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Carbothermal Preparation and Characterisation of Ca-α-sialon

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Abstract

Ca-α-sialon can be synthesised by simultaneous carbothermal reduction–nitridation of a mixture of fine SiO_2, Al_2O_3, $CaSiO_3$ *and carbon black powder at 1500°C. For the first time a single phase material is obtained in a one step process. The main intermediate product in these processes is a β-sialon with a low z-value* ($z < 1{\cdot}2$)*. After formation of this β-sialon the calcium is incorporated in the lattice to form the Ca-α-sialon.*

1 Introduction

Si_3N_4 and Si_3N_4 based ceramics like sialon materials are interesting for high temperature engineering applications. These materials have very good thermal shock behaviour, high wear resistance, good corrosion resistivity, oxidation resistance and high strength.[1–4] The preparation of the sialon materials, either α or β, can be performed in several different ways. Reaction sintering is the most widely used method among them. The disadvantages are the relatively expensive starting materials and the limited possibilities to produce complex shapes of fully densified materials. An alternative way of producing sialon starting with relatively inexpensive materials is the route of carbothermal reduction and nitridation of oxide materials. The carbothermal reduction and nitridation of kaolin clay is well known for the synthesis of β-sialon.[5–7] The overall reaction for the production of β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$) when $z = 3$ is:

$$3\ (2\ SiO_2\ Al_2O_3 \cdot 2\ H_2O) + 15\ C + 5\ N_2 \rightarrow 2\ Si_3Al_3O_3N_5 + 15\ CO + 6\ H_2O \qquad (1)$$

This reaction can be separated into several stages. Some of the intermediate products are mullite and SiC.[5,6]

As mentioned, besides the β-sialon α-sialon also exists. The structure of these latter materials is stabilised by a modifying cation such as Y, Li, Mg and Ca. The general formula for α-sialon is $Me_{m/val}Si_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$ where m and n indicate the replacement of (Si–N) by (Al–O) and *val* is the valency of the metal ion. The synthesis of α-sialon materials by reaction sintering is widely used, especially for the Y-α-sialon materials which are intensively studied.The carbothermal reduction, however, is hardly ever investigated and reported about. In this paper, the possibility is investigated of preparing Ca-α-sialon by carbothermal reduction in a single step from oxidic starting powders. To determine the most convenient starting materials, it is important to know what kind of intermediate products are formed. This is one of the reasons why the mechanism of the carbothermal reaction has been studied here.

The composition chosen is $Ca_{0{\cdot}8}Si_{9{\cdot}2}Al_{2{\cdot}8}O_{1{\cdot}2}N_{14{\cdot}8}$. Starting with $CaSiO_3$ the overall reaction is as follows:

$$0{\cdot}8\ CaSiO_3 + 8{\cdot}4\ SiO_2 + 1{\cdot}4\ Al_2O_3 + 22{\cdot}2\ C + 7{\cdot}4\ N_2 \rightarrow Ca_{0{\cdot}8}Si_{9{\cdot}2}Al_{2{\cdot}8}O_{1{\cdot}2}N_{14{\cdot}8} + 22{\cdot}2\ CO \qquad (2)$$

This composition has been chosen for practical reasons because it is well within the single phase area of Ca-α-sialon,[8] and single phase material is likely to be obtained.

Some years ago, Mitomo *et al.*[9] prepared α-sialon (Ca and Y) by carbothermal reduction and nitridation. In that study relatively expensive starting materials such as tetraethyl–orthosilicate, aluminium–isopropoxide, calcium–ethoxide and yttrium nitrate were used. These were mixed with carbon black, precipitated and fired at different temperatures. This study showed that α-cristobalite, mullite, Si_2N_2O and β-Si_3N_4 were the main intermediate crystalline products. These were obtained, next to some amount of α-sialon, after firing at temperatures at 1450°C or lower. In a second step the material was transformed to single phase α-sialon by firing it at higher temperatures.

2 Experimental Methods

2.1 Preparation

Pure oxide materials were used to investigate the formation of single phase Ca-α-sialon. The starting materials were SiO_2 (Aerosil OX50, Degussa), C (Elftex 125, Cabot, stoichiometric amount according to reaction eqn (2)), Al_2O_3 (grade 'C', γ + δ Al_2O_3, Degussa) and $CaSiO_3$ (Wollastonite SG, Rheinische Kalksteinwerke). In some experiments $CaCO_3$ (Merck p.a., purity > 99%) or CaO (decomposed $CaCO_3$) were used as a source for calcium. The SiO_2 and Al_2O_3 powders have a high specific surface area (± 50 m^2/g). This means a high reactivity which can cause sintering of particles during the powder preparation.

An important parameter in carbothermal processes is the mixing of the powders to improve the contact between reactants and reduce the diffusion path length. Wet mixing and dry mixing were the two methods that were used. They are described briefly below.

2.2 Wet mixing

The starting powders are dispersed in water or isopropanol in a polyethylene bottle with Si_3N_4 milling balls on a roller bench for ± 48 h. The next stage is evaporating the isopropanol, pressing tablets of the powder, or slip casting the aqueous suspension. For slip casting tablets, the suspension has to meet certain requirements. The powder particle size distribution should be narrow and if possible the particle size should be below 1 μm. It is important that the suspension is stable and not too viscous. To obtain a stable suspension with SiO_2 and Al_2O_3, the pH should be either below pH = 2 (otherwise the SiO_2 and Al_2O_3 will form a gel) or above 9. However in the latter case, a very small amount of the SiO_2 will dissolve and the ionic strength will increase, which will flocculate the suspension. In order to check these properties sedimentation experiments were done in all cases. For dispersing the carbon a surfactant is required. Several surfactants were tried and among these CG-6 (i.e. ammonium salt of poly acrylic acid) supplied by ICI worked best for this system. It also helped to disperse the other powders. The suspensions which were used for slip casting had a pH < 2 because the surfactant worked better at this pH than at higher pH-values. After mixing, the suspension was ultrasonically treated to break the agglomerates and then slip cast in a plastic ring (ϕ 45 mm) placed on a gypsum plate.

2.3 Dry mixing

Pelletising is another way to produce green bodies which can be fired. The starting powders are dry mixed in an Eiger mixer (Labor Mixer R02) until the mixture looked homogeneous. Then water is sprayed on the powder which caused agglomeration of the powder. The size of the pellets obtained is related to the amount of water added and the speed of the mixer (typical values 5–10 mm). These pellets are dried at 100°C and can be used for the synthesis of Ca-α-sialon.

The density of the tablets and pellets are roughly estimated by measuring the weight and volume (pellets = 1·0 g/cm^3, tablets = 0·7 g/cm^3). The slip cast tablets are less dense and more porous than the pellets, so the influence of porosity on the reaction can be observed.

2.4 Synthesis

The different experiments and conditions are summarised in Table 1. For these experiments a constant amount of slip cast tablets were used in a horizontal tube furnace with flowing nitrogen. The exceptions were Experiment A, during which pieces of mixed starting powder bonded with binder were used. (These can be considered as pellets; agglomerates are formed after evaporation of isopropanol) and Experiment E in which pellets were used. The experiments with starting mixtures A–D were carried out in a horizontal tube furnace with a diameter of 25 mm. Experiment E was carried out in a tube furnace with a diameter of 50 mm. The amount of pellets used was 200 g and the bed length was 20 cm. The temperature was in the range 1350 – 1650°C for 3 – 65 h. The progress of the reaction was followed by measuring the CO content in the exhaust gas mixture with a CO-monitor (Defor Gas Analyser, Maihak).

Additionally some of the tablets were refired for 1 or 2 h between 1550 and 1700°C in a graphite resistance furnace in a static nitrogen atmosphere to see if the amount of α-sialon would increase. The tablets were embedded in a mixture of BN, Si_3N_4 and AIN powder to prevent dissociation at these relatively high temperatures. The influence of a milling step between the first and second firing was investigated as well. The milling could be performed in a mortar, because the material was not very hard. This powder was pressed uniaxially followed by isostatic pressing.

To get some insight into the mechanism of the carbothermal reduction, several experiments were carried out at 1500°C as a function of the firing time. In these experiments pellets were used and all the reaction parameters were kept constant, except for the time, which varied from 20 to 1000 min. The volume of the reaction bed in the horizontal tube furnace (ϕ 25 mm) was 10 ml and the N_2 flow was 12·5 l/h.

Table 1. Approximate phase composition after the first firing of a mixture of SiO_2, Al_2O_3, $CaSiO_3$ and C in N_2 at different temperatures

Starting materials	*Temperature [°C]*	*Time [h]*	*N_2-flow [l/h]*	*α/β ratio*	*Composition**
A	1450	14	12	0·27	α-sialon, β-sialon
B	1450	14	12	0·39	α-sialon, β-sialon
B	1450	6	12	0·79	α-sialon, β-sialon
B	1450	6	12	0·25	α-sialon, β-sialon
C	1450	6	12	—	β-sialon
B	1450	5·5	12	—	β-sialon
B	1450	7·5	12	0·49	α-sialon, β-sialon
B	1450	7·5	6	0·67	α-sialon, β-sialon
B	1450	3	12	—	β-sialon
B	1350	6	12	0·33	α-sialon, β-sialon
D	1350	6	12	0·45	α-sialon, β-sialon
D	1450	6	12	—	β-sialon
D	1350	12	12	—	SiO_2
D	1450	6	5	—	Si_2ON_2
E	1500	65	30	>20	α-sialon
E	1500/1650	15/2$^+$	30	—	SiC

(A) SiO_2, Al_2O_3, CaO + C in isopropanol with binder.
(B) SiO_2, Al_2O_3, $CaSiO_3$ + C in water.
(C) SiO_2, Al_2O_3, $CaSiO_3$ + C in water, lower mass content.
(D) Same as B but excess of $CaSiO_3$ (2×).
(E) SiO_2, Al_2O_3, $CaSiO_3$ + C, pelletised.
(*) Amorphous and secondary phases neglected.
($^+$) No cooling inbetween.

3 Characterisation

To investigate the phase compositions in the product material, X-ray diffraction was applied (Rigaku Geigerflex diffractometer) using Cu–Kα radiation. To determine the ratio of α-sialon to β-sialon the following equation was used:[10]

$$\alpha/\beta = [I_{\alpha(102)} + I_{\alpha(210)}] \,/\, [I_{\beta(101)} + I_{\beta(210)}] \qquad (3)$$

This equation is applicable in the case of pure α and β Si_3N_4 and is assumed to be valid for sialon materials too, because the structures are very similar. To estimate the α-sialon content only α and β sialon phases were taken into account. Amorphous phases and (traces of) secondary phases were neglected. Therefore in Table 1 only an indication is given of the compounds present in the sample; the concentration for each component is not calculated. The lattice parameters of the materials were determined from slow scans (0·0125°/s). The ten strongest reflections observed were applied to calculate the lattice parameters using a computer program based on the SIMPLEX method.[11]

To determine the relation between the nitrogen content and the content of α-sialon the nitrogen content was determined by a reverse Kjelldall titration.[12] The sample is destructed with molten lithium hydroxide, the formed NH_3 is dissolved in boric acid which was titrated with hydrochloric acid to determine the nitrogen-content. Particle size was determined by sedigraph measurements (Micromeritics Sedigraph 5100). The powder was suspended in water and ultrasonically treated to break agglomerates before the measurements.

4 Results and Discussion

4.1 Synthesis of Ca-α-sialon

The conditions of the experiments and the results are displayed in Table 1. As can be seen, the applied conditions at 1450°C or lower temperatures are not appropriate for preparing single phase α-sialon from the starting SiO_2, Al_2O_3 and $CaSiO_3$ powders. The main products in this range of temperatures are α-sialon and a β-sialon when these starting powders are used. Even after a very long time the composition of the samples does not differ significantly. In all samples an amorphous phase is present. This phase cannot be characterised by X-ray diffraction; the phase is assumed to consist of aluminates and silicates. Evaporation of SiO influences the yield of the sialon material. When the reaction time is longer the silicon loss increases. This explains the higher ratio after 6 h compared to the ratio after 14 h (Experiments 2 and 3). Although the circumstances were the same in Experiments 3 and 4, the results were quite different. This is probably due to the fact that two different batches of tablets were used. Apparently one batch was not as homogeneously mixed as it should have been. This could explain the large difference in the α/β ratio. According to the results of Experiments 13 and 14 (main products SiO_2 and Si_2ON_2) the temperature of 1350°C is not sufficient for the reaction to have proceeded far enough for the sialon materials to be detected. SiO_2 and Si_2ON_2 are well known intermediates in the formation of β-sialon too.[6] In Experiment 14 the N_2-flow is too low to supply a sufficient amount of nitrogen in 6 h to form sialon material. In the samples reacted for a short time there were remains of starting materials present. The z-values of the formed β-sialon material in the samples fired below 1500°C vary between approximately 0·4 and 1·2. A value of 1·4 at the most can be expected from the starting composition. At a temperature below 1500°C the highest content of α-sialon is about 40%, both for the slip cast tablets and pelletised starting material. Increasing the temperature to 1500°C resulted in an almost single phase Ca-α-sialon (> 95 wt%). The rest (5 wt%) is uncertain because of the detection limit of the X-ray diffraction analysis. However, when the holding time at 1500°C is not long enough, a significant amount of residual carbon is left in the mixture. The mixture contains hardly any sialon material (at least not above the detection limit). When the temperature is raised to 1650°C the main product is SiC instead of α-sialon. Refiring the tablets, which were fired at temperatures below 1500°C, at elevated temperatures (1550–1700°C) resulted in a decrease of the α-sialon content. On the contrary, milling and pressing tablets and refiring these tablets in the same temperature range results in products with high α-sialon content. α-sialon contents of up to 95 wt% are achieved (see Table 2).

This means that on the one hand it has been confirmed that Ca-α-sialon can be obtained in a two step process,[9] but on the other hand it has been shown in this paper that it is possible to use a single step process.

Table 2 shows the influence of porosity on the conversion to α-sialon. From this it can be seen that porosity has little or no effect on the reaction (at least in this range of porosity).

Figure 1 shows the transformation percentage to α-sialon after milling and a second firing at higher temperatures. The highest amount of Ca-α-sialon was obtained at 1700°C. No SiC could be detected, indicating a complete consumption of carbon in the first step.

Table 2. Comparison of α-sialon content between first and second firing of tablets and pellets with intermediate grinding. (The numbers are averages)

	First firing (1450°C)	*Second firing (1700°C)*
Tablets	30% α-sialon, 70% β-sialon	> 95% α-sialon
Pellets	35% α-sialon, 65% β-sialon	> 95% α-sialon

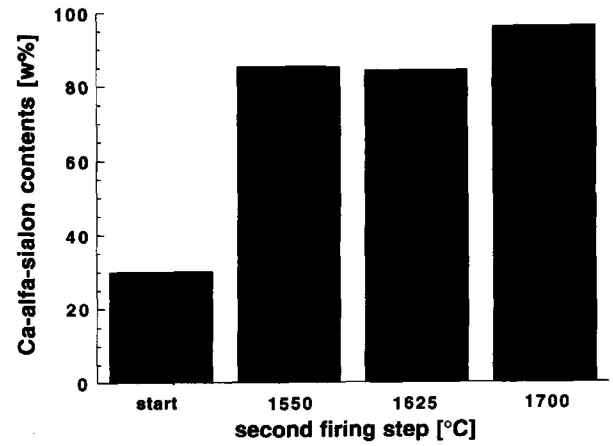

Fig. 1. Transformation to α-sialon after the second firing. (Start = initial amount of Ca-α-sialon before the second firing).

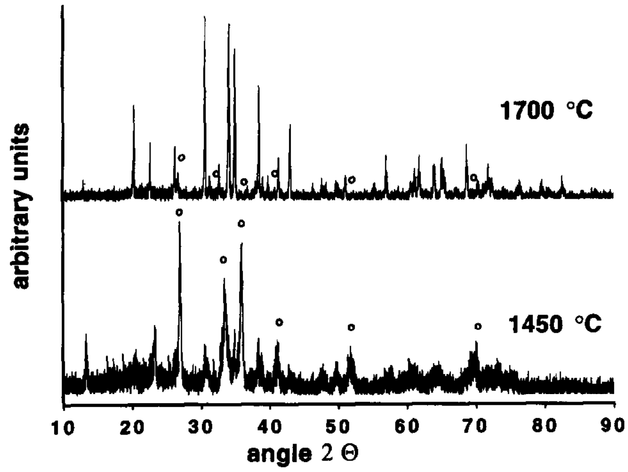

Fig. 2. X-ray diffraction patterns of material after first firing at 1450°C (bottom) and firing at 1700°C (top).The circles indicate peaks of β-sialon.

The phase change during the refiring process is shown in Fig. 2. The lower part presents a diffractogram of a sample fired at 1450°C. According to the baseline (which is not straight) a significant amount of amorphous phase is still present after firing at 1450°C. The diffractogram in Fig. 2 after refiring at 1700°C shows narrow and sharp peaks and a straight baseline. The unit cell dimensions of α-sialon calculated from this diffractogram are a = 0·784 and c = 0·571 nm. From these lattice parameters an m-value in the general formula for α-sialon of ± 1·4 can be estimated. This means that most of CaO is incorporated in the crystalline material and the rest is present in the amorphous or unidentified phase. The powder which is obtained after firing twice is more difficult to mill than powder which is synthesised at 1500°C. The particle size (agglomerate size) of this powder as synthesised is approximately 5–8 μm while the agglomerate size of the refired powder is about 10–20 μm.

4.2 Reaction mechanism

The results from the experiments concerning the investigation of the mechanism of the reaction are presented in Fig. 3 and discussed in the next paragraph. In a relatively short time the sialon products are formed. From X-ray diffraction patterns it follows that in the beginning of the reaction a significant amount of amorphous phase is present. This complicates the identification and quantitative determination of several components during this initial period. The main intermediate product is β-sialon material with low z-values ($z < 1{\cdot}2$). In shortly reacted samples some SiC seems to be present. Sometimes the samples contain O'-sialon. Calcium aluminates or silicates were hardly found except the starting $CaSiO_3$. The intermediate products are consumed very fast otherwise there should have been a plateau at a certain level in the curves.

To monitor the progress of the reaction the cell parameters of Ca-α-sialon are calculated. The values are shown in Table 3. These show that the further the reaction proceeds the smaller the cell parameters become. The cell parameters of the α-sialon converge to the values of the desired product. As expected, if the amount of nitrogen increases the cell parameters will decrease.[13]

Table 3. Cell parameters of Ca-α-sialon calculated during progress of the reaction.

Time [min]	a *[nm]*	c *[nm]*
100	0·787	0·572
125	0·785	0·568
250	0·784	0·569
500	0·785	0·569
750	0·784	0·569
1000	0·784	0·568

In Fig. 4, the data from the nitrogen determination are plotted, showing that even at a low (40 wt%) Ca-α-sialon concentration the nitrogen content is high. This means that nitridation has proceeded so far that most of the nitrogen required for the formation of the Ca-α-sialon is available in the sample. Approaching 100 wt% of Ca-α-sialon the nitrogen content rises up to almost the theoretical value (35·0 wt%)

On the basis of the results mentioned previously the following mechanism of the formation of Ca-α-sialon is proposed. The first step is the formation of a β-sialon with a z-value of 1·2 (Theoretically $z = 1{\cdot}4$, because it was aimed at $Si_{9\cdot2}/\ Al_{2\cdot8}$). The theoretical value of the nitrogen content of a β-sialon is 33·8 wt% if the z-value is 1·2. In Fig. 4 it is shown that with a low (40 wt%) Ca-α-sialon concentration combined with a high content of β-sialon (60 wt%) the nitrogen content nearly reaches the theoretical value for a β-sialon material with a z-value of 1·2. The end of the curve shows that the nitrogen content rises to the theoretical value of Ca-α-sialon which is 35·0 wt%. The molar concentration of nitrogen is increased from 13·2 to 14·8 (see eqns 4 and 5). In summary, the first step is:

$$4{\cdot}6\ SiO_2 + 0{\cdot}7\ Al_2O_3 + 9{\cdot}9\ C + 3{\cdot}3\ N_2 \rightarrow \underset{(\beta\text{-sialon})}{Si_{4\cdot6}Al_{1\cdot4}O_{1\cdot4}N_{6\cdot6}} + 9{\cdot}9\ CO \qquad (4)$$

In the second step calcium and the extra nitrogen are being incorporated:

$$0{\cdot}8\ CaO + 2\ Si_{4\cdot6}Al_{1\cdot4}O_{1\cdot4}N_{6\cdot6} + 2{\cdot}4\ C + 0{\cdot}8\ N_2 \rightarrow \underset{(\alpha\text{-sialon})}{Ca_{0\cdot8}Si_{9\cdot2}Al_{2\cdot8}O_{1\cdot2}N_{14\cdot8}} + 2{\cdot}4\ CO \qquad (5)$$

It is assumed that an eutectic liquid of $CaSiO_3$ (providing CaO) and β-sialon promotes the formation of Ca-α-sialon. During this formation it is expected that Si–N as well as Al–O bonds have to be broken but how exactly the formation takes place is not in the scope of this work and is

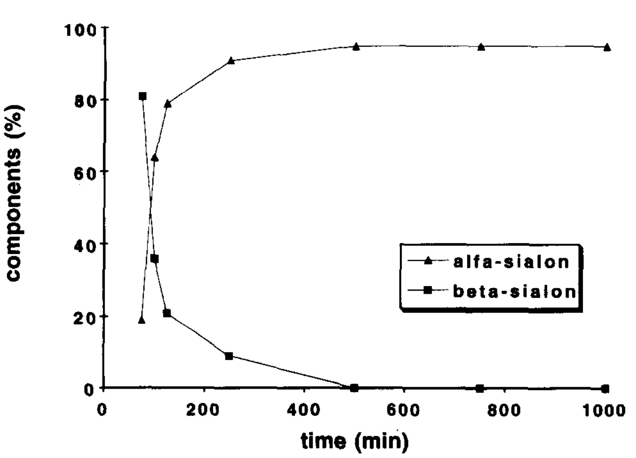

Fig. 3. The α and β sialon content of the mixture after firing at 1500°C for different times.

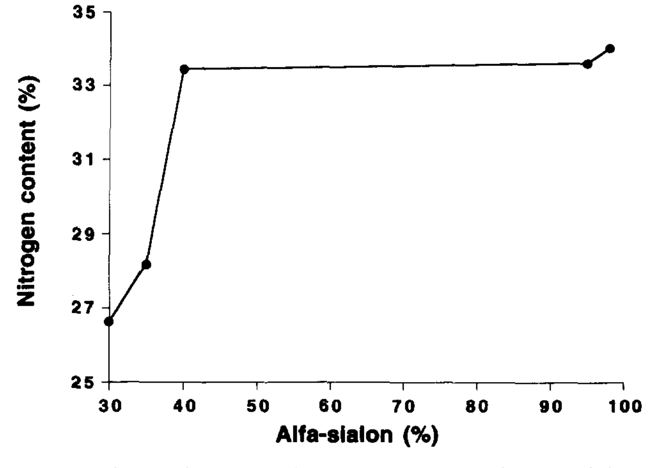

Fig. 4. Relation between nitrogen content and Ca-α-sialon content in the mixture. Experiments were carried out in a large horizontal tube furnace (ϕ 50 mm, 200 g pellets, 30 l/hr N_2-flow, 1500°C).

not investigated. The conversion of the mixed α/β-sialon which was obtained after firing at a temperature lower than 1500°C to a single phase α-sialon by firing it at a higher temperature can be compared to reaction sintering.[13] The carbon was fully consumed in the first step due to complete nitridation. Ca is then incorporated into the material in the second step at a higher temperature without further nitridation, different from the second step of the carbothermal reaction given by eqn (5).

5 Conclusions

The carbothermal reduction and nitridation of oxidic powder precursors is a possible route to prepare single phase Ca-α-sialon in a relatively inexpensive way. There are two methods to obtain single phase material. The first way is firing first at 1450°C, milling the obtained α/β mixture and refiring it at 1550–1700°C. Results from this route are comparable with the results found in Ref.[9] The second way is firing at 1500°C where the reaction can be completed in *one* step to form single phase materials. The main intermediate product in the carbothermal reduction of the oxides is β-sialon with a low z-value ($< 1{\cdot}2$). A proposal for the formation mechanism of single phase Ca-α-sialon has been made. Firstly, a β-sialon with low z-value is formed, followed by the incorporation of the Ca-ions. Nitrogen content determination and calculation of the cell parameters support this proposed mechanism. In contrast with the formation of β-sialon, SiC is not a major intermediate product.

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