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Determination of the Concentration of Oxygen Dissolved in the AlN Lattice by Hot Gas Extraction from AlN Ceramics

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Abstract

A method for the selective determination of the concentration of oxygen dissolved in the AlN lattice of AlN ceramics by hot gas extraction is presented. For this analysis the ceramic has to be crushed to fragments smaller than a critical size that depends on the type of microstructure (40–100 μm). Estimated accuracy for the determination of lattice dissolved oxygen is better than 0·05 wt%, which makes the method useful for studies relating phase composition and microstructure of AlN ceramics to their thermal conductivity. Results obtained so far on AlN(Y_2O_3) ceramics indicate that the maximum concentration of oxygen in AlN after sintering at ~1800°C is only ~0·6 wt%, less than the limit found in other studies.

Eine Methode zur selektiven Bestimmung des im AlN-Gitter gelösten Sauerstoffgehaltes in AlN-Keramiken durch Heißgasextraktion wird vorgestellt. Für diese Analyse muß die Keramik auf eine Korngröße unterhalb einer kritischen Größe zerkleinert werden, die von der Art des Gefüges abhängt (40–100 μm). Die Genauigkeit der Sauerstoffanalyse wird auf besser als 0·05 Gew% geschätzt, damit ist die Methode brauchbar für Untersuchungen zum Zusammenhang zwischen Phasenreinheit und Gefüge von AlN-Keramiken und ihrer Wärmeleitfähigkeit. Nach den bisher vorliegenden Ergebnissen an AlN(Y_2O_3)-Keramiken beträgt die maximale Sauerstofflöslichkeit im AlN-Gitter bei Sintertemperaturen von etwa 1800°C nur ~0·6 Gew.%, weniger, als in anderen Arbeiten gefunden wurde.

On présente une méthode de détermination sélective de la concentration d'oxygène dissolu dans les cristaux de AlN dans les céramiques à base de AlN par extraction à haute température. Pour cette analyse les céramiques sont broyées à une granulométrie maximale qui dépend de la microstructure (40–100 μm). La précision de l'analyse est suffisante (<0·05%) pour rendre la méthode utile pour des études qui concernent les relations entre la pureté des phases, la microstructure et la conductibilité thermique des céramiques à base de AlN. D'après les résultats actuels sur les céramiques AlN(Y_2O_3) la solubilité maximale de l'oxygène dans les cristaux de AlN n'est que ~0·6% après frittage à ~1800°C, ce qui est moins que les limites trouvées dans d'autres études.

1 Introduction

High thermal conductivity is one of the attractive features of AlN ceramics. Values as high as 280 W/mK have been measured on pure single crystals parallel to their *c*-axis.[1] A quantitative correlation between the concentration of oxygen dissolved in the lattice of AlN single crystals—and associated with Al vacancies—and thermal conductivity has been given by Slack *et al.*[2] In single- or polyphase polycrystalline AlN ceramics there are other factors besides the concentration of oxygen dissolved in the AlN lattice (called 'lattice dissolved oxygen' below) that can affect thermal conductivity. Yet it has been shown in several studies[3–5] that lattice dissolved oxygen can have the decisive influence on thermal conductivity in such ceramics also.

For this reason, methods for the selective determination of the concentration of lattice dissolved oxygen are highly desirable. The total oxygen concentration in AlN and other nitrogen ceramics can be measured by methods such as hot gas

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extraction or neutron activation. In principle, the concentration of lattice dissolved oxygen can be derived indirectly from the total oxygen concentration and a qualitative X-ray analysis of the phases present in the ceramic.[5] This method, however, is restricted to simple systems like AlN with Y_2O_3 as sintering aid. The oxygen content bound in oxide phases can also be calculated directly from quantitative X-ray phase analysis data, in conjunction with known Y_2O_3 contents.[6] The accuracy of this method, however, is rather limited, particularly if several oxide phases are present, or if their concentration is low. It fails completely if oxide phases are X-ray amorphous. Large errors can result, consequently, if the lattice dissolved oxygen is calculated from the difference of the total oxygen and the oxide-bound oxygen derived from such data. Direct measurements of oxygen concentrations in individual AlN grains by microprobe or electron energy loss spectrometry (EELS)[7] are time-consuming and difficult to put on a statistically sound basis.

For AlN powders, a modified hot gas extraction analysis has recently been described, that allows separate determination of lattice dissolved oxygen and oxygen that is bound in surface oxide layers or separate oxide particles.[8] In essence, this method makes use of the fact that the lattice dissolved oxygen is protected against carbothermal reduction by the stability of the AlN matrix. It is extracted simultaneously with the nitrogen, at temperatures much higher than those required to reduce the oxide phases. In the present paper it will be shown that this method, with certain modifications and limitations, can also be applied to sintered AlN ceramics.

2 Experimental

A commercial hot gas extraction analyser (TC-436, LECO Co., St Joseph, MI, USA) was used for oxygen and nitrogen determinations. Graphite powder (No. 501-073, LECO Co., St Joseph, MI, USA) was added to the samples, in order to accelerate the carbothermal reduction of the oxide phases. AlN ceramics investigated were partly from commercial sources, partly laboratory-made (details of preparation in Ref. 5). They all contained Y_2O_3, CaO or CaC_2 as oxide sintering aids. A few ceramic samples were prepared from AlN powders that had been preoxidized in order to study the extraction behaviour of samples containing large amounts of the binary $AlN–Al_2O_3$ phases (γ-AlON and pseudo-polytypes). The phases present in the ceramics were determined by X-ray diffraction and scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray microanalysis (EDX).

The work was started on the assumption that the procedure developed for powder analysis should also be applicable to AlN ceramics, provided that the ceramics be analysed in fragments small enough for the oxide phases to be extracted sufficiently fast, i.e. prior to the attack of the AlN grains. To test this assumption, samples of AlN ceramics containing 5 wt% Y_2O_3 were crushed. Fragments were separated into six fractions ranging from $<25\,\mu m$ to $>250\,\mu m$ and then analysed by the method developed for powders.[8]

A reproducible release of oxygen in three different fractions analogous to the results on powders was indeed found for sufficiently small fragment sizes. The phases present in the ceramics after the different steps of oxygen release were next investigated by X-ray diffraction. If the assumption of selective extraction of the oxide phases were correct, then obviously no oxide phases should be detectable by X-ray diffraction after this extraction step, but some form of reaction products instead. On massive samples a slow carbothermal reduction of the oxide phases is observed during sintering or heat treatment at temperatures above ~1600°C in graphite-heated furnaces. In this case the reaction takes place at the sample surface, with the microstructure in the interior rearranging to accommodate the loss of oxide phases.[9] By contrast, hot gas extraction analysis, as used here, is a fast process of only a few minutes duration. Therefore, porosity was assumed to form within the ceramic fragments upon the loss of the oxide phases. Microstructures prior to and after partial oxygen extraction were therefore examined by SEM.

3 Results and Discussion

For comparison Fig. 1 shows the release of oxygen and nitrogen from AlN powder (grade F, Tokuyama Soda Co., Tokyo, Japan), mixed with an equal quantity of graphite, as a function of extraction time and temperature. Oxygen is extracted in three fractions. Fraction III, released at the highest temperatures simultaneously with the nitrogen, is the lattice dissolved oxygen and fraction II is extracted from oxide phases. Oxygen from phases or bonds of low thermochemical stability (e.g. in hydroxides) is released at the lowest temperatures as fraction I.[8] In Fig. 2 extraction results are shown for an AlN ceramic sintered with 5 wt% Y_2O_3 for 1 h at

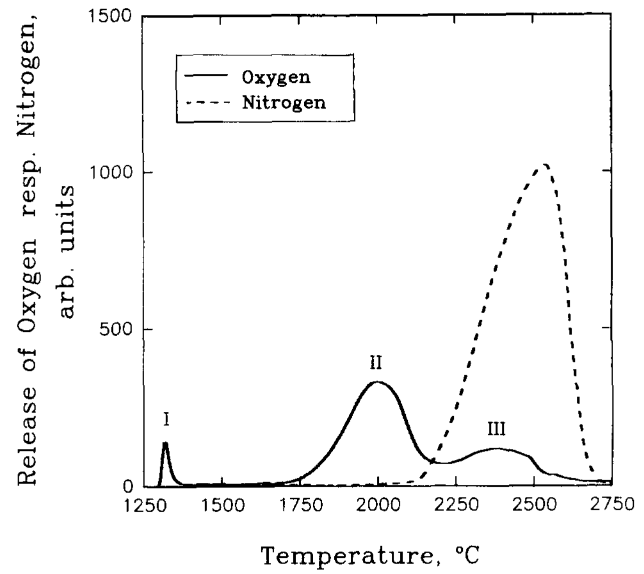


Fig. 1. Selective hot gas extraction of oxygen and nitrogen from AlN powder (Tokuyama Soda Co., grade F); heating rate 360 K/min.

1750°C. Experimental conditions were the same as for the powder analysis, but fragment size of the AlN ceramic was varied as indicated. As can be seen, oxygen is released from the ceramic fragments with sizes smaller than 100 μm in the same time/temperature sequence as from AlN powders. For fragments coarser than 100 μm the second and third oxygen peak overlap considerably, the peak shapes not being reproducible.

The limiting fragment size for reproducible separation of the peaks apparently depends on the type of AlN ceramic. A commercial material (Shapal SH-15, Tokuyama Soda Co., Tokyo, Japan) is an extreme example that required fragmentation to sizes below 40 μm.

Quantitative data can be extracted from the peak intensities, if the peaks are well separated. The best reproducibility for fraction I oxygen is obtained by first extracting this fraction, then measuring the total residual oxygen content and subtracting this from the overall oxygen content that was present before partial extraction. For peak II this method fails with AlN (Y_2O_3) ceramics, because the Y-containing reaction products after peak II oxygen extraction tend to pick up oxygen again very fast and therefore cannot be handled conveniently. For this reason, in contrast to the method used for AlN powders, the peak II area is directly used for the oxygen determination, and it is calibrated with AlN–Y_2O_3 and AlN–Y_2O_3–Al_2O_3 mixtures. Figure 3 shows the relation between the amount of oxygen introduced by oxide additions to AlN powder and the integrated peak II oxygen signal. A calibration factor of 0·99 ± 0·02 can be deduced from the data. The true amount of type II oxygen is then obtained after proper baseline correction. Extrapolation of the calibration curve to zero oxide addition gives a peak II oxygen signal equivalent to 0·6 wt%, in full agreement with the fraction II content of the AlN powder (Tokuyama Soda Co., grade F) as determined before.[8] Oxygen peak III, the fraction released simultaneously with the nitrogen content, is again determined by difference. As can be seen in Figs 1 and 2 there is some peak II/peak III overlap. The onset of N_2 release marks the beginning of peak III oxygen release, but only approximately the end of peak II oxygen release. For the sake of simplicity, in the present paper the beginning of N_2 release is used for peak II cutoff. The error introduced by this

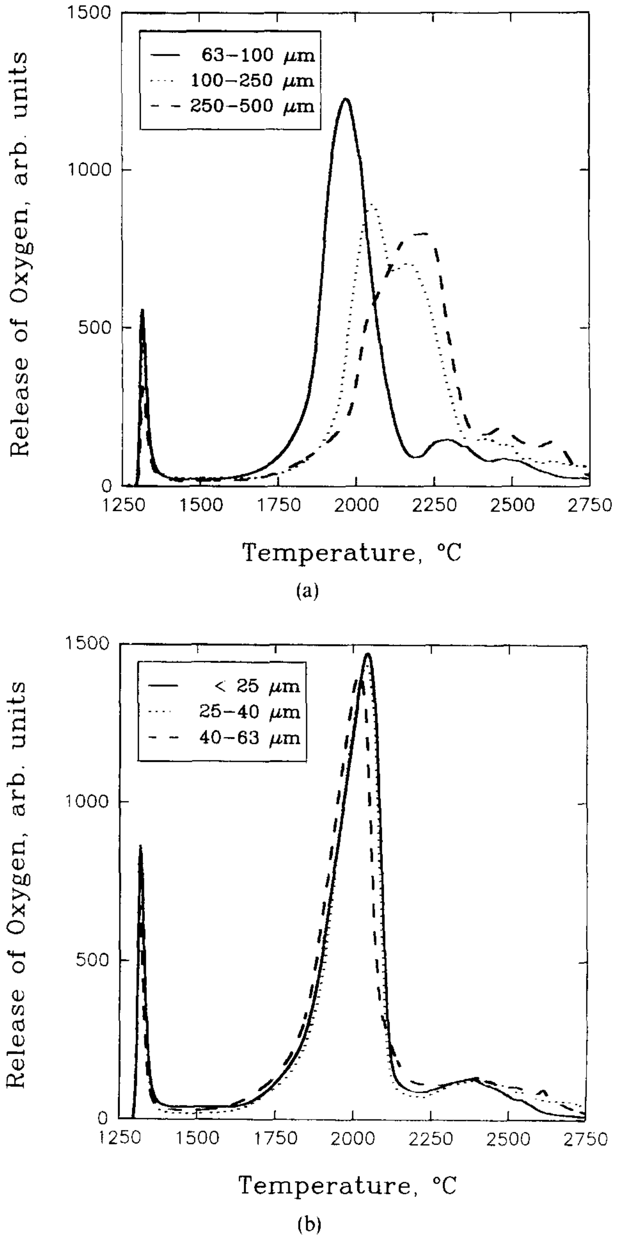


Fig. 2. Release of oxygen from AlN ceramic (Tokuyama Soda Co., grade F with 5 wt% Y_2O_3, sintered for 1 h at 1750°C) as a function of fragment size; heating rate 360 K/min.

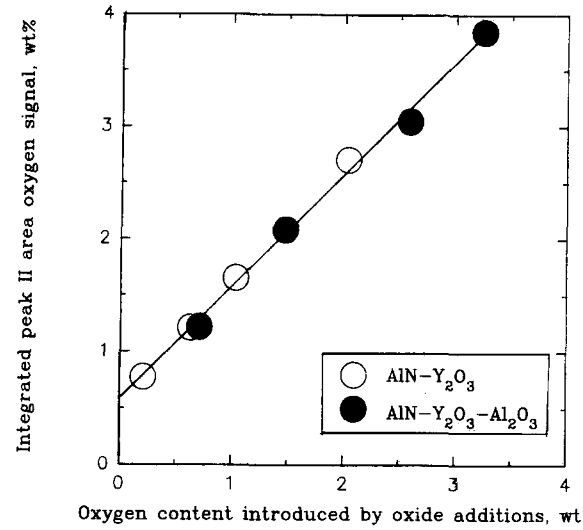


Fig. 3. Calibration of integrated peak II oxygen signal with $AlN–Y_2O_3$ and $AlN–Y_2O_3–Al_2O_3$ mixtures. Calibration factor from slope of calibration curve is 0·99 ± 0·02.

method can be reduced by analytical peak fitting procedures; this work is in progress.

Oxygen contents measured in different AlN ceramics are shown in Tables 1 and 2. The ceramic fragments pick up a considerable amount of type I and II oxygen. This oxygen is bound to the surface, as indicated by the dependence on fragment size (see also Fig. 2). As should be expected, the amount of oxygen uptake also depends on the time span between crushing and measurement. Similar effects have been noted in attrition-milled powders.[8]

Table 1. Oxygen contents in AlN (5 wt% Y_2O_3) ceramic, sintered for 1 h at 1750°C

Fragment size (*μm*)	*Oxygen* (*wt%*)			
	Total	*Type I*	*Type II*	*Type III* (*lattice dissolved*)
250–500	1·912	0·000		
100–250	1·931	0·006		
63–100	1·946	0·033	1·737	0·176
40–63	2·017	0·059	1·784	0·174
40–63[a]	2·084	0·091	1·824	0·169
25–40	2·138	0·112	1·865	0·161
< 25	2·349	0·129	2·054	0·166
e.s.d.	±0·015	±0·03	±0·015	±0·03

[a] Measured 7 days after crushing (otherwise within 3 h).

For the ceramic analysed in Table 1, oxygen fraction III is constant for fragment sizes < 100 μm (< 40 μm in Table 2), which indicates that extraction of type II oxygen is indeed complete within the time/

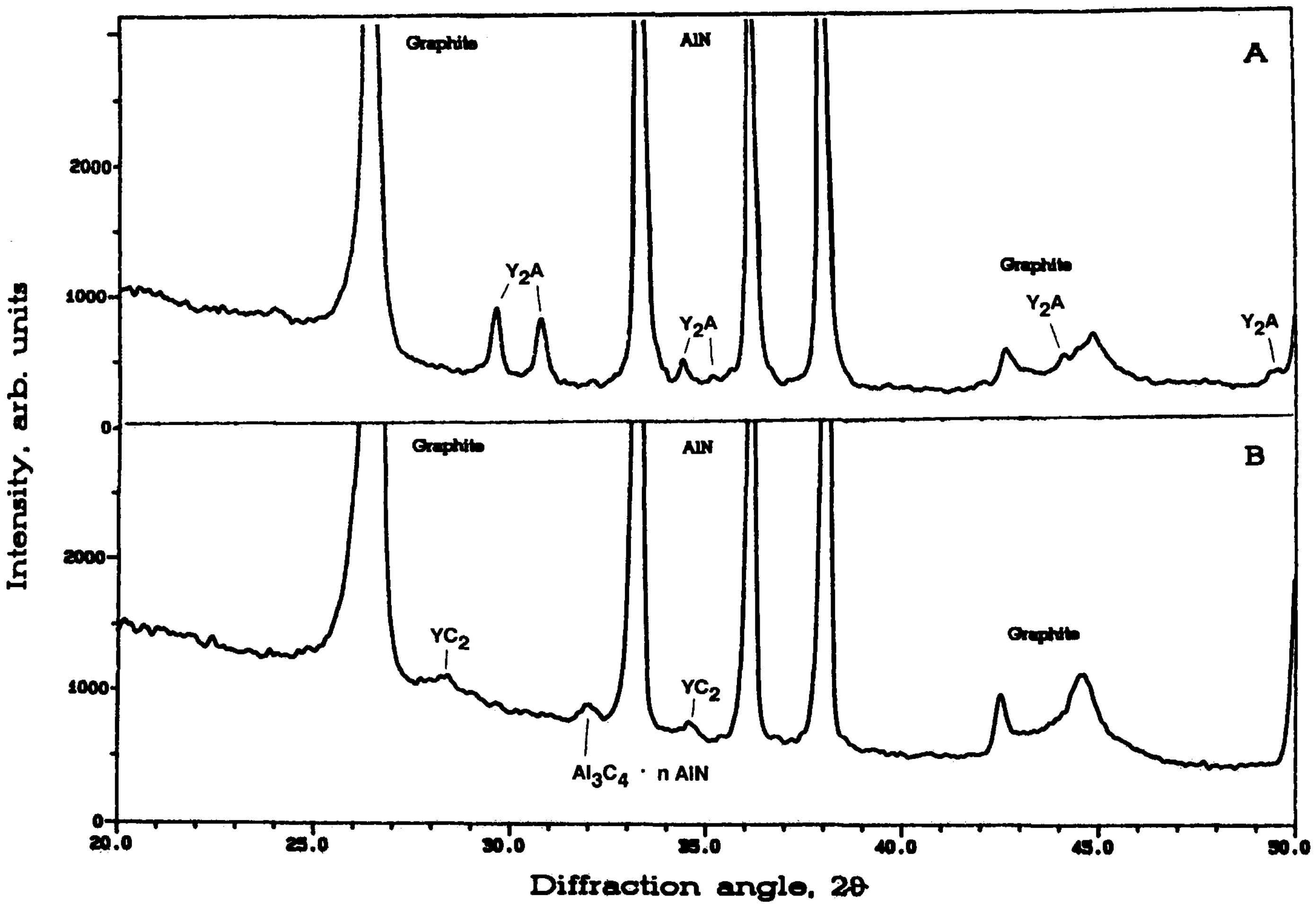
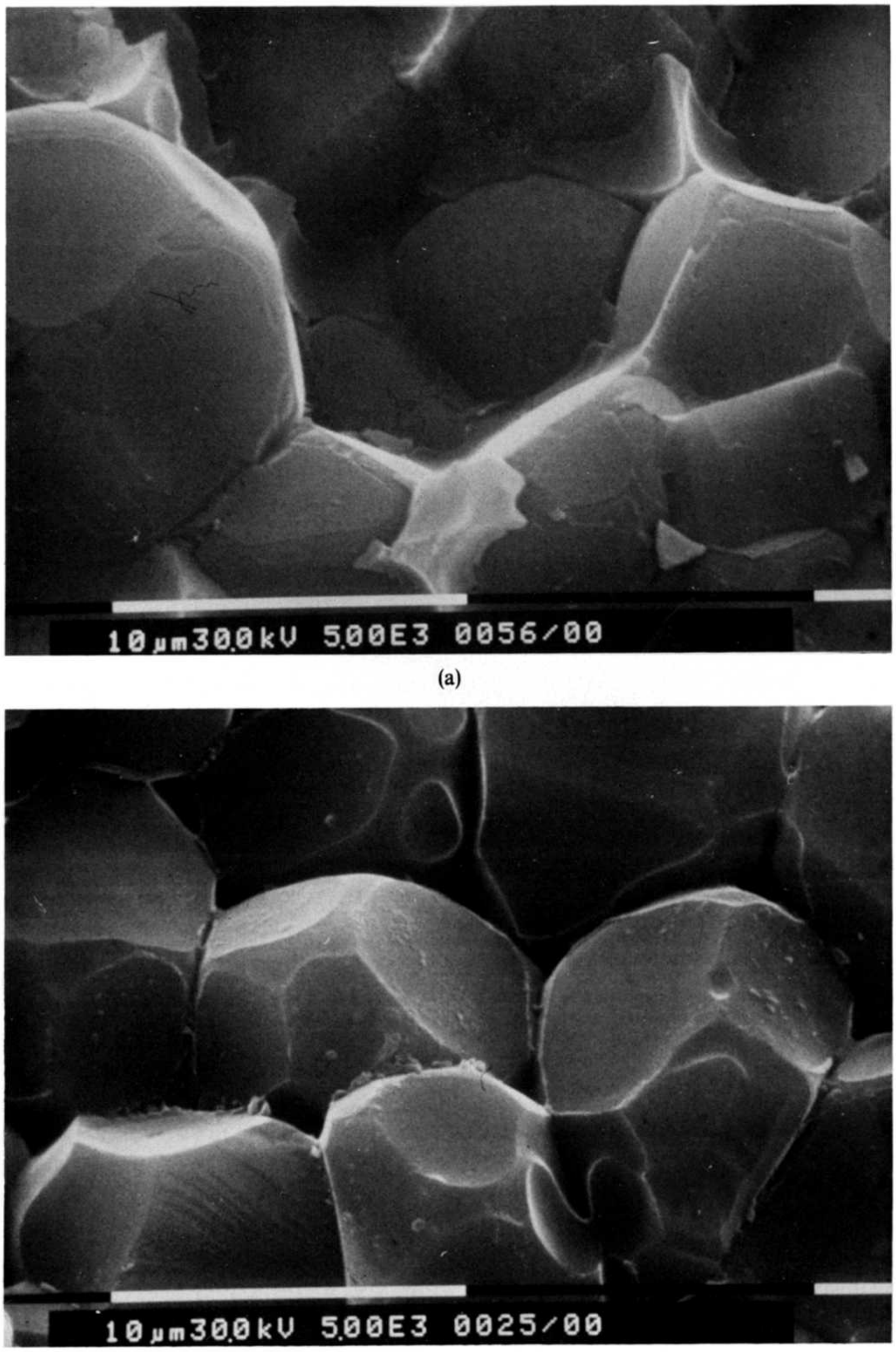


Fig. 4. X-Ray diffraction diagrams of AlN (5 wt% Y_2O_3) ceramic–graphite mixture before (A) and after (B) peak II extraction ($Y_2A = Y_4Al_2O_9$, JCPDS No. 22-987, YC_2, JCPDS No. 11-602, $Al_3C_4.n AlN$ from Ref. 10).

temperature span available prior to nitrogen release. X-Ray diffraction analysis confirms the hypothesis that the oxide phases in the sufficiently small ceramic fragments are reduced before the AlN itself is attacked.

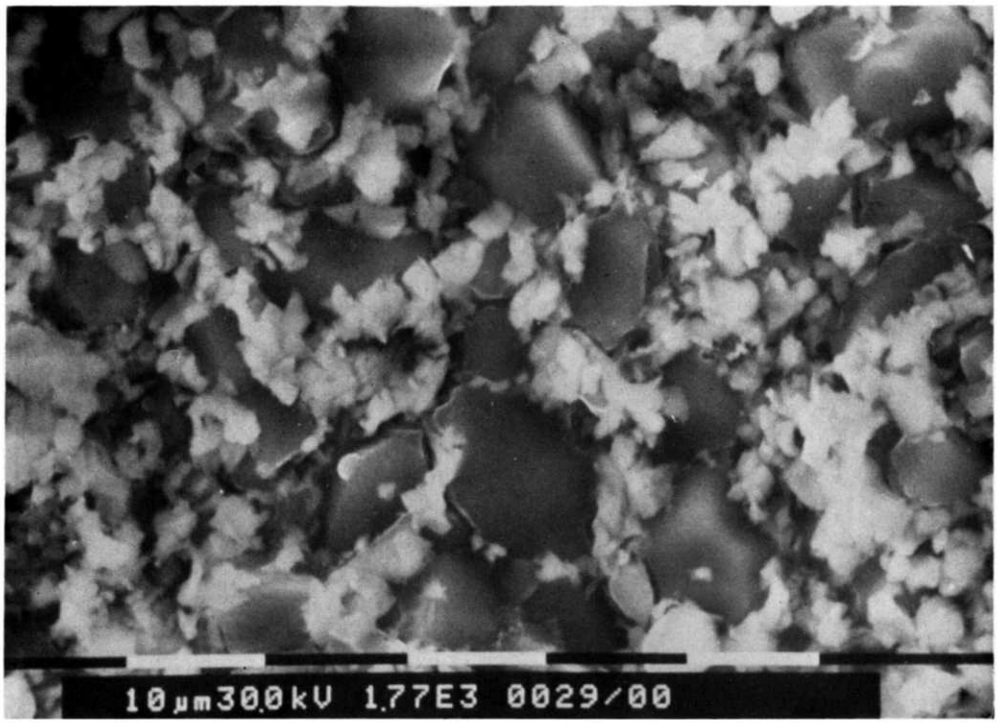
Figure 4 shows diffraction diagrams of an AlN (5 wt% Y_2O_3) ceramic–graphite mixture before and after type II oxygen extraction. The AlN diffraction peaks are unchanged, whereas the Y-aluminate peaks present in the as-sintered sample are missing after extraction. Instead, new peaks have appeared that can be assigned to YC_2 and aluminium carbonitrides.[10] The presence of these phases is in full agreement with the supposed reaction sequence.

Microstructural changes during the selective extraction of the oxide phases are revealed by SEM.



(b)

Fig. 5. SEM micrographs of AlN (5 wt% Y_2O_3) ceramic: (a) Fracture surface as sintered; (b) fracture surface of fragment, fractured after type II oxygen extraction; (c) surface of fragment after type II oxygen extraction.



(c)

Fig. 5.—*contd.*

Table 2. Oxygen contents in a commercial AlN ceramic (Shapal SH-15, Tokuyama Soda Co.)

Fragment size	*Oxygen (wt%)*			
(µm)	*Total*	*Type I*	*Type II*	*Type III (lattice dissolved)*
63–100	2·413	0·033		
40–63	2·451	0·032		
25–40	2·558	0·062	2·272	0·224
<25	2·629	0·055	2·341	0·233
e.s.d.	±0·015	±0·03	±0·015	±0·03

Figure 5(a) shows a fracture surface of an AlN (5 wt% Y_2O_3) ceramic as sintered. In Fig. 5(b) the fracture surface of a fragment of the same ceramic, but after extraction of the type II oxygen, can be seen. The fracture is mostly intergranular. Open porosity is clearly present, and its geometry is strikingly similar to that of the oxide phases in Fig. 5(a). Comparison of Fig. 5(a) and 5(b) shows that indeed, as was expected, the oxide phases have completely migrated out to the fragment surface, leaving behind an interconnected open channel system. As the fracture path follows this channel system, the former spatial distribution of the oxide phases now becomes exposed very clearly.

The fraction of the surface of a given AlN grain that is in direct contact with neighbouring AlN grains can be estimated from Fig. 5(b). This microstructural feature should be strongly related to thermal conductivity and will be dealt with in a separate paper.

Figure 5(c) shows the outer surface of a ceramic fragment, also after type II oxygen extraction. The solid products of the carbothermal reduction of the oxides have accumulated at the surface; EDS analysis shows large Y concentrations in these reaction products. Investigation of the microstructure also reveals the reason for the fact that finer fragmentation was necessary in order to fully extract peak II oxygen prior to AlN attack in the commercial material: Fig. 6(a) again is a fracture surface prior to extraction, Fig. 6(b) after peak II extraction. In this material the oxide phases ($Y_3Al_5O_{12}$ and $YAlO_3$ as found by X-ray diffraction) are present as isolated lumps instead of a continuous network. After partial extraction closed pores are left behind. It appears reasonable that the oxide phases, being liquids at the extraction temperature, can be sucked out faster to the surface through the network system than from isolated grains, thus, in the latter case, requiring finer fragmentation. On the other hand, it has been shown[11] that oxide liquids can migrate rather fast through dense, pure, polycrystalline AlN ceramics.

In summary, all the data from chemical, phase and microstructural analysis available so far support the hypothesis that the hot gas extraction procedure as originally developed for powders[8] can also be used for sintered AlN(Y_2O_3) ceramics that have been crushed to a sufficiently small fragment size.

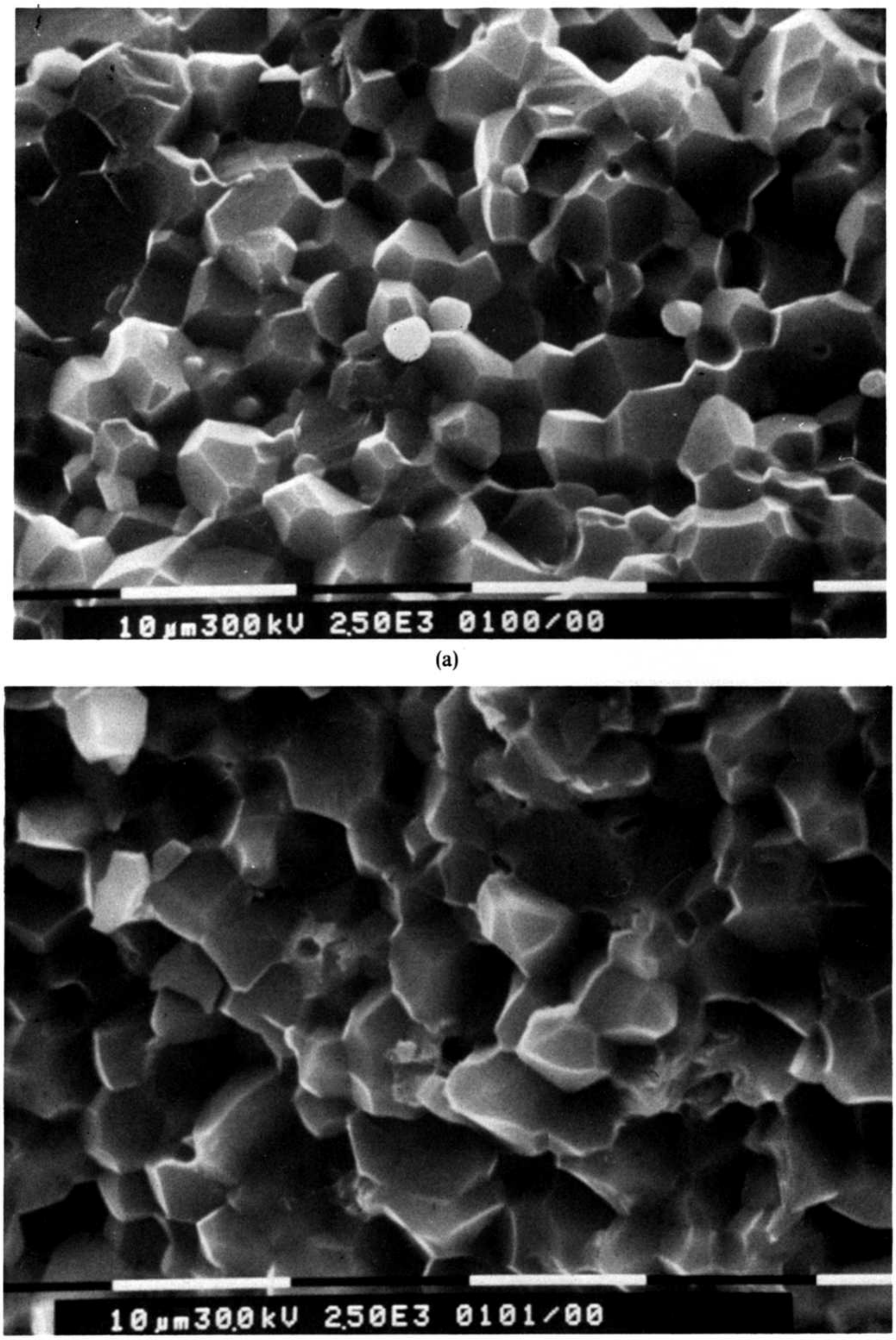


Fig. 6. SEM micrographs of a commercial AlN ceramic (Shapal SH-15, Tokuyama Soda Co.): (a) Fracture surface as sintered; (b) fracture surface of fragment, fractured after type II oxygen extraction.

However, because of the high reactivity of the Y-containing reaction products, a modified method for fraction II oxygen evaluation has to be applied. Discrimination between oxygen bound in oxide phases and oxygen dissolved in the AlN lattice is then possible. Ceramics containing CaO and CaC_2 as sintering aids showed the same sequence of oxygen release. It is assumed, therefore, that the method is generally applicable, but that different calibration coefficients may have to be used.

The standard deviations of the hot gas extraction measurement are rather small, around 0·03 wt% (Tables 1 and 2). Systematic errors may still be present, residual peak II/III overlap and baseline

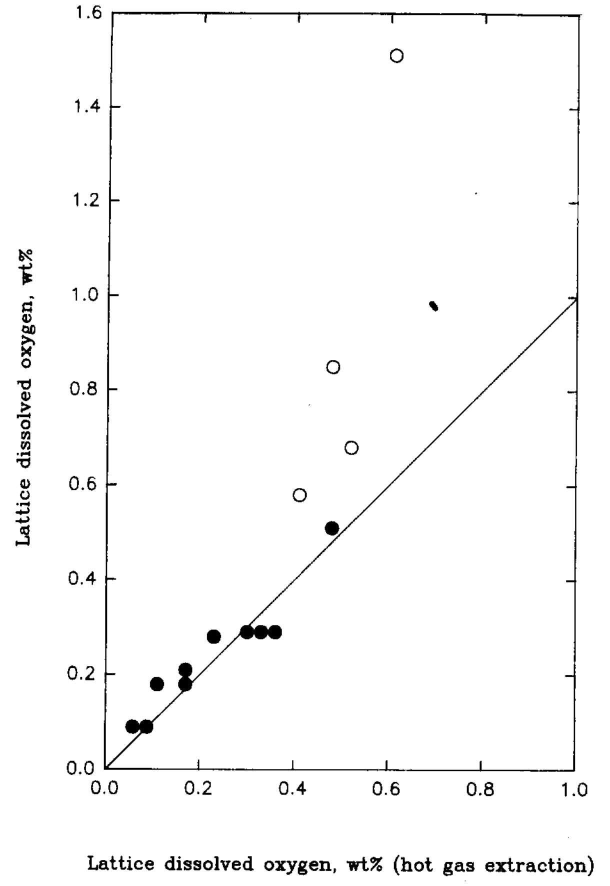


Fig. 7. Comparison of lattice dissolved oxygen measured by hot gas extraction and phase associations after Buhr *et al.*[5]

uncertainty being major possible sources. From the scatter of the data used for calibration (Fig. 3) it is estimated that such errors are below 0·05 wt%.

As stated in the introduction an alternative method to determine the lattice dissolved oxygen from phase associations has been described by Buhr *et al.*[5] The results from the two methods are compared in Fig. 7. Hot gas extraction analysis was done on the same samples as described in Ref. 5 and on additional ones made in the same way. As can be seen, there is a fair correlation (correlation coefficient 0·95) for data points with oxygen contents below ~0·5 wt% (full symbols). Lattice dissolved oxygen contents much larger than 0·5 wt%, as determined by the phase associations method, are not confirmed by hot gas extraction (open symbols in Fig. 7). In the case of the two samples where the phase associations method gave oxygen contents above 0·8 wt%, X-ray diffraction clearly indicated the presence of γ-AlON (~$Al_{23}O_{27}N_5$) besides $Y_3Al_5O_{12}$ and AlN. After peak II oxygen extraction, the X-ray diffraction peaks of γ-AlON were completely absent. The same was found on samples that contained a large amount of γ-AlON (~10% as estimated from X-ray diffraction intensities). No release of N_2 simultaneous with peak II oxygen was found in these cases. It is therefore assumed that γ-AlON reacts with graphite forming CO and solid AlN and/or the Al-carbonitrides mentioned above. γ-AlON thus behaves essentially in the same way as the pure oxide phases, which is understandable in view of its limited thermal stability.[12]

For the remaining two data points in Fig. 7 (samples 0·2 a and 1·0 a from Ref. 5 containing 0·2 resp. 1·0 wt% Y_2O_3 and sintered with program a: 1 h, 1750°C) the presence of 0·5–0·7 wt% γ-AlON would be sufficient to incorporate all the oxygen in excess of the amount determined by hot gas extraction. By comparison with the diffraction peaks of the other two samples, this amount would be definitely below the X-ray detection limit. Ceramic samples from preoxidized AlN powders sintered at 1950°C for 3 h contained the 27R-pseudopolytype[12] ($Al_9O_3N_7$). This phase, in contrast to γ-AlON, only releases its oxygen content at much higher temperatures upon extraction, approaching the decomposition temperature of AlN. Consequently, the separation of peak II and peak III oxygen is lost if large amounts of this phase are present besides AlN and aluminates.

4 Conclusions

Hot gas extraction, a well-established method to determine oxygen concentrations in non-oxide materials, can be modified to discriminate between lattice dissolved oxygen and oxygen bound in oxide phases of AlN ceramics. For this purpose the ceramic has to be crushed to fragments smaller than a critical size that depends on the type of microstructure, $<40\,\mu m$ being satisfactory in all kinds of AlN ceramics studied so far. Crushing and storage can, if no precautions are taken, affect oxygen fractions I and II, but not III. All fractions can be determined with estimated accuracies better than 0·05 wt%, which makes the method promising for studies relating phase composition and microstructure of AlN ceramics to their properties, particularly thermal conductivity. The selective extraction of all oxide phases during hot gas extraction analysis takes place very rapidly, apparently without rearrangements of the microstructure, the space formerly occupied by the oxide phases being left as porosity without changes of shape. This also offers a new tool for microstructural characterization.

The hot gas extraction method presented here is limited to ceramics that do not contain large amounts of Al-oxynitride pseudopolytypes. The

27R-pseudopolytype in particular gives off its oxygen content at temperatures slightly lower than that of AlN. The oxygen content in these phases is concentrated in periodic stacking faults of the polytype structure. As the difference in oxygen release temperatures of 27R and AlN is rather small, it must be concluded that occasional unperiodic stacking faults or, in fact, other extended structural defects will release their associated oxygen impurities upon extraction in a way that cannot be separated from the behaviour of lattice dissolved oxygen *sensu stricto*. The term 'lattice dissolved oxygen' as used here is therefore meant to cover all oxygen included in the AlN crystallites.

The results obtained so far on this total lattice dissolved oxygen indicate that the maximum solubility of Al_2O_3 in AlN at 1800°C is only approximately 0·5 mol% Al_2O_3 (0·6 wt% oxygen). This is much less than the limit given by Slack[1] (1·35 mol% Al_2O_3 for 2000°C) that was used by Buhr *et al.*[5] for the proposed AlN_{ss}–$Y_3Al_5O_{12}$ phase boundary.

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