JOURNAL OF MATERIALS SCIENCE 24 (1989) 355-358

Scanning electron microscope observations of polymorphic transitions occurring on a $12CaO \cdot 7Al_2O_3$ surface under electron beam action

A. DERDACKA-GRZYMEK, Z. KONIK, J. IWANCIW, A. STOK
Interbranch Institute of Building and Refractory Materials, Academy of Mining and Metallurgy, Cracow, Poland

The compound $12CaO \cdot 7Al_2O_3$ has been widely studied for a long time. There are many controversies concerning its polymorphism and other properties in the literature. The variable conditions of synthesis, i.e. temperature, atmosphere, as well as the different cooling rate conditions allowed us to obtain an optically anisotropic polymorphic modification of the $12CaO \cdot 7Al_2O_3$ in vacuum. X-ray investigation of that anisotropic phase indicated that the "*d*"-values (in nm) of the diffraction maxima did not correspond to that of the isotropic cubic phase presented in the literature. The polymorphic transition temperature was determined and reported earlier. SEM observations shed new light on the $12CaO \cdot 7Al_2O_3$ polymorphism problem. A sample of CaO/Al_2O_3 of weight ratio 0.94, which has been synthesized and cooled in air, was examined under the scanning electron microscope. The sample was exposed to electron beam action for 20 min. In the dark spots formed during this operation, "bulges" appeared which then enlarged and cracked. On the surface a transverse crack was visible. This phenomenon could also be observed in other areas of the sample surface during exposure. This phenomenon is connected presumably with the polymorphic transition of the $12CaO \cdot 7Al_2O_3$ phase.

1. Introduction
The phenomenon of polymorphism has been widely applied in some technological processes. In addition to the polymorphic transition $\beta \rightarrow \gamma$ Ca_2SiO_4, the polymorphic transition of calcium aluminate $12CaO \cdot 7Al_2O_3$ is of particular importance in associated alumina and cement production by the Grzymek method [1]. In this technique, alumina is extracted from calcium aluminate $12CaO \cdot 7Al_2O_3$ (the component of self-disintegrating sinter) by the use of sodium carbonate solution. The $12CaO \cdot 7Al_2O_3$ phase decomposes in sodium carbonate solution at different rates, depending on the burning temperature of the sinter, kiln atmosphere and cooling rate. The variable conditions of synthesis are the reason for the non-homogeneity of the $12CaO \cdot 7Al_2O_3$ phase, resulting from the occurrence of two polymorphs; optically isotropic and anisotropic [2–4].

There still remain some discrepancies in the literature concerning the $12CaO \cdot 7Al_2O_3$ polymorphic transition and the character of its melting process. Explanation of the phenomenon relating to $12CaO \cdot 7Al_2O_3$ polymorphism allows improvement of the sintering and cooling of self-disintegrating sinter and therefore to an increase in the effectiveness of alumina production. The scanning electron microscopy, in addition to other measurements, is of significant importance in anisotropic $12CaO \cdot 7Al_2O_3$ synthesis, as well as in the transition temperature from anisotropic to isotropic $12CaO \cdot 7Al_2O_3$ phase determination.

2. Synthesis of regular, optically isotropic $12CaO \cdot 7Al_2O_3$ phase
The raw mixture of CaO and Al_2O_3 of weight ratio 0.94, was synthesized at 1673 K in an oxidizing atmosphere and cooled in air. The sample was studied by X-rays and observed by optical and scanning electron microscopy. The XRD analysis proved the occurrence of regular, isotropic $12CaO \cdot 7Al_2O_3$ phase, also denoted α phase. The microscopic observations of a polished section revealed that this sample was not homogeneous and consisted of isotropic and anisotropic phases. The isotropic phase formed colourless crystals of irregular shape. Some were isometric, characteristic of $12CaO \cdot 7Al_2O_3$ regular phase. The anisotropic phase formed mainly crystals of skeletal structure, of irregular or prismatic shape.

2.1. SEM observations of α-$12CaO \cdot 7Al_2O_3$ phase synthesized in an oxidizing atmosphere
The aluminate sample was exposed for 20 min point action of an electron beam. In the dark spots after this exposure, the formation of "bulges", their growth and

0022-2461/89 $03.00 + .12 © 1989 Chapman and Hall Ltd.

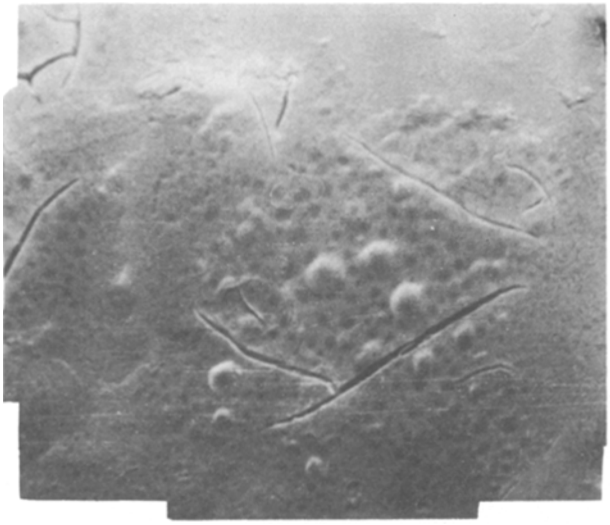

Figure 1 SEM of the surface of $12CaO \cdot 7Al_2O_3$ synthesized at 1673 K in an air atmosphere before electron beam action, × 6000.

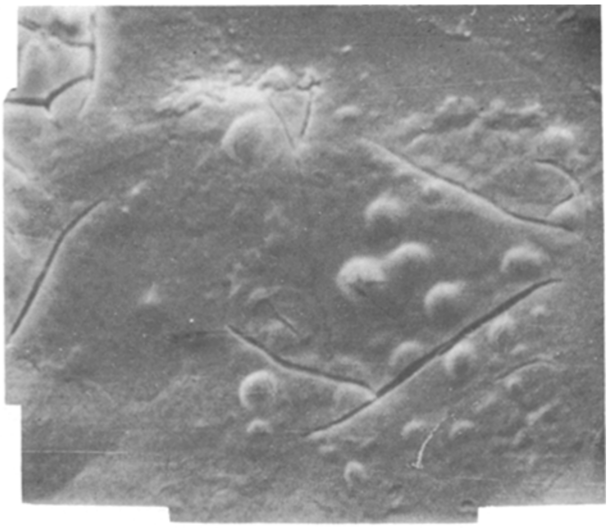

Figure 4 SEM of the surface of $12CaO \cdot 7Al_2O_3$ synthesized at 1673 K in an air atmosphere after 20 min exposure, showing a transverse crack, × 6000.

Figure 2 SEM of the surface of $12CaO \cdot 7Al_2O_3$ synthesized at 1673 K in an air atmosphere during electron beam action, × 2700.

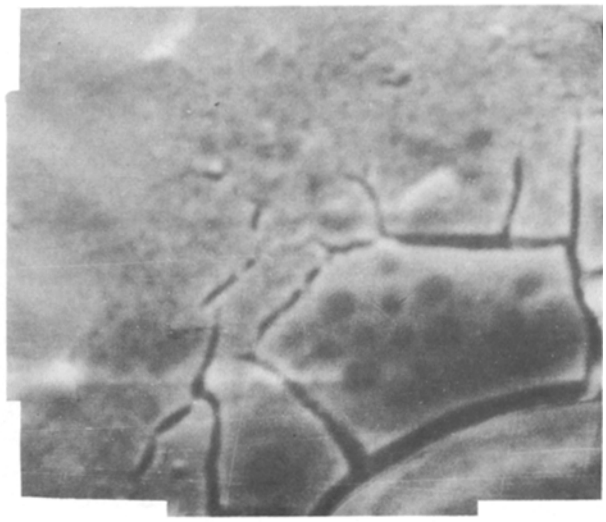

Figure 5 A higher magnification new of an area of Fig. 4, × 19000.

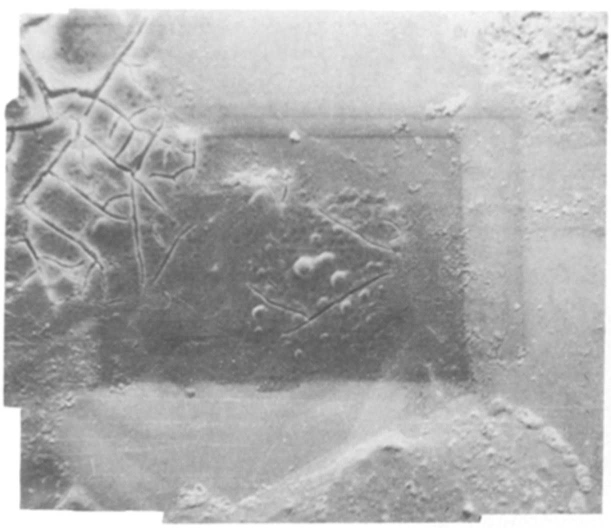

Figure 3 SEM of the surface of $12CaO \cdot 7Al_2O_3$ synthesized at 1673 K in an air atmosphere after 20 min exposure. The growth and crack of the new "bulge" is visible, × 6000.

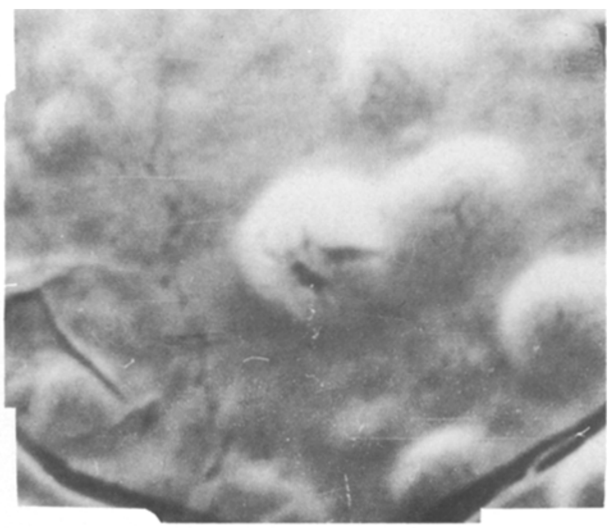

Figure 6 SEM of $12CaO \cdot 7Al_2O_3$ synthesized at 1673 K in an air atmosphere showing another spot on the surface before electron beam action, × 13 000.

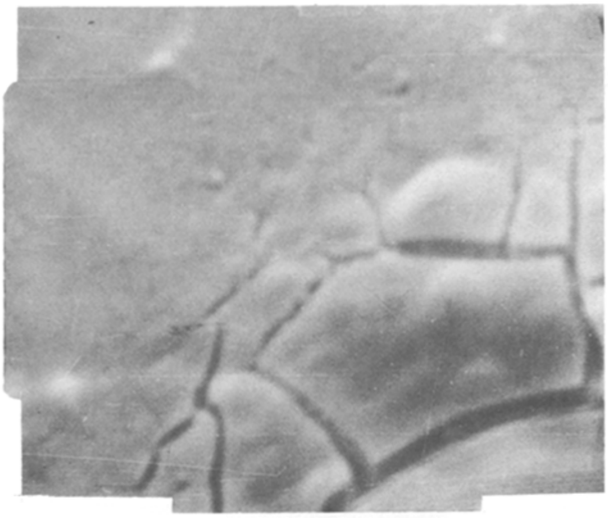

Figure 7 SEM of $12CaO \cdot 7Al_2O_3$ synthesized at 1673 K in an air atmosphere showing another spot on the surface after 15 min exposure. The growth of the new "bulge" is visible, × 13 000.

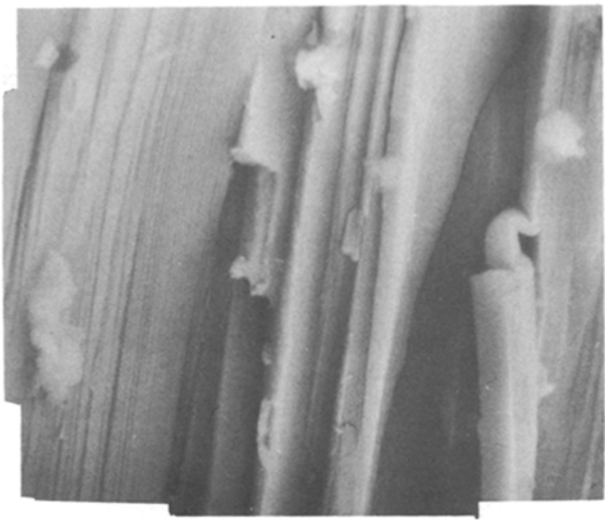

Figure 9 SEM of $12CaO \cdot 7Al_2O_3$ synthesized in vacuum showing the anisotropic phase crystals of prismatic habit, × 3000.

cracking were observed. A transverse crack on the sample surface could be also noticed (Figs 1 to 5). The same phenomena have been observed after action of the electron beam on another spot (Figs 6 to 8). We suppose that they are connected with polymorphic transition in the $12CaO \cdot 7Al_2O_3$ phase.

3. Synthesis of optically anisotropic $12CaO \cdot 7Al_2O_3$ phase

Taking into account the SEM results obtained for isotropic $12CaO \cdot 7Al_2O_3$ phase, the synthesis of $12CaO \cdot 7Al_2O_3$ under vacuum was carried out from a mixture of CaO and Al_2O_3 weight ratio 0.94. This mixture was heated at 1823 K in a chamber of a "Setaram" thermoanalyser at the rate of $10\,K\,min^{-1}$ (vacuum of 3×10^{-2} to 2×10^{-4} torr).

The sample was stored at 1823 K for 30 min and subsequently cooled to 293 K at the rate of $8\,K\,min^{-1}$. The product thus obtained was studied by X-rays and observed using optical and scanning electron microscopy. From the XRD pattern it results that this product is not the isotropic $12CaO \cdot 7Al_2O_3$ regular phase or a mixture of other known calcium aluminates (this phase is denoted γ-$12CaO \cdot 7Al_2O_3$). Microscopic observations of a polished section revealed the structure to be built up of plate-like and prismatic coarse crystals which were optically anisotropic.

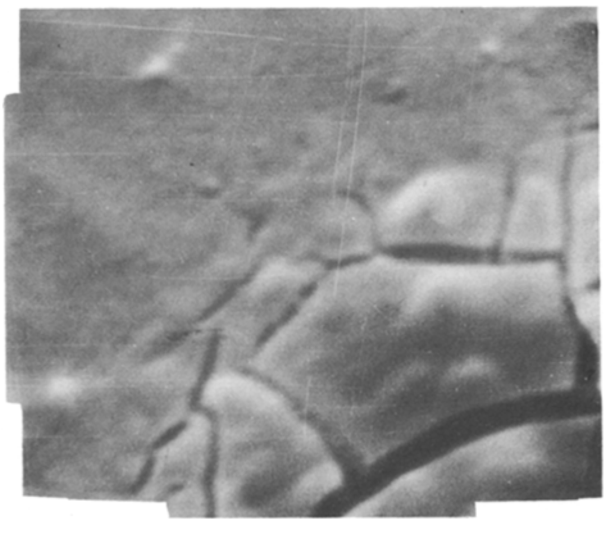

Figure 8 SEM of $12CaO \cdot 7Al_2O_3$ synthesized at 1673 K in an air atmosphere showing another spot on the surface after 20 min exposure. the growth of a new "bulge" is visible, × 13 000.

3.1. SEM observations of γ-$12CaO \cdot 7Al_2O_3$ phase synthesized in vacuum

SEM observations confirmed the plate-like and prismatic structure of this $12CaO \cdot 7Al_2O_3$ phase and showed the differences in the morphology of α- and γ-$12CaO \cdot 7Al_2O_3$ surfaces (Fig. 9).

4. $\gamma \rightarrow \alpha$ $12CaO \cdot 7Al_2O_3$ polymorphic transition temperature

Two $12CaO \cdot 7Al_2O_3$ polymorphs can be produced from the raw mixture of CaO and Al_2O_3, weight ratio 0.94, depending on the conditions of synthesis. Optically anisotropic γ-$12CaO \cdot 7Al_2O_3$ was heated at 1473 K in air. The product was studied by XRD and microscopy. The XRD pattern corresponded to regular, optically isotropic α-$12CaO \cdot 7Al_2O_3$. Microscopic observations confirmed that this phase was identical to α-$12CaO \cdot 7Al_2O_3$. It should be stated that the α and γ phases are the polymorphs of $12CaO \cdot 7Al_2O_3$ and the polymorphic transition $\gamma \rightarrow \alpha$ takes place at 1473 K.

5. Conclusions

1 .Scanning electron microscopic examination of α-$12CaO \cdot 7Al_2O_3$ phase allowed observation of the changes occurring on the surface under the electron beam action. These changes are presumably due to the polymorphic transition of $12CaO \cdot 7Al_2O_3$.

2. Further experiments allowed the production in vacuum, from the raw mixture of $CaO/Al_2O_3 = 0.94$, the optically anisotropic γ-$12CaO \cdot 7Al_2O_3$ phase differing from the α-$12CaO \cdot 7Al_2O_3$ regular isotropic phase and the XRD pattern and microstructure.

3. α and γ phases are the polymorphs of the compound $12CaO \cdot 7Al_2O_3$. The transition temperature of the γ phase to α is 1473 K in air.

References

1. J. GRZYMEK, A. DERDACKA-GRZYMEK, Z. KONIK, A. STOK and M. GAWLICKI,The complex production of aluminium oxide and iron from laterite raw materials applying the calcium aluminate polymorphism, in "Light Metals", edited by H. O. Bohner (AIME, 1985) pp. 87–99.
2. J. GRZYMEK, A. DERDACKA-GRZYMEK, Z. KONIK, A. STOK and M. PYZALSKI, *Baustoffindustrie* **3** (1985) 72.
3. J. GRZYMEK, A. DERDACKA-GRZYMEK, Z. KONIK, A. STOK, M. PYZALSKI and J. IWANCIW, "Some physicochemical properties of $12CaO \cdot 7Al_2O_3$ phase in relation to Al_2O_3 production from self-disintegrating sinters", in "Light Metals" (AIME, 1987) pp. 91–7.
4. J. GRZYMEK, A. DERDACKA-GRZYMEK, Z. KONIK, M. PYZALSKI, J. IWANCIW and A. STOK, "The effect of synsthesis and cooling conditions on phase properties of the $12CaO \cdot 7Al_2O_3$", 8th International Congress on the Chemistry of Cément, Rio de Janeiro, Communications Theme 3, Vol. IV (Financiadora de Estudos e Frojetos, 1986) pp. 401–6.

Received 15 January
and accepted 10 June 1988