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High temperature thermal analysis study of the reaction between magnesium oxide and silica

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Abstract

The reaction between SiO_2 and MgO at temperatures up to 1500°C was studied using thermal analysis, with X-ray diffraction as a supplementary technique. The results indicated that the reaction is slow and takes place with 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. A complete reaction of the starting materials to form Mg_2SiO_4 may only be achievable by maintaining the mixture at 1500°C for extended periods of time (longer than 1 h) depending on the geometry of the reactants.

INTRODUCTION

Forsterite (Mg_2SiO_4) is a high-melting-point material with refractory characteristics desirable for high temperature applications. It is a product of the thermal decomposition of chrysotile asbestos, $Mg_3(Si_2O_5)(OH)_4$ [1]. The formation of forsterite, however, seems always to be accompanied by the formation of an undesirable, relatively low melting compound, namely enstatite ($MgSiO_3$), which limits the practical applicability of forsterite. In the present work, the reaction of SiO_2 with MgO is examined in an attempt to gain more understanding of the reaction route and to seek a practical thermal treatment that would lead to the formation of forsterite alone.

EXPERIMENTAL

Materials and procedure

The starting materials were reagent grade MgO and high purity spectroscopic grade SiO_2 powders. A Du Pont 9900TA system with HTDTA and

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951TGA modules was used in the study. At different stages of processing, the reaction products were examined by X-ray diffraction (XRD) as a supplementary technique.

In the experiments, 20–40 mg samples were subjected to programmed heating at 20°C min^{-1} to the desired temperature in a stream of helium with a flow rate of 50 ml min^{-1}.

RESULTS AND DISCUSSION

The reaction of MgO with SiO_2 was studied to gain more knowledge on the high temperature solid–solid reactions in this binary system. The work was carried out as part of a research and development study undertaken by CANMET to produce magnesium silicate sand, a desirable high-melting-point material suitable for refractory applications.

In the MgO–SiO_2 binary system [2], two stable compounds, namely forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$), exist. The former is the more

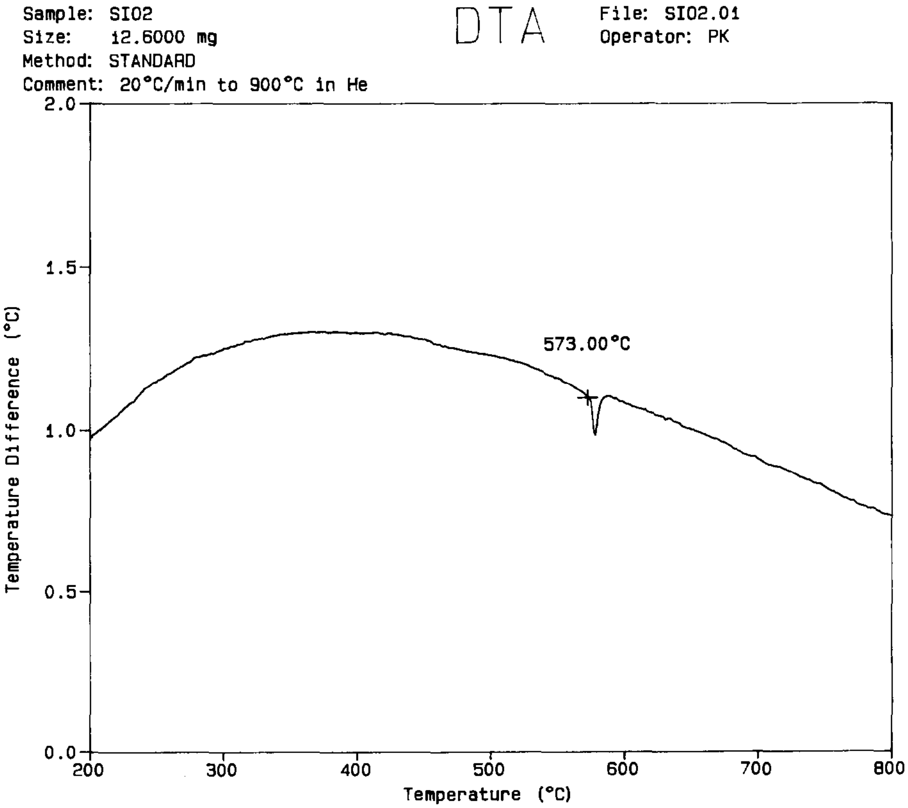

Fig. 1. DTA diagram for SiO_2 starting material.

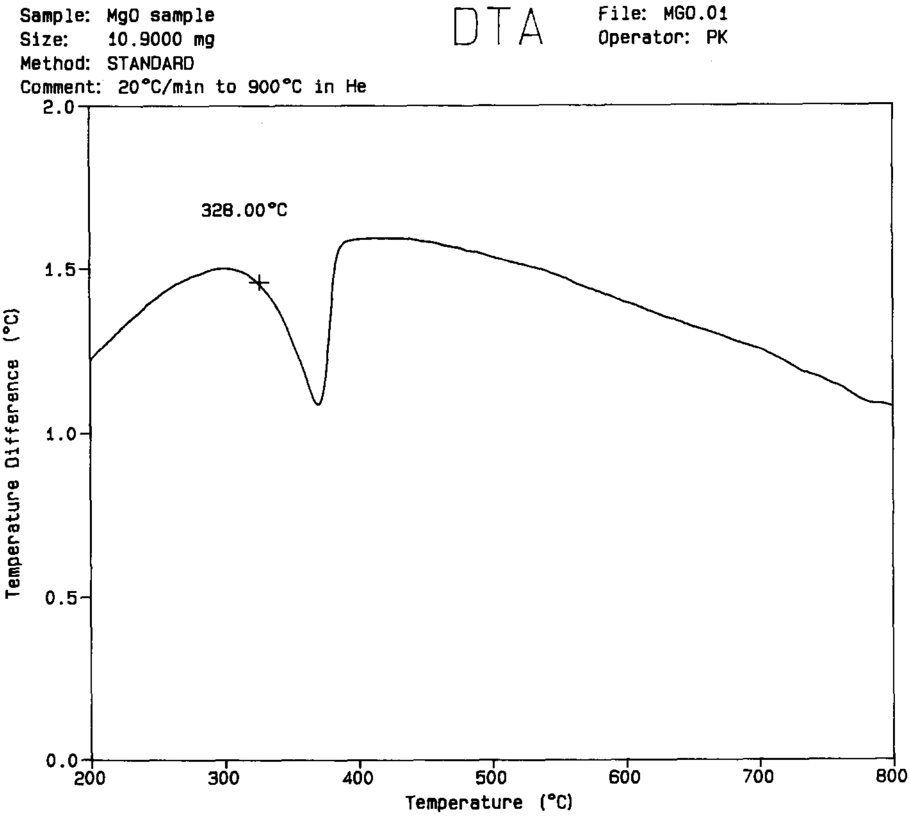

Fig. 2. DTA diagram for MgO starting material.

refractory material with a fusion point around 1900°C, compared with about 1550°C for the latter.

The present study was done using high temperature differential thermal analysis (HTDTA), with XRD as a supplementary technique. For the HTDTA, the samples were heated to the desired temperature at 20°C min^{-1} in helium. Platinum crucibles were used most of the time as sample containers.

Figure 1 shows the DTA diagram of the silica starting material, with the characteristic reversible α/β quartz polymorphic transformation appearing at about 573°C. Figure 2 shows the DTA diagram of reagent grade MgO. An endothermic peak at 328°C on the diagram corresponds to the dehydration of $Mg(OH)_2$ contained in the sample. As this was a significant peak, a separate experiment using thermogravimetry (TG) was carried out to determine the amount of hydroxide in the reagent grade MgO. Figure 3 shows the TG diagram obtained, which indicates a total weight loss at 400°C of about 10%. The weight loss in the range 250–400°C (9.6%) corresponds to the dehydroxylation of magnesium hydroxide and amounts

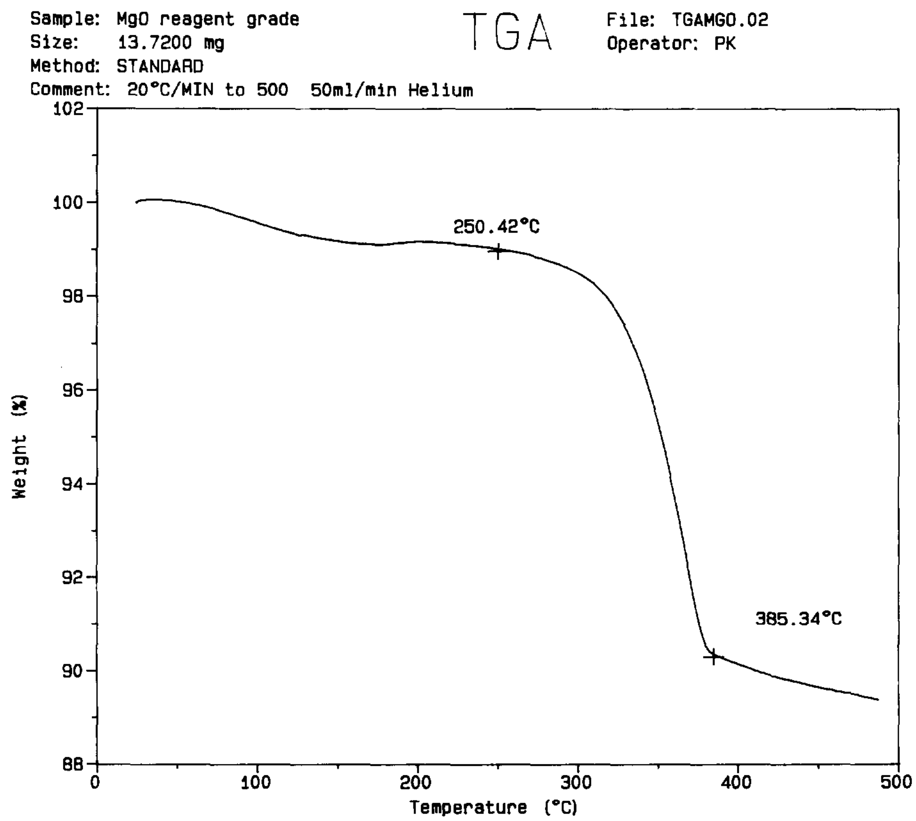

Fig. 3. TG diagram for MgO starting material.

to 31% of $Mg(OH)_2$ in the sample. The dehydroxylation of magnesium hydroxide takes place according to

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

Solid mixtures of the two reagent grade materials were prepared and subjected to different heating schemes in the HTDTA module. Reaction products obtained after the heat treatment were examined by XRD. Figure 4 shows a reproducible DTA diagram for a mixture of reagent grade MgO (corrected for contained hydroxide) and SiO_2 with a molar ratio of 1.8 : 1, heated to 1500°C at 20°C min^{-1}. This MgO : SiO_2 ratio is lower than that required for the formation of Mg_2SiO_4. In addition to the endothermic peaks of the dehydration of magnesium hydroxide and the polymorphic transformation of quartz, a reproducible endothermic baseline drift is detected, starting around 1250°C. The 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 indicated that the reaction of MgO with SiO_2 was not complete even after heating the mixture up to 1500°C, and that there

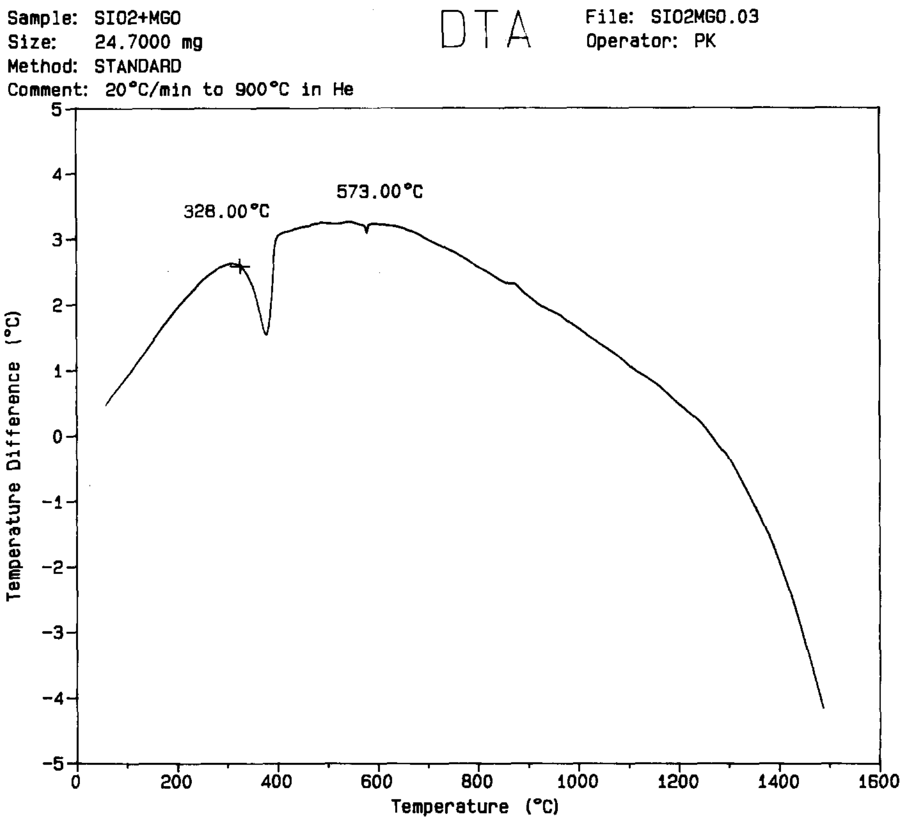

Fig. 4. DTA diagram for an MgO–SiO_2 mixture with a molar ratio of 1.8:1, in helium.

may be another reaction taking place above 1250°C, as indicated by the endothermic drift of the baseline at this temperature.

This experiment was repeated using an MgO–SiO_2 mixture with a molar ratio of 2.7:1 (more MgO than stoichiometrically required for the formation of Mg_2SiO_4). A similar DTA diagram was obtained, and the XRD analysis of the product indicated the presence of the same constituents detected in the last experiment, 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 1 h. A DTA diagram similar to that in Fig. 4, except for an isothermal portion, was obtained. The 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).

In another experiment, the magnesium oxide starting material was pre-dried for 1 h in nitrogen to decompose the contained hydroxide, and was 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°C min^{-1} and was

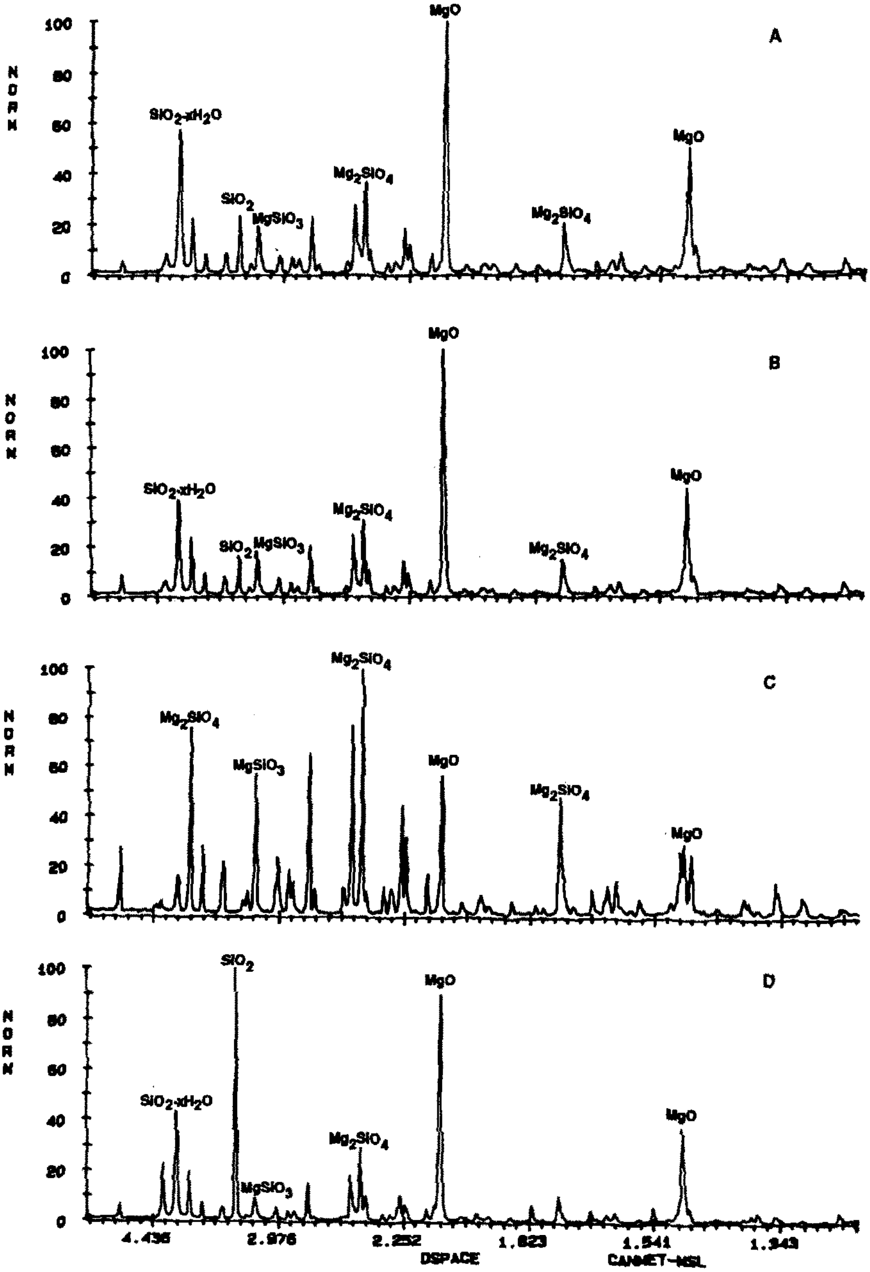

Fig. 5. XRD patterns of MgO–SiO_2 mixtures: A, 1.8:1, heated to 1500 °C; B, 2.7:1, heated to 1500°C, C, 2:1, maintained for 1 h at 1500°C, D, 2:1, maintained for 1 h at 1200°C.

held isothermally at this temperature for 1 h. The DTA diagram was identical to that in Fig. 4 up to 1200°C except for the absence of a hydroxide dehydration peak. The XRD analysis of the product indicated the presence of the same constituents as those found in the product of the sample heated to 1500°C, but with a higher silica content (Fig. 5D).

In the temperature range of interest (1000–1500°C), the possible reactions in the $MgO–SiO_2$ binary system are

$$SiO_2 + 2MgO = Mg_2SiO_4 \tag{2}$$

$$SiO_2 + MgO = MgSiO_3 \tag{3}$$

$$Mg_2SiO_4 + SiO_2 = 2MgSiO_3 \tag{4}$$

$$MgSiO_3 + MgO = Mg_2SiO_4 \tag{5}$$

Reactions (2), (3) and (5) are thermodynamically favorable over a wide range of temperatures, whereas reaction (4) is thermodynamically favorable only up to 1464°C [3]. Reaction 2, however, is much more favorable 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 Mg_2SiO_3 may also be attributed to reaction (4) which, although it is the least favorable thermodynamically, may be kinetically faster than the other reactions. This question may be addressed in a future study.

The appearance of MgO and SiO_2 in the XRD patterns of the products of samples heated to 1200°C (even after maintaining the sample isothermally at this temperature for 1 h) 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 residual SiO_2 and MgO were still 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 1 h. In this case, MgO and $MgSiO_3$ were still present in the product, but with 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 evident in the product. More reaction took place in mixtures that were maintained isothermally for 1 h at 1500°C. With a longer time at this temperature, it is likely that the reaction would proceed to completion with the formation of Mg_2SiO_4, the desirable product.

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