# Release of Foreign Matter During Sintering of Aluminium Nitride and Silicon Nitride

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## Abstract

*The release of trace amounts of foreign matter from AlN and Si₃N₄ green and sintering bodies during annealing and sintering operations was studied. These trace amounts were labelled with radioactive isotopes and the release behaviour as a function of the temperature, time and gas atmosphere was investigated. A decisive influence on release rates was found depending on whether the foreign matter was imbedded in the lattice or at the grain boundaries. For the release of Na from AlN a two-step process was found with a maximum release rate from grain boundaries at 900°C and from the nitride lattice at 1650°C. The release of rare earth and alkaline earth impurities was only observed if strongly reducing carbon compounds were present in the gas atmosphere within the investigated temperature range (<1850°C).*

*Die Freisetzung von Fremdstoffen aus AlN und Si₃N₄ bei Glüh- und Sintervorgängen wurde unter Verwendung gamma-aktiver Isotope in Abhängigkeit von Temperatur, Zeit und Gasatmosphäre untersucht. Die Freisetzung ist wesentlich davon abhängig, ob sich der Fremdstoff im Gitter oder in den Korngrenzenbereichen befindet. Für die Freisetzung von Na aus AlN wurde ein Zweistufenprozeß gefunden mit einem Maximum bei 900°C für die Freisetzung aus dem Korngrenzenbereich und ein zweites Maximum bei 1650°C für die Freisetzung aus dem Gitter. Die Freisetzung der Seltenen Erden und Erdalkalielemente wurde im untersuchten Temperaturbereich (<1850°C) durch die Gegenwart stark reduzierender Kohlenstoffverbindungen stark beschleunigt.*

*Les auteurs ont étudié la libération de traces d'éléments étrangers à AlN et à Si₃N₄, lors des opérations de recuisson et de frittage, au départ de masses frittées et à cru. Les quantités de traces ont été dosées avec des isotopes radioactifs et leur libération a été examinée selon la température, le temps et l'atmosphère gazeuse. Les vitesses de libération sont fortement influencées par la localisation des éléments étrangers: à l'intérieur du réseau ou aux joints de grains. En ce qui concerne la libération du Na à partir d'AlN, les auteurs ont identifié un processus en deux étapes avec une vitesse maximum de libération par les joints de grains à 900°C et par le réseau nitrure à 1650°C. La libération de terres rares et d'impuretés de rare-terreux et d'alcalino-terreux a été observée uniquement lorsque des composés carbones fortement réducteurs étaient présents dans l'atmosphère.*

## 1 Introduction

The release of foreign matter from ceramic materials is governed by three processes: (a) the diffusion in the matrix to grain boundaries, (b) the diffusion within grain boundaries to the gas phase, and (c) subsequent desorption. As a result, depending on the vapour pressure of foreign matter, segregation in boundary layers may occur.[1]

With respect to non-oxidic materials, only very few data are available which allow the release

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rates of foreign matter during annealing and sintering processes to be estimated. They refer mostly to diffusion in thin layers.[2-6]

This paper intends to investigate experimentally the release rates of foreign matter from AlN and $Si_3N_4$ during sintering in order to obtain information about the behaviour of impurities and sintering additives during this treatment.

## 2 Experimental

### 2.1 Sample preparation

AlN green bodies (tablets 8 mm diameter; 2 mm height) were prepared by mixing AlN powder in hexane (see Table 1 ) with 2 wt% CaO, or 2·7 wt% $CaF_2$, respectively, in a planetary mill. A solution of wax E (BUNA) in hexane (4 wt% of wax relative to AlN) and an alcoholic solution of uranyl nitrate (about 1 ppm of $^{235}U$ relative to AlN) were added, followed by additional milling. The sample was evaporated to dryness, sieved (200 $\mu m$ mesh size), cold die-pressed (150 MPa) and heated for 2 h at 750°C in nitrogen to remove organic compounds.

The preparation of the $Si_3N_4$ samples was made accordingly. A mixture of 5 wt% both of $Y_2O_3$ and $Al_2O_3$ was used as a sintering additive.

The sintering curves for a 1 h treatment of AlN and $Si_3N_4$ are depicted in Fig. 1.

### 2.2 Release experiments

The samples, which were pretreated as already described, were irradiated in the SAPHIR reactor of the Paul Scherrer Institute. The neutron flux was $3 \times 10^{13}$ n $cm^{-2}$ $s^{-1}$. The irradiation time lasted between 10 min and 20 h. After a cooling time of 15 to 300 h the samples were measured with a high-purity Germanium detector for γ-decaying nuclides. Two types of radionuclides were produced; firstly, isotopes from (n,γ) pro-
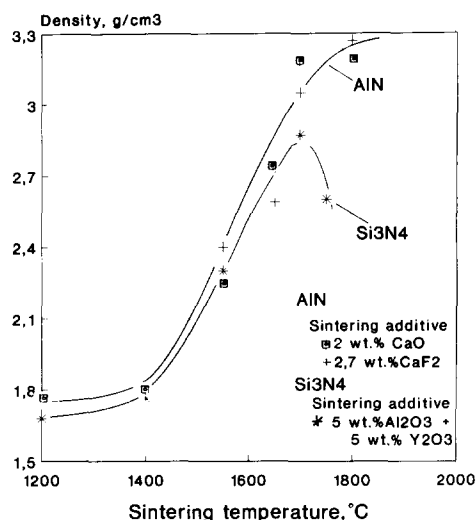


**Fig. 1.** Sintering density of AlN and $Si_3N_4$ as a function of temperature. Sintering time 1 h. Gas medium Ar + 2 vol.% $H_2$.

cesses and, secondly, fission products from $^{235}U$. After counting, the samples were thermically treated followed by a second measurement. From the two measurements it was possible to determine the release rates $F_i$ for individual isotopes after some corrections for radioactive decay between the two measurements. The γ-lines, which were used for the assignment of individual nuclides are summarized in Table 2.[7] The value $[1 - F_i]$ is the residue in the sample after the treatment.

Thermal treatment was performed in an $Al_2O_3$ tubular oven (Hochtemperatur-Materialien und -Geräte GmbH, Berlin). The samples were put into the oven in a Mo/W boat. As gases 10 litres $h^{-1}$ of a mixture containing Ar (99·998 vol %) + $H_2$

**Table 1.** Characteristics of powders

| Material | Grain Size ($d_{50}$; $\mu m$) | Surface area ($m^2/g$) | Impurity level, (ppm) | | |
| --- | --- | --- | --- | --- | --- |
| | | | $Na^a$ | $Cr^a$ | $O^b$ |
| AlN Grade $C^c$ | 1·0 | 4·7 | 8 | 8 | 16 000 |
| $Si_3N_4$ LC-12$^c$ | 0·6 | 18 | <10 | 26 | 16 000 |
| $Al_2O_3^d$ | 0·5 | 9·5 | 44 | — | — |
| $CaO^e$ | 13 | — | 2180 | — | — |
| $CaF_2$, p.A.$^f$ | 2·6 | — | 43 | — | — |
| $Y_2O_3^g$ | 4·8 | — | 5 | — | — |

$^a$ ICP-AAS.
$^b$ Hot gas extraction.
$^c$ H. C. Starck.
$^d$ Alcoa A 16.
$^e$ Sojuschimexport.
$^f$ VEB Chemiewerk Nünchritz.
$^g$ Coprecipitation and freeze drying.

**Table 2.** Isotopes and their mechanism of production

| Isotope | Half-life | Measured γ-energy (keV) | | Mechanism of production |
| --- | --- | --- | --- | --- |
| $^{24}Na$ | 15·02 h | 1368·5 | 2753·9 | n, α; n, γ |
| $^{46}Sc$ | 83·83 d | 888·9 | 1120·5 | n, γ |
| $^{51}Cr$ | 27·70 d | 320·1 | | n, γ |
| $^{72}Ga$ | 14·1 h | 834·0 | 2202·7 | n, γ |
| | | 2507·8 | | |
| $^{91}Sr$ | 9·52 d | 555·6 | 749·8 | SP |
| $^{95}Zr$ | 64·03 d | 724·2 | 756·7 | Daughter of $^{95}Zr$ |
| $^{95}Nb$ | 43·98 d | 765·8 | | SP |
| $^{97}Zr$ | 17·0 h | 657·9 | 743·4 | SP |
| $^{99}Mo$ | 2·75 d | 181·1 | 739·4 | SP |
| $^{103}Ru$ | 39·25 d | 497·1 | | SP |
| $^{131}I$ | 8·02 d | 284·3 | 364·5 | SP |
| $^{132}Te$ | 3·26 d | 228·2 | | SP |
| $^{133}I$ | 20·8 h | 529·9 | 875·3 | SP |
| $^{135}Xe$ | 9·08 h | 249·8 | | SP |
| $^{140}Ba$ | 12·75 d | 423·7 | 537·3 | SP |
| $^{141}Ce$ | 32·5 d | 145·4 | | SP |
| $^{143}Ce$ | 33·0 h | 293·3 | 664·5 | SP |
| $^{152}Eu$ | 13·33 a | 778·9 | 964·1 | n, γ |
| | | 1085·9 | 1408·0 | |
| $^{152m}Eu$ | 9·32 h | 841·6 | | n, γ |
| $^{181}Hf$ | 42·4 d | 482·0 | | n, γ |
| $^{187}W$ | 23·9 d | 685·8 | | n, γ |

SP: Fission product of $^{235}U$.

(1·95 vol.%) + $H_2O$ (0·04 vol.%) or a mixture of $N_2$ (99·999) + electrolytically produced $H_2$ were used. The heating and cooling rates in the oven were 25 K min$^{-1}$ and the temperature hold-up times were between 1 and 6 h.

## 2.3 Initial distribution of products

The initial distribution of the radioactive nuclides in the samples closely depends on the formation mechanism. Fission products have recoil energies of about 80 to 100 MeV resulting in recoil ranges (depending somewhat on the fission nuclide and the matrix) of about 3 mg cm$^{-2}$. For a material with a density of 1·8 g cm$^{-3}$ (3·27 g cm$^{-3}$) this corresponds to a recoil range of about 17 $\mu$m (9 $\mu$m).[9] Hence, the recoil range is more than one order of magnitude higher than the individual agglomerate sizes, especially the primary particles of the powder. Therefore it can be assumed that there is a homogeneous distribution of fission products in the matrix even if the added uranium is concentrated on the powder surfaces.

On the other hand, products from (n,$\gamma$) processes (i.e. neutron activation processes) are not displaced. Their distribution is therefore identical with that of the initial nuclides. In the present case, this means that the non-fission Eu and Hf radionuclides were produced from impurities in the sintering additive $Y_2O_3$ and the Cr and W isotopes as part of the grinding abrasion.

The distribution of Na, however, should be different for AlN and $Si_3N_4$. In both cases the radionuclide $^{24}$Na is produced from Al via (n,$\alpha$) reactions. In $Si_3N_4$ Al is contained in the sintering additive. The produced $^{24}$Na should therefore be in the oxidic phase. For AlN $^{24}$Na should be produced homogeneously in the grains of the matrix. In addition, it is also produced via Na impurities in the sintering additives (see Table 1). This latter source leads to $^{24}$Na-enriched grain boundary layers.

**Table 3.** Temperature at which a certain fraction of the elements is released (sintering time 1 h)

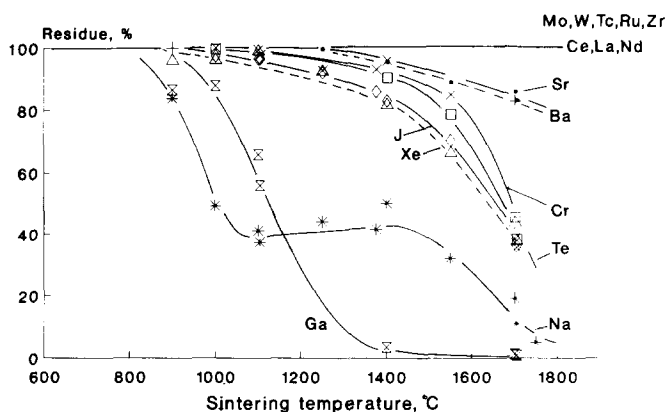| Element | Fractional release | | | | | |
|---|---|---|---|---|---|---|
| | 20% | | 50% | | 80% | |
| | AlN | $Si_3N_4$ | AlN | $Si_3N_4$ | AlN | $Si_3N_4$ |
| Na | 850 | 1 180 | 1 020 | 1 280 | 1 660 | 1 360 |
| Sr | 1 800$^a$ | — | — | — | — | — |
| Ba | 1 750$^a$ | — | — | — | — | — |
| Eu | — | 1 850 | — | — | — | — |
| Ga | 980 | — | 1 130 | — | 1 250 | — |
| Cr | 1 500 | 1 700 | 1 700 | — | — | — |
| Te | 1 560 | 1 200 | 1 700 | 1 500 | — | 1 650 |
| I | 1 430 | 1 220 | 1 660 | 1 530 | — | 1 750$^a$ |
| Xe | 1 430 | 1 300 | 1 660 | 1 600 | — | — |

$^a$ Extrapolated values.



**Fig. 2.** Different residues in aluminium nitride as a function of the sintering temperature. Isothermal sintering time 1 h. Gas medium Ar + 2 vol.% $H_2$.

## 3 Results and Discussion

### 3.1 Release behaviour from green bodies

Figures 2 and 3 show the results from heated green bodies in Ar + 2 vol.% $H_2$. The residue of foreign matter which is left in the ceramic material after sintering is shown versus temperature. The isothermal retention time at the given temperature for each release measurement lasted 1 h. Table 3 summarizes all temperatures that resulted in a measurable release of a radionuclide.

Sodium shows (besides Ga in AlN) the highest release rates for both materials. Significant release is observed already at relatively low temperatures. The elements Te, I and Xe indicate a rather similar behaviour. The data for Cr exhibit a significantly different behaviour for both nitrides. Generally, in AlN higher release rates are observed if compared to $Si_3N_4$ at the same temperatures. Significant release of alkaline earth elements and of Eu is found only for temperatures above 1700°C. The elements Nb, Mo, W, Tc, Ru, Zr and Hf and the trivalent lanthanides and Sc remain in the matrix during the temperature regime and the gas media which were investigated.

The reasons for the different release behaviour of the elements are due to their different diffusion properties in polycrystalline nitrides and due to their vapour pressures.[1]
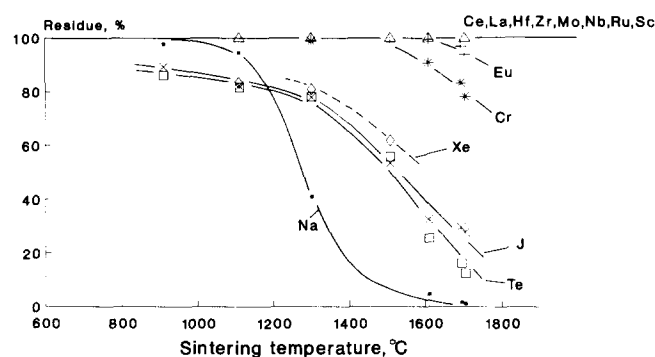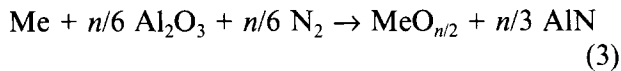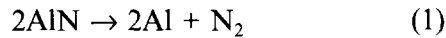


**Fig. 3.** Different residues in silicon nitride as a function of the sintering temperature. Isothermal sintering time 1 h. Gas medium Ar + 2 vol.% $H_2$.

For an estimate of the release behaviour the chemical state of the corresponding element has to be known. This state, in a first approximation, can be deduced from an analysis of the possible reactions. For AlN the following reactions are possible:

$$2AlN \rightarrow 2Al + N_2 \tag{1}$$

$$Me + x/2\ N_2 \rightarrow MeN_x \tag{2}$$

$$Me + n/6\ Al_2O_3 + n/6\ N_2 \rightarrow MeO_{n/2} + n/3\ AlN \tag{3}$$

($n$ = valence state of the metal)
With trace amounts of $H_2O$ vapour in the gas the following reaction is possible:

$$2\ AlN + 3\ H_2O \rightarrow Al_2O_3 + N_2 + 3\ H_2 \tag{4}$$
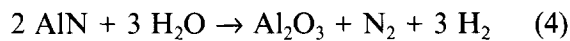
Reactions of $H_2O$ with foreign atoms are less likely, because reaction (4) occurs mainly at the sample surface, whereas the main part of the foreign species is contained in the matrix as well as in the inner pores of the sample.

According to these reactions the foreign substances are expected to exist in the form of metals, nitrides or oxides. Thermodynamic calculations favour the elemental form of the elements Mo, W, Ru, Cr, Ga and Na, the oxide form for Sr, Ba, La, Ce, Nd and Eu, and the nitride form for Nb, Zr and Hf[9] in equilibrium with AlN. Considering the vapour pressures of the compounds in equilibrium with AlN it is obvious that the elements Mo, Nb, W, (Tc), Ru, Zr, Hf and the trivalent lanthanides are not released because of their low vapour pressure. Due to the higher vapour pressures of Na, Ga, Cr, Te, I and Xe these elements are likely to be desorbed after reaching the bulk surface via diffusion. The oxides of the alkaline earth elements and of the bivalent Eu are between the two groups already listed. At 2000 K a threshold is obviously reached at which a perceptible release from the nitride surface is possible.

How far the release rates are effected by the concentration of foreign matter depends on the interaction mechanisms. In Y-doped $ThO_2$ a delayed release of $^{95}Nb$ was found relative to that from pure $ThO_2$.[10] On the other hand, measured release rates of Kr, I and Rb from $UO_2$ did not exhibit any influence for up to 4% oxidic additives.[11]

Looking at Figs 2 and 3 it is interesting to note that there is an exceptionally high release rate of sodium and an unusual shape of the curve for AlN. In Fig. 4 the Na residue after sintering is shown for different substances. From the basic BeO, Na has already entirely escaped at temperatures below 1300°C, independent of the gas (air and hydrogen).[12] At identical temperatures a higher Na content remained in $Al_2O_3$ compared to
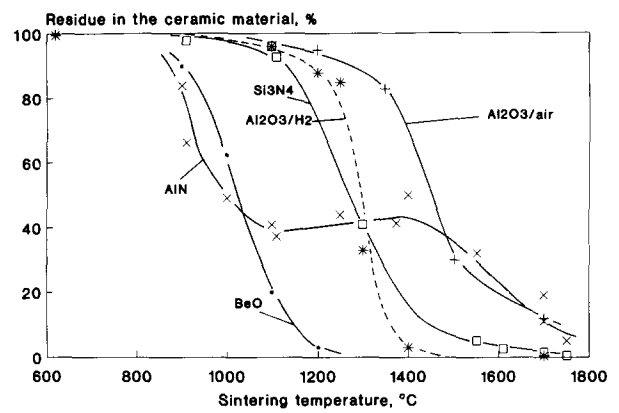


**Fig. 4.** Residue of sodium in different ceramic materials as a function of the sintering temperature.

BeO. However, release rates for Na from $Al_2O_3$ depended on the gas atmosphere.[13] For hydrogen a similar pattern was found as for $Si_3N_4$.

The release behaviour of Na from AlN is more complicated. The shape of the curve could be explained on the assumption of two different fractions of Na. The first fraction of Na is concentrated in the CaO containing grain boundaries, with a release behaviour similar to that of BeO. The second fraction is expected to be distributed within the AlN matrix. Due to the lower transport coefficient the latter fraction is temperature delayed in its release behaviour.

Ga exhibits remarkably high release rates from AlN (see Fig. 2). If the exceptionally high diffusion coefficients of Ga in AlN are excluded, then the observation could indicate an enrichment of that element on the surface of the AlN grains. This is only possible if Ga is enriched on the surfaces already during the nitriding of Al.

### 3.2 Influence of the gas atmosphere on the release rates

Table 4 summarizes the results of measured release rates from AlN and $Si_3N_4$ obtained in different gas media. Modification of the atmosphere via

**Table 4.** Influence of gas atmosphere on the release of elements from AlN and $Si_3N_4$

| Element | Gas atmosphere | | | | | | |
|---------|------|------|------|------|------|------|------|
| | Ar + H₂ | | Ar +H₂+C | N₂ | | N₂ + C | |
| | AlN | Si₃N₄ | AlN | AlN | Si₃N₄ | AlN | Si₃N₄ |
| Ba | 16 | 0 | 41 | 22 | 14 | 24 | 27 |
| Ce | 0 | 0 | 11 | 0 | 0 | 0·6 | 0·3 |
| Nd | n.d. | n.d. | n.d. | n.d. | 0 | 3 | n.d. |
| Eu | n.d. | 5 | n.d. | n.d. | 32 | n.d. | 42 |
| Cr | 58 | n.d. | 28 | 58 | n.d. | 52 | n.d. |
| Te | 64 | 86 | 53 | 57 | 62 | 25 | 83 |
| I | 66 | 72 | 64 | 58 | 65 | 26 | 82 |

Sintering conditions: 1700°C, 1h.
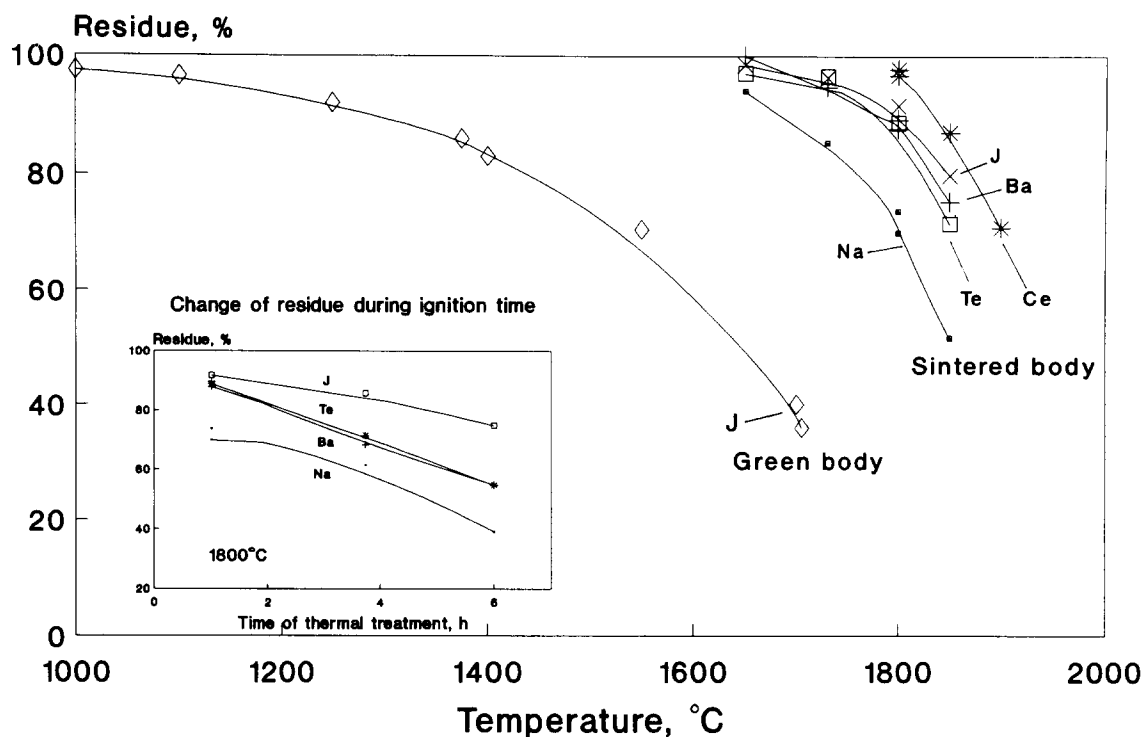Fractional release in %.
n.d.: Not detected.

**Fig. 5.** Different residues in sintered aluminium nitride as a function of the heating temperature. Heating time 1 h. Gas atmosphere Ar + 2 vol.% $H_2$. Also shown is the release behaviour of iodine from non-sintered aluminium nitride (from Fig. 2). The insert depicts the release behaviour of Na, Ba, Te and I at 1800°C for different heating times.

carbon was achieved by wrapping the samples in a graphite foil. Most remarkable is the different release behaviour of the trivalent lanthanides. Only in the case of graphite wrapping did these elements show some release. Partly increased release rates was also found for the divalent Ba.

The influence of carbon containing sintering gases on the solid-state chemical interactions between AlN and sintering additives has repeatedly been mentioned.[9] Compounds such as $(CN)_2$ or HCN have been proposed as carbon carriers.[14] This leads to conditions which favour carbo-reduction or carbo-nitriding reactions. As a result of such reactions the partial pressure of the metallic species increases which favours the release behaviour.

### 3.3 Release from AlN sintering samples

All results discussed so far were obtained from samples where the green bodies were irradiated at the SAPHIR reactor. In Fig. 5 results are depicted from samples which were irradiated after the sintering procedure (sintering density 3·16 g cm⁻³). These samples were again heated after the irradiation to determine the release rates, as shown in Fig. 5. For comparison, as an example, the release behaviour of iodine from green bodies is shown.

The temperature of equal release rates for sintered samples is shifted by several hundred degrees towards higher values. This could be caused by increased diffusion lengths both in the grain volume and along the grain boundaries. Since for sintered

samples no open pores exist, capillary diffusion as a fast transport mechanism is entirely absent.

The behaviour of the release rates from the AlN samples as a function of the heating time is also shown in Fig. 5 (insert). For the observed release rates of about 10% to 60% a linear relationship as a function of the heating time was observed.

Figure 6 makes an intercomparison of the release rates of Na from different AlN samples: green bodies, sintered samples and single crystals (kindly supplied by Dipl.-Ing. Sternizke, TH Darmstadt). The different behaviour can be explained by the different shares of Na in the grains and in the phase between the grains. Na contained as impurity in the sintering additive $CaO/CaF_2$ migrates to the surface and evaporates. For the sintered material and the powder made of single crystals this part of Na has already disappeared.
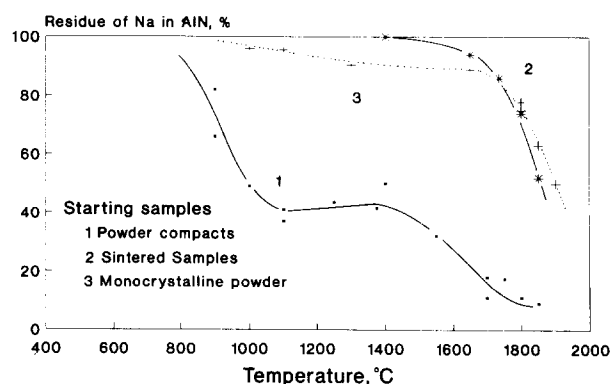


**Fig. 6.** Residue of sodium from different aluminium nitride samples. Heating time 1 h. Gas atmosphere Ar + 2 vol.% $H_2$.

From the powder made of single crystals about 10% of Na is released up to 1600°C. This part obviously comes from the surface cover of the AlN particles by $Al_2O_3$. Above 1500°C for all three sample types release of Na mainly occurs from the $^{24}$Na produced via (n,α) reactions with Al. This part of Na is embedded in the AlN lattice. Due to the high temperature at which this release mechanism starts it can be concluded that the very slow volume diffusion dominates. This release mechanism should be independent of the grain size, as already observed in oxidic nuclear fuel samples.[15]

## Acknowledgement

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