

## Aluminium reduction and nitriding of aluminosilicates

A.D. Mazzoni<sup>\*,1</sup>, E.F. Aglietti<sup>1</sup>

CETMIC (Centro de Tecnología de Recursos Minerales y Cerámica), C.C. 49 (1897), M.B. Gonnet, Buenos Aires, Argentina

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### Abstract

High-alumina compounds are reduced with aluminum by applying simultaneous nitriding. Andalusite, mullite and kaolinite are employed as raw materials. The sequence of reaction was followed using thermal techniques (ATD-TG-DTG) and XRD. The reactions that occur are similar for all the aluminosilicates employed. Silicon and aluminum nitride appear at low temperatures. The final phases are sialon and alumina. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Andalusite; Mullite; Kaolinite; SiAlON; Nitriding; TG-DTA

### 1. Introduction

Alumina-base ceramics are some of the most useful materials in engineering activities. Their electrical and mechanical properties are suitable for application at ambient environment. However, the properties need to be improved for use under severe conditions. Many authors have reported that the dielectric and mechanical properties of hot-pressed alumina improved by the addition of small amounts of Si<sub>3</sub>N<sub>4</sub> and AlN (in situ formation of sialons) [1]; the samples containing different phases as: β-sialons, sialon polytypes, etc.

The β'-sialons have a structure derived from β-Si<sub>3</sub>N<sub>4</sub>, corresponding to the formula Si<sub>6-Z</sub>Al<sub>Z</sub>O<sub>Z</sub>N<sub>8-Z</sub> with 0 < Z ≤ 4.2 [2,3]. These phases have structural properties similar to those of β-Si<sub>3</sub>N<sub>4</sub> and chemical properties combining those of Si<sub>3</sub>N<sub>4</sub> and alumina, according to their composition [2,3] There are six polytype sialons near the AlN corner in the Si-

Al-O-N phase diagram (Fig. 1). The structure of these phases is determined by the metal(M)/non-metal(X) ratio and it can be expressed by the formula M<sub>m</sub>X<sub>m</sub>, where *m* takes values of 4, 5, 6, 7, 9 or 11. The polytype sialons are the phases 8H, 15R, 12H, 21R and 2H<sup>δ</sup>.

Sialon polytypes have been used as replacements of aluminium nitride and are reported to be successful in overcoming some of the hydrolysis problems encountered when aluminium nitride is used [4].

At present, there exists a tendency to use abundant and cheap raw materials to obtain ceramic powders (oxygenated as well as nitrogenous). Ceramic powders can be manufactured from well-characterized raw materials. These powders are then purified in order to control the degree of impurities. The reactions studied in this work are developed within this category of materials.

The formulation of alumina-sialon mixtures (principally β'-sialon and/or polytypes) may be achieved in several ways: by reacting elemental (metallic) Al with SiO<sub>2</sub> [5,6]; and by heat treatment of volcanic ash [7] or aluminosilicates [8] in nitrogen atmosphere. In

\*Corresponding author. Tel.: +54-221-4840247; fax: +54-221-4710075; e-mail: cetmic@netverk.com.ar

<sup>1</sup>CONICET and UNLP research member.

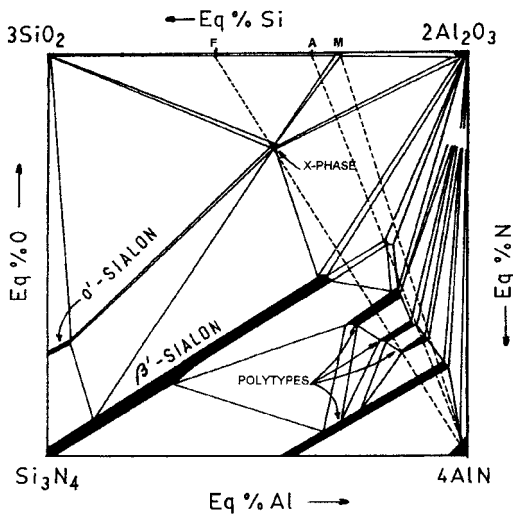


Fig. 1. Phase diagram of the Si–Al–O–N system at 1400°C.

previous studies, clay–Al–N<sub>2</sub> and mullite–Al–N<sub>2</sub> systems were studied by Mazzoni [8] and Mazzoni et al. [9] using silica-rich natural aluminosilicates and Al in N<sub>2</sub>.

In this work, the stages and sequences of the reactions between alumina-rich natural aluminosilicates and A in the presence of N<sub>2</sub> were studied.

The systems studied were: ‘andalusite–Al–N<sub>2</sub>’, ‘mullite–Al–N<sub>2</sub>’ and ‘kaolinite–Al–N<sub>2</sub>’ and the reactions and mechanisms were followed and analyzed up to 1650°C using thermal analysis.

## 2. Experimental methods

The minerals used were andalusite from South Africa; kaolin from Georgia, USA, and synthetic mullite (FOSECO). The chemical analyses of these aluminosilicates are presented in Table 1.

The aluminium used was of 99.9% purity. The aluminium as well as the minerals utilized have a

particle size smaller than 44 μm (mesh 325 ASTM). The nitrogen used contained <5 ppm of O<sub>2</sub> and H<sub>2</sub>O.

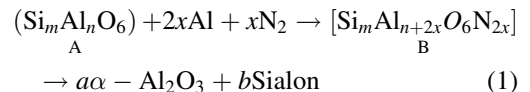
Mixtures of mineral–Al with different A content were prepared; their compositions are presented in Table 2. These mixtures were prepared by wet mixing of the calculated amounts of mineral and Al. Afterwards, they were dried and uniaxially pressed (38.3 Mpa) into cylindrical pellets. The pellets were then milled for thermal analysis.

Differential thermal analyses and gravimetric analyses were carried out simultaneously in a Netzsch STA 409 equipment. Samples were placed in alumina crucibles and α-Al<sub>2</sub>O<sub>3</sub> was used as a reference. The heating rate (β) was 5 K/min. The equipment was evacuated and then filled with N<sub>2</sub> to eliminate the oxygen present. This operation was repeated thrice. The experiments were performed in N<sub>2</sub> at a flow rate of 100 ml/min and a manometric pressure of 0.05 Mpa.

The phases formed during heating and the final reaction products were followed and analyzed by XRD with a Philips PW 1140/00 diffractometer. Peak areas were used to calculate the amounts of crystalline phases which were expressed in arbitrary units (AU) and were used to demonstrate the evolution of the reaction products. Thermodynamic data were obtained using JANAF tables [10].

## 3. Results and discussion

The general equation describing the aluminothermy of aluminosilicates in a nitrogen atmosphere is:



where: *a*, *b*, *m*, *n*, *x* are stoichiometric coefficients, A a point on the SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> axis (Fig. 1), and B a point in the Si–Al–O–N phase diagram (Fig. 1).

Table 1  
Chemical composition of the aluminosilicates (in wt%)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O + K <sub>2</sub> O	Loss on ignition
Kaolin	44.1	39.5	0.52	2.10	0.06	0.08	0.05	13.6
Mullite	26.1	72.2	0.40	0.2	0.2	0.2	0.51	0.00
Andalusite	39.3	57.7	1.05	0.18	0.18	0.06	0.40	0.80

Table 2  
Composition and nomenclature of the aluminosilicates–Al mixtures studied

Aluminosilicate sample	Kaolin (F)		Mullite (M)		Andalusite (A)		
	F340	F300	M300	M210	A200	A300	A350
Al/M, F or A ratio (wt/wt)	0.340	0.300	0.300	0.210	0.200	0.300	0.350
Al content (wt%)	25.4	23.1	23.1	17.4	16.67	23.08	25.93

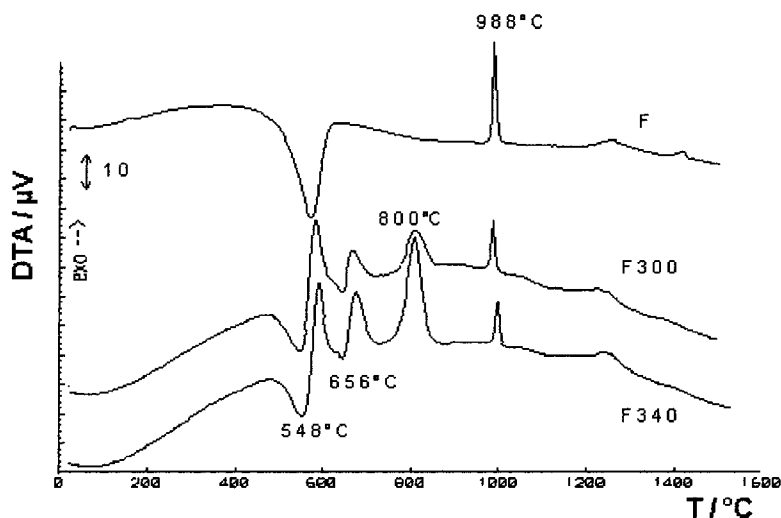


Fig. 2. DTA of kaolinite (F) and kaolinite–Al mixtures (F<sub>300</sub>, F<sub>340</sub>).

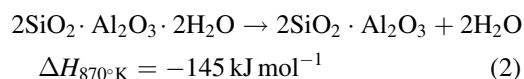
The amounts of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and sialons depend on the amount of Al in the mixture as well as on the aluminosilicate composition. Using silica-rich raw minerals [9], sialons may be obtained as principal phases but with alumina-rich aluminosilicates, the majority phase will be  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with a secondary phase formed by mixtures of sialons (principally  $\beta'$ -sialons and polytype sialons). This fact was observed with andalusite or mullite.

The analyses by DTA-DTG of 'kaolinite–Al–N<sub>2</sub>' allowed us to establish a sequence of reactions occurring during sample heating and when the reaction-sintering temperature is reached.

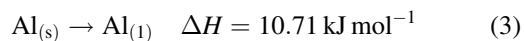
Results obtained in the 'kaolinite–Al–N<sub>2</sub>' system are represented in Figs. 2 and 3 and they are compared with those of pure kaolinite.

The first effect detected is an endothermic peak in DTA accompanied with mass loss, this peak is also detected in pure 'kaolinite' corresponding to the

reaction:



This endothermic peak appears at 548°C in samples with Al, whereas in the pure mineral it appears at 570°C. This shift is produced by the appearance of another neighbouring endothermic peak at 656°C without mass change. This one corresponds to the Al melting:



This peak shows an S-shaped effect in its upper limit and a distortion in its lower limit because of interaction with the previous peak.

While increasing temperature, the kaolinite–Al sample reveals an endothermic band with a maximum at 800°C that grows with the Al content. This is

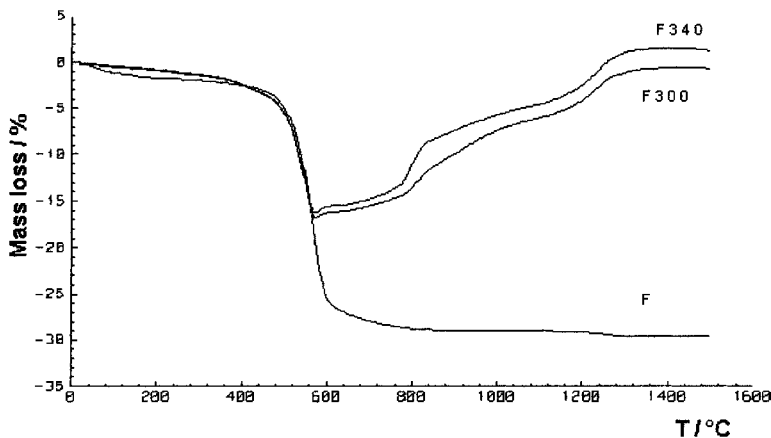
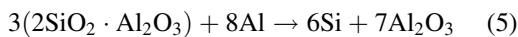
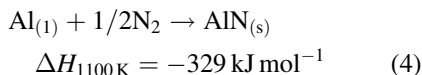


Fig. 3. TG of kaolinite (F) and kaolinite–Al mixtures (F<sub>300</sub>, F<sub>340</sub>).

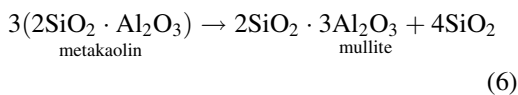
attributed to a combination of reactions and can be expressed through the following equations:



The reaction described in Eq. (4) is strongly exothermic. The reaction in Eq. (5) is exothermic but it is difficult to calculate  $\Delta H$  since there are no thermodynamic values of metakaolin.

The XRD analysis permits to confirm the formation of Si, AlN and transition alumina. The mass increase observed by TG produces a well-defined DTG peak at 1100 K, (827°C) described by the reaction in Eq. (4). The difference of weight seems to indicate that near 47 to 49% of the aluminium is consumed by this reaction. The remnant Al is not sufficient to reduce all the metakaolin formed in Eq. (2). This is confirmed by the presence of the exothermic peak of the metakaolin thermal transformation at 988°C [11]. This peak is also present in the pure kaolinite thermal treatment but of a larger size.

The reaction that occurs in kaolinite without Al is:

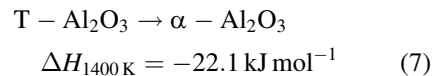


This reaction involves the appearance of mullite (a crystalline phase) from the metakaolin that is an amorphous phase. This reaction does not produce

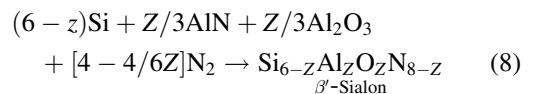
any change in weight. This fact can be verified by XRD.

The peaks, at 980° and 548°C proper, of kaolinite tend to decrease with increasing Al content.

At temperatures >1200°C, the transition alumina is transformed to the  $\alpha$  phase by the following reaction:



The final stage of the reaction is associated with a mass increase due to the nitriding process. This is caused by the nitriding of silicon that appears from the reaction in Eq. (5). The nitrogenous phase formed is  $\beta'$ -sialon:



This is an exothermic reaction although it was not easily detected by the equipment. The thermal effect can be seen in the F340 sample.

Figs. 4 and 5 summarize the results for andalusite–Al–N<sub>2</sub> reactions while Figs. 6 and 7 provide results for mullite–Al–N<sub>2</sub>.

Figs. 4–7 do not include the behaviour of pure aluminosilicates since they do not present thermal effects under heating. Mullite does not have DTA peaks or mass variations in the temperature range studied. The andalusite has a negligible weight loss caused by impurities (0.2%) and one peak of thermal

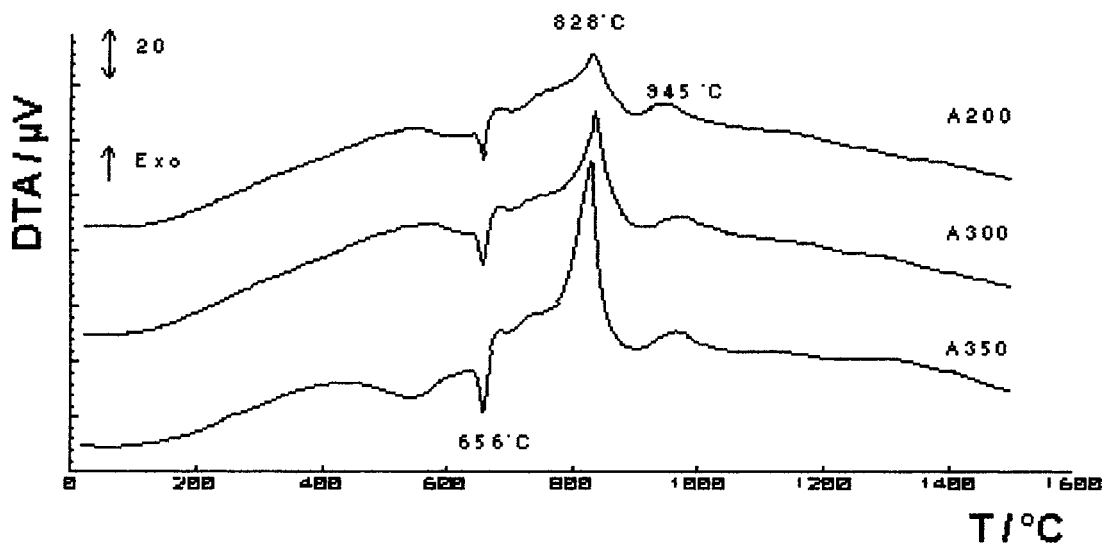


Fig. 4. DTA of andalusite–Al mixtures.

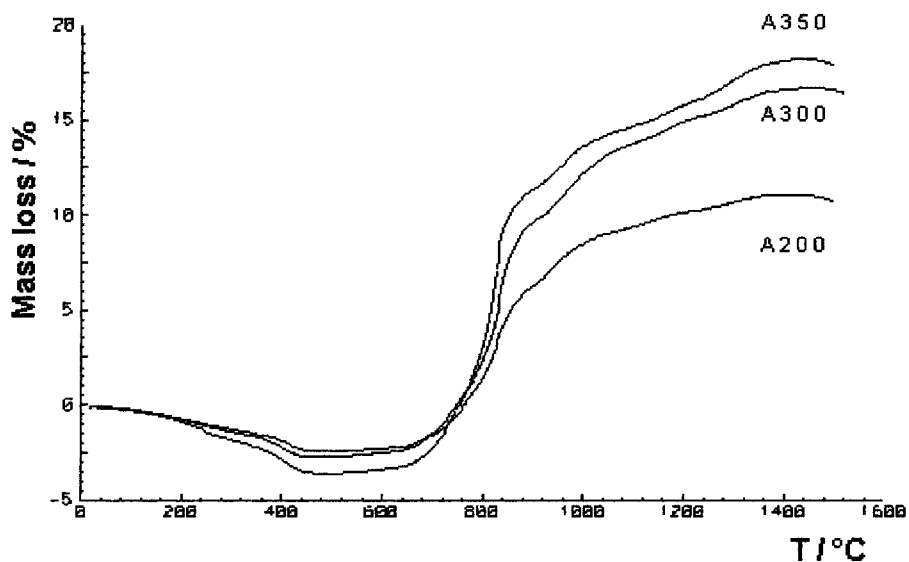
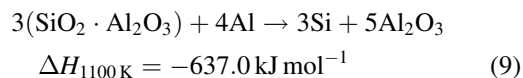


Fig. 5. TG of andalusite–Al mixtures.

decomposition at high temperatures which is not detected in our test conditions. Thus, all the peaks of these figures can be attributed to aluminothermy and nitriding reactions.

The andalusite samples present the peak of aluminium melting (656 °C) and an exothermic band around 828 °C, accompanied by a weight gain corresponding to AlN formation (reaction in Eq. (4)). The alumi-

nothermy of andalusite is also produced according to Eq. (9):



The aluminothermic reduction of SiO<sub>2</sub>-rich impurities of the mineral would have to be examined.

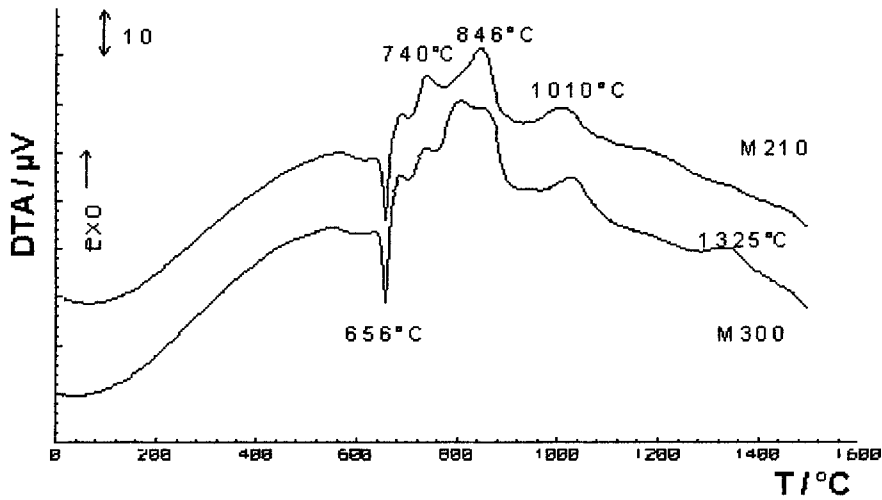


Fig. 6. DTA of mullite-Al mixtures.

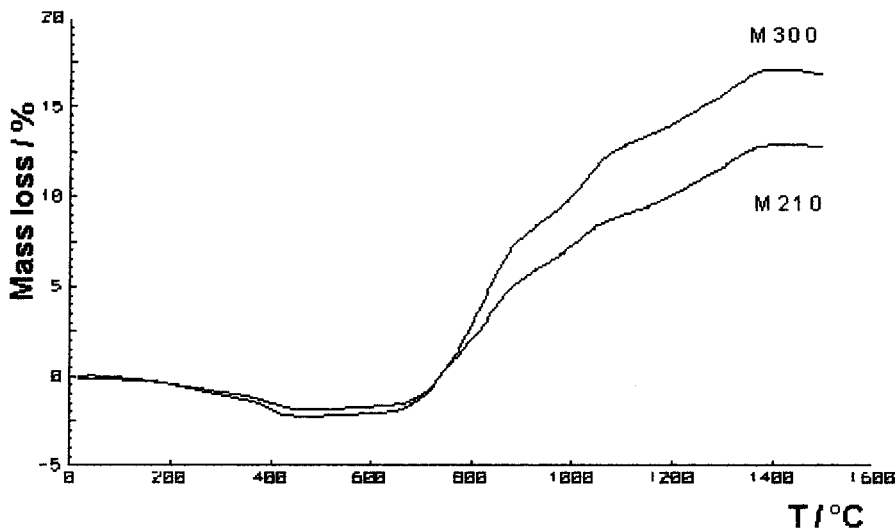
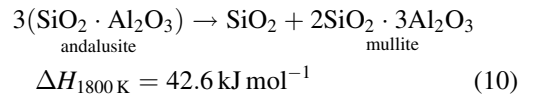


Fig. 7. TG of mullite-Al mixtures.

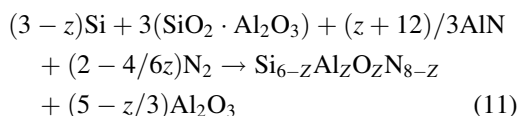
The small exothermic peak found around 945°C cannot be attributed to any specific reaction since crystalline phases detected before, and after, the reaction were similar. The TG record in this zone shows a small gain, but the most important fact is that at this temperature there is a change in the slope of the TG curve between the zone of aluminium nitriding and the zone of Si nitriding. At higher temperatures, the andalusite begins its thermal decomposition according to:



The mullite appears in the sample although the andalusite phase is found even at the maximum test temperature.

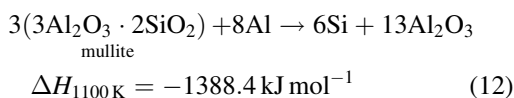
The incorporation of nitrogen (weight gain) at temperatures >950°C with sialon formation, principally the β'-sialon, may be explained in a global way

by the following reaction:



The alumina formed in reactions depicted in Eqs. (9) and (10) is the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase, without detection of transition alumina.

The mullite behaviour is very similar to that observed for andalusite showing aluminium melting and the exothermic band around 845°C is due to reactions in Eqs. (4) and (12).



The band at 1010°C is equivalent to the one at 945°C in the andalusite. The weight gain at temperatures >1010°C is produced by the reaction of Si, AlN, andalusite and  $\text{N}_2$  to form sialons (Eq. (11)).

The change in the form between the peaks at 656° and 840°C is probably produced by movements of the base line (thermal conductivity) because no mass or phase changes are detected.

It is important to note that all nitrogen is introduced during heating and that during the soaking time at constant temperature the phases present only react in such a way as to lead to equilibrium in accordance with the Si–Al–O–N diagram.

The products obtained at the end of the heating treatment for mullite–aluminium samples are:  $\beta'$ -sialon,  $\alpha$ - $\text{Al}_2\text{O}_3$  and mullite while in andalusite–Al samples we also found remnant andalusite. The persistence of the original phases (mullite–andalusite; although there is sufficient Al for their total reduction) is produced by the competition between reaction in Eq. (4) (AlN formation) and those in Eqs. (9) and (12) (Si formation).

TG diagrams show that in andalusite samples, close to 65% Al is consumed in the reaction of Eq. (4). The remnant aluminium is not sufficient to reduce the total

andalusite even in the A350 mixture and this was confirmed through the obtained final phases.

For the mullite–Al samples, >58% of the aluminium is transformed in AlN and the remnant is not sufficient to complete the mineral reduction.

#### 4. Conclusions

The reactions of aluminothermy of alumina-rich minerals in  $\text{N}_2$  atmosphere permit to obtain alumina–sialon mixtures. By means of thermal analysis, it is possible to observe different stages and sequences of reactions with temperature increases. The principal intermediate phases formed are AlN and Si, that react with the remnant aluminosilicate forming alumina and sialon phases. The three minerals studied present a similar behaviour and they are in agreement with the Si–Al–O–N phase diagram. Simultaneous TG-DTG-DTA is an adequate technique to study such reactions.

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#### References

- [1] K. Takatori, O. Kamigaito, J. Mater. Sci. Lett. 7 (1988) 1024.
- [2] C.C. Sorrell, J. Aust. Ceram. Soc. 19 (1983) 48.
- [3] K.H. Jack, J. Mater. Sci. 11 (1976) 1135–1158.
- [4] M.B. Trigg, J. Aust. Ceram. Soc. 21 (1985) 24.
- [5] S. Umabayashi, K. Kobayashi, Am. Ceram. Soc. Bull. 56 (1977) 578.
- [6] P. Albano, A.N. Scian, E. Pereira, Thermochim. Acta 202 (1992) 35.
- [7] S. Umabayashi, K. Kobayashi, J. Am. Ceram. Soc. 58 (1975) 464.
- [8] A.D. Mazzoni, Mater. Chem. Phys. 43 (1996) 38.
- [9] A.D. Mazzoni, E.F. Aglietti, Thermochim. Acta 298 (1997) 123–128.
- [10] JANAF, Thermochemical Tables, second edn., 1970; 1985.