Effect of Oxygen on Sintering of Aluminium Nitride with Y_2O_3 Sintering Aid

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 Y_2O_3 助剤での窒化アルミニウムの焼結に及ぼす酸素量の影響

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Aluminium nitride (AlN) powders with 0-1.2 mass% of carbon and 5 mass% of Y_2O_3 addition were sintered at 2023 and 2073 K under a nitrogen atmosphere, and the sintered samples were characterized by their oxygen content, composition of the secondary phase, microstructure, density, and thermal conductivity. With an increase of carbon addition, the oxygen content decreased linearly and the secondary phase changed from aluminium-rich to yttrium-rich. The microstructure, density and thermal conductivity of the sintered samples were also found to depend strongly on the oxygen content. The correlation between the oxygen content and the sintering behavior of AlN with Y_2O_3 sintering aid has been discussed.

Key-words : Aluminium nitride, Oxygen content, Sintering, Phase composition, Microstructure, Density, Thermal conductivity

1. Introduction

Aluminium nitride (AlN) is an attractive material because it has high thermal conductivity combined with good electrical insulation, low dielectric constant and low thermal expansion coefficient, and can be pressureless-sintered with additives to theoretical density.^{1),2)} These properties make AlN a leading candidate as a substrate for power circuits and multichip modules, and as a packaging material for integrated circuits.

Oxide additives, particularly Y_2O_3 or CaO, are efficient densification aids for pressureless sintering of AlN.³⁾ They not only enable full densification of AlN at relatively low temperature, but also increase its thermal conductivity. It has been suggested that a secondary phase, also called a grain boundary phase, is formed at sintering temperature as a result of reactions between the oxide additives and the oxygen impurity in AlN, and accelerates its sintering. The formation of the secondary phase also reduces AlN lattice defects caused by dissolved oxygen, which cause phonon scattering, and improves its thermal conductivity. The sintering of AlN is known to be strongly affected by the kinds and addition levels of the sintering aids.

On the other hand, AlN tends to absorb moisture

and oxygen during pulverizing and handling in the air due to its chemical activity. There exists about 0.8-2.0 mass% oxygen as an impurity in commercial AlN powders. It is expected that the oxygen content in AlN powder will affect the formation of the secondary phase and thus the sintering of AlN.

Sakai and Iwata investigated the effect of the oxygen content level as an impurity on the densification behavior of pure AlN by a hot-pressing process, and reported that oxygen accelerates the densification of AlN and improves the mechanical strength of the sintered samples.⁴⁾ Kuramoto et al. studied the effect of oxygen content on the thermal conductivity of the pressureless-sintered AlN with CaO additive, and concluded that thermal conductivity of AlN is inversely proportional to the logarithm of the oxygen content.⁵⁾ Other investigations on the correlation between oxygen content and thermal conductivity of the AlN with Y_2O_3 additive were conducted by several research groups,^{6),7)} in which the oxygen content was changed by the control of both sintering temperature and sintering period, and the thermal conductivity of AlN was reported to be increased by decreasing oxygen content. However, few detailed studies have been performed on the correlation between oxygen content and sintering behavior as well as properties of AlN with sintering additives.

In the present study, AlN powders with an addition of Y_2O_3 and carbon were sintered, in order to study the effect of the oxygen content on the sintering of AlN under constant conditions such as particle size, sintering additive and sintering condition except for oxygen content. The relations among the oxygen content and sintering behavior, phase composition, densification, and thermal conductivity of the samples were investigated.

2. Experimental procedure

2.1 Starting materials

The starting materials were (a) AlN powder (Toyo Aluminium K. K.) with a mean particle size of 0.72 μm , a specific surface area of 10.04 m^2/g , and an oxygen content of 2.7 mass%; (b) Y_2O_3 powder (Dof 5, Mitsubishi Kasei Co.) with a mean particle size of 1.55 μm and a specific surface area of 12.0

m²/g; and (c) carbon black (#2300, Mitsubishi Kasei Co.) with a mean particle size of 15 nm and a specific surface area of 260 m²/g. The chemical composition of the AlN powder is listed in Table 1.

2.2 Sample preparation

The starting materials were mixed in 2-propanol for 12h using a plastic bottle mill with nylon balls. The added amount of Y₂O₃ was 5 mass% for all the samples, and the addition of carbon was changed from 0 to 1.20 mass%, as shown in Table 2. After drying, the mixed powder was pressed into pellets and cold isostatically pressed (CIPed) under 98 MPa for 2 min. The CIPed pellets were placed in a BN crucible and sintered in a graphite resistance furnace at the temperature of 2023 K as well as 2073 K for 3h under a 0.1 MPa nitrogen gas atmosphere (see Table 2). The heating and cooling rates were 5 and 2 K/min, respectively.

2.3 Characterization

For the sintered samples, the bulk density was measured by a displacement method in water. The fractured surfaces were observed by a scanning electron microscope (SEM). The oxygen and carbon contents were measured by a hot gas extraction

method, and yttrium content was analyzed by an inductively coupled plasma (ICP). The crystalline phases were determined by X-ray diffraction (XRD), and the composition of the secondary phase was calculated using the relative intensities of the diffraction lines of (211) for Y₃Al₅O₁₂ (YAG), (121) for YAlO₃ (YAL), and (112) for Y₄Al₂O₉ (YAM), respectively. Thermal conductivity was measured at room temperature by a laser flash method.

3. Results and discussion

3.1 Chemical composition

The chemical composition of the sintered samples is listed in Table 3. The residual carbon in all the samples showed the same value and was smaller than that observed in the raw powder, with no relation to either the amount of the added carbon or the sintering temperature. This indicates that all added carbon had either reacted with the oxygen in the raw powder or evaporated during sintering. The yttrium content in the sintered samples was measured to be very close to the added amount, showing no evaporation of yttrium during sintering.

The oxygen content in the sintered samples listed in Table 3 was calculated by subtracting the Y₂O₃'s oxygen from the total observed oxygen. The oxygen content in the samples without carbon addition (samples A-4 and B-4) decreased as compared to that of the raw powder, which may be due to the evaporation of the absorbed oxygen on the surface of the raw powder. It is observed that the oxygen content decreased with an increase of carbon addition. A tendency toward reduction, although small, is also seen in the oxygen content as sintering temperature increases, being consistent with the report by Watari et al.⁶⁾

Figure 1 shows the correlation between the reduction of oxygen content (O), in comparison with those without carbon addition, and the amount of added carbon (C) in the sintered samples. It is seen

Table 1. Chemical Composition of the AlN Powder

Element	Content	Element	Content
Cu	5 ppm	Ni	3 ppm
Fe	45 ppm	Cr	3 ppm
Si	50 ppm	Ti	1 ppm
Mn	2 ppm	O	2.7 mass%
Mg	2 ppm	N	33.0 mass%
Zn	2 ppm	C	0.03 mass%

Table 2. Carbon Addition and Sintering Condition of the Samples

Samples	C Addition (mass%)	Sintering Temp. (K)
A-1	1.20	2023
A-2	0.85	"
A-3	0.50	"
A-4	0	"
B-1	1.20	2073
B-2	0.85	"
B-3	0.50	"
B-4	0	"

Table 3. Chemical Composition and Properties of the Sintered Samples

Samples	Chemical Composition (mass%)			Relative Density	Thermal Conductivity
	Y ₂ O ₃	C	O ¹⁾	(%)	(W/mK)
A-1		0.02	0.84	79.8	106.6
A-2		"	1.34	80.5	99.0
A-3		"	1.71	86.1	110.4
A-4		"	2.28	99.6	100.1
B-1	4.9	"	0.84	95.6	177.7
B-2	"	"	1.24	96.0	163.9
B-3	"	"	1.70	96.4	160.5
B-4	5.1	"	2.25	99.6	98.9

1) Oxygen content was calculated by subtracting the Y₂O₃ oxygen from the total oxygen content.

Fig. 1. Relationship between oxygen reduction and carbon addition in the sintered samples.

that oxygen reduction increases linearly with an increase in the addition of carbon by the following formula.

$$O \text{ (mass\%)} = 1.17 C \text{ (mass\%)} \quad (1)$$

This result indicates that about 1.1 mol of carbon is required to remove 1 mol of oxygen from the raw powder. Using formula (1), it is believed that the oxygen in AlN ceramics can be controlled accurately by the addition of carbon. Yan et al.⁸⁾ studied the residual carbon on the surface of the binder-burnout AlN powder with X-ray photoelectron spectroscopy (XPS), and indicated that almost all the oxygen in the samples with C/O atomic ratio higher than 1.0 was removed by the carbon-deoxidation reaction during sintering. Our result is close to theirs, although the source of carbon was not the same in the two cases. Thus the chemical reaction between carbon and oxygen in this study can also be considered to obey the following reaction formula reported by Yan et al.⁸⁾

Greater consumption of carbon compared to formula (2) to remove the oxygen from the samples may be due to the evaporation of a part of carbon black in the present sintering condition.

3.2 Phase composition

The secondary phase observed by XRD in the sintered samples varied with the residual oxygen, as shown in Table 4. The phases of both YAL and YAM coexisted in the samples with lower oxygen content (samples A-1 and B-1), while only YAG existed in those with higher oxygen content (samples A-4 and B-4). In the other samples, both YAG and YAL phases were observed (samples A-2, A-3, B-2, and B-3).

These results may be explained by using the Y_2O_3 - Al_2O_3 phase diagram, as shown in Fig. 2. In this study, we assume that all the oxygen in the powder exists as Al_2O_3 when it reacts with Y_2O_3 . With constant addition of Y_2O_3 , it is clear that the composition of the secondary phase is determined by the amount of Al_2O_3 , or oxygen content. The amount of secondary phase in each sample was calculated, according to the added amount of Y_2O_3 and the resid-

Table 4. Composition of the Secondary Phase in the Sintered Samples

Sample	Phase Composition (% cal.)			Phase Composition (% mea.)		
	YAG	YAL	YAM	YAG	YAL	YAM
A-1	0	53	47	0	25	75
A-2	33	67	0	30	70	0
A-3	82	18	0	85	15	0
A-4	100	0	0	100	0	0
B-1	0	53	47	0	38	62
B-2	18	82	0	19	81	0
B-3	82	18	0	76	24	0
B-4	100	0	0	100	0	0

Fig. 2. Phase diagram of Al_2O_3 - Y_2O_3 system.

ual oxygen content shown in Table 3, and listed in Table 4. The calculated values agree well with the measured ones in all the samples, suggesting that the reaction of Al_2O_3 and Y_2O_3 occurs in a nearly equilibrium state. It is considered that the phase composition of the secondary phase can be controlled with the control of the oxygen content and Y_2O_3 in AlN(Y_2O_3) ceramics.

3.3 Densification

The relative density of the sintered samples is listed in Table 3. The 100% density was calculated from the fractional summation of the crystalline density of hexagonal AlN (3.261 g/cm³, from JCPDS card 25-1133) and cubic Y_2O_3 (5.031 g/cm³, from JCPDS card 41-1105). The samples having higher oxygen content showed density as high as 99.6% at both sintering temperatures of 2023 and 2073 K. The density of the samples tends to decrease with a decrease of the oxygen content, particularly at lower sintering temperature (for sample A-1, density as low as 79.8% was obtained), although the starting powders had the same particle size, which is known

to strongly affect the sintering of AlN.

In the case without sintering aid, the oxygen was reported to cause the cation vacancy in AlN and increase the diffusion coefficient for the densification process, and thus accelerate the densification of AlN.⁴⁾ But in the present case, the effect of oxygen on the sintering of AlN should be related with the Y_2O_3 additive. It is believed that the ratio of oxygen content and Y_2O_3 additive affects the composition of the secondary phase, and changes the liquid phase temperature and densification process. With the same Y_2O_3 addition, the increase of oxygen content easily causes the formation of the secondary phase with higher Al_2O_3 content and lowers its melting temperature, thus promoting the densification of AlN (see Fig. 2).

3.4 Microstructure

The fractured surfaces of the sintered specimens were examined by SEM, and two selections are shown in Fig. 3. The difference in the degree of densification of the samples with different oxygen content is distinguishable. Little grain growth and many intergrain pores are seen in the sample with lower oxygen content (sample A-1), while grain growth is evident for the sample with higher oxygen content (sample A-4). The degree of densification observed in SEM is consistent with the density measurements.

3.5 Thermal conductivity

The thermal conductivity of the sintered samples is summarized in Table 3. The samples sintered at 2023 K, including sample A-4, which has higher sin-

tering density, all showed lower thermal conductivity at about 100 W/m·K. For those sintered at 2073 K, no increase of thermal conductivity was observed in the sample with higher oxygen content (sample B-4), while higher thermal conductivity over 160 W/m·K was obtained in the other low-oxygen content samples. It is also observed that the thermal conductivity of the samples increases with a decrease of the oxygen content.

According to the phonon scattering model for AlN, the thermal resistance, the reciprocal of the thermal conductivity, increases linearly with increase of lattice oxygen content.¹⁾ This model is supported by several experimental results obtained from not only single-crystal but polycrystalline AlN.^{9),10)} It is considered that the lattice oxygen is created due to the diffusion of oxygen impurities into the AlN lattice during sintering. In the case of high oxygen content, the aluminium-rich phase, YAG, forms and residual oxygen diffuses easily to the AlN lattice due to thermodynamic considerations of the Al_2O_3 - Y_2O_3 phase diagram, thus reducing its thermal conductivity. The reduction of the oxygen content further changes the secondary phase from aluminium-rich to yttrium-rich, and few oxygen will enter into the AlN lattice, so a corresponding increase in thermal conductivity can be obtained.

4. Conclusions

AlN powders with 5 mass% of Y_2O_3 and 0–1.20 mass% of carbon addition were sintered at 2023 and 2073 K under a nitrogen atmosphere. An investigation was made for the correlation between the oxygen content, which was controlled by the amount of the added carbon, and the sintering of the powders as well as the properties of the sintered samples. The results were shown as follows:

- (1) The oxygen reduction in the sintered samples was linearly proportional to the amount of added carbon. It takes about 1.1 mol of carbon to remove 1 mol of oxygen from the AlN samples during sintering.
- (2) With constant Y_2O_3 addition, the secondary phase in the sintered samples changes from aluminium-rich to yttrium-rich as oxygen content decreases. The phase composition is consistent with that calculated according to the Al_2O_3 - Y_2O_3 phase diagram.
- (3) The density of the sintered samples decreases with decrease of the oxygen content.
- (4) The thermal conductivity of the sintered samples with relative density over 95% increases as oxygen content decreases.

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Fig. 3. SEM photographs of fractured surface of the samples sintered at 2023 K for 3h.

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