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Preparation of sialon alumina powders with aluminium in nitrogen atmosphere

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Abstract

The stages and sequence of the reactions between silica-rich natural aluminosilicates and Al in N_2 presence were studied. In this case diatomite-Al-N_2 and bentonite-Al-N_2 reactions were studied up to 1650°C using TG–DTG–DTA and XRD techniques. Thermal effects associated with the nitridation reactions were determined. The final phases formed were sialon–alumina mixtures with silicon and aluminium nitride as important intermediaries. The phases formed were the same as those predicted by the Si-Al-O-N phase diagram. © 1997 Elsevier Science B.V.

Keywords: Diatomite; Bentonite; Aluminium; SiAlON; Preparation; TG–DTA

1. Introduction

Advanced ceramics in which alumina and sialons are included have important technological applications due to their good physicochemical properties [1–3].

Sialon–alumina composites present dielectric and mechanical properties superior to the pure alumina materials. They contain mainly the β'-sialon phase [3]. β'-sialons are the most widely known phases of the Si-Al-O-N system. These phases correspond to the formula $Si_{6-Z}Al_ZO_zN_{8-Z}$ with $0 < Z \leq 4.2$. Their hexagonal crystalline structure derives from β-Si_3N_4[1]. Other important crystalline phases in the Si-Al-O-N system are the polytype sialons which have properties similar to the sialons.

There are six polytype sialons near to 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 can be expressed by the formula $M_mX_m + 1$, where m values are 4, 5, 6, 7, 9 or 11. Polytype sialons have been used to replace aluminium nitride as they successfully overcome some of the hydrolysis problems encountered when aluminium nitride was used [4].

The principal method of achieving ceramics from the Si-Al-O-N system is the one performed through reaction and sintering of Si_3N_4, SiO_2, Al_2O_3 and AlN mixtures in adequate proportions [1,2]. The alumina–sialon composites may be achieved by reaction and sintering of Si_3N_4 with Al_2O_3 powders [3].

The formation of sialon–alumina mixtures (principally β'-sialon and/or polytypes) may be obtained by alternative methods such as the reaction of metallic aluminium with SiO_2 [5,6] or the heat treatment of volcanic ash [7] in N_2 atmosphere. In our previous

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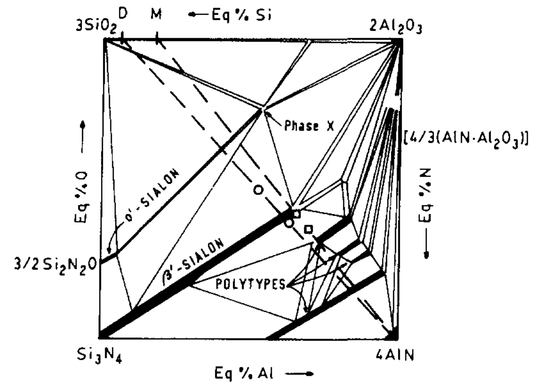

Fig. 1. Phase diagram of the system Si-Al-O-N at 1400°C.

work the 'clay-Al-N_2,' 'mullite-Al-N_2,' 'andalusite-Al-N_2' and 'bentonite-Al-N_2' systems were studied [8,9].

In this work, the stages and sequences of the reactions between silica-rich natural alumino-silicates and Al in the presence of N_2 are studied. In this case, 'diatomite-Al-N_2' and 'bentonite-Al-N_2' reactions were followed and analyzed up to 1650°C.

2. Experimental methods

The minerals used were diatomite from Catamarca, Argentina and bentonite Minard from Neuquen, Argentina. The chemical analyses of these minerals are shown in Table 1.

The aluminium used has 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 less than 5 ppm of O_2 and H_2O.

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

Differential thermal analyses and gravimetric analysis were carried out simultaneously in a Netzsch STA 409 equipment. Samples were placed in alumina crucibles and α-Al_2O_3 was used as a reference. The heating rate (β) was 5 K/min. The equipment was evacuated and then filled with N_2 to eliminate the oxygen present. This operation was repeated three times. The experiments were performed in N_2 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 show the evolution of the reaction products. Thermodynamical data were obtained using JANAF tables [10].

3. Results

Reactions between diatomite and bentonite with Al in the presence of N_2 with temperatures higher than 1200°C correspond to global reactions of the following type:

$$\underset{\text{bentonite}}{(7.105SiO_2.Al_2O_3)} + 2X\,Al + XN_2 \rightarrow [S_{7.105}Al_{(2+2X)}O_{17.21}N_{2X}] \rightarrow A\alpha\text{-}Al_2O_3 + B(Si_{6-Z}Al_ZO_ZN_{8-Z}) + C\text{ polytypes} \qquad (1)$$

$$\underset{\text{diatomite}}{(21.861\,SiO_2.Al_2O_3)} + 2X\,Al + XN_2 \rightarrow [Si_{21.861}Al_{(2+2X)}O_{46.722}N_{2X}] \rightarrow A\alpha\text{-}Al_2O_3 + B(Si_{6-Z}Al_ZO_ZN_{8-Z}) + C\text{polytypes} + DO'\text{-sialon} \qquad (2)$$

Table 1
Chemical composition of the minerals (in weight %)

Minerals	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	$Na_2 + K_2O$	LOI (1000°C)
Diatomite	82.3	6.4	0.37	1.7	0.7	0.6	3.54	2.82
Bentonite	59.64	14.27	0.52	4.37	1.33	1.7	3.52	14.23

Table 2
Mixtures mineral-Al studied

Mineral	Diatomite		Bentonite	
Sample	D 525	D 787	B 567	B 787
Al/mineral (wt/wt) ratio	0.525	0.787	0.567	0.787
Al % (wt)	34.42	44.04	36.18	44.04

where: A, B, C, D, Z, X: stoichiometric coefficients

[] means one point in the diagram of Si-Al-O-N phases (Fig. 1).

In reactions (1) and (2), reduced formulae expressed in SiO_2 and Al_2O_3 for diatomite and bentonite were considered. Thus, the diatomite is represented as 21.86 $SiO_2.Al_2O_3$ and the bentonite as 7.10 $SiO_2.Al_2O_3$. When sialon–alumina composites are obtained by means of this type of reaction, several important stages occur during heating. These stages are indicated by thermal effects and weight variations that permit them to follow simultaneously by TG–DTA. The intermediary phases formed were observed by XRD.

Figs. 2–4 show the thermal analysis results of (diatomite–Al) mixtures and Figs. 5–7 show the results corresponding to (bentonite–Al) mixtures.

The curves of the pure minerals do not present important thermal effects or weight changes above 200°C. The bentonite shows a peak at 600°C due to hydroxyl loss (–OH), so the other thermal effects correspond to mineral -Al-N_2 reactions.

The four (mineral–Al) mixtures show as a first thermal effect a sharp endothermic peak at approx. 655°C without weight change. This peak corresponds to aluminium melting:

$$Al_{(S)} \rightarrow Al_{(l)} \quad \Delta H = 10.71\,\mathrm{kJ\,mol^{-1}} \qquad (3)$$

This peak shows an S-shaped effect for the four (mineral–Al) mixtures produced probably by an important change in the thermal conductivity. This effect is less visible in those samples containing more aluminium since it is masked by the successive peaks.

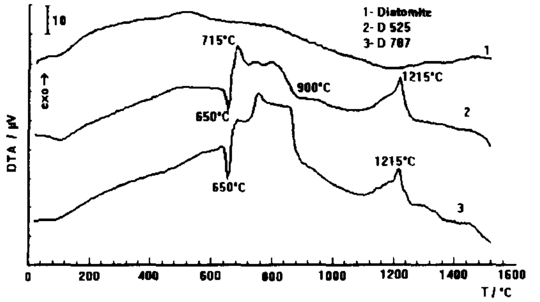

Fig. 2. DTA curve of diatomite and diatomite–Al mixtures (in N_2 atmosphere).

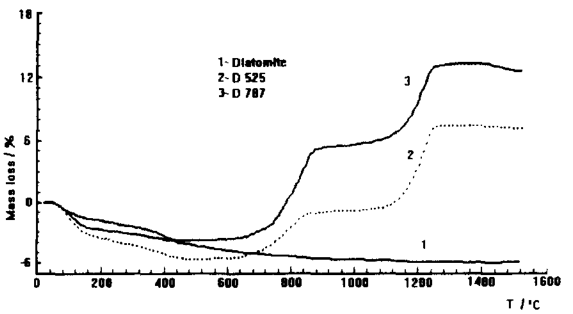

Fig. 3. TG curve of diatomite and diatomite–Al mixtures (in N_2 atmosphere).

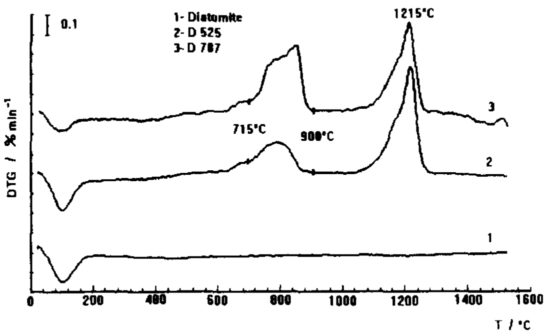

Fig. 4. DTG curve of diatomite and diatomite–Al mixtures (in N_2 atmosphere).

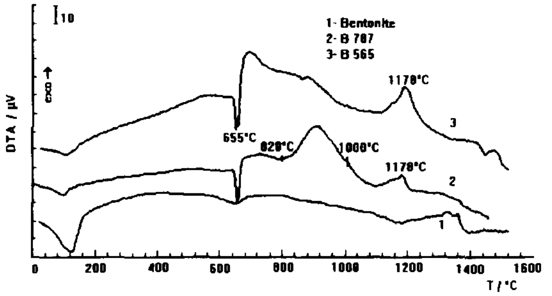

Fig. 5. DTA curve of bentonite and bentonite–Al mixtures (in N_2 atmosphere).

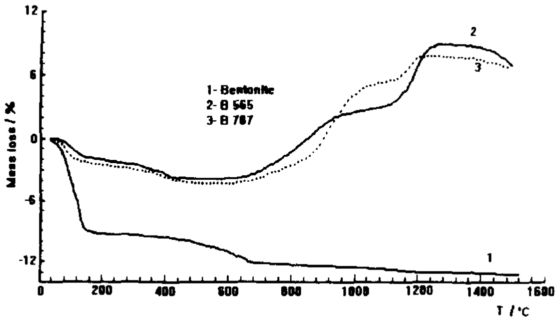

Fig. 6. TG curve of bentonite and bentonite–Al mixtures (in N_2 atmosphere).

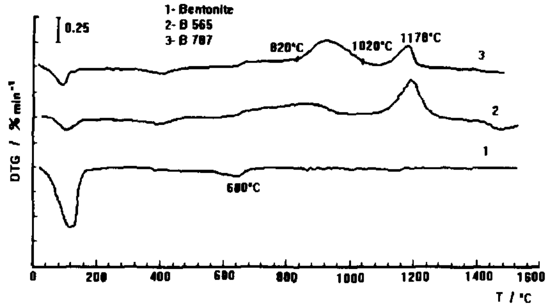

Fig. 7. DTG curve of bentonite and bentonite– Al mixtures (in N_2 atmosphere).

The (diatomite–Al) mixtures exhibit a broad exothermic band between 715 and 900°C (Fig. 2) that increases with the increment of Al content. This band is associated with the weight increase between 720 and 920°C as it is observed in TG–DTG curves (Fig. 4). The analysis by XRD of the phases present before and after this band shows the formation of important quantities of Si, AlN and transition alumina together with Al disappearance.

This band may be attributed to the following reactions:

$$\underset{\text{Diatomite}}{21.861\,SiO_2.Al_2O_3} + X\,Al \rightarrow \tfrac{3}{4}X\,Si$$
$$+\left(21.861-\tfrac{3}{4}X\right)SiO_2+\tfrac{1}{2}(X+2)Al_2O_3 \quad (4)$$

$$Al_{(l)}+\tfrac{1}{2}N_2 \rightarrow AlN_{(s)}$$
$$\Delta H_{1100\,K}=-329.3\,kJ\,mol^{-1} \quad (5)$$

Reactions (4) and (5) are exothermic while the weight gain is attributed only to reaction (5) by N_2 addition (nitriding reaction).

The (bentonite–Al) mixtures show an exothermic band between 820 and 1000°C, a higher temperature range compared with the diatomite–Al mixture, and associated with a mass increase (Figs. 5–7). The XRD analysis of the phases present before and after this thermal band shows that reactions (5) and (6) take place.

$$\underset{\text{bentonite}}{7.105\,SiO_2.Al_2O_3} + X\,Al \rightarrow \tfrac{3}{4}X\,Si$$
$$+\left(7.105-\tfrac{3}{4}X\right)SiO_2+\tfrac{1}{2}(X+2)Al_2O_3 \quad (6)$$

The Si appearance is easily explained thermodynamically by partial silica reduction of the minerals by the metallic Al with alumina formation (reaction (7)).

$$3SiO_2+4Al \rightarrow 3Si+2Al_2O_3 \quad (7)$$

This reaction has free energy: $\Delta G_{1100\,K}=-517\,kJ\,mol^{-1}$ and $\Delta H_{1100\,K}=-630\,kJ\,mol^{-1}$

Haussone et al. [11] have shown that AlN formation is associated with an exothermic band between 800 and 1000°C. This exothermic effect is strongly influenced in its temperature and heat by metallic impurities and by the presence of aluminium salts. In reactions (4) and (6) it is easy to understand the shifting of this band since both minerals have other ions as impurities (see chemical analysis) probably affecting this thermal effect.

Finally, the four mixtures studied present a third exothermic band. This band appears at approx. 1215°C for the (diatomite–Al) samples (Fig. 2) and at about 1178°C for the (bentonite–Al) samples. This third band is associated with a weight gain, with DTG peaks centered at 1215°C for the diatomite and at 1178°C for the bentonite. The XRD analysis of the samples before and after this thermal effect shows the disappearance of Si, AlN and transition alumina, while β'-sialon, α-Al_2O_3 and other sialons (polytypes) appear. Consequently, these bands are associated with reactions of the following type:

$$(6-Z)Si+Z/3\,AlN+Z/3\,Al_2O_3$$
$$+(4-4/6Z)N_2 \rightarrow \underset{\beta'\text{-Sialon}}{Si_{6-Z}Al_ZO_ZN_{8-Z}} \quad (8)$$

$$T\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$
$$\Delta H_{1400\,K}=-22.1\,kJ\,mol^{-1} \quad (9)$$

The appearance of the O′-sialon phase may be observed in the mixtures with the low aluminium content:

$$(2-\mathrm{X})\mathrm{SiO_2} + (6-3\mathrm{X})\mathrm{Si} + 2\mathrm{X}\,\mathrm{Al_2O_3} + (4-2\mathrm{X})\mathrm{N_2} \rightarrow \underset{O'\text{-Sialon}}{4[\mathrm{Si_{2-X}Al_XO_{1-X}N_{2-X}}]} \qquad (10)$$

Enthalpies of reactions (8) and (10) are exothermic and their values depend on Z and X (thermodynamic data not available). In most of the cases β'-sialon is accompanied by a polytype sialon whose formation occurs as in:

$$\mathrm{A\,Si} + \mathrm{B\,AlN} + \mathrm{C\,Al_2O_3} + \mathrm{D\,N_2} \rightarrow \text{Polytype sialons} \qquad (11)$$

Summing up, the third band is produced by a combination of reactions (8), (9) and (10) or (8), (9) and (11). This is consistent with the variation of crystalline phases, weight increase and the exothermic effect observed.

The Si formed increases with the SiO_2 content (chemical analysis) of the mineral studied as is expected. Considering other minerals, the Si formed increases according to the sequence: (mullite-Al-N_2), (andalusite-Al-N_2) [12], (clay-Al-N_2) [8], (bentonite-Al-N_2) and (diatomite-Al-N_2).

While increasing the Al content in the mixtures, the first weight gain (700 and 920°C) is greater than the second weight gain (1178 and 1215°C) confirming the sequence of reactions proposed.

When the highest reaction temperature is reached (between 1350 and 1650°C) the final phases are already formed: β'-sialon, α-Al_2O_3, O′-sialon or polytype sialons. During the time in which the temperature is maintained constant, the variation of the relative quantities of these phases tends towards the phases in equilibrium predicted by the phase diagram (Fig. 1). Fig. 8 shows the evolution of the phases for temperatures higher than 1200°C. At these temperatures (higher than 1200°C), the loss of SiO(g) occurs, not allowing the system to come to equilibrium. The reaction is of the type:

$$\mathrm{A[Si_{6-Z}Al_ZO_ZN_{8-Z}]} + \mathrm{B\,Al_2O_3} \rightarrow \mathrm{C\,SiO(g)} + \mathrm{A'[Si_{6-Z'}Al_{Z'}O_{Z'}N_{8-Z'}]} + \mathrm{E\,Polytype}. \qquad (12)$$

A, A′, B, C, D, E: stoichiometric coefficients with $Z < Z'$.

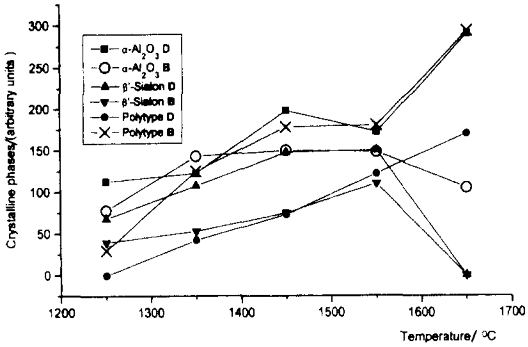

Fig. 8. Crystalline phase evolution for temperatures higher than 1200°C and reaction time of 180 min (D: Diatomite 787; B: Bentonite 787).

This phenomenon occurs provided that alumina and sialons are together under N_2 flow since in the range of temperatures used (lower than 2000°C) the equilibrium atmosphere contains N_2 and SiO(g) [12]. This phenomenon is independent of the preparation method.

4. Conclusions

Reactions occurring between an aluminosilicate-Al-N_2 at temperatures higher than 1200°C permit sialon–alumina mixtures be to obtained. The intermediate stages and the fast reactions occurring during heating may be followed by thermal analysis techniques. Si is an important intermediary in the sequence of these reactions when the mineral is SiO_2-rich. Simultaneous TG–DTG–DTA is an adequate technique to study these type of reactions. The phases formed are as predicted by the Si-Al-O-N phase diagram.

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