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Note

THE CRYSTALLIZATION KINETICS OF $12CaO \cdot 7Al_2O_3$ GLASS

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ABSTRACT

Various experimental techniques, viz. thermal analysis, IR spectroscopy and X-ray diffraction have been used to analyse the crystallization kinetics of $12CaO \cdot 7Al_2O_3$ glass ($C_{12}A_7$). The IR spectra and diffraction results confirm the presence of this compound in the final glass with initial molar composition of 7.04% SiO_2, 30.29% Al_2O_3 and 62.67% CaO. Use of the Flynn and Wall method has shown that the crystallization process follows two different mechanisms: three-dimensional growth for a low heating rate (up to 5 K min^{-1}), and two-dimensional growth for a higher heating rate. The crystallization process is also accompanied by an increase in weight.

INTRODUCTION

The use of thermal analysis techniques facilitates the investigation of different crystallization mechanisms. Many papers have described the use of DTA [1], but only a few processes allow the use of TG methods as well, since crystallization is a physical process which usually occurs without any variation in weight. Other works [2] have described the glass compound $12CaO \cdot 7Al_2O_3$ ($C_{12}A_7$) as being at equilibrium with the humidity of the oven at 950–1350 °C. These data deal with the obtaining of an unique compound in an isothermal regime, whereas we are concerned with a ternary mixture in a dynamic regime of temperature, where only a small part of the final compound crystallizes in a $C_{12}A_7$ lattice.

EXPERIMENTAL

The work was carried out on a glass of the system $CaO–Al_2O_3–SiO_2$ of molar composition 7.04% CaO, 30.29% Al_2O_3 and 62.67% SiO_2. The glass had been milled to a particle size of less than 56 μm. The equipment used was: a derivatograph Q 1500 D, MOM Budapest (Paulik, Paulik and Erdey type) with a static air atmosphere in the temperature range 20–1500 °C, with TG sensitivity of 20 mg, using Al_2O_3 as reference material, alumina crucibles, and heating rates of 2.5, 3.75, 5, 7.5 and 15 K min^{-1}; an IR Spectrometer Specord M 80 (Jena type) of wavelength range 4000–200 cm^{-1}; a diffractometer (HZG-3 type) with Cu $K\alpha$ radiation, at a tension of 30 kV and an intensity of 30 mA, with 2θ within the range 1.5–30°.

RESULTS AND DISCUSSION

The thermal analysis carried out on the glass indicates a crystallization process accompanied by an increase in weight. The diagrams for different heating rates are given in Fig. 1. In all cases, a constant percentage of about 0.2% weight increase was observed.

The X-ray diffractogram of the product after the exothermal effect occurred indicates the presence of $C_{12}A_7$ (see Table 1).

Figure 2 shows the IR spectra of the same product. The peaks of $C_{12}A_7$ can be seen, as given in the literature [3], but there also occurs the peak of an

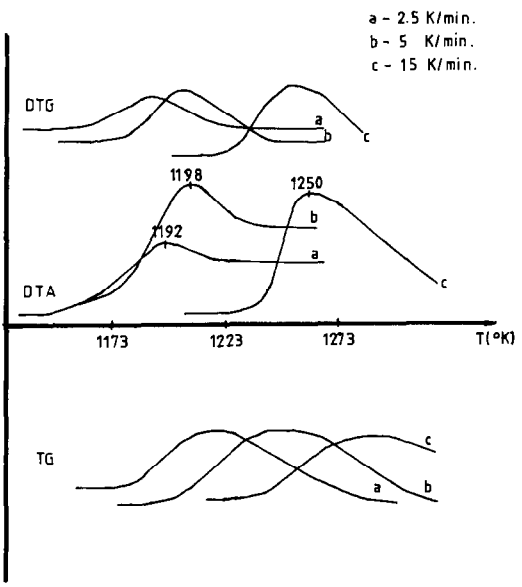

Fig. 1. TG, DTG and DTA curves for the glass at different heating rates.

TABLE 1

Observed interplanar distances and relative intensities for $C_{12}A_7$ glass as compared with ASTM data

ASTM data	Our results	
d_{hkl}	d_{hkl}	I/I_A
4.890	4.875	95
2.998	2.988	45
2.680	2.680	100
2.447	2.434	50
2.189	2.187	40
1.945	1.938	30
1.662	1.662	30
1.601	1.599	30

OH group at 3600 cm^{-1}. Accordingly, the following reaction probably took place during the crystallization process [3]

$$\underset{\text{amorphous}}{12CaO \cdot 7Al_2O_3} + H_2O \rightarrow \underset{\text{crystal}}{Ca_{12}Al_{14}O_{32}(OH)_2} \quad (1)$$

The kinetics of this reaction were investigated by means of the Flynn and Wall method at constant heating rate [4], using data from the thermogravimetric curves. Various kinetic functions were tried [5] and the best correlation coefficients were obtained for three-dimensional growth at heating rates lower than or equal to 5 K min^{-1}, and for two-dimensional growth at higher heating rates. The results are given in Table 2. It should be noted that the values of the activation energy at 5, 7.5 and 15 K min^{-1} are closely similar, regardless of the change of mechanism.

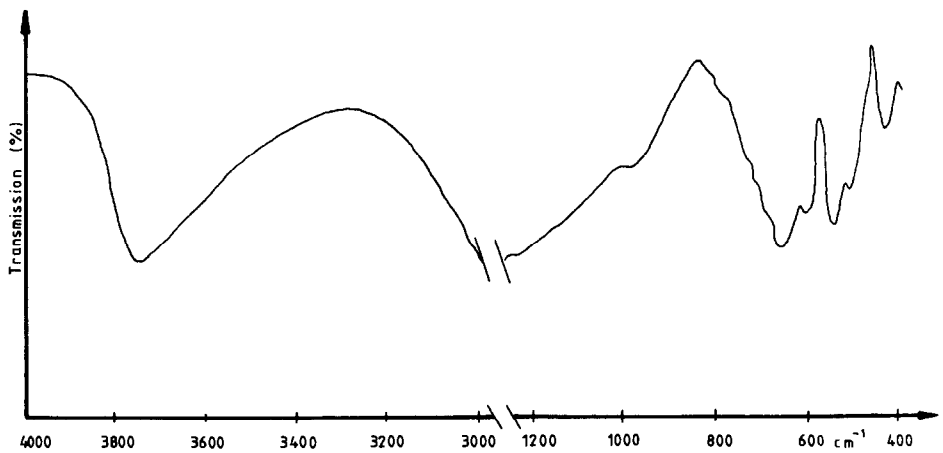

Fig. 2. IR spectrum of the glass.

TABLE 2

Kinetic parameters of the crystallization process

Heating rate (K min^{-1})	Kinetic function $g(\alpha)$	Activation energy (kcal mol^{-1})	Correlation coefficient
2.5	$[-\ln(1-\alpha)]^{1/3}$	93	0.9977
3.75		91	0.9961
5		82	0.9941
7.5	$[-\ln(1-\alpha)]^{1/2}$	88	0.9943
15		86	0.9919

TABLE 3

Degree of crystallinity of the final compound at different heating rates

Heating rate (K min^{-1})	Degree of crystallinity (%)
2.5	15.4
3.75	15.4
5	18.5
7.5	17.7
15	15.4

Since reaction (1) will lead to a total gain in weight of 1.3% and we have recorded only 0.2%, it appears that the degree of crystallinity of the final compound should be of about 15%. More precise results are given in Table 3.

CONCLUSIONS

The crystallization process of a glass of molar composition 7.04% CaO, 30.29% Al_2O_3 and 62.67% SiO_2 was investigated. The final product was analysed by X-ray diffractometry and IR spectroscopy, and the results indicate the presence of $C_{12}A_7$ and OH groups. The TG curve shows an increase in weight during the crystallization process, so we assume the occurrence of a reaction between amorphous $12CaO \cdot 7Al_2O_3$ and water.

The kinetic parameters of the reaction were evaluated by means of the Flynn and Wall method. The results indicate a change of mechanism from three-dimensional to two-dimensional growth with increasing heating rate.

The degree of crystallinity of the final product was also computed, by comparing the observed with the theoretical weight change, and was found to be of about 15%, with a maximum of 18.5% for the heating rate of 5 K min^{-1}.

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