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The Influence of the Anions of Calcium-Containing Sintering Aids for Aluminium Nitride

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Abstract

Various calcium compounds were used as sintering additives for aluminium nitride, in order to investigate the influence of their anions on the sintering and the resulting properties of the AlN ceramic. With the exception of CaS, all sintering additives used form CaO and hence calcium aluminate liquid phases. Due to the different melting or decomposing temperatures of the calcium compounds as well as various chemical reactions and the volatility of the halides, for instance, considerable differences in the determined properties occurred. Most of the calcium compounds used remove oxygen from the AlN. The sintering atmosphere also shows an influence on the thermal conductivity of the samples, because the nitrogen takes part in some chemical reactions.

Verschiedene Calciumverbindungen wurden als Sinterhilfsmittel für Aluminumnitrid eingesetzt, um den Einfluß der Anionen auf die Sinterung und die resultierenden Eigenschaften der AlN-Keramik zu untersuchen. Mit Ausnahme von CaS führten alle eingesetzten Sinterhilfsmittel zur Bildung von CaO und damit zu Calciumaluminatschmelzphasen. Aufgrund unterschiedlicher Schmelz-bzw. Zersetzungstemperaturen der Calciumverbindungen, verschiedener chemischer Reaktionen sowie der Flüchtigkeit z.B. der Halogenide, traten z.T. erhebliche Unterschiede in den ermittelten Eigenschaftswerten auf. Durch die meisten verwendeten Calciumverbindungen wird Sauerstoff aus dem AlN-Gitter entfernt. Die Sinteratmosphäre beeinflußt ebenfalls die Wärmeleitfähigkeit der Proben, da der Stickstoff aus der Sinteratmosphäre an einigen Reaktionen teilnimmt.

Divers composés du calcium ont été utilisés comme additifs de frittage du nitrure d'aluminium, afin d'étudier l'influence de leurs anions sur le frittage et les propriétés finales des céramiques en AlN. A l'exception de CaS, tous les additifs de frittage utilisés forment du CaO et de là des phases liquides d'aluminate de calcium. En raison des différentes températures de fusion et de décomposition des composés de calcium, ainsi que des diverses réactions chimiques et de volatilité des halogénures, par exemple, on remarque des différences considérables dans les propriétés mesurées. La plupart des composés du calcium utilisés enlevent de l'oxygène à l'AlN. L'atmosphère de frittage a aussi une influence sur la conductivité thermique des échantillons car l'azote intervient dans certaines réactions chimiques.

1 Introduction

The good thermal conductivity, together with other physical properties, such as low dielectric permittivity, low dielectric losses, and a thermal expansion behaviour matching that of silicon, makes aluminium nitride interesting as a substrate material for highly integrated microelectronic units.

Because of the increasing complexity of microelectronic devices and the decreasing switching times, the removal of the heat discharge is of increasing importance. In the case of insufficient heat dissipation, the maximum operating temperature can easily be exceeded and the function carriers are destroyed.[1]

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The thermal conductivities of aluminium nitride often differ extremely from the theoretical value, because all defects, such as pores and grain boundary segregations, as well as contaminations (point defects) within the AlN lattice cause a considerable decrease of the thermal conductivity.[2,3]

In this connection the quantity of oxygen in the lattice plays an important role. Oxygen occupies nitrogen sites in the AlN lattice and hence causes aluminium vacancies according to the following equation:

$$Al_2O_3 \rightleftharpoons 2Al_{(Al)} + 3O_{(N)} + V_{(Al)}$$

AlN is mainly covalent bonded, and that is why conventional powders can be sintered to high densities only with the aid of a liquid-phase sintering mechanism. This requires the addition of a sintering aid. Calcium oxide, forming liquid phases with Al_2O_3 at the sintering temperature, is a well-proven sintering aid for AlN.[4]

In the present paper the influence of the anions of calcium compounds on the sintering process and the resulting properties of AlN ceramics is investigated. The following compounds were chosen: CaO (added as $Ca(NO_3)_2 . 4H_2O$), CaF_2, CaC_2, $CaCN_2$, CaS, $CaCl_2$, CaH_2, $CaCO_3$, Ca_3P_2 and $Ca(C_3H_5O)_2$ (calcium lactate).

2 Experimental

AlN is mainly covalent bonded, and that is why (oxygen content: 1·5 wt%) was used as the starting material. The AlN powder was mixed with the dopants and the pressing aids (ethanolic solution of polyvinylbutyral and stearic acid) in an agate mortar. In the case of moisture-sensitive dopants ($CaCN_2$, CaH_2, CaS and CaC_2), this was performed by heating the dopant and paraffin in cyclohexane in a glass bulb. The suspension was continuously stirred, and the AlN was added. The quantity of dopants was 3 wt% related to the calcium content in CaO.

After drying in air or vacuum in the case of the moisture-sensitive dopants, the powder was cold isostatically pressed into small cylinders (height and diameter: 5 mm) using a pressure of 480 MPa. The pressing aid was burnt out at 500°C for 1 h in air.

One group of samples was sintered in a high-temperature carbon tube furnace (Nernst-Tamman) in a nitrogen atmosphere. The samples were put into a small, open graphite crucible and completely embedded in AlN. The sintering temperature was 1850°C, the soaking time was 3 h; heating and cooling rates were 800 K/min in the case of dopants resistant to hydrolysis. Samples containing moisture-sensitive dopants were heated to 500°C using a heating rate of 200 K/h. Subsequent treatment was the same as already mentioned. Some aluminium nitride samples doped with $CaCO_3$, $CaCN_2$, Ca_3P_2 and calcium lactate ($Ca(C_3H_5O)_2$) were sintered using another high-temperature furnace (HTO 2300/2-SN, Fa. LEW, Henningsdorf). In this case the samples were located in a closed graphite crucible which was coated inside with molybdenum, also embedded in AlN. Besides nitrogen, argon was also used as sintering atmosphere.

The following properties of the sintered samples were determined: sintering density, residual contents of oxygen and calcium evaluated by hot gas extraction (LECO TC 136) and ICP analysis (Leeman Labs 2.5), respectively. The thermal conductivity was measured using a light-flash method as described in Ref. 5. Furthermore, X-ray diffraction analysis (Siemens D 500), SEM of fractured samples (Cambridge Instruments) and electron microanalysis (EDX, Tracor Northern) were performed.

The operating characteristics of the applied calcium-containing sintered aids are investigated, and possible reasons for the substantial differences in the obtained sintering density and thermal conductivity are presented.

3 Results and Discussion

Using a calcium-containing sintering additive, liquid calcium aluminate phases are formed. Table 1 shows a choice of these calcium aluminates and the corresponding values of the free standard reaction enthalpy at a temperature of 2000 K, $\Delta G_{R,2000}$ in kJ/mol, referred to 1 mol of converted Al_2O_3.[6,7]

Possible reactions between the calcium compounds and the oxygen (in the form of Al_2O_3) to give CaO and other reaction products are presented in Table 2. The ΔG_R values characterize the possibility of the reactions from the thermodynamical point of view. A small positive value can be shifted to the negative range, for instance, if the mentioned calcium aluminates are formed. Furthermore, the kinetic conditions have to be considered, because volatilizing reaction products can shift the chemical equilibrium and even enable a reaction with a positive ΔG_R value.

Table 1. Free standard reaction enthalpies of calcium aluminate (choice)

Calcium aluminate	*CaO/Al_2O_3 ratio*	*$\Delta G_{R,2000}$ (kJ/mol)*
$CaO . 2Al_2O_3$	1:2 (0·5)	−47
$CaO . Al_2O_3$	1:1 (1·0)	−53
$12CaO . 7Al_2O_3$	12:7 (~1·7)	−126
$3CaO . Al_2O_3$	3:1 (3·0)	−199

Table 2. Possible calcination reactions during the sintering process (the values for the free standard reaction enthalpies are related to 1 mol Al_2O_3)

Sintering additive	*Possible reactions to form CaO*			*Free standard reaction enthalpy (kJ/mol) (T in K)*	*Annotation*
$CaCO_3$	$CaCO_3 \rightleftharpoons CaO + CO_2$	(1)		—	$p_{CO_2} = 1$ bar at 841 C
CaX_3	$3CaX_2 + Al_2O_3 \rightleftharpoons 3CaO + 2AlX_3$	(2)	$X = F$	$\Delta G_{2000} = +362$	$p_{AlF_3} = 1$ bar at 1180°C
$(X = F, Cl)$			$X = Cl$	$\Delta G_{2000} = +414$	$p_{AlCl_3} = 1$ bar at 450 C
	$2CaF_2 + Al_2O_3 \rightleftharpoons 2CaO + AlOF + AlF_3$	(3)		$\Delta G_{2000} = +350$	—
CaS	$3CaS + Al_2O_3 + N_2 \rightleftharpoons 3CaO + 2AlN + 3S$	(4)		$\Delta G_{2000} = +590$	$T_s \approx 2400$°C
	$3CaS + Al_2O_3 \rightleftharpoons 3CaO + Al_2S_3$	(5)		$\Delta G_{2000} = +394$	—
CaH_2	$3CaH_2 + N_2 \rightleftharpoons Ca_3N_2 + 3H_2$	(6)		$\Delta G_{1089} = -143$	$T_s = 817$°C (1089 K)
	$Ca_3N_2 + Al_2O_3 \rightleftharpoons 3CaO + 2AlN$	(7)		$\Delta G_{1089} = -385$	—
	$3CaH_2 + Al_2O_3 + N_2 \rightleftharpoons 3CaO + 2AlN + 3H_2$	(8)		$\Delta G_{1089} = -528$	—
CaC_2	$CaC_2 + Al_2O_3 + N_2 \rightleftharpoons CaO + 2AlN + 2CO$	(9)		$\Delta G_{2000} = -14$	$T_s \approx 2300$°C
	$2CaC_2 + 3Al_2O_3 \rightleftharpoons 2CaO + 3Al_2O + 4CO$	(10)		$\Delta G_{2000} = +193$	—
$CaCN_2$	$6CaCN_2 + Al_2O_3 \rightleftharpoons 3CaO + 3CaC_2 + 2AlN + 5N_2$	(11)		$\Delta G_{1573} = -82$	Sublimation and decomposition at ≈ 1300 C (≈ 1573 K)
Ca_3P_2	$Ca_3P_2 + Al_2O_3 \rightleftharpoons 3CaO + 2AlP$	(12)		$\Delta G_{2000} = +51$	—
	$Ca_3P_2 + Al_2O_3 + N_2 \rightleftharpoons 3CaO + 2AlN + 2P$	(13)		$\Delta G_{2000} = -119$	—
	$Ca_3P_2 + Al_2O_3 + 2N_2 \rightleftharpoons 3CaO + 2AlN + 2PN$	(14)		$\Delta G_{2000} = -8$	
$Ca(C_3H_5O)_2$	$Ca(C_3H_5O)_2 \rightleftharpoons CaO + (2CH_4 + COH_2) + 3C$	(15)		—	—
	$3C + Al_2O_3 + N_2 \rightleftharpoons 2AlN + 3CO$	(16)		$\Delta G_{2000} = -16$	—
	$9C + 2Al_2O_3 \rightleftharpoons Al_4C_3 + 6CO$	(17)		$\Delta G_{2000} = +141$	-

The densities and thermal conductivities obtained for the AlN samples for all the sintering aids used are summarized in Fig. 1. There are notable differences in the densities, but, with exception of calcium lactate using an argon atmosphere, all densities were higher than 90% of the theoretical density of AlN (3·26 g/cm^3). Densities of more than 98% of the theoretical density were obtained using CaO, $CaCl_2$, CaF_2 and CaS. By contrast, the addition of CaC_2, CaH_2, CaP_3, $CaCN_2$ and Ca lactate resulted in densities below 96%.

Although the density represents an important fact for the thermal conductivity, it does not solely determine its value (see Fig. 1). A high relative sintering density of about 99% with $CaCl_2$ and 98% with CaS does not automatically cause a high value of the thermal conductivity as shown by 86 W/m K ($CaCl_2$) and 73 W/m K (CaS). Otherwise, the samples sintered with calcium lactate or CaH_2 show comparatively high thermal conductivities of 102 and 92 W/m K, respectively, despite the relatively low sintering densities of 88 and 91%.

$CaCO_3$ decomposes at a relatively low temperature and forms CO_2 and calcium aluminate liquid phases with oxygen impurities (Al_2O_3) contained in the AlN. $Ca(NO_3)_2 . 4H_2O$, also an oxide precursor, melts at 40°C and transforms into the anhydrous salt above 100°C. This salt melts at about 561°C and begins to decompose into CaO and nitric oxides at red heat.

The halides react with Al_2O_3 according to eqn (2) (Table 2), although the positive ΔG_R values of this

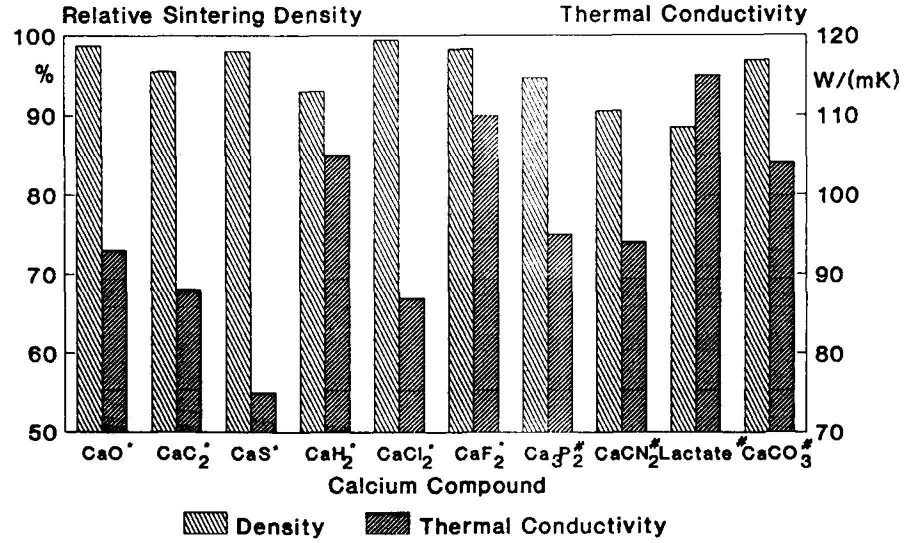


Fig. 1. Comparison of different calcium compounds with regard to the density and thermal conductivity of AlN ceramics. Sintering conditions: 1850°C, 3 h, N_2; graphite crucible: ★, open; #, closed.

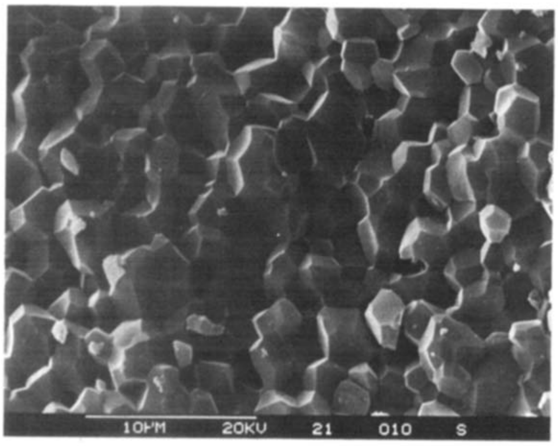


Fig. 2. Fracture surface of an AlN sample (SEM, 3000:1), sintering additive CaF_2.

reaction cannot be moved into the negative range by the formation of Al-oxyfluorides according to eqn (3) or the formation of calcium aluminates already mentioned. Nevertheless, reaction (2) seems to be possible because AlF_3 and $AlCl_3$ are volatile and leave the sintered body. By contrast, stable complexes are formed in the presence of low valence cations, for instance, $LiAlF_4$ was detected by X-ray diffraction at a temperature of 1750°C if LiF was added as a sintering aid.[8] In summary, the use of calcium halides as sintering additives should result in the formation of oxidic calcium compounds and in the formation of volatile aluminium halides.

The SEM micrograph of the fracture surface (Fig. 2) shows a sample sintered with CaF_2, which is characterized by a mean grain size of 2–5 μm and a predominantly intercrystalline fracture mode. Similar AlN microstructures were produced by adding the other calcium compounds. Secondary phases, located in the triple points, could not be identified using X-ray, because their content was lower than 3–5%, and hence below the detection limit (see also Fig. 3).

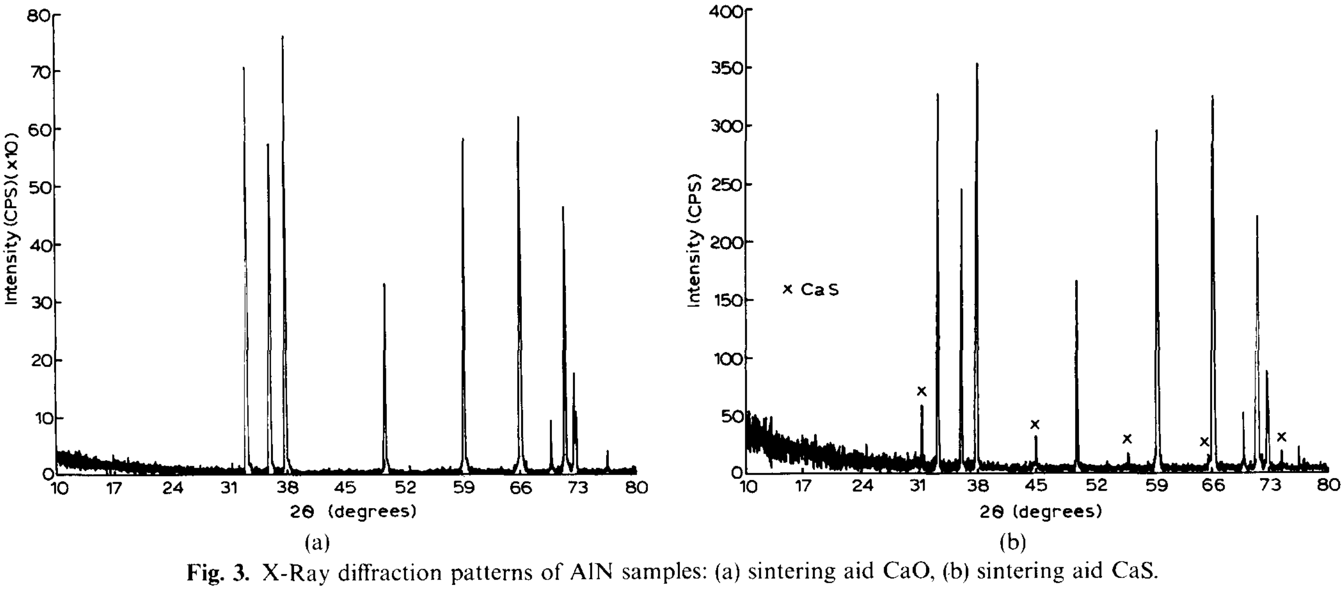
CaS melts at 2400°C. A lowering of the melting point can be assumed but no reaction between CaS and AlN/Al_2O_3 is expected, because of the highly positive ΔG value. This assumption is confirmed by the XRD, as well as by the high calcium and the low oxygen content (see also Figs 3 and 4); however, CaS must have contributed to the densification, because the relative density reached was about 98%. The low thermal conductivity of the samples sintered with CaS can possibly be caused by an incorporation of sulphur into the AlN lattice. This could have embrittled the lattice and lead to the transcrystalline fracture mode, recognizable in Fig. 5. The round particles in the grain boundary junctions could be identified as CaS using EDX.

CaH_2 decomposes at 816°C, in the presence of nitrogen; however, calcium nitride is formed, which is thermically unstable and melts at 1195°C. Therefore, eqn (8) can be assumed using CaH_2 as a sintering aid. The free standard reaction enthalpy is negative, already in a lower temperature range. This negative value further decreases with temperature due to the positive reaction entropy.

CaC_2 melts at about 2300°C. It is unstable in contact with AlN and reacts in the presence of nitrogen according to eqn (9). The CO formed should also remove the oxygen. In a nitrogen-free atmosphere, evaporating Al-suboxides can be formed instead of AlN (see eqn (10)). In this case the mass removal as well as the decreasing amount of liquid phase can be the reason for the reduced sintering densities and thermal conductivities.

$CaCN_2$ decomposes at about 1300°C. In presence of some substances, however, the decomposing temperature is distinctly lowered. At first the formation of CaC_2 is expected and subsequently a reaction according to eqn (9) or (10). The total reaction is summarized in eqn (11).

Figure 6 shows that the thermal conductivity



(a) (b)

Fig. 3. X-Ray diffraction patterns of AlN samples: (a) sintering aid CaO, (b) sintering aid CaS.

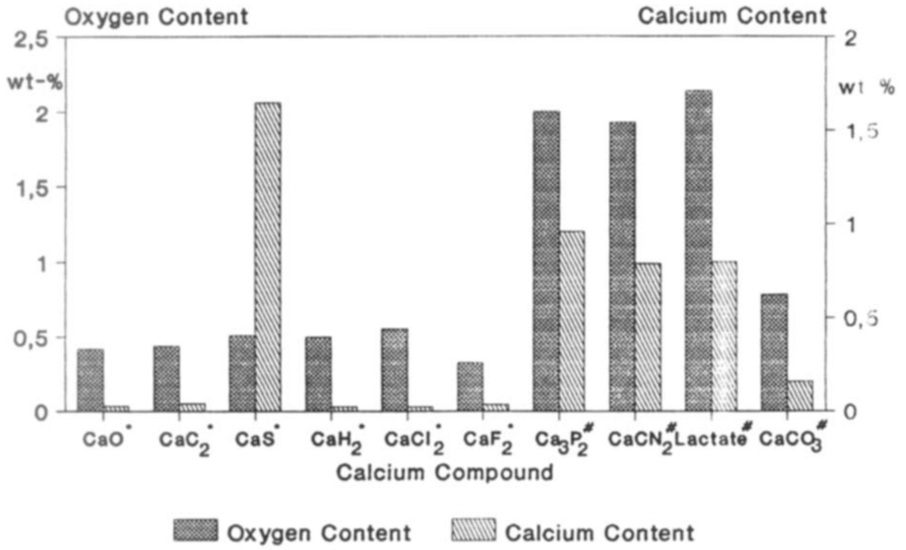


Fig. 4. Quantities of residual oxygen and calcium in sintered AlN samples. Sintering conditions: 1850°C; 3 h. N_2; graphite crucible: ★, open; #, closed.

increases, in spite of a slightly diminished density, with an increasing addition of CaF_2, due to decreasing residual quantities of oxygen and calcium. The residual amounts for all sintering aids are summarized in Fig. 4. The diagram shows distinctly the differences between samples sintered in a closed graphite crucible or in an open one. In case of the open crucible the liquid phase had been nearly completely evaporated. By contrast, if a closed crucible was used, a notably higher quantity remained in the samples, however, without possessing a negative effect on the thermal conductivity.

The influence of the sintering atmosphere on the density and the thermal conductivity of the AlN samples is shown in Fig. 7. The effect is strong, especially if nitrogen takes part in the reaction of the sintering aids with AlN or Al_2O_3, and it is insignificant without such an interaction, as, for instance, in the case of CaO and $CaCO_3$.

Despite the samples sintered with $CaCN_2$ the relative sintering densities showed only small differences. By adding $CaCN_2$, a relative density was obtained which was about 13% higher in a nitrogen atmosphere than in an argon atmosphere.

The highest thermal conductivity of 112 W/m K was obtained in the case of $CaCO_3$ with argon as the sintering gas. After sintering with nitrogen, 95 W/m K were measured.

The values of the thermal conductivities of samples doped with Ca_3P_2 and $CaCN_2$ were about 20% lower, if the sample was sintered in argon instead of nitrogen, and always lower than those of samples doped with $CaCO_3$. Ca_3P_2 melts above 1600°C. The reaction with Al_2O_3 according to eqn (13) can only occur in a nitrogen atmosphere; the reaction to AlP according to eqn (12), however, is only possible at temperatures above the sintering

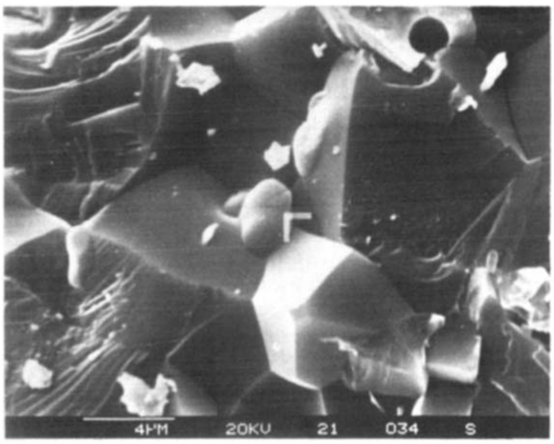


Fig. 5. Fracture surface of a AlN sample sintered with CaS (SEM, 4000:1), the arrow marks a residue of the added CaS.

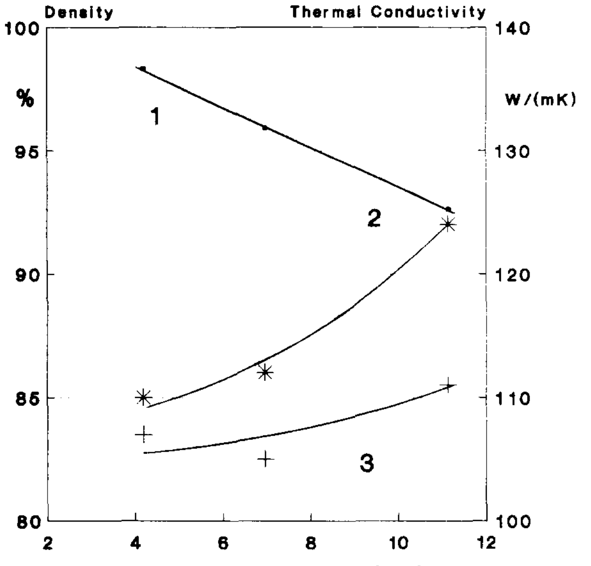


Fig. 6. Thermal conductivity and density of AlN samples versus the addition of CaF_2. Sintering conditions: 1850°C, 3 h, N_2; open graphite crucible. 1, Relative sintering density; 2, measured thermal conductivity; 3, thermal conductivity related to 100% of the relative sintering density.

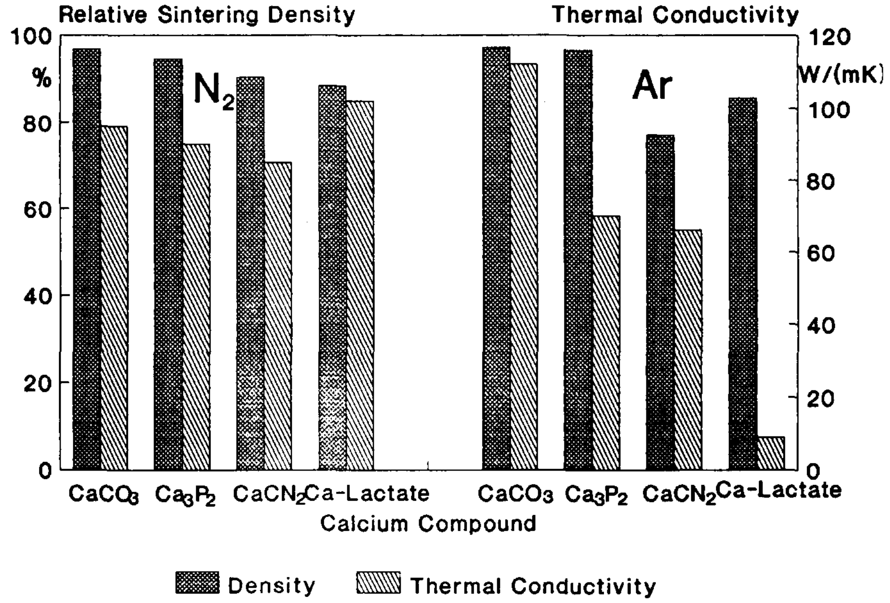


Fig. 7. The influence of the sintering atmosphere on the density and the thermal conductivity of AlN samples. Sintering conditions: 1850°C, 3 h, N_2; closed graphite crucible.

range. That is why Ca_3P_2 leads to the formation of a liquid phase which predominantly consists of calcium aluminates in the case of a nitrogen atmosphere and of the phosphide in an inert atmosphere.

The greatest differences regarding the sintering atmospheres were noticed using calcium lactate as a sintering additive. The samples sintered in a nitrogen atmosphere showed the highest values of the thermal conductivity, but in case of the argon atmosphere the lowest of all. One reason for this strong influence of the atmosphere could be the following: in the presence of nitrogen, the carbon which remains after evaporation of water and hydrocarbons from the lactate reacts with Al_2O_3 according to eqn (16). The oxygen is removed as carbon monoxide. In an argon atmosphere, however, aluminium carbide is formed according to eqn (17), which remains in the AlN lattice and leads to a drastic decrease of the thermal conductivity.

4 Summary

The use of various calcium compounds as sintering aids for AlN leads to substantial differences in respect of the sintering densities and thermal conductivities of the resulting AlN ceramics.

All the sintering aids used, with the exception of CaS, form CaO and hence calcium aluminate liquid phases. This process is supported by the volatility of the decomposition and reaction products. Therefore, such as in the case of the halides, even reactions possessing a positive free standard reaction enthalpy can take place.

With the exception of $CaCO_3$ and CaS, oxygen is removed by all sintering aids used. In the case of CaC_2, $CaCN_2$ and the lactate the oxygen is removed from the AlN by means of chemical reactions forming carbon monoxide.

In summary, the use of calcium-containing sintering aids leads to values of the thermal conductivity which are comparable to those of yttrium-doped AlN ceramics. Their low costs and, moreover, the shorter soaking times required are two notable advantages.

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