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INVESTIGATION OF REFRACTORY OXIDES BY HIGH-TEMPERATURE DTA

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Aim of this work in connection with the development of materials in the periclase-forsterite-zirconia system was the determination of melting temperature and melting enthalpy of refractory compounds. The possibility of determination of the melting and solidification of minor phases in refractory materials should be proved.

The forsterite melting enthalpy was determined equal 783 J/g with a standard deviation of 22 J/g.

The addition of zircon to periclase leads to the formation of an eutectic $MgO–ZrO_2–Mg_2SiO_4$ melt. 1750°–1755°C was determined as its solidification temperature. Cooling leads to the crystallization of forsterite and cubic-ZrO_2 from the melt.

Keywords: high temperature DTA, refractory oxides

Introduction

High temperature refractory oxides (Mg_2SiO_4, $MgO+ZrSiO_4$) were investigated with a commercial DTA apparatus (Netzsch STA 429). Aim of the work in connection with the development of materials in the periclase-forsterite-zirconia system was the determination of melting temperature and melting enthalpy of refractory compounds. The possibility of determination of the melting and solidification of minor phases in refractory materials should be proved.

Temperatures up to 2400°C and the temperature differences were measured with W/Re thermocouples. Closeable crucibles from pyrolytic-coated graphite were used. These crucibles directly contain metallic calibration substances (here Pt) and a second crucible made from W which does not react with the oxide samples and the coated graphite. The closeable crucibles suppress evaporation and protect the sample holder against the melt.

The calibration of the instrument was made with Au, Pt, Al_2O_3 regarding temperature and sensitivity [1]. Platinum (melting point 1769°C) was used as an in-situ calibration standard in the reference crucible during all measurements for

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purposes of control. Helium with an oxygen partial pressure smaller than 1 ppm was used as protective gas.

Determination of the melting enthalpy of forsterite (Mg_2SiO_4)

The olivine forsterite (Mg_2SiO_4) was prepared by dispersing appropriate amounts of very fine SiO_2 (Aerosil Degussa) in an aqueous solution of $Mg(NO_3)_3 \cdot 6H_2O$. The suspension was dried under stirring. The dry powder was calcinated at 700°C for 12 hours, pressed to discs and sintered at 1400°C for 5 hours. The complete formation of Mg_2SiO_4 was proved by means of XRD. Chemical composition was controlled by wet chemical analysis.

The heat of fusion of Mg_2SiO_4 has not yet been measured [2]. It was the impulse for the determination of forsterite melting enthalpy. It can be calculated using thermodynamic values [3] equal+17.0 kcal/mol=+506 J/g at 1898°C.

The melting point of forsterite is 1890±20°C [4]. In the JANAF-tables [5] a melting temperature of 1885°C and a ΔH°_{m}=+20.6±2 kcal/mol=+612±60 J/g is published. Forsterite melts congruently. The reaction $MgSiO_3+MgO \rightarrow Mg_2SiO_4$ is possible, due to a negative $\Delta_R G$ value. Papers dealing with thermodynamic properties of magnesia silicates [6–8] do not mention the melting enthalpy of Mg_2SiO_4.

The free heat of formation of forsterite at the melting temperature is $\Delta G^{\circ}m.t.=-33$ J/mol, and that of enstatite ($MgSiO_3$) is $\Delta G^{\circ}m.t.=-17$ J/mol [9].

Enstatite melts incongruently at 1560°C. This feature of stability is related to the crystal chemistry. The orthosilicate forsterite, containing discrete SiO_4^{4-} ions, is more stable as the metasilicate enstatite with chain structure.

The prepared forsterite was melted in the high-temperature DTA apparatus under 3 various (20, 10, 5 deg/min) heating rates. Figure 1 shows that the onset-temperature of the endothermic melting peak is not influenced by the heating rate. It was determined at 1855°–1860°C. This is 30 K lower than expected.

Under cooling with 3 various rates (20, 10, 5 deg/min) forsterite solidified without hysteresis at 1860°C. The determination of the melting enthalpy was performed using in-situ temperature and sensitivity calibration with Pt. Figure 2 shows an example of the results of peak integration at 5 deg/min heating rate. In Table 1 the determined melting enthalpy after 4 DTA runs with heating and cooling is summarized. The forsterite melting enthalpy was determined as equal to 783 J/g with a standard deviation of 22 J/g, not significant from the rate of temperature change. This value is larger than calculated from thermodynamic data.

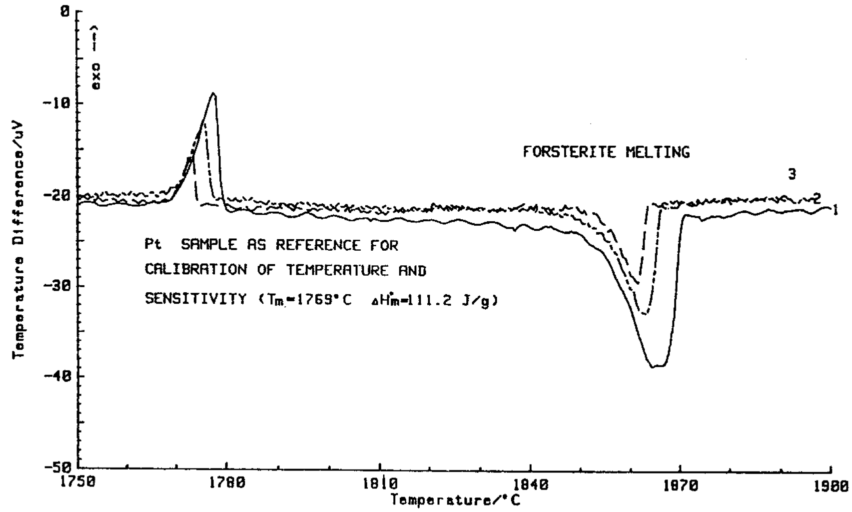

Fig. 1 DTA of forsterite (Mg_2SiO_4) melting under various heating rates (1–20 deg/min, 2–10 deg/min, 3–5 deg/min), sample weight 25 mg

Solidification temperature of the melting phase in periclase (MgO) doped with zircon ($ZrSiO_4$)

To enhance the thermomechanical properties of periclase refractories, it is useful to connect the coarse periclase grains with a high-melting binding phase. This binding phase should be crystalline and not glassy.

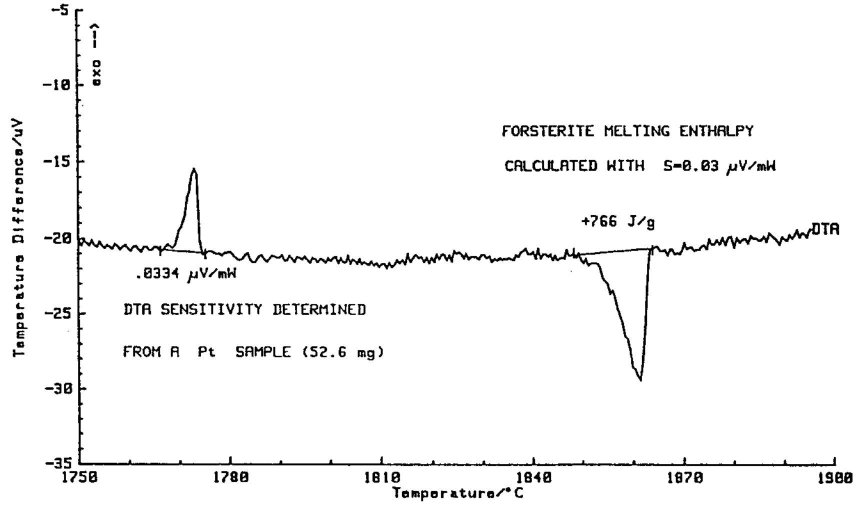

Fig. 2 Determination of forsterite (Mg_2SiO_4) melting enthalpy, 5 deg/min heating rate, sample weight 25 mg

Table 1 Mg_2SiO_4 melting enthalpy values (sample weight 25 mg)

No.	heating rate/ deg·min^{-1}	up	down	melting enthalpy/ J·g^{-1}
1.	20	+		781
	20		+	770
2.	20	+		749
	20		+	784
3.	10	+		826
	10		+	789
4.	5	+		766
	5		+	799
		melting enthalpy ΔH°_{m}=		783
		standard deviation σ=		22

Reaction sintering of MgO with small amounts of $ZrSiO_4$ to form forsterite and zirconia is common [10]. Forsterite-zirconia composites can be prepared from periclase-zircon mixtures following the equation:

$$ZrSiO_4+2MgO \rightarrow Mg_2SiO_4+ZrO_2$$

It should be mentioned that the reaction according to this equation leads to an increase of the volume of 3.6 vol-%, if the formation of cubic-ZrO_2 is considered. This can drive apart periclase grains. Therefore, it is only advantageous to use fine zircon and fine periclase in such amounts that the hollow space between the coarse periclase grains can be filled with the reaction products [11].

We investigated compositions of MgO with 5, 10, 15 wt% $ZrSiO_4$ as raw material oxide mixtures and after firing at 1650°–1700°C, 48 hours in an industrial tunnel kiln. The periclase was of high purity due to its origin from $MgCl_2$-solution. The zircon was a fine Australian zircon sand. The grain size of both periclase and zircon powders was determined by sedimentation analysis (Sedigraph 5000D Micromeritics). The d_{50}-values were 12 μm and 2 μm respectively.

The solidification of the melting phase for 10 and 15 wt% $ZrSiO_4$ could be determined with high-temperature DTA at 1755°C. For example see Fig. 3. The formation of the melting phase between 1740°–1775°C is difficult to observe and it is disturbed by the Pt melting at the reference site. For samples fired under industrial conditions into their equilibrium state, the solidification temperature was determined. Separation of the fine grained binding phase or milling of the samples has not influenced the result. Taking into account the melting temperature of 1855°–1860°C of forsterite, it can be concluded that a melting phase was formed. Its melting and solidification temperature is lowered by ZrO_2. The available phase diagram $MgO-ZrO_2-SiO_2$ [12] shows only forsterite rich compositions. A phase diagram:

eutectic $MgO-CaO$ – eutectic $MgO-Mg_2SiO_4$ – eutectic $MgO-ZrO_2$ published in a patent [13] contains an eutectic composition $MgO-ZrO_2-Mg_2SiO_4$ with a melting temperature of 1750°±10°C. This corresponds with the determined melting temperature in this work.

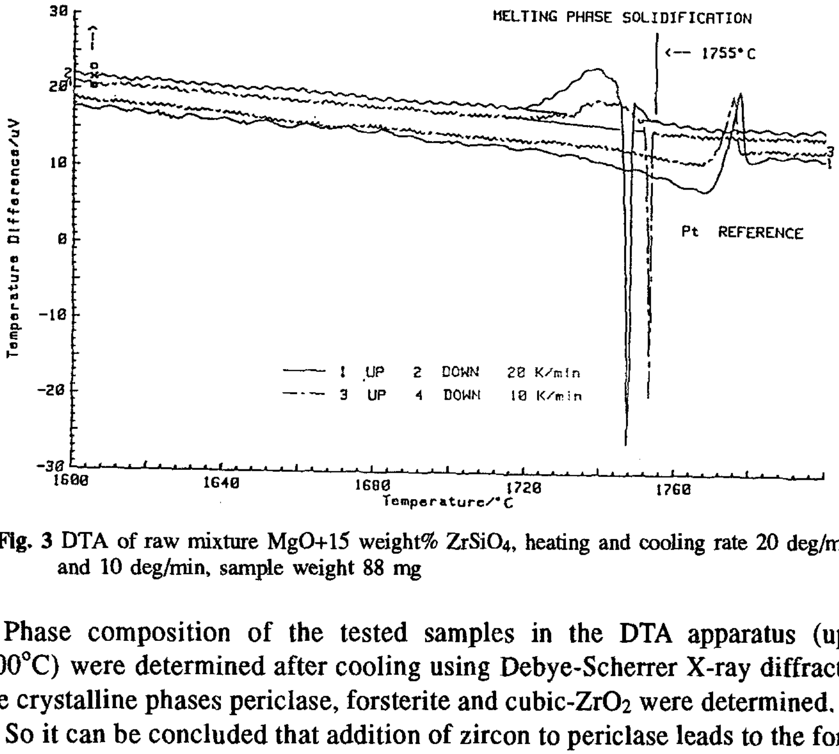

Fig. 3 DTA of raw mixture MgO+15 weight% $ZrSiO_4$, heating and cooling rate 20 deg/min and 10 deg/min, sample weight 88 mg

Phase composition of the tested samples in the DTA apparatus (up to 1900°C) were determined after cooling using Debye-Scherrer X-ray diffraction. The crystalline phases periclase, forsterite and cubic-ZrO_2 were determined.

So it can be concluded that addition of zircon to periclase leads to the formation of an eutectic $MgO-ZrO_2-Mg_2SiO_4$ melt. Its solidification temperature was determined as 1750°–1755°C. Cooling leads to the crystallization of forsterite and cubic-ZrO_2 from the melt.

The consequences for the high temperature plastic deformation and the thermomechanical properties of periclase refractories doped with zircon should be proved.

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Zusammenfassung — Ziel dieser Arbeit ist die Bestimmung von Schmelztemperatur und Schmelzenthalpie der feuerfesten Verbindungen in Verbindung mit der Entwicklung von Substanzen im System Periklas–Forsterit–Zirkonerde. Es sollte die Möglichkeit zur Bestimmung von Schmelzen und Erstarren von Minor-Phasen in feuerfesten Substanzen geprüft werden.

Die Schmelzenthalpie von Forsterit wurde mit einem Wert von 783 J/g und einer Standarddeviation von 22 J/g ermittelt.

Der Zusatz von Zirkonerde zu Periklas führt zur Bildung einer eutektischen $MgO–ZrO_2–Mg_2SiO_4$-Schmelze, deren Erstarrungstemperatur mit 1750°–1755°C ermittelt wurde. Beim Abkühlen kristallisieren aus der Schmelze Forsterit und kubisches ZrO_2 aus.