Review: The Crystallization of Cordierite Glass

Part 2 The study of devitrification behaviour by differential thermal analysis and infra-red spectrophotometry

A. G. GREGORY, T. J. VEASEY
Department of Minerals Engineering, University of Birmingham, UK

The analytical methods of differential thermal analysis and infra-red spectrophotometry and their applications to the study of glass crystallization are reviewed. The development of these methods for an investigation of the devitrification of a cordierite-type glass is described and the results of preliminary experiments are discussed.

1. Introduction
The crystallization of cordierite-type glasses has been studied in detail by several different analytical methods and the results of these studies were reviewed in Part 1 of this work [1]. In the present study [2] both differential thermal analysis and infra-red spectrophotometry were employed as the main analytical methods and complementary data were obtained from X-ray diffraction and optical microscope methods. This paper will describe and discuss the methods that were adopted and a later publication will deal with the results of an investigation of the crystallization of a cordierite-type glass in detail.

2. Differential thermal analysis
The technique of DTA has been extensively employed as a standard analytical method in chemical, mineralogical and ceramic applications and the literature dealing with the basic principles is extensive. Amongst the most useful works are those of Mackenzie [3], Smothers and Chiang [4], Mackenzie and Mitchell [5], Wendlandt [6], Garn [7], and Mackenzie [8]. Most of these authors first dealt with the theory of DTA and then discussed the practical requirements which are necessary for the production of accurate and reproducible data. The early theories of DTA [9-17] were well documented and described in detail and the problems involved in the development of quantitative methods have also received considerable attention [11, 18-24]. Although the literature is extensive and the method of quantitative DTA has been widely used it must be stressed that extreme care must be taken to ensure rigid standardization of the experimental procedure before any kind of quantitative assessment is attempted. In addition, the nature of the reaction being studied must be carefully considered.

Several DTA methods have been developed to study reaction kinetics and have been reviewed elsewhere [25-28]. One of the most useful papers on the measurement of reaction kinetics was published by Kissinger [29]. From the basic assumption that the temperature of maximum deflection in DTA is also the temperature at which the reaction rate is at a maximum, for decompositions of the type (solid $\rightarrow$ solid + gas), Kissinger concluded by detailed theoretical analysis that the activation energy for simple decomposition reactions could be evaluated from DTA at different heating rates. He defined a shape index by which the order of the reaction could be estimated and found that the dominant factor which determined the shape and position of the peak was the nature of the reaction itself. More recent work has used the same basic equation [30] and the technique of analogue computing to study DTA reaction kinetics in terms of a mathematical model. Garn [31] investigated the suitability of certain test materials for the calibration of DTA apparatus and found that it is quite improbable that any single expression will provide an accurate representation of solid$_1$ $\rightleftarrows$ solid$_2$ phase transformations. All of these publications are useful background for prospective users of DTA but there have been several works more directly concerned with the applications of the method in
2.1. Applications of DTA in glass technology

Robredo [32, 33] published a comprehensive review of the application of DTA to glass research and technology which contained numerous references. The subject matter was divided into sections dealing with the applications in the study of (a) reactions between the components of the glass batch, (b) structure and thermal treatments and (c) phase changes—including phase separation, crystallization and polymorphism. The latter part was of particular interest and was divided under headings related to the compositions of the glass-forming systems that have been studied by the method. The work of Krasilnikova et al [34, 35] on the determination of the proportion of glassy to crystalline products in the Na~O-SiO2 system was described. The systems Li2O-SiO2 and Li2O-Al2O3-SiO2 have been extensively studied by DTA and several works were referenced [36-42], and the results of Kalinina et al [39] and Kalinina and Filipovich [43] were presented as examples. Thakur and Thiagarajan [44] studied crystallization of CaO-Al2O3-SiO2 glasses with additions of TiO2 and Na2O to determine the influence of these additives on crystallization temperature and Pavlushkin et al [45] used DTA to study the influence of MgO and FeO on the crystallization of similar glasses. More important for the purposes of the present work was the section on the studies of crystallization of MgO-Al2O3-SiO2 glasses. The work of Toropov and Sirazhiddinov [46] was described and some of their thermal analysis curves were presented. Robredo also cited several other studies of the cordierite system [47-50] which had employed DTA. The DTA method for this type of study has been widely used in the Soviet Union and other work dealing with the system included the papers of Kitaigorodskii and Khodakovskaya [51], Kitaigorodskii and Usvitksii [52], Pavlushkin and Ellern [53] and Blinov [54]. There are numerous references in the Soviet literature to other uses for DTA in glass technology research, particularly in the determination of crystallization behaviour, and the review by Robredo gave an excellent summary of such applications. It is worth noting that Karkhanavala and Hummel [55] and Tyrrell, Gibbs and Shell [56] used DTA in their important investigations of cordierite polymorphism which were described earlier [1].

Thus it can be seen that DTA has been widely used in glass technology for many years and has become particularly important in the study of crystallization processes. The possibilities of the technique can be increased even more with improvement in instrumentation and more rigorous standardization; for example, a recent publication [57] has described a micro-DTA/hot-stage microscope apparatus which has been successfully used for studies of the crystallization of Li2O-Al2O3-SiO2-TiO2 glasses. In the present study DTA was used to determine the crystallization behaviour of the base glass and to evaluate nucleation catalyst efficiency and a full discussion of the method is presented later.

3. Infra-red spectrophotometry

The predominant use of the infra-red spectrophotometer for many years has been for the structural analysis of organic materials. With advanced instrumentation and the introduction of new techniques over the past decade the importance of infra-red analysis of inorganic materials such as rocks, minerals, ceramics and glasses has become apparent. The character of each spectrum is determined by the vibrational modes of the atomic or molecular structure and is a complex function of the interatomic distances, bond angles, bond forces and relative masses of the constituent atoms. Consequently the infra-red analytical technique is very sensitive to short-range ordering and can provide useful complementary information to X-ray analysis. The advantages for the study of glasses are obvious and it is found that glass will give as strong a spectrum as crystalline material and that many more specific absorptions appear as secondary peaks when the structure becomes more ordered during the devitrification process.

A useful introduction to the technique was published by Lyon [58] and the theoretical aspects were discussed by Harrick [59] and an earlier publication by Lyon [60] contained an impressive number of specimen spectra of natural materials. Most of these results were obtained using the absorption method which depends upon dispersing and mounting of a powdered specimen, at a very low level of concentration, in a transparent potassium bromide disc. The disc can be prepared by pressing in a heated vacuum die at pressures up to 65 tons per square inch, thus producing an homogeneous, transparent mounting medium.

The method has been described in detail by