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Densification and structural development in the sintering of AlN ceramics with $CaCN_2$ additives

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Abstract

The effect of $CaCN_2$ addition on the densification and structural development for sintered AlN ceramics was investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and electron diffraction (ED). Dense sintered specimens (bulk density >3.16 g cm^{-3}) with 0.5–3.0 wt.% $CaCN_2$ additives were obtained depending on sintering temperature and time. When added with $CaCN_2$ from 0.50 to 3.0 wt.% and sintered at 1650–1800°C, all of the sintered samples exclusively belonged to the same AlN phase and no other phases were found in the XRD patterns. A large fraction of intergranular fractures was found in the SEM observations of the AlN samples sintered without and with $CaCN_2$ additive. The characterization of the AlN powders sintered with $CaCN_2$ additive was performed with a microstructural analysis using TEM and ED. In the TEM and ED pattern, the minor phase, $3CaO{\cdot}Al_2O_3$, appeared around the AlN grain boundaries.

Keywords: AlN; $CaCN_2$; Grain boundaries; Microstructure-final; Sintering

1. Introduction

Aluminum nitride (AlN) and AlN-based materials containing elements such as O, C and Si have attracted much attention of researchers in advanced ceramics. AlN is recognized as having a considerable potential for use in fabricating high-performance heat-conducting substrates for semiconductors because it is chemically inert and has high electrical resistivity.[1] The thermal conductivity of a high-purity AlN single crystal is theoretically estimated to be 320 W (mK)$^{-1}$,[2,3] which is 80% that of copper metal. On the other hand, AlN also exhibits excellent thermal shock behavior, hence it has a potential application in Al and ferrous alloy industries.[4]

AlN also shows low sinterability because it is a covalent material with the wurtzite type structure.[5] However, it has been found that several sintering aids such as CaC_2,[5] Y_2O_3,[5,6] $Ca(NO_3)_2{\cdot}4H_2O$,[7] CaO,[5,7] Eu_2O_3,[1] and $CaCO_3$[8] are reported to be useful for the fabrication of fully dense ceramics. Kurokawa et al.[5] have pointed out that when AlN powders containing sintering additives such as CaC_2, CaO, Y_2O_3 and C are hot-pressed in BN-lined graphite die at 1800°C and 100 kg cm^2 in 1 atm of N_2 gas for 2 h, most of AlN ceramics are fully densified, but when more than 1.0 wt.% carbon is added, relative densities are around 70% of the theoretical density. When the AIN powder are added with $Ca(NO_3)_2{\cdot}4H_2O$ (equivalent to 0.5 wt.% CaO additive) sintered at 2000°C and 200 kg cm^{-2} in 1 atm N_2 atmosphere for 3 h, the bulk density is 3.26 g cm^{-3}.[7] On the other hand, VanDamme et al.[1] have also pointed out that dense sintered AlN specimens are obtained using 1–4 wt.% Eu_2O_3 additive and firing at 1800°C for 1 h in a graphite furnace with a N_2 gas flow of about 1 l min^{-1}. Otherwise, Komeya et al.[8] have also found that when AlN powder containing sintering additive $CaCO_3$ 0.5 wt.% (0.3 wt.% as a CaO) attained the full density of 3.25 g cm^{-3} by sintering at 1800°C for 1 h, which would be consistent with over 99% for relative density. This densification is compared to 2.60 g cm^{-3} for AlN compacts with no additions. In sintering at 1750°C, typical effective densification phenomena were observed for $CaCO_3$ content.[8] This phenomenon seems to be based on the formation of aluminates in the AlN-oxides system which gives a liquid phase at high temperatures. However, an extensive

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literature search shows that details of the sintering of aluminum nitride with $CaCN_2$ additive has not been clarified.

In the present paper, the densification and structural development in the sintering of AlN ceramics with $CaCN_2$ additives have been studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction (ED). The objectives of this investigation are to demonstrate (i) the effect of $CaCN_2$ addition on the sintering and densification behavior of AlN powders, (ii) the structural evolution of the AlN powders with $CaCN_2$ additives during sintering, and (iii) effect of $CaCN_2$ addition on the grain growth and microstructure development for sintered AlN ceramic.

2. Experimental procedure

2.1. Sample preparation and sintering

The AlN powders were of commercial grade (supplied by Tokuyama Soda Co., Japan). Impurity contents and physical properties of the AlN starting powders are listed in Table 1.

Calcium cyanamide (0–4.0 wt.%) ($CaCN_2$, purity 99.5%, supplied by TCI Chemical Co., Japan) was used as a sintering additive to prepare specimens. Each mixture was blended for 4 h in a laboratory ball mill using Al_2O_3 balls and ethanol. The powder mixture was dried at 110°C in NH_3 atmosphere for 2 h, mechanically blended with 1.0 wt.% ethyl cellulose binder (E.C., purity 49%, supplied by Hayashi Pure Chem. Indust. Ltd., Japan) in a high shear mill for 2 h and sieved after granulation. The powder mixture after granulation was isostatically pressed at l47 MPa into a pellet of 1.49 mm in height and 15.0 mm in diameter. The green compacts are preheated to 150°C for 1 h under NH_3 atmosphere to remove ethanol and moisture and heated at 900°C for 3 h to eliminate organic binders.

The preheated compact was sintered in a closed BN crucible at 1650–1800°C in N_2 atmosphere (purity $>99.9\%$) maintained at 1.08 atm for various times in a graphite heated tube furnace. Linear heating rate of 5°C min^{-1} from room temperature to 900°C and 2.5° C min^{-1} from 900 to 1650∼1800°C, respectively, were applied. After sintering, the surface of the pellet was polished prior to the measurements of density, XRD, SEM and TEM.

Table 1
Impurity element contents and physical properties of AlN starting powder

Impurity element	Content (ppm)	Physical property
Si	20	Particle size (μm) 1.3
C	390	Surface area ($m^2\ g^{-1}$) 3.3
Ca	49	
O_2	8300	

2.2. Analysis

After sintering, the bulk density of the sintered samples was measured using an Archimedes method and Eq. (1)

$$\text{Bulk density} = D/(W-S)\left(\text{g cm}^{-3}\right) \tag{1}$$

where D: weight of a dried sample, S: weight of a sample in water, W: weight of a wet sample.

The value of linear shrinkage was calculated from Eq. (2)

$$S = (\Delta L/L) \times 100\% \tag{2}$$

where S: linear shrinkage, L: diameter of green compact, ΔL: difference of a green compact diameter before and after sintering.

The XRD patterns of the sintered compacts were obtained using an X-ray diffractometer (Model Rad II A, Rigaku, Tokyo) with CuK_α radiation and Ni filter, operated at 30 kV, 200 mA and a scanning rate (2θ) of 0.25 min^{-1}.

The fracture surface of the sintered specimens was examined by SEM (Jeol 840, Tokyo, Japan). Specimens for transmission electron microscope observations were prepared by cutting with a diamond saw, grinding and polishing the 50 μm thick, and finally ion milling with Ar^+-ions. ED examinations were made on carefully thinned foils of the specimens.

3. Results and discussion

3.1. Densification behavior

Fig. 1 shows the bulk density of the sintered AlN specimens as a function of $CaCN_2$ content and sintering temperature. It indicates that, when sintered at 1650°C for 1 h, the effective densification is observed in the range of 2.0–3.0 wt.% $CaCN_2$ additive (bulk density varies from 2.90 to 3.02 g cm^{-3}) but the bulk density decreases rapidly in the specimens with over 3.0 wt.% $CaCN_2$ content. During sintering at 1700°C for 1 h, the bulk density sharply increases from 2.25 to 3.16 g cm^{-3} for the specimens added with $CaCN_2$ content varying from 0 to 2.0 wt.%. On the other hand, when sintered at 1700 and 1800°C for 1 h, respectively, the bulk density increases with sintering temperature for 0–1.0 wt.% $CaCN_2$. The maximum bulk density is 3.22 g cm^{-3} for the specimens containing 1.0 and 0.50 wt.% $CaCN_2$, and sintered at 1750 and 1800°C, respectively. Besides, for the AlN samples added with 3.0 wt.% $CaCN_2$ and

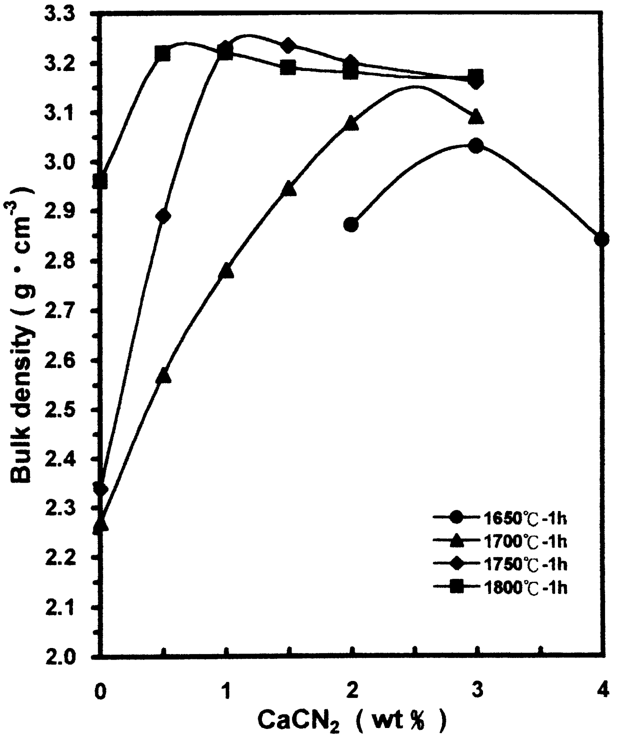

Fig. 1. Relationship between $CaCN_2$ content and bulk density for the AlN compact sintered at various temperatures for 1 h.

sintered at 1650 and 1700°C for 1 h, the bulk density above 3.00 g cm^{-3} is obtained.

The linear shrinkage of the samples with 0–4.0 wt.% $CaCN_2$ additive during sintering at 1650, 1700, 1750 and 1800°C for 1 h, respectively, at a constant heating rate of 2.5°C min^{-1}, is shown in Fig. 2. It indicates that, when sintered at 1650°C for 1 h, the linear shrinkage increases from 14.58 to 15.85% with $CaCN_2$ additive increased from 2.0 to 3.0 wt.%. On the other hand, the linear shrinkage decreases from 15.83 to 14.00% for the $CaCN_2$ content increased from 3.0 to 4.0 wt.%. Besides, when the samples are sintered at 1700°C for 1 h, the linear shrinkage increases from 6.00 to 16.67% with $CaCN_2$ additive content increased from 0 to 3.0 wt.%. For the specimens sintered at 1750 and 1800°C for 1 h, respectively, the same linear shrinkage 20.83% is attained.

The relation between linear shrinkage and $CaCN_2$ additive content in sintering at 1750°C for various times is shown in Fig. 3. When the samples are sintered at 1750°C for 1 h, the linear shrinkage increases from 7.53 to 20.83% with $CaCN_2$ additive content increasing from 0 to 1.5 wt.%. When the samples contain 1.5 to 3.0 wt.% $CaCN_2$ sintered at 1750°C for 1–12 h, the linear shrinkage still maintains at 20.83% for all samples. This result can be attributed to an increasing amount of liquid phase clusters per unit grain boundary area with sintering time for the same $CaCN_2$ additive content.

Figs. 2 and 3 also indicate that during the sintering at 1750°C for 1 h, the linear shrinkages are 14.17 and 16.67% for the samples containing 0.50 and 1.0 wt.% $CaCN_2$, respectively. On the other hand, the linear shrinkage attains to 20.83% for the samples with the $CaCN_2$ additive content from 1.5 to 3.0 wt.%. For the soaking time of 3 h, the linear shrinkage is 20.83%, no matter what $CaCN_2$ additive content it contains.

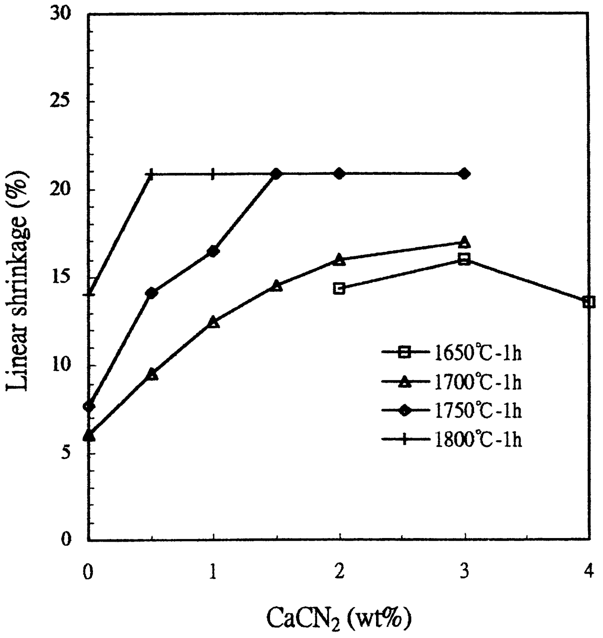

Fig. 2. Effect of $CaCN_2$ content on the linear shrinkage of the AlN compacts sintered at various temperatures for 1 h.

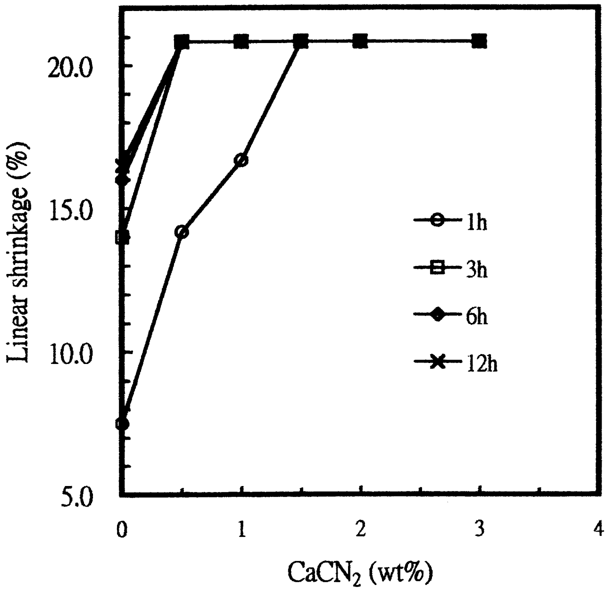

Fig. 3. Relation between $CaCN_2$ content and linear shrinkage for the AlN compacts sintered at 1750°C for various times.

Kubo et al.[9] have pointed out that for the AlN powder with the surface area of 95–175 m^2 g^{-1} the sintering temperature is less than 1600°C and for the conventional pure powders with the surface area of 1.0–5.3 m^2 g^{-1}

usually around 1850°C or higher.[10,11] In the present study, the surface area of the powders is about 3.3 $m^2 g^{-1}$. Thus, the difference in sintering temperature can be attributed to the surface area or the ($CaCN_2$) additive grains.

From Figs. 1–3, it is obvious that the density exhibits a complex dependence in the sintering temperature–time plot due to simultaneous densification and decomposition. Terwilliger and Lange[12] have modeled this process by assuming that the decomposition vapor causes the pore growth. The consequence of an increasing amount of vapor raises the pore pressure and thereby limits density. Swelling occurs because the decomposition reaction increases the pore size and net porosity.[13]

3.2. Phase evolution

The XRD patterns of the AlN powders added with various $CaCN_2$ additives and sintered at 1750°C for 1 h are shown in Fig. 4. Evidently, all of the peaks in the pattern belong to the single hexagonal AlN[14] and no other phases are found in the sintered specimens, irrespective of the different contents of $CaCN_2$ additives. For the AlN powders added with various $CaCN_2$ additives and sintered at 1650, 1700 and 1800°C for 1 h, respectively, the XRD patterns are the same as in Fig. 4, revealing the same single hexagonal AlN.

The TEM bright field micrograph and the corresponding electron diffraction (ED) pattern of the area indicated by an arrow in the AlN powders added with 3.0 wt.% $CaCN_2$ and sintered at 1750°C for 12 h are shown in Fig. 5. From Fig. 5(a), it is found that the uniform grain size is about 1.5 μm, the well-faceted grains develop upon grain growth and the grain boundaries contain a minute secondary phase. The ED pattern of the grain boundaries is shown in Fig. 5(b), showing $\left[\bar{1}\bar{2}1\right]$ zone axis of $3CaO\cdot Al_20_3$.

Kurokawa et al.[5] have pointed out that a minor phase of $CaAl_2O_4$ is present in the AlN samples with 4 wt.% CaO additive. On the other hand, none of the AlN samples added with CaC_2 shows a second phase.[5] Kuramoto and Taniguchi[7] found that the single phase of AlN in the sintered compact with $Ca(NO_3)_2\cdot 4H_2O$ (equivalent to 0.5 wt.% CaO). Komeya et al.[8] also found that the lower $CaCO_3$ (below 5 wt.%) added samples are substantially identical to $CaO\cdot 6Al_2O_3$, $CaO\cdot 2Al_2O_3$ and spinel phase. Besides, when added with 5 wt.% $CaCO_3$, $CaO\cdot Al_2O_3$ also appears. In the present study, when the maximum amount of an additive (4.0 wt.% $CaCN_2$, equivalent to 2.8 wt.% CaO) is added to the AlN powders, followed by sintering between 1650 and 1800°C for 1 h, the XRD patterns of the AlN samples with added $CaCN_2$ additive does not show a second phase, but the ED pattern provide the evidence for the presence of $3CaO\cdot A1_2O_3$.

According to Figs. 4 and 5, neither residual $CaCN_2$ nor CaO is found in the XRD and ED patterns. When $CaCN_2$ is used as a sintering aid it decomposes during sintering to form a low-melting-temperature liquid phase. Some residual oxygen impurities of the AlN powders are also localized at the grain boundaries to form $3CaO\cdot Al_2O_3$.

3.3. Effect of $CaCN_2$ addition on the grain growth

The relation between grain size and $CaCN_2$ additive content in sintering at various temperatures for 1 h is

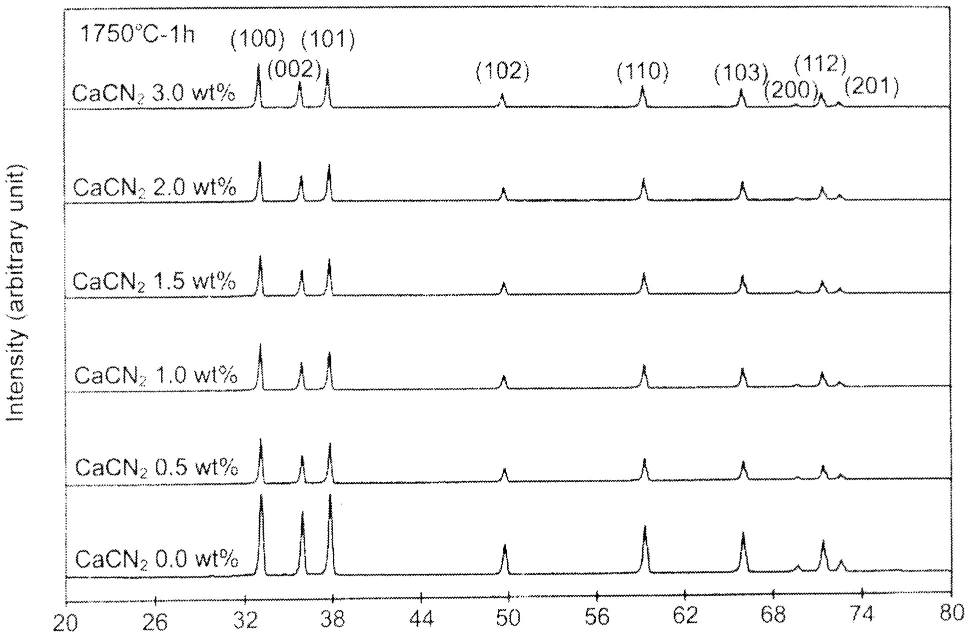

Fig. 4. XRD patterns of the AlN compacts added with various $CaCN_2$ contents and sintered at 1750°C for 1 h.

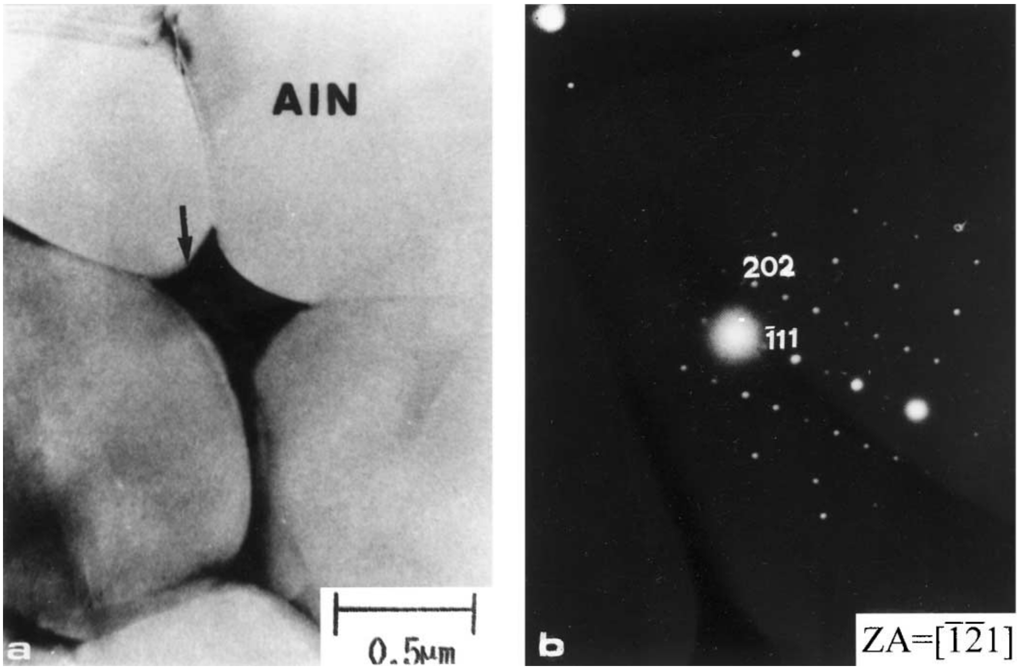

Fig. 5. TEM micrographs of the AlN compacts added with 2.0 wt.% $CaCN_2$ and sintered at 1750°C for 12 h: (a) BF image, (b) the ED pattern of the grain boundaries indicated by an arrow, showing the presence of $3CaO{\cdot}Al_2O_3$ with zone axis $[\bar{1}\bar{2}1]$.

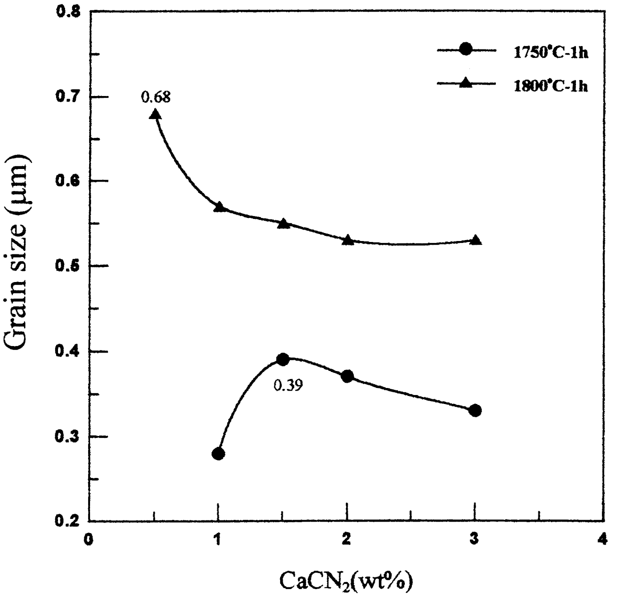

Fig. 6. Relation between $CaCN_2$ content and grain size for the AlN compact sintered at various temperatures for 1 h.

shown in Fig. 6. When the samples are sintered at 1800°C for 1 h, the grain size decreases from 0.68 to 0.55 μm with the $CaCN_2$ content increased from 0.50 to 3.0 wt.%. On the other hand, for the samples sintered at 1750°C for 1 h, the grain size increases from 0.28 to 0.39 μm with the $CaCN_2$ content increased from 1.0 to 1.5 wt.%, but the grain size decreases from 0.39 to 0.34 μm when the $CaCN_2$ content increases from 1.5 to 3.0 wt.%.

The $CaCN_2$ additive shows the greatest effect for the lower sintering temperature and smaller initial grain size. From Figs. 2 and 6, it is found that a decrease in grain growth rate is accompanied by a lower densification rate. The slower grain growth of the primary phase undergoing from mixed solid phases is probably due to the reduction in volume fractions of the respective phase, increased diffusion distance, changes in the interfacial energies, and interfacial reactions.[13]

During initial liquid formation, transients in the interfacial energies can have an effect on the grain connectivity. A decrease in solid diffusivity is one approach to slowing the grain growth rate. A change in the stoichiometry of the solid component can result in slower growth if the deficient species has the lower diffusion rate. Also chemical additives can alter the interfacial energy interfering with the interfacial dislocation and reprecipitation.[13] Lassner et al.[15] also pointed out that the typical inhibitor acts to slow down the interfacial material transport during solution-reprecipitation.

3.4. Microstructure observation by SEM

The effect of the $CaCN_2$ addition on the microstructure of the sintered AlN ceramics was observed by SEM. Fig. 7 shows the SEM morphology of the AlN samples with 0.50 wt.% $CaCN_2$ additive sintered at 1750°C for various times. It reveals that the grains grow with sintering time. In Fig. 3, for the samples with 0.50 wt.% $CaCN_2$ and sintered at 1750°C for 1 h, the linear shrinkage is only 14.17%. But when sintered at 1750°C

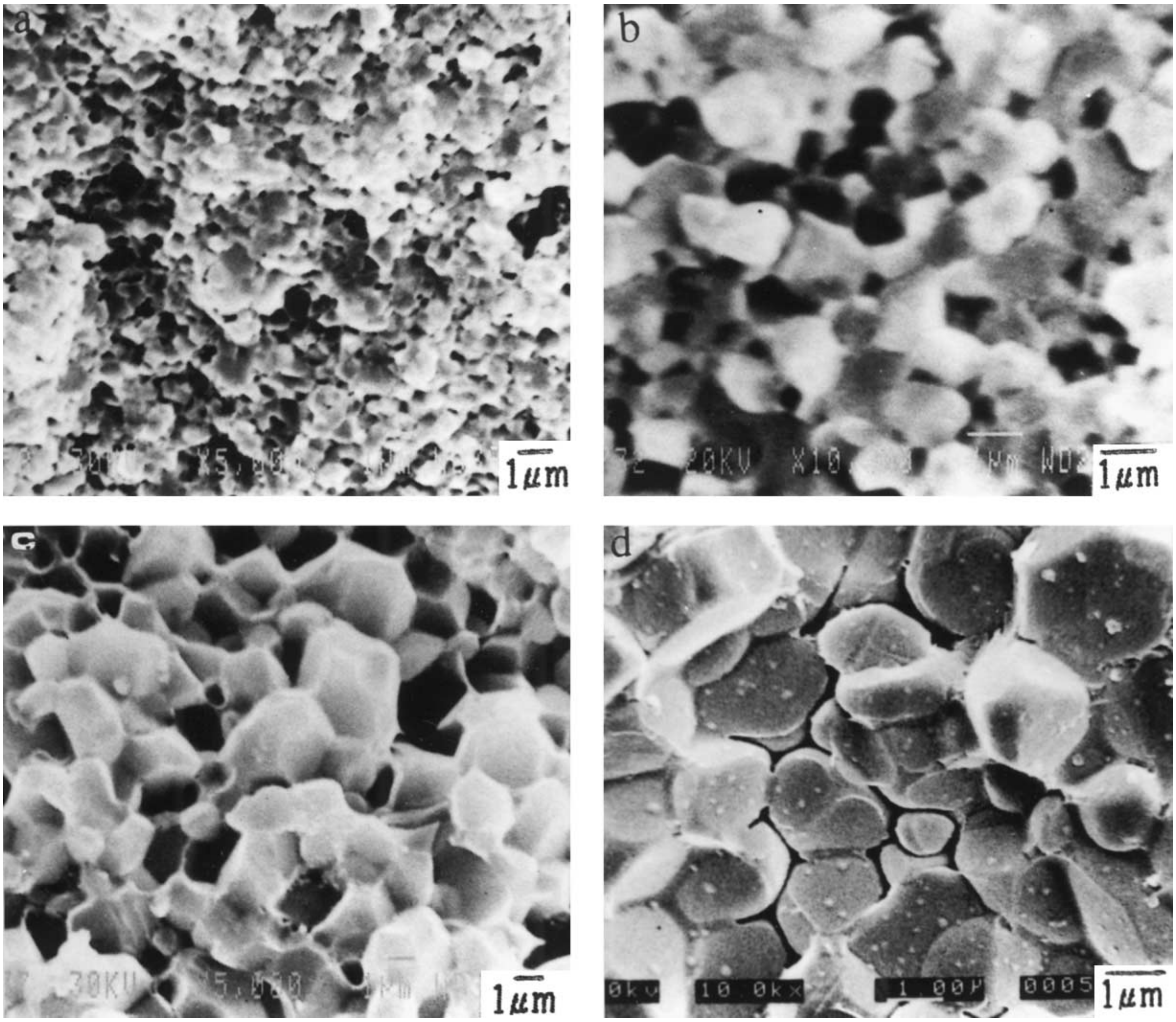

Fig. 7. SEM micrographs of the fractured surfaces for the AlN specimens with 1.0 wt.% $CaCN_2$ and sintered at 1750°C for different times: (a) 1 h, (b) 3 h, (c) 6 h and (d) 12 h.

for 3–12 h, the linear shrinkage approaches the same value, namely 20.83%. The amount of the $CaCN_2$ additive directly influences the volume fraction of the liquid phase. Dimension change during sintering depends on liquid phase contact. According to Figs. 3 and 7, when the $CaCN_2$ additive is maintained at 0.50 wt.% and the compacts are sintered at 1750°C for 3, 6 and 12 h, respectively, the $CaCN_2$ decomposes completely and melts so that the amount of the liquid phase attains to the maximum and obtains the highest linear shrinkage. On the other hand, when sintered at 1750°C for 3, 6 and 9 h, respectively, the liquid phase is contact with AlN or Al_2O_3 on the AlN surface induces the solution-reprecipitation and the amount of the liquid phase maintains constant during sintering time greater than 3 h, forming CO and CO_2 gases,[5] leading to the same linear shrinkage value.

The SEM micrographs of the fractured surfaces of the specimens with various $CaCN_2$ additives sintered at different temperatures for 1 h are shown in Fig. 8. Micrographs shows that the grain sizes of the AlN specimens containing 2.0 wt.% $CaCN_2$ and sintered at 1700, 1750 and 1800°C for 1 h are about 0.32, 0.38 and 0.53 µm, respectively. Apparently, the fracture mode is quite same among the different AlN samples. Many intergranular fractures are found in the sintered AlN samples with various $CaCN_2$ additives. Well-faceted grain morphology is associated with predominant intergranular fracture. From Fig. 8, it is also found that, for the AlN samples containing different $CaCN_2$ additives and sintered at the same temperature, the grain size of the AlN samples containing 3.0 wt.% $CaCN_2$ additive is less than that with 2.0 wt.% $CaCN_2$.

From Fig. 8, it is also seen that the solid AlN particles wet each other due to enough amount of the liquid phase and hence it is facile to obtain a densified sample. Aside from this feature, the sintered samples exhibit appreciable grain growth with increasing sintering temperature for the samples containing the same amount of $CaCN_2$ additive.

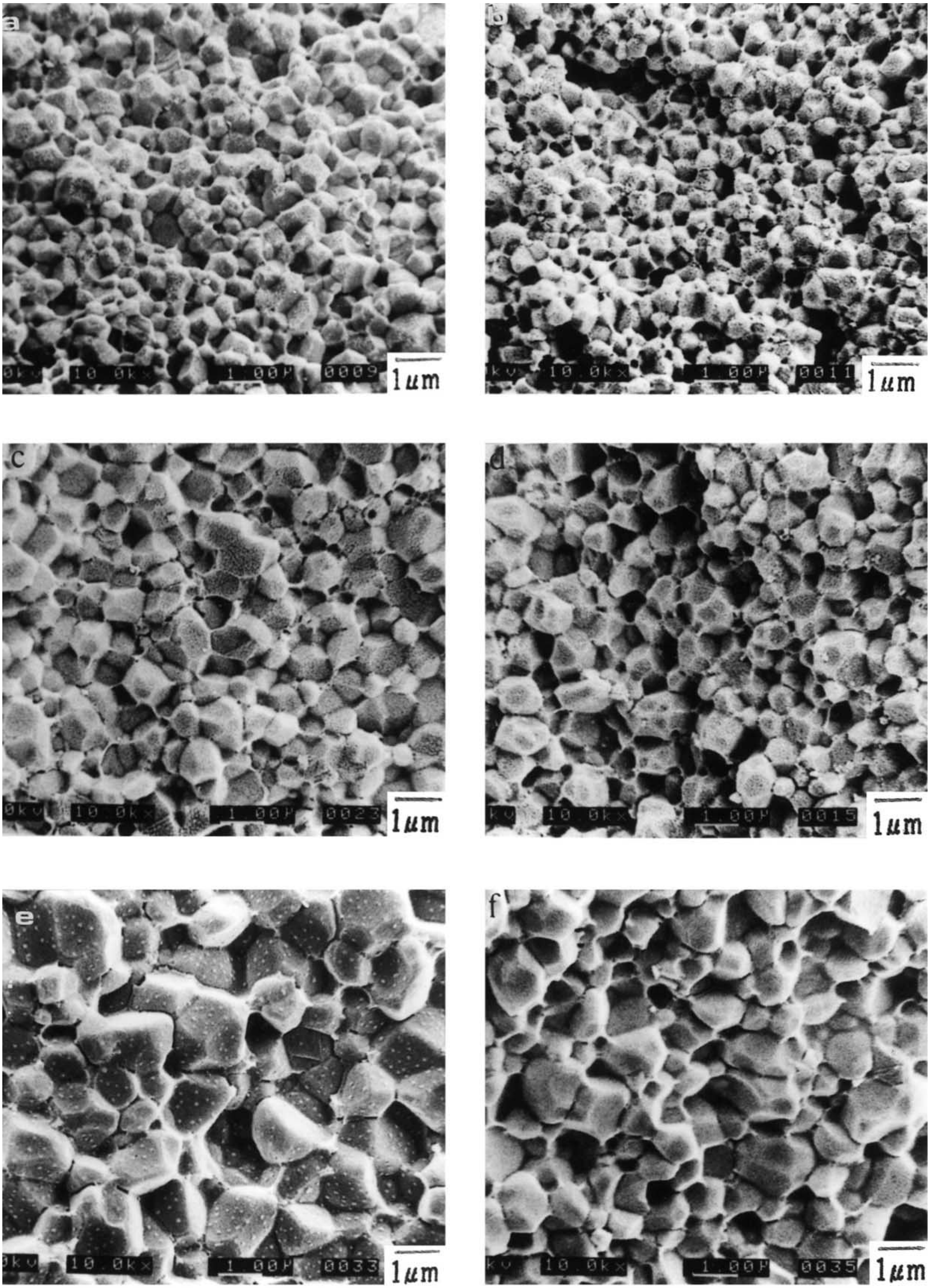

Fig. 8. SEM micrographs of the fractured surfaces for the AlN compacts with various $CaCN_2$ additives and sintered at different temperatures for 1 h: (a) 2.0 wt.% $CaCN_2$ at 1700°C, (b) 3.0 wt.% $CaCN_2$ at 1700°C, (c) 2.0 wt.% $CaCN_2$ at 1750°C, (d) 3.0 wt.% $CaCN_2$ at 1750°C, (e) 2.0 wt.% $CaCN_2$ at 1800°C and (f) 3.0 wt.% $CaCN_2$ at 1800°C.

4. Conclusions

A study of $CaCN_2$ addition on the densification and structural development in sintered AlN ceramics is summarized as follows:

1. The maximum bulk density, 3.22 g cm^{-3}, is obtained for the specimens containing 1.0 and 0.5 wt.% $CaCN_2$ sintered at 1750 and 1800°C, respectively. On the other hand, for the AlN samples with 3.0 wt.% $CaCN_2$ additive sintered at 1650 and 1700°C for 1 h, respectively, the bulk density is above 3.00 g cm^{-3}.
2. When sintered at 1650°C for 1 h, the linear shrinkage increases from 14.58 to 15.83% with $CaCN_2$ additive increased from 2.0 to 3.0 wt.%. On the other hand, the linear shrinkage decreases from 15.83 to 14.00% with $CaCN_2$ content increased from 3.0 to 4.0 wt.%. For the specimens sintered at 1750 and 1800°C for 1 h, respectively, the linear shrinkage for all AlN samples containing $CaCN_2$ additive greater than 1.5 wt.% attains to 20.83%.
3. When the samples are sintered at 1750°C for 1 h, the linear shrinkage increases from 7.53 to 20.83% with $CaCN_2$ additive content increasing from 0 to 1.5 wt.%. For the samples containing 1.5–3.0 wt.% $CaCN_2$ sintered at 1750°C for 1–12 h, the linear shrinkage maintains 20.83% for all samples.
4. The XRD patterns of the AlN samples containing various $CaCN_2$ additive and sintered at 1650–1800°C for 1 h have shown a single hexagonal AlN.
5. When $CaCN_2$ is used as a sintering aid it decomposes during sintering to form a low-melting-temperature liquid phase. Some residual oxygen impurities of AlN powders are localized at the grain boundaries to form $3CaO{\cdot}Al_2O_3$.
6. The SEM observations have shown many intergranular fractures in the sintered AlN samples with $CaCN_2$ additive. The well-faceted grain morphology is associated with a predominant intergranular fracture.

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