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HIGH-TEMPERATURE THERMAL ANALYSIS STUDY OF THE REACTION BETWEEN MAGNESIUM OXIDE AND SILICA

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The reaction between SiO_2 and MgO at temperatures up to 1500°C was studied using thermal analysis, with X-ray diffraction being used to identify reaction products. The reaction is slow and results in the formation of Mg_2SiO_4 and $MgSiO_3$, with minor amounts of $SiO_2 \cdot nH_2O$ and residual amounts of unreacted SiO_2 and MgO. Complete reaction of the starting materials to form Mg_2SiO_4 can only be achieved by maintaining the mixture at 1500°C for extended periods of time (> 1 h).

Keywords: high-temperature DTA, magnesium oxide, silica, thermal analysis, XRD

Introduction

Forsterite (Mg_2SiO_4) is a widely used refractory material with a fusion point of about 1900°C. It may be produced by the thermal decomposition of crysotile asbestos, $Mg_3(Si_2O_5)(OH)_4$ [1]. In the $MgO\text{-}SiO_2$ binary system [2], two stable compounds, namely forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$), exist. Forsterite, formed by this route, however, always seems to be accompanied by enstatite, which has a fusion point of about 1550°C and consequently limits the practical applicability of the forsterite product. The present investigation examines the reaction of SiO_2 with MgO in an attempt to gain more understanding of the reaction route and to identify a practical thermal treatment that would lead to the formation of forsterite alone.

Experimental

The starting materials were reagent-grade MgO and high-purity spectroscopic-grade SiO_2 powders. A DuPont 9900TA system with HTDTA and 951TGA

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modules was used. In the experiments, 20–40 mg samples were heated at 20 deg/min in platinum crucibles to the desired temperature in helium flowing at 50 ml/min. Reaction products were identified by X-ray diffraction.

Results and discussion

Figure 1 shows the DTA curve of the silica starting material, with the characteristic reversible α–β quartz polymorphic transformation appearing at about 573°C. Figure 2 shows the DTA curve of MgO; an endothermic peak at 328°C corresponds to dehydration of $Mg(OH)_2$. As this was a significant peak, thermogravimetry (TG) was carried out to determine the amount of hydroxide present. The TG curve (Fig. 3) indicates a total weight loss at 400°C of about 10%, corresponding to about 30% $Mg(OH)_2$ in the sample. The dehydroxylation of magnesium hydroxide takes place according to the following scheme:

$$Mg(OH)_2 = MgO + H_2O \tag{1}$$

Solid mixtures of the two reagent-grade materials were prepared and subjected to different heating schemes in the HTDTA module. Figure 4 shows a reproducible DTA curve for a mixture of MgO (corrected for contained hydroxide) and SiO_2 with a molar ratio of 1.8:1, heated to 1500°C. This MgO/SiO_2 ratio is lower than that required for the formation of Mg_2SiO_4. In addition to the endothermic peaks due to dehydration of magnesium hydroxide and the polymorphic transformation of quartz, a reproducible endothermic baseline drift is detected, starting around 1250°C. XRD analysis of the product (Fig. 5a) indicated the presence of MgO, SiO_2, Mg_2SiO_4, $SiO_2{\cdot}nH_2O$ and $MgSiO_3$. These results indicate that the reaction of MgO with SiO_2 is not complete even after

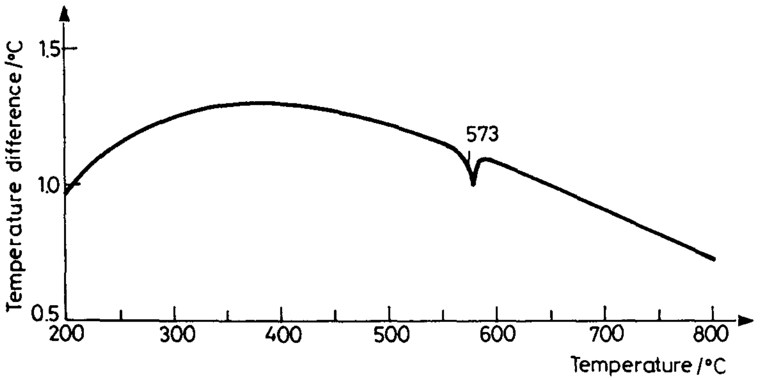

Fig. 1 DTA curve for the SiO_2 starting material

heating the mixture to 1500°C, and that there may be another reaction taking place above 1250°C as indicated by the endothermic drift of the baseline above this temperature.

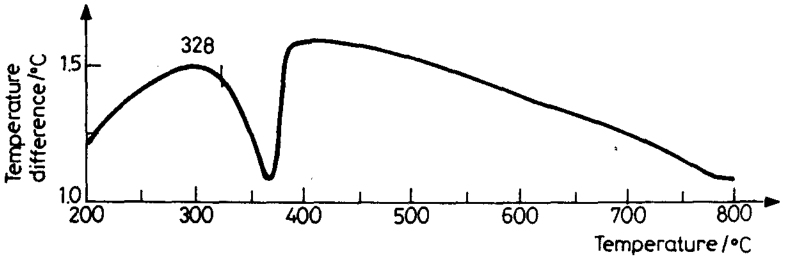

Fig. 2 DTA curve for the MgO starting material

This experiment was repeated using MgO/SiO_2 mixture with molar ratio of 2.7:1 (more MgO than stoichiometrically required for the formation of Mg_2SiO_4). A similar DTA curve was obtained and XRD analysis of the product indicated the presence of the same constituents detected in the previous experiment, but with perhaps somewhat less SiO_2 (Fig. 5b).

A similar experiment was carried out using a stoichiometric mixture of MgO/SiO_2 (2:1). This time, after heating to 1500°C, the sample was maintained isothermally for an hour. A DTA curve similar to that in Fig. 4, except for an isothermal portion, was obtained. XRD analysis of the product indicated the presence of Mg_2SiO_4, MgO, $MgSiO_3$ and minor amounts of $SiO_2 \cdot nH_2O$. Significantly, no SiO_2 was detected (Fig. 5c).

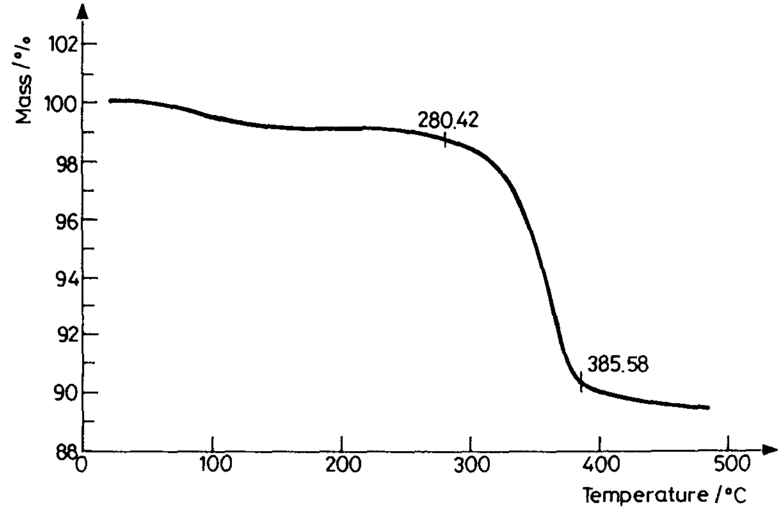

Fig. 3 TG curve for the MgO starting material

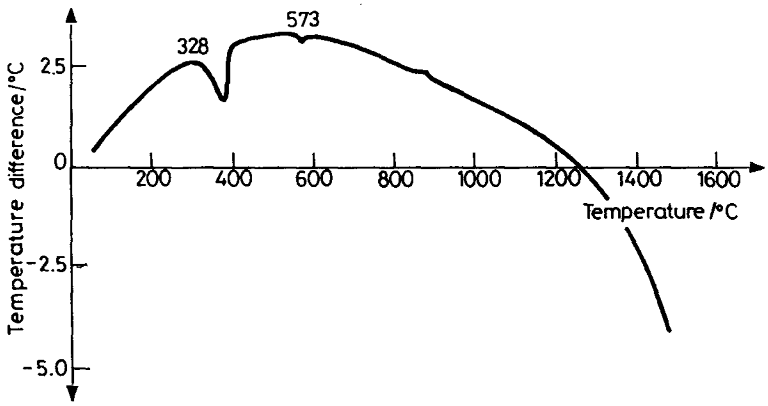

Fig. 4 DTA curve for a MgO/SiO_2 mixture with a molar ratio of 1.8:1

In a final experiment, the magnesium oxide starting material was pre-dried for an hour in nitrogen to decompose the contained hydroxide and was then mixed with SiO_2 in the molar ratio 2:1. The mixture was heated to 1200°C (before the onset of the endothermic drift) at 20 deg/min and was held isothermally at this temperature for one hour. The DTA curve was identical to that in Fig. 4 up to 1200°C except for the absence of the dehydroxylation peak. XRD analysis of the product indicated the presence of the same constituents as those found in the sample heated to 1500°C, but with a higher silica content (Fig. 5d).

In the temperature range of interest, 1000°–1500°C, possible reactions in the MgO/SiO_2 binary system are as follows:

$$SiO_2 + 2MgO = Mg_2SiO_4 \quad (2)$$

$$SiO_2 + MgO = MgSiO_3 \quad (3)$$

$$Mg_2SiO_4 + SiO_2 = 2MgSiO_3 \quad (4)$$

$$MgSiO_3 + MgO = Mg_2SiO_4 \quad (5)$$

Reactions 2, 3 and 5 are thermodynamically favoured at a wide range of temperatures, while reaction 4 is thermodynamically possible only up to 1464°C [3]. Reaction 2, however, is much more favourable in the temperature range of interest. This may explain, at least partially, the persistent appearance of $MgSiO_3$ together with Mg_2SiO_4 in all XRD patterns obtained for the products of reaction between MgO and SiO_2 at 1200° and 1500°C. The formation of $MgSiO_3$ may also be attributed to reaction 4 which, although it is the least favourable thermodynamically, may be kinetically faster than the other reactions. This question will be addressed in a future study.

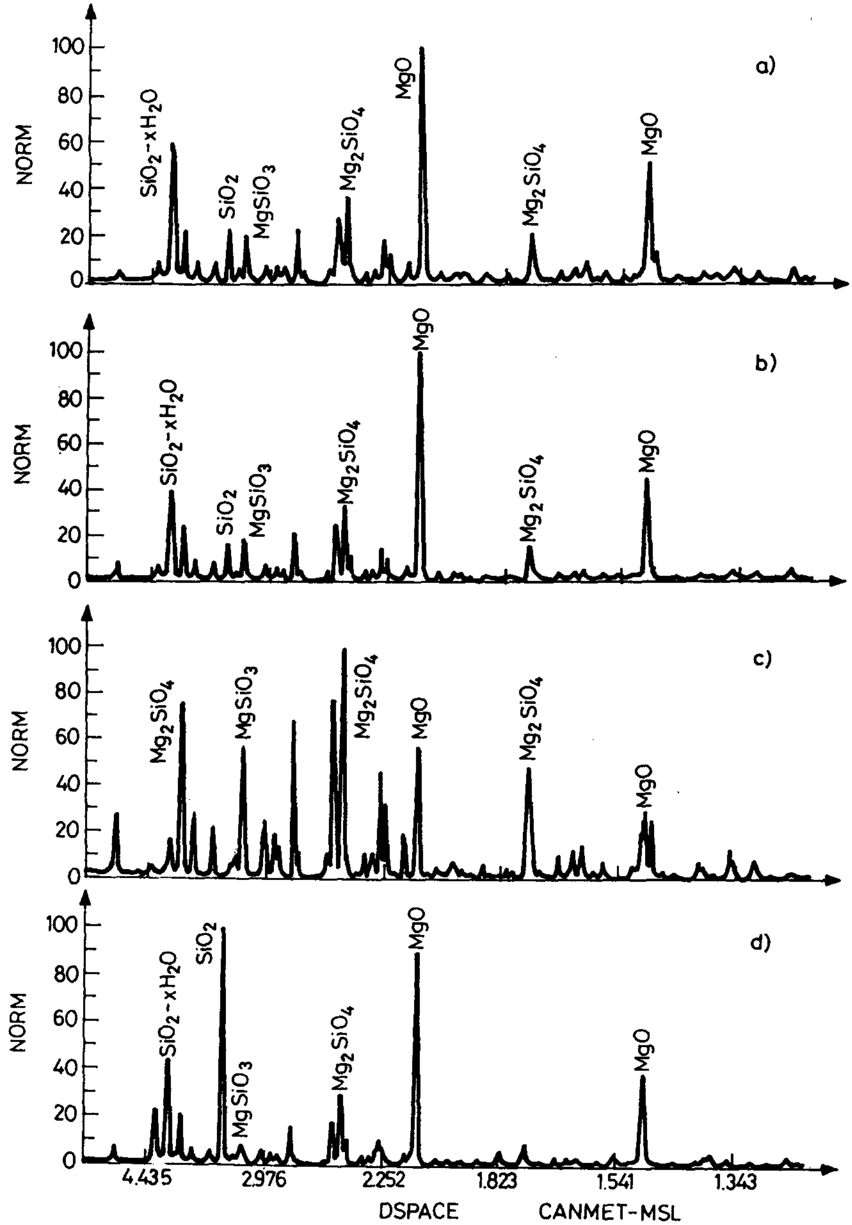

Fig. 5 XRD patterns of the MgO/SiO$_2$ mixtures: a) 1.8/1, heated to 1500°C; b) 2.7/1, heated to 1500°C; c) 2/1, maintained for 1h at 1500°C; d) 2/1, maintained for 1h at 1200°C

The appearance of MgO and SiO$_2$ in the XRD patterns of samples heated to 1200°C (even after maintaining the sample isothermally at this temperature for an hour) indicates that solid–solid reactions taking place in this binary system are very slow. By heating to 1500°C, more reaction seems to have taken place, but still residual SiO_2 and MgO were evident in the product. The depletion of SiO_2 was evident only when the mixture was heated to 1500°C and maintained isothermally at this temperature for an hour. With even longer time at 1500°C, reaction 5 may proceed to completion with the formation of Mg_2SiO_4

In conclusion, the reaction between SiO_2 and MgO seems to proceed slowly with the formation of Mg_2SiO_4 and $MgSiO_3$ at temperatures up to 1500°C, but significant amounts of unreacted SiO_2 and MgO remain in the product. More reaction took place in mixtures that were maintained isothermally for one hour at 1500°C. With longer time at this temperature it is likely that the reaction would proceed to completion with formation of Mg_2SiO_4, the desirable product.

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Zusammenfassung — Mittels Thermoanalyse und Röntgendiffraktion (zur Identifizierung der Reaktionsprodukte) wurde die Reaktion zwischen SiO_2 und MgO bei Temperaturen bis zu 1500°C untersucht. Es handelt sich um eine langsam verlaufende Reaktion, welche neben geringen Mengen von $SiO_2 \cdot nH_2O$ und unreagierten Restmengen von SiO_2 und MgO die Bildung von Mg_2SiO_4 und $MgSiO_3$ zur Folge hat. Eine vollständige Reaktion des Ausgangsmateriales zu Mg_2SiO_4 kann nur durch ein längeres (1 h) Behandeln der Probe bei 1500°C erreichen.