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Effect of Y_2O_3 on low temperature sintering and thermal conductivity of AlN ceramics

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Abstract

The effect of Y_2O_3 on the densification and thermal conductivity of AlN ceramics sintered at the temperature of 1650 °C was studied using CaF_2–Y_2O_3 system as additives. XRD was employed to identify the phases formed during sintering. The results show that AlN ceramics with Y_2O_3 addition have a low shrinkage at temperatures below 1600 °C because the solid reaction between Y_2O_3 and Al_2O_3 decreases the amount of the calcium aluminates liquid due to the consumption of Al_2O_3. At 1650 °C, Y_2O_3 promotes the densification due to the formation of liquid $CaYAlO_4$. The observation by TEM and HREM reveals that the inhomogeneous grain-boundary phases containing different phase compositions move to the three-grain junctions to form discrete pockets during the sintering. The measurement of the lattice parameters and the thermal conductivity of AlN ceramics shows that Y_2O_3 has no prominent effect on the purification of the AlN lattice at this sintering temperature. The higher thermal conductivity in the presence of Y_2O_3 mainly comes from the enhancement of the densification.

Keywords: AlN; Grain boundary phases; Sintering; Thermal conductivity

1. Introduction

Aluminum nitride is considered to be a promising substrate and package material for high power integrated circuits because of its high thermal conductivity, low dielectric constant, thermal expansion coefficient close to that of silicon and high electrical resistivity.[1–3] However, AlN is difficult to sinter due to its highly covalent bonding. For full densification, rare-earth and/or alkaline earth oxides are often added as sintering aids in the fabrication of AlN ceramics.[4,5] These sintering aids play a double role during the sintering. One is to help form the liquid phase that promotes the densification by the process of liquid-phase sintering. The other is to improve the thermal conductivity by decreasing the oxygen impurities in the AlN lattice. Y_2O_3 is an effective additive to achieve dense AlN ceramics most likely due to the liquid-phase formation of yttrium aluminates at temperatures around 1800 °C since the eutectic temperature of Y_2O_3 and Al_2O_3 is around this region.[6] Also, it purifies the AlN lattice by forming YAP and YAM with low activity of Al_2O_3 in them, which increases the thermodynamic driving force for oxygen removal, and thus increases the thermal conductivity of AlN ceramics.[7,8] Recently more and more attention has been given on the low temperature sintering of AlN ceramics considering reducing manufacturing cost and benefiting cofiring of multilayer substrates.[9–15] In these studies, Y_2O_3 is often used as one of the additives.[9,11,12,13] However, its effect on the densification and thermal conductivity is not clear enough. Jarrige et al.[12] found that Y_2O_3 increases the viscosity of the calcium aluminates and limits the composition change of the liquid to refractory phases by displacing the composition of the secondary phases at 1700 °C. However, they did not give the effect of Y_2O_3 on the thermal conductivity of the sintered specimens. At the temperature lower than 1700 °C, whether Y_2O_3 has an important role on the elimination of oxygen defects in the AlN lattice is also unknown. In this paper, CaF_2 and Y_2O_3 were used as additives to study the effect of Y_2O_3 on the densification and thermal conductivity of AlN ceramics at the temperature of 1650 °C.

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2. Experimental

Specimens were prepared through a conventional ceramic fabrication process. Commercially available AlN powder (grade US, Toyo Aluminium K. K.), as described by Table 1, was used as a starting material. Powders of AlN with additives of CaF_2 (analytical reagents) and Y_2O_3 (analytical reagents) were ball-milled by planetary milling for 2 h using ethanol as a mixing medium. After drying and binder-adding, the powder mixture was uniaxially die-pressed into pellets 10 mm in diameter and 5 mm thick and then de-waxed at 550 °C. The pellets were then placed into a BN crucible and sintered at 1650 °C for 1 min, 2 h, 4 h, 6 h and 12 h respectively in a graphite furnace with a flowing nitrogen atmosphere. The compositions of the specimens were shown in Table 2.

The shrinkages and the densities of the sintered pellets were measured by vernier caliper and Archimedes displacement method, respectively. X-ray diffraction (XRD) with CuK_α was used to identify the produced phases. The fracture surfaces of the pellets were observed by scanning electron microscopy (SEM, OPTON, CSM950). The liquid phases between the grains were examined by transmission electron microscopy (JEM, 200CX) and high resolution transmission electron microscopy (JEM, 2010F). To determine the lattice parameters, the samples with and without Y_2O_3 addition fired for 1 min, 4 h and 8 h at 1650 °C were scanned from 90 to 140° at the rate of 0.1°/min using CuK_α radiation. The thermal conductivity at room temperature was measured by a laser flash technique.

To identify the phases in the sintering, Al_2O_3 was added in the additives as one of the reactants, as described by Table 2. Then the mixed powders fired at 1200 °C were identified by XRD. As the liquid may occur at a higher temperature, the mixed powders, laid on the single AlN pellets, were fired at 1650 °C in a graphite furnace with a flowing nitrogen atmosphere, just like the sintering of AlN ceramics. After being fired for different times, the AlN pellets penetrated by the liquid were identified by XRD to achieve the phase compositions in the liquid.

Table 1
Properties of the starting AlN powder

Chemical composition (wt.%)					Average particle size (μm)	Specific surface ($m^2\ g^{-1}$)
N	O	C	Si	Fe		
33.2	1.11	0.04	0.0059	0.0023	1.46	4.50

Table 2
Compositions of different samples in the experiments

Sample	CaF_2 (wt.%)	Y_2O_3 (wt.%)	Al_2O_3 (wt.%)	AlN (wt.%)
CA	2	0	0	98
YA	0	2	0	98
CYA1	2	2	0	96
CYA2	2	3.5	0	94.5
CAO	44.4	0	55.6	0
YAO	0	44.4	55.6	0
CYAO	30.8	30.8	38.4	0

3. Results

3.1. Shrinkage

Fig. 1 shows the shrinkage of the samples with different amounts of Y_2O_3 addition. Compared with sample CA, the samples with Y_2O_3 addition have lower shrinkages at temperatures lower than 1600 °C. However, the shrinkages of samples CYA1 and CYA2 increase quickly and exceed that of sample CA above 1600 °C. After sintered at 1650 °C for 12 h, sample CYA1 shrinks 17.9%, higher than that of the sample without Y_2O_3 addition, which is 16.3%. It also can be seen in the figure that sample CYA1 has the largest shrinkages in the three samples with Y_2O_3 addition, which indicates that 2 wt.% Y_2O_3 benefits achieving a maximum of shrinkages. The different shrinkages of the samples with Y_2O_3 addition are most likely attributed to the effects of Y_2O_3 on the liquid phases during the different sintering temperatures, as the following explains in detail.

3.2. Phase compositions

The phases in the sintered samples CAO and CYAO were summarized in Table 3. At 1200 °C, CaF_2 reacts with Al_2O_3 to form $CaAl_4O_7$, $CaAl_2O_4$ and $Ca_{12}Al_{14}F_2O_{32}$. When Y_2O_3 is added with CaF_2, the additional phases $Y_4Al_2O_9$ (YAM) and $CaYAl_3O_7$ are identified. Since both Ca–Al–O compounds and yttrium aluminates are formed at this temperature, the amount of Y_2O_3 influences the formation of Ca–Al–O compounds due to the

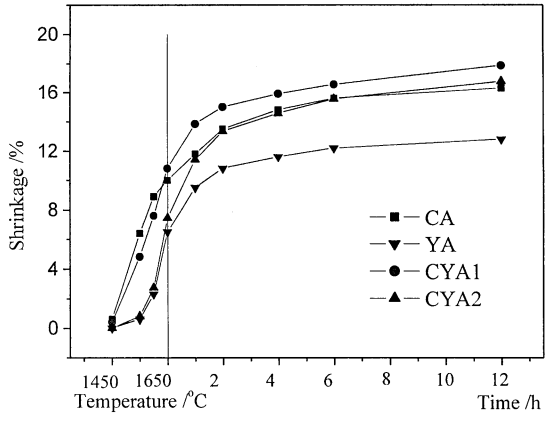

Fig. 1. The shrinkage of samples during the firing.

consumption of Al_2O_3. Thus, when sintered at temperatures lower than 1650 °C, the lower shrinkage in the samples with Y_2O_3 addition may be attributed to the decreased amount of the calcium aluminates liquid, which generally promotes the densification of AlN ceramics. At 1650 °C, a trace of $CaAl_4O_7$ remains in sample CAO, while in sample CYAO, $CaYAlO_4$ is an additional phase besides the calcium aluminates and YAM. After being sintered for 8 h, Ca–Al–O compounds except for a trace of $CaAl_2O_4$ are nearly undetectable in sample CAO, which implies evaporation of the Ca–Al–O compounds in a carbon-containing nitrogen atmosphere, as mentioned by Greil.[16] But in sample CYAO sintered for 8 h, the compounds containing $CaO–Y_2O_3–Al_2O_3$ still exist, which implies that these phases are stable at this temperature. Since the quick shrinkages of the samples with Y_2O_3 addition and phase $CaYAlO_4$ occur near 1650 °C, it is possible that the liquid phases containing $CaYAlO_4$ promote the densification of AlN ceramics during sintering at 1650 °C.

Using XRF, the contents of elements Ca and Y are detected in the polished sample CYA1 sintered for different times at 1650 °C. As shown in Fig. 2, Ca content decreases with the soaking time, which associates with the evaporation of calcium aluminates. After being sintered for 6 h, the decrease of Ca content becomes slow, which implies that $CaYAlO_4$ is stably remaining in the sample. Y content has a different change from Ca content in that it decreases quickly after being sintered for 6 h. This may come from the removal of the liquid containing the yttrium aluminates from the interior to the surface of the specimens during the sintering.

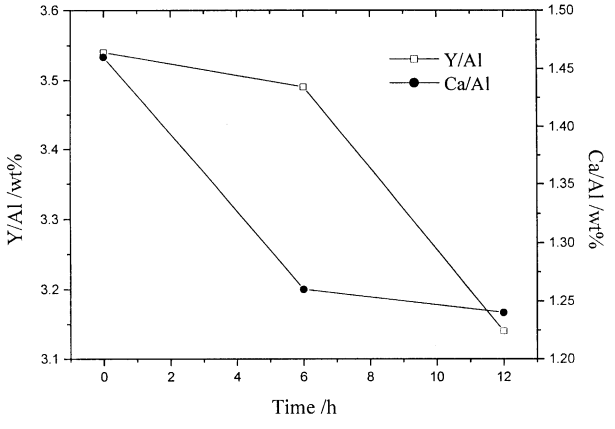

Fig. 2. Y and Ca contents in the sample CYA1 sintered at 2650 °C for different time.

3.3. Microstructure

Figs. 3 and 4 show the microstructure of the fracture surface of samples CA and CYA1 sintered at 1650 °C for 1 min, 6 h and 12 h, respectively. From the photographs, it is observed that a large quantity of liquid congregates together in the samples sintered for 1 min but is homogeneously distributed between the grains after 6 h. This shows that the liquid goes through a process from occurrence to redistribution during the sintering. In sample CA the grains have an inhomogeneous size distribution. However, they are more homogeneous in sample CYA1, which implies that $CaYAlO_4$ improves the growth of the AlN grains. Furthermore, the fracture is along the grains in sample CA sintered for 12 h, but in sample CYA1, it is visible that fracture surfaces across some grains, as shown in Fig. 4(c). This implies that the bonding between the AlN grains can be enhanced in the presence of Y_2O_3.

As shown in Fig. 5, the dihedral angles between the grains of both sample CA and CYA1 sintered for 4 h are close to 120°, which implies the grain-boundary phases have a less wetting to the AlN grains. This agrees with the high viscosity of the secondary phases as Jarrige et al. mentioned.[12] The less wetting also results in the less final shrinkages of samples CA and CYA1 compared with the results achieved by Wang et al.[17] In sample without Y_2O_3 addition, the amount of the grain-boundary phases is so small that the clean grain boundaries remain due to the evaporation of the grain-boundary phases, as shown in Fig. 5(a). In the sample with Y_2O_3, a few of grain-boundary phases move to the three-grain junctions, thus also resulting in the sharp grain boundaries, as shown in Fig. 5(b).

The high resolution TEM picture of the grain-boundary phases in sample CYA1 sintered for 4 h is shown in Fig. 6. Two fields with different atom arrangements are observed from the figure. The interlayer spacings along the orthogonal directions in the field I are 1.038 and 1.045 nm, approximately equal to the plane spacings of (010) and (100) of phase YAM, which are 1.0469 and 1.0528 nm, respectively. The selected area electron diffractive pattern at this area also indicates the existence of YAM phase as shown in this figure. In the field II, the interlayer spacings along the two perpendicular directions are 0.379 and 1.163 nm, in agreement with the plane spacings of (100) and (010) of $CaYAlO_4$ phase, which are 0.364 and 1.187 nm, respectively.

Table 3
Phase compositions of different samples during the firing

	CAO	CYAO
1200 °C for 1 h	CaF_2, Al_2O_3, $CaAl_2O_4$, $CaAl_4O_7$, $Ca_{12}Al_{14}F_2O_{32}$	CaF_2, $Ca_{12}Al_{14}F_2O_{32}$, $Y_4Al_2O_9$, $YAlO_3$, $CaYAl_3O_7$
1650 °C for 1 min	$CaAl_2O_4$	$Y_4Al_2O_9$, $Y_3Al_5O_{12}$, $Ca_2Al_2O_5$, $CaYAl_3O_7$, $CaYAlO_4$
1650 °C for 8 h	Trace of $CaAl_2O_4$	$Y_4Al_2O_9$, $CaYAl_3O_7$, $CaYAlO_4$

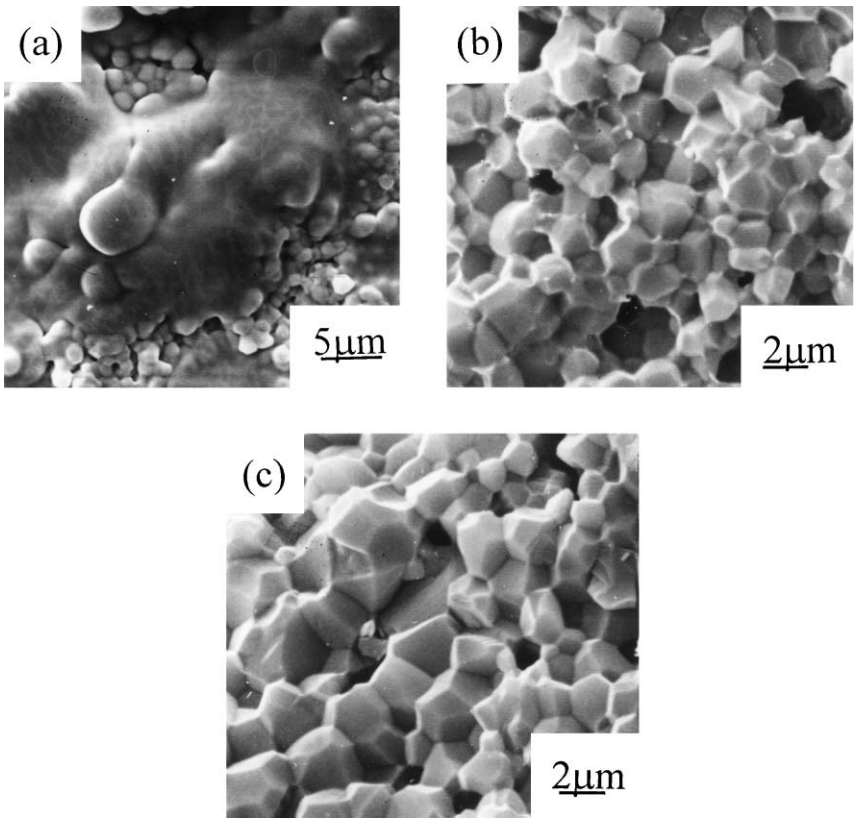

Fig. 3. Microstructures of sample CA sintered at 1650 °C for (a) 1 min, (b) 6 h, and (c) 12 h by SEM.

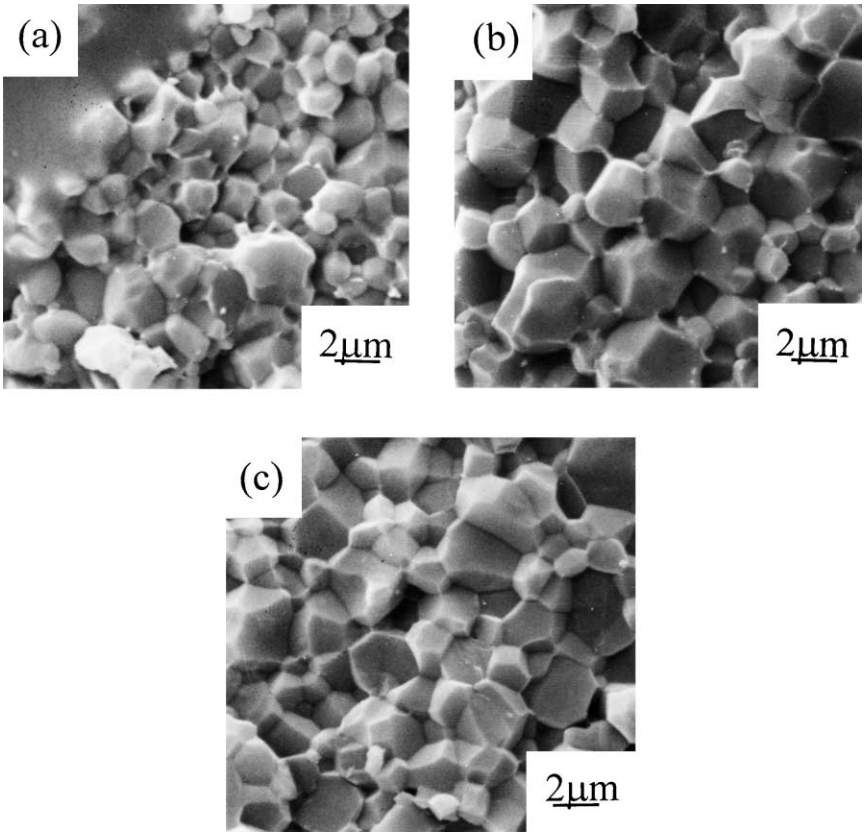

Fig. 4. Microstructures of sample CYA1 sintered at 1650 °C for (a) 1 min, (b) 6 h, and (c) 12 h by SEM.

These results are consistent with that identified by XRD, as shown in Table 3, where the two phases of YAM and $CaYAlO_4$ are identified in this sample. By EDS as indicated in Table 4, the different contents of Ca and Y elements are examined from the edge to the middle of the grain boundary phases, which also implies the inhomogeneous phase compositions in the grain-boundary phases. It is noted that the atoms of phase YAM in field I and that of phase $CaYAlO_4$ in field II arrange through a co-lattice transition. This implies that the promotion of the liquid $CaYAlO_4$ on shrinkage can be reduced if the solid YAM is enough in the liquid.

3.4. Thermal conductivity

The qualitative information about the oxygen concentration in the AlN lattice and, indirectly, of its thermal conductivity is obtained by the careful determination of the AlN lattice parameters. A reduction of the c lattice parameter corresponds to higher oxygen concentration and lower thermal conductivity of the AlN grains.[1,18,19] Table 5 shows the lattice parameters, densities, and thermal conductivities of samples CA and CYA1 sintered for different time at 1650 °C. The densities of samples CA and CYA1 increase with

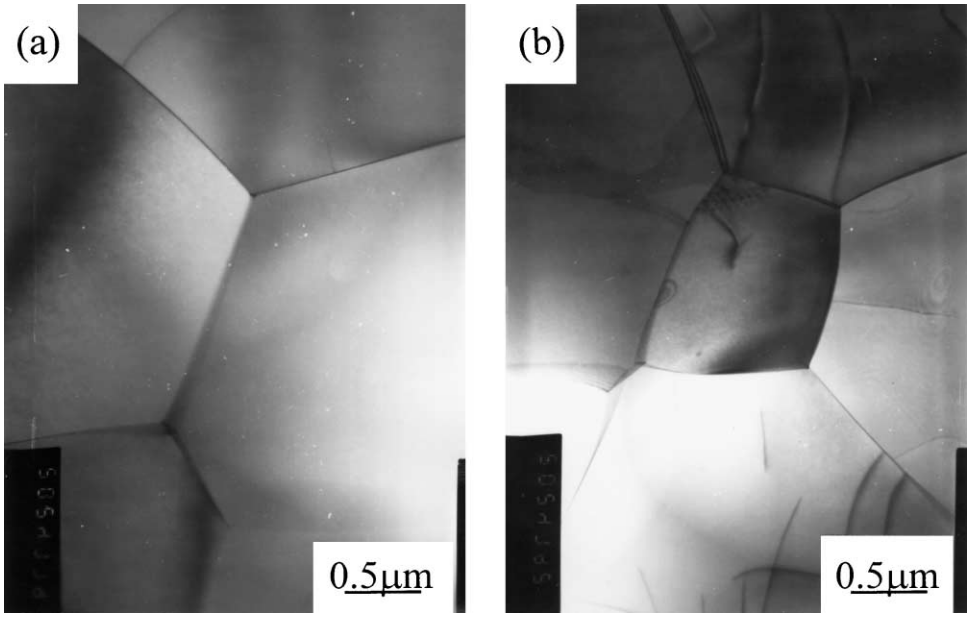

Fig. 5. TEM of samples (a) CA and (b) CYA1 sintered for 4 h at 1650 °C.

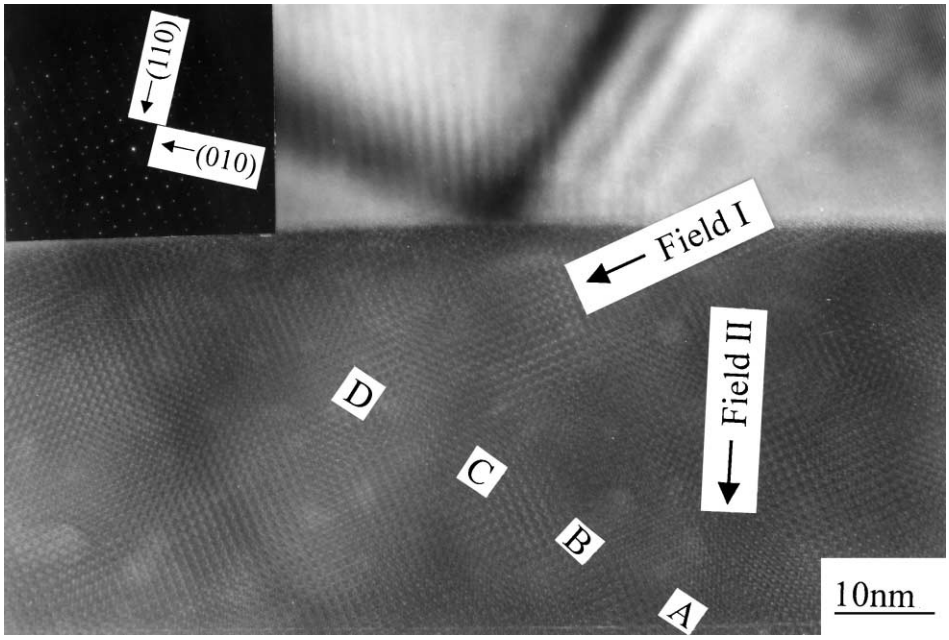

Fig. 6. High-resolution electron microscope study on the grain boundary phases of sample CYA1 sintered for 4 h at 1650 °C.

Table 4
Contents of the elements Ca and Y in the grain boundary phases shown in Fig. 6

Position	Ca (wt.%)	Y (wt.%)	Ca/Y (atoms)
A	0.5	1.11	1
B	0.63	1.48	0.73
C	1.04	1.93	0.51
D	1.95	12.72	0.34

Table 5
Lattice parameters, densities and thermal conductivities of samples CA and CYA1 sintered for different time at 1650 °C

Sample	a (nm)	c (nm)	Density (g/cm^3)	Thermal conductivity (W/m·K)
CA for 1 min	0.31118	0.49794	2.82	85
CA for 4 h	0.31118	0.49791	3.18	121
CA for 8 h	0.31119	0.49787	3.18	120
CYA1 for 1 min	0.31119	0.49790	3.01	109
CYA1 for 4 h	0.31118	0.49789	3.24	137
CYA1 for 8 h	0.31118	0.49788	3.26	148

the sintering time, which is consistent with the shrinkages at this temperature. Since the purification of the AlN lattice produces an increase of the c-axis, the decrease of c-axis during the sintering implies that the oxygen diffuses into AlN lattice and increases the defects in it, thus deteriorating the thermal conductivity. As shown in Table 5, the c-axis in sample CA sintered from 1min to 4h decreases from 0.49794 to 0.49791nm, so the increasing thermal conductivity from 85 to 121 kJ/m·K mainly comes from the enhancement of the densification. It can be seen that the density and thermal conductivity of sample CA sintered from 4 to 8 h have no change, which implies that the detriment to thermal conductivity due to the increase of the oxygen-related defects has counteracted the promotion of the decreasing grain boundary phases on it since the c-axis has a decrease from 0.49791 to 0.49787 nm. In sample CYA1 sintered from 1 min to 8 h, there is no increase on the c-axis length, which indicates that Y_2O_3 has no prominent effect on the elimination of oxygen defects from the lattice. Furthermore, the c-axis of sample CYA1 sintered for 8 h has a very small difference from that of sample CA, which also implies that the promotion of Y_2O_3 on the removal of oxygen from the lattice is not obvious. Thus, the higher thermal conductivity of sample CYA1 than that of CA is mainly attributed to its higher densification.

4. Discussions

During the sintering, oxygen covering on the surfaces of the AlN particles diffuses into the lattice to produce aluminum vacancies, which decreases the thermal conductivity of AlN ceramics by scattering phonons. The additives decrease the oxygen defects by two routes: (i) the additives react with the oxygen to form aluminates, and thus decrease the oxygen content on the surface of AlN particles; and ii) the grain-boundary phases with low oxygen activity occur round the AlN grains, which removes oxygen from the lattice to the surface. To eliminate the oxygen defects in the AlN lattice, they are important that the additives contact with the AlN particles sufficiently in the route (i), and the grain-boundary phases with low oxygen activity are continuous and have the effective wetting to the AlN grains in the route (ii).

It is suggested that oxygen homogeneously distributes on the surface of the AlN particles. So it is difficult for all the oxygen to react with the additives if the liquid formed by the reaction does not wet all the AlN particles. In sample CA sintered at 1650 °C, as shown in Fig. 3, the liquid goes through a process of redistribution, which makes the oxygen on the surface of the less wetted particles by the liquid have enough time to diffuse into the lattice, thus resulting in the decrease of c-axis. Furthermore, small quantity of liquid remains between the grains, as shown in Fig. 5(a), which makes it difficult to remove the oxygen from the lattice to the surface due to the lack of the driving force produced by the liquid round the grains. So the c-axis decreases greatly and the thermal conductivity is deteriorated during the sintering. In sample CYA1, the small quantity of calcium aluminates liquid below 1650 °C not only slows the shrinkage but also decreases the close contact of Y_2O_3 with the oxygen on the surface of the AlN particles, which results in a lower c-axis at the beginning of 1650 °C compared with that of sample CA. During the sintering, liquid $CaYAlO_4$ with Y_2O_3 and YAM promotes the reaction between them and the oxygen, thus slowing the decrease of the c-axis. However, the effect of the liquid on the removal of the oxygen from the lattice to the surface is not prominent since the grain-boundary phases containing YAM and $CaYAlO_4$ move to the three-grain junctions as the firing time goes on, as shown in Figs. 5(b) and 6, which results in a less wetting to the AlN grains. So the c-axis of sample CYA1 decreases during the sintering. The higher thermal conductivity of the samples with Y_2O_3 is mainly attributed to the enhancement of the densification.

5. Conclusions

Y_2O_3 has an important effect on the densification of AlN ceramics sintered at a low temperature of 1650 °C. Below this temperature, the shrinkage of the sample with Y_2O_3 additive is slow because the solid phase reaction between Y_2O_3 and Al_2O_3 decreases the formation of the calcium aluminates liquid. At 1650 °C, the shrinkages of the samples with Y_2O_3 addition increase quickly due to the formation of liquid $CaYAlO_4$. After

sintered for 12 h, the shrinkage of the sample with 2 wt.% Y_2O_3 addition reaches 17.9%, higher than that of the sample without Y_2O_3 addition, which is 16.3%. In the grain-boundary phases, YAM co-exists with $CaYAlO_4$ through a co-lattice transition, which limits the promotion of liquid $CaYAlO_4$ on the shrinkage if the amount of YAM is too much. When the amount of Y_2O_3 addition increases from 2 to 3.5 wt.%, the shrinkage of the sample decreases to 16.8%. The existence of liquid $CaYAlO_4$ decreases the diffusion of oxygen from surface to the AlN lattice at some extent. However, the removal of the oxygen from AlN lattice is difficult because the liquid phase moves to the triple grain junction to form discrete pockets, which causes a less wetting to the AlN particles during the sintering. The increasing thermal conductivities of the samples with Y_2O_3 addition mainly rely on the enhancement of the densification.

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