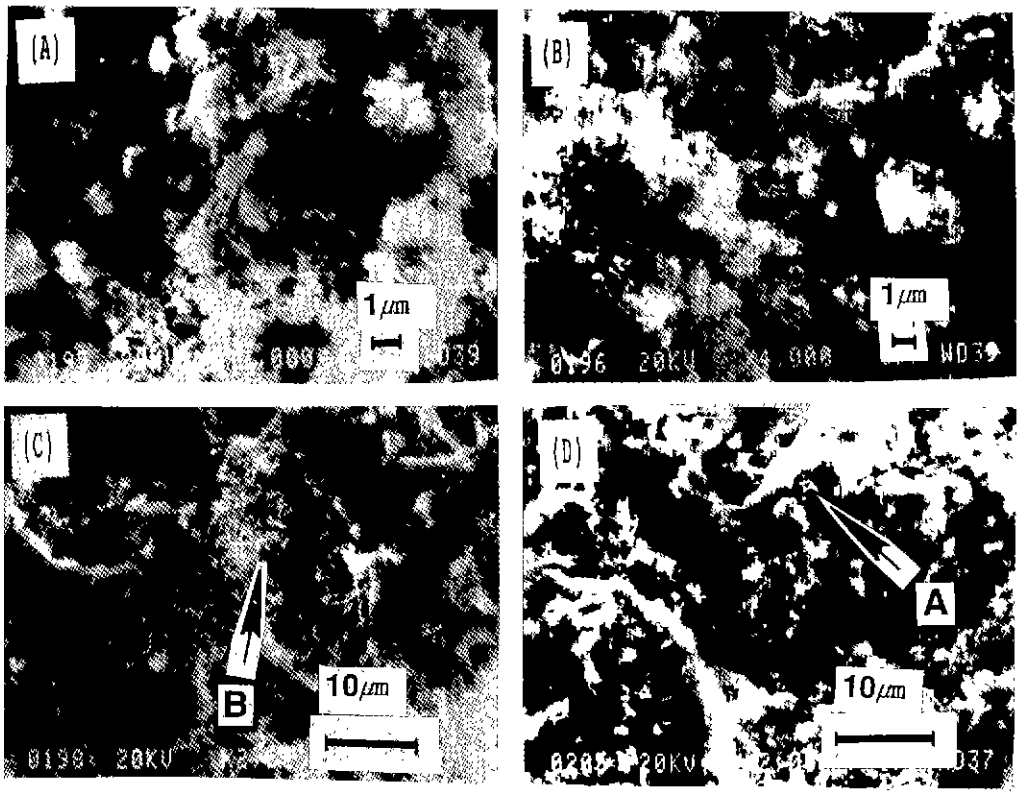

Fig. 5. SEM micrographs after firing at (A) 1200°C, (B) 1350°C, (C) 1500°C and (D) 1600°C under controlled atmosphere.

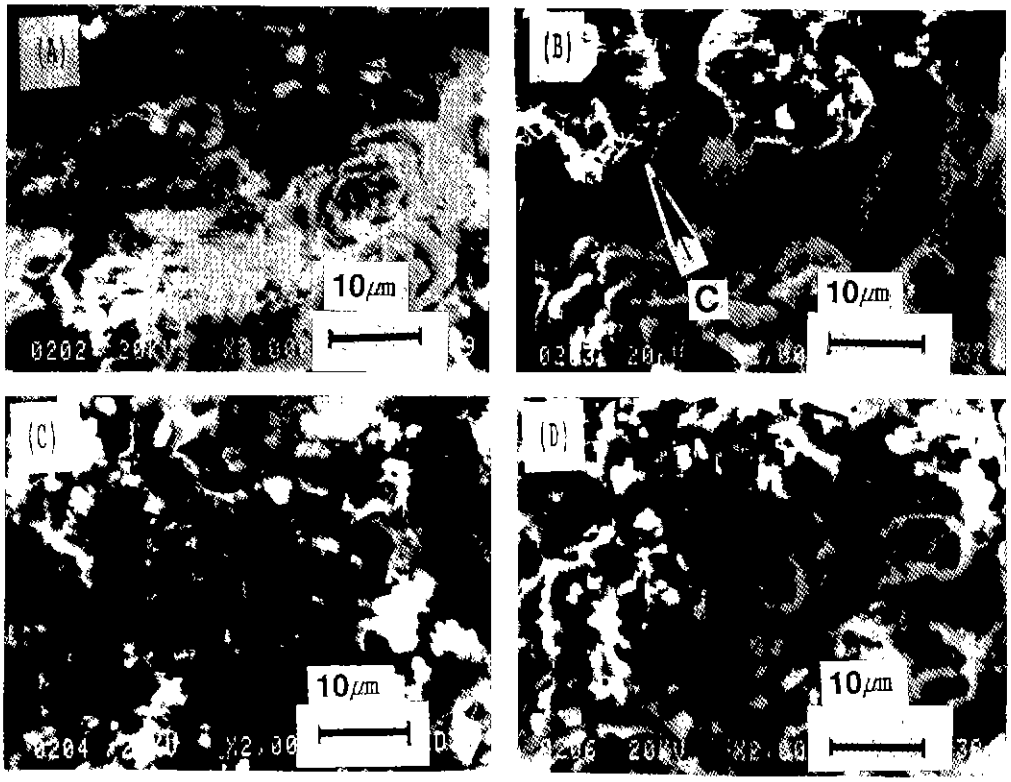

Fig. 6. SEM micrographs after atmospheric firing at (A) 1200°C, (B) 1350°C, (C) 1500°C and (D) 1600°C.

AlN or Al_2O_3. Table 1 shows the result of EDX according to the points A, B and C in Figs. 5 and 6. Point "A" was regarded as whiskers from a reduction atmosphere. In case of sintering in air, no whiskers were observed at 1600°C. As shown in Table 2, the quantative analysis indicates that the composition is similar to that of the point "C". The phase was confirmed to be Al_2O_3-AlN-mullite by XRD analysis. It can be also concluded that the silicon carbide was formed from SiO_2 under a reduction atmosphere.

A carbon (content=0.39%) formation is described by the reaction (4) as follows:

$$SiC(s) + 2CO(g) = SiO_2(g) + 3C(s) \quad (4)$$

The result of bending strength and porosity in various sintering temperatures and atmospheres is illustrated in Figs. 7 and 8, respectively. In Fig. 7, in case of sintering under controlled atmosphere, the bending strength decreased as the termperature is increased up to 1500°C. On the contrary, the maximum bending strength exists at 1350°C in case of sintering under atmosphere.

It could be concluded that the porosity was increased with increasing volume extension by formation of Al_2O_3 and the strength could be increased by forming a rod from coalescence of Al whiskers. Meanwhile, it could be seen that porosity and strength were decreased at 1200°C and 1500°C, whereas those were increased at 1350°C and 1500°C in air atmosphere. It was considered that the existence of molten aluminium promoted bonding strength between Al_2O_3 and AlN grains. Porosity increased in oxidation than reduction atmosphere.

Porosity under oxidation atmosphere was higher than that under reduction atmosphere, because Al changed into Al_2O_3 by oxidation.

Table 1. Result of Point Analysis of the Specimen (D) in Figs. 5 and 6 by EPMA.

Position / Component	A	B	C
Na_2O	.485	.245	.000
MgO	.452	.749	.000
Al_2O_3	80.879	95.330	83.141
SiO_2	17.708	2.165	16.675
K_2O	.000	.117	.027
CaO	.273	.745	.132
TiO_2	.005	.166	.024
MnO	.056	.000	.000
Fe_2O_3	.143	.085	.000
ZrO_2	.000	.388	.000

The linear expansion changed from +1.3% to +1.5% under a reduction atmosphere and from +1.2% to +2.8%

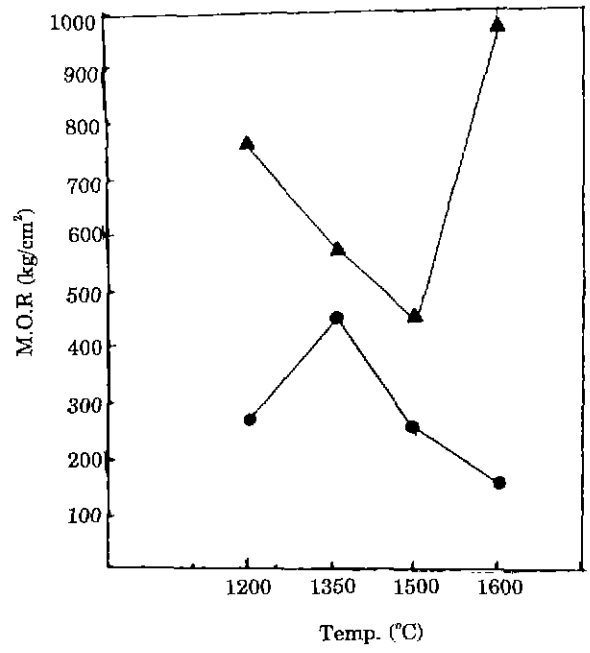

Fig. 7. Modulus of rupture as a function of temperature (▲—▲: controlled atmosphere, ●—●: air atmosphere).

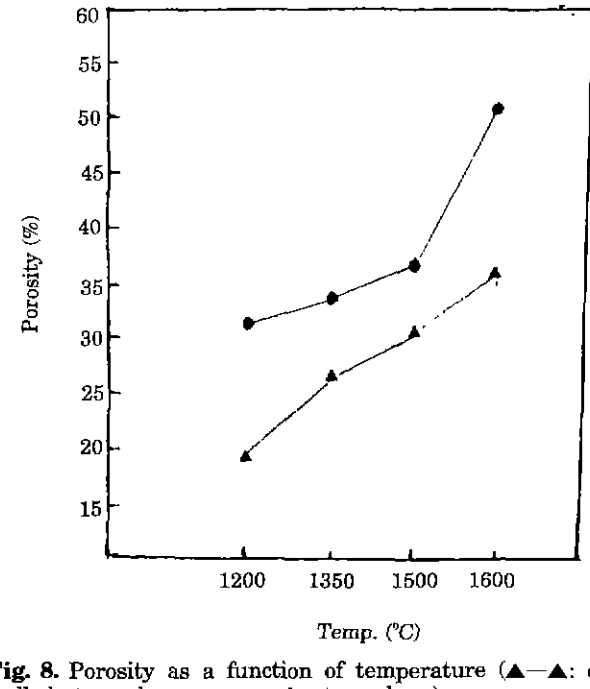

Fig. 8. Porosity as a function of temperature (▲—▲: controlled atmosphere, ●—●: air atmosphere).

Table 2. Chemical Composition of the Specimen After Firing at 1600°C (by XRF, carbon analyser, and chemical titration).

Firing / Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	C	SiC	AlN
Air atmosphere	10.48	81.10	0.10	0.13	0.02	0.14	-	-	8.01
Controlled atmosphere	-	73.42	0.51	0.11	0.05	0.10	0.39	10.03	15.37

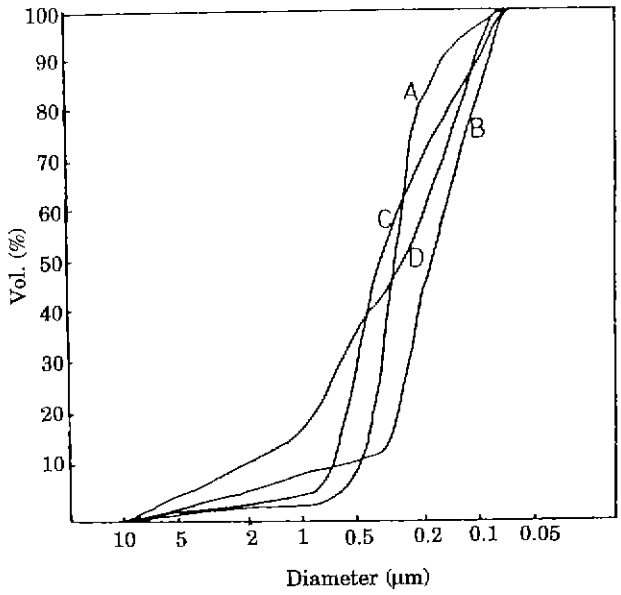

Fig. 9. Pore size distribution after firing at (A) 1200°C, (B) 1350°C, (C) 1500°C and (D) 1600°C under controlled atmosphere.

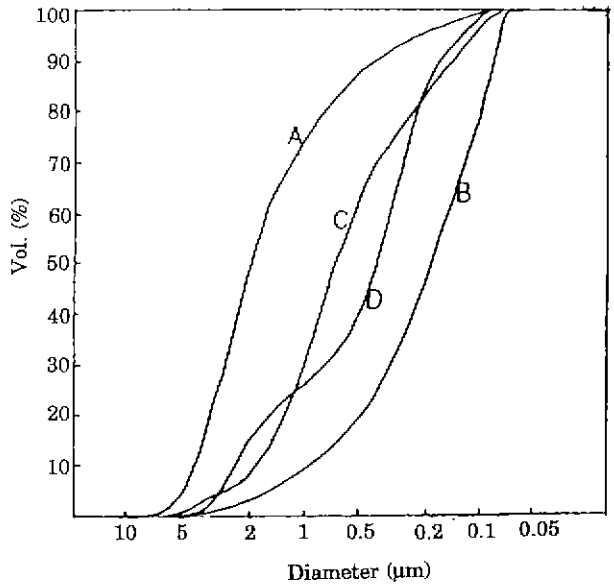

Fig. 10. Pore size distribution after firing at (A) 1200°C, (B) 1350°C, (C) 1500°C and (D) 1600°C under air atmosphere.

under an air atmosphere. As for pore size, there was no difference in average pore size from 0.2 to 0.5 μm, but on the contrary, the difference could be shown in the pore size distribution. Especially, specimen fired at 1600°C had pore size distribution from 0.1 to 10 μm. It has been considered that a lot of Al_2O_3 were formed by Al oxidation, and SiC did not exist below 1600°C.

Figures 9 and 10 showed that the pore size increased and pore size distribution was broadened by Al_2O_3 formation from Al. The average pore size was increased in lower firing temperature.

The pore size decreased by densification due to Al oxidation, but the width of pore size distribution was broadened. Also the distribution was similar to those for oxidation and reduction firing atmospheres at 1600°C because of the formation of second phases such as SiC and mullite and volume expansion oxidation of Al.

IV. Conclusion

Porous composites of Al_2O_3-AlN based mullite and SiC can be prepared by aluminum reaction synthesis and sintering under controlling atmosphere to improve durability of gas filter body.

Also it was possible to obtain porous materials with high strength by firing in a low temperature instead of hot pressing, HIP and post sintering. The porous materials of Al_2O_3-AlN-mullite could be obtained at 1600°C in an air atmosphere firing and resulted in a porosity of 51.59% and high strength of 168 kg/cm^2. In case of Al_2O_3-AlN-SiC, it showed a porosity of 33.33% and a strength of 977 kg/cm^2. The average pore size has been changed from 0.2 to 0.5 μm in reduction atmosphere and to 2 μm in air atmosphere. It is concluded that densification occurred due to volume expansion by the oxidation of Al.

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