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Phase Equilibria in the High Magnesia Corner of the System $MgO-ThO_2-B_2O_3$ at 1200° C

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Phase equilibria in the high magnesia corner of the system $MgO-ThO_2-B_2O_3$ were investigated at 1200°C using X-ray powder diffraction techniques. The two magnesium borates reported previously at this temperature were confirmed, but no magnesium thorate and no ternary phases were found. Solid solution effects were investigated; for the binary phases by comparison of patterns, for magnesium oxide and thorium oxide by comparison of lattice parameters. No solid solutions were detected.

Phase equilibria in the system $MgO-ThO_2$ were investigated at 1500°C, again no binary compound was found and no solid solution detected. A suggestion is made to reconcile the latter observation with previous work.

1. Introduction

An attempt has been made to determine the phase equilibria in the high magnesia corner of the $MgO-ThO_2-B_2O_3$ system.

1.1. Previous Work

The ternary system has not been investigated at any temperature, but data exists for the two binary systems [1, 2] concerned.

According to Davis and Knight [1], in the magnesium oxide-boric oxide system there are two binary compounds stable at 1200°C; namely $2MgO.B_2O_3$ and $3MgO.B_2O_3$.

Although the magnesium oxide-thorium oxide system has not been studied thoroughly, the 1600° isothermal of the ternary magnesium oxide-thorium oxide-hafnium oxide has been reported by Mark [2]. According to this work thorium oxide will accept approximately 48 mole % of magnesium oxide into solid solution while thorium oxide is insoluble in magnesium oxide.

X-ray powder data exists for all three primary oxides in the system, but as the melting point of boric oxide is 450°C [3] this would be a liquid at the investigating temperature. The powder patterns of both magnesium oxide [4] and thorium oxide [5] are known very accurately.

2. Experimental

The investigation was started by preparing the binary compounds and by examining compacts in the magnesium oxide-thorium oxide system.

The starting materials were Analar magnesium oxide (not less than 99.2% pure on the ignited basis), Analar thorium nitrate hexahydrate (not less than 99% pure) and Analar boric acid (not less than 99.5% pure). The magnesium oxide was pre-heated at 900°C for 1 h in a platinum boat and stored in sealed bottles before weighing; the other components were weighed as thorium nitrate hexahydrate and boric acid. The amounts weighed were such as to give 1 g compacts after firing.

The starting materials were pre-fired. In this the thorium nitrate hexahydrate was decomposed by heating for 20 to 30 min at 800 to 900°C: magnesium oxide and/or boric acid was added and the mixture was further heated for 5 min at 800 to 900°C. Boric acid, because of its volatility was not pre-fired with the thorium nitrate hexahydrate. All pre-firing was carried out in platinum boats.

After pre-firing, the mixture was ground to a very fine powder, mixed thoroughly and pressed for 5 min in a ½ in. diameter steel die at a pressure of 35,000 lb/sq in. No binder was used.

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The compacts were placed on platinum foils and fired in air, and the temperature of the electrically heated furnace was controlled at 1200 ± 5°C. The specimens were air quenched.

Each compact was ground and a little used as an X-ray powder specimen which was then examined in an 11.46 cm diameter Debye-Scherrer camera using filtered copper radiation. Examination of the binary compounds indicated that thermal equilibrium was reached within 4 h and this time was used for all ternary compacts.

However, compacts containing only magnesium oxide and thorium oxide were fired for considerably longer periods in an attempt to induce either reaction or solid solutions; in these cases firing times of 26 to 28 h were used.

At a later stage in the investigation magnesium oxide, thorium oxide and the magnesium oxide-thorium oxide binary compacts were re-fired for 14 h at 1500°C.

3. Results

3.1. At 1200°C

3.1.1. *Magnesium Oxide-Boric Oxide Binary System*

In this system the presence of two magnesium borates was confirmed:

$2MgO.B_2O_3$; the pattern obtained in that of the triclinic form [6].

$3MgO.B_2O_3$; the present pattern agrees with that of Berger [7].

3.1.2. *Magnesium Oxide-Thorium Oxide Binary System*

No intermediate phase was found in this system. In addition both these compounds produced sharp diffraction lines at high Bragg Angles and because of this it was possible to obtain accurate cell sizes after extrapolation against the Nelson-Riley function [8]. The extrapolation was carried out using the ICT Atlas computer and a modified version of Wait's program [9]. This program not only applies a least-squares extrapolation to the results, but also calculates the standard deviation. This was carried out for all major and minor phases, see table I (trace phases gave insufficient diffraction lines). An examination of these results indicated that there was no detectable solid solution of magnesium oxide in thorium oxide or vice versa.

3.1.3. *Ternary Compacts*

Solid Solution Effects. Comparison of the patterns containing binary phases gave no evidence for the existence of solid solution effects. However, due to the lack of diffraction lines in the back reflection region the accuracy of this method is poor and the possibility of slight solid solution cannot be discounted. In the case of magnesium oxide and thorium oxide, again extrapolated cell sizes were obtained and again there was no evidence of any solid solution effects.

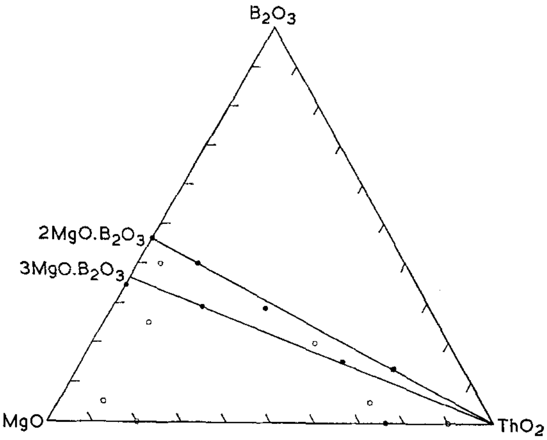

Figure 1 Phase equilibria in the high magnesia corner of the system MgO-ThO_2-B_2O_3 at 1200°C. Closed circles indicate compacts which were analysed chemically; open circles indicate compacts at nominal chemical composition.

Thermal Equilibrium Diagram. In all, fifteen binary and ternary compacts were made, and fired at 1200°C, of these, eight were chemically analysed. Table I lists these compacts, their nominal composition, their actual composition (if obtained) and the interpretation of the X-ray diffraction patterns.

The subsolidus compatibility triangles at 1200°C consistent with these analyses are shown in fig. 1, but, as already mentioned, some solid solution in the binary compacts cannot be discounted.

The discrepancies between the nominal and actual compositions, are, in general, fairly small, averaging 0.8 wt %. There is no evidence of loss of boric oxide by volatilisation.

3.2. At 1500°C

After re-firing the magnesium oxide-thorium oxide compacts for 14 h at 1500°C, no intermediate phase was found and there was no

TABLE I Specimens prepared, chemical composition and X-ray analysis

Specimen No.	Chemical composition (wt %)						Phase analysis		
	Nominal MgO	ThO_2	B_2O_3	Actual MgO	ThO_2	B_2O_3	Major	Minor	Trace
1	80	20					ThO_2 +MgO		
2	25	75		24.0	75.9		ThO_2	MgO	
3	10	90					ThO_2		MgO
4	85	10	5				ThO_2 +MgO		$3MgO.B_2O_3$
5	25	70	5				ThO_2	MgO	$3MgO.B_2O_3$
6	65	10	25				ThO_2+ $3MgO.B_2O_3$	MgO	
7	63.5		36.5	65.6		34.3	$3MgO.B_2O_3$		
8	50.5	20	29.5	50.7	20.0	29.2	ThO_2	$3MgO.B_2O_3$	
9	26.7	57.8	15.5	26.6	57.7	15.6	ThO_2		$3MgO.B_2O_3$
10	55	5	40				$3MgO.B_2O_3$ +$2MgO.B_2O_3$	ThO_2	
11	34	36.5	29.5	37.0	34.2	28.8	ThO_2	$3MgO.B_2O_3$ +$2MgO.B_2O_3$	
12	30	50	20				ThO_2	$3MgO.B_2O_3$	$2MgO.B_2O_3$
13	53.7		46.3	53.7		46.5	$2MgO.B_2O_3$		
14	47	14	39	46.9	13.3	40.0	ThO_2	$2MgO.B_2O_3$	
15	15	72	13	15.3	70.8	13.7	ThO_2		$2MgO.B_2O_3$

detectable solid solution of either oxide in the other.

4. Discussion

The lack of solid solution, mentioned in the previous section is not entirely unexpected. Van Vlack [10] points out that, in close packed crystal structures, there can be extensive solid solution if the size of the host and substitutional ions do not differ by more than 15%, but that this limitation is relaxed if the structures are not close-packed. In addition, solid solution is limited if the host and substitutional atoms have different valency, or for compounds having different structures.

Van Vlack [11] gives the ionic radii for six-fold co-ordination as Mg^{2+} 0.78 Å, Th^{4+} 1.10 Å and B^{3+} 0.25 Å, hence the three ions have widely different ionic radii. In addition these ions have different valencies and the three oxides have different structures, magnesium oxide has the sodium chloride structure, thorium oxide has the calcium fluoride structure while boric oxide is hexagonal [12]. In short, the conditions are very unfavourable for the formation of solid solutions.

However, according to Mark [2], at 1600°C there is extensive solid solution of magnesium oxide in thorium oxide. His diagram indicates that approximately 48 mole % of magnesium oxide is accepted into solid solution. At first sight this appears irreconcilable with the present work, the 100°C difference between 1500 and 1600°C is unlikely to account for this difference. However, 48 mole % of magnesium oxide in thorium oxide is equivalent to 12 wt % and in the present work the limit of detectability of magnesium oxide in thorium oxide would appear to be a little less than 10 wt % (the compact containing 10 wt % of magnesium oxide gives three very weak powder diffraction lines). Hence Mark's [2] results can be reconciled if he used the disappearing phase technique in X-ray diffraction analysis as the only method of determining the extent of solid solution. Unfortunately he gives no details of the technique used for phase analysis, and there is no way of checking this suggestion [13].

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