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DETERMINATION OF PHASE EQUILIBRIA IN THE SYSTEM BeO-ThO₂

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ABSTRACT

A study of the BeO-ThO₂ system has shown that a eutectic occurs at 70 m/o BeO (18.1 w/o) and 2155° C ± 5° (3911°F). The solid solubility of ThO₂ in BeO below the eutectic temperature is less than 0.016 m/o ThO₂ (0.16 w/o), and the solid solubility of BeO in ThO₂ is less than 0.1 m/o BeO (0.0095 w/o). Small amounts of ThO₂ have no effect on the β to α BeO phase inversion.

I. SUMMARY

An investigation of the BeO-ThO₂ indicates that this system has a eutectic reaction occurring at 70 m/o BeO (18.1 w/o) and 2155° C ± 5°. Ceramographic techniques were used on melted and heat treated specimens for this determination. The solid solubility of ThO₂ in BeO was determined on specimens that were first melted and then heat treated at pre-selected temperatures. The solid solubility of ThO₂ in BeO at temperatures below the eutectic is less than 0.016 m/o ThO₂ (0.16 w/o) and approaches a maximum solubility at the eutectic of slightly less than 0.03 m/o (0.32 w/o). Above the eutectic temperature a decrease occurs in the solid solubility as the temperature approaches the melting point of BeO. X-ray diffraction was used to determine the solid solubility of ThO₂ in BeO. Selected specimens were analyzed by spectrographic methods for maintenance of composition. The solid solubility of BeO in ThO₂ was less than 0.1 m/o BeO (0.0095 w/o) in the solid state. Ceramographic inspections were used for this determination since X-ray diffraction was unable to detect small amounts of BeO.

The BeO phase inversion between 2000° C (3630° F) and 2100° C (3810° F) was substantiated by high temperature X-ray diffraction. This inversion was below the eutectic temperature in the BeO-ThO₂ system. High temperature X-ray diffraction indicated that small amounts of ThO₂ had no detectable effect on the temperature of the phase inversion.

II. INTRODUCTION

The object of this research program was to study the phase relationships in the system, BeO-ThO_2 . The main objective was to establish the eutectic composition and temperature and limits of solid solubility. Of interest to this investigation was the effect of the high-temperature BeO phase inversion on the system. Ceramographic and X-ray diffraction were the primary methods used in these studies.

III. PREVIOUS AND RELATED INVESTIGATIONS

The BeO-ThO₂ system has been the subject of several investigations. These investigations have indicated that a simple eutectic reaction occurs and the limits of solid solubility are not extensive. Von Wartenburg¹ determined the liquidus curve for this system and found a low melting point at about 70 m/o BeO and 2210° C (4010° F) (see Figure 1). More recently, Geach and Harper² reported the eutectic to occur at about 60 m/o BeO and 2360° C (4280° F). Geach and Harper indicated that the melting point may have been too high, which is borne out by an inspection of Figure 2. The observed melting point of both the BeO and ThO₂ are about 400° C above the accepted values. Geller³ et al., investigated the ternary system BeO-Al₂O₃ - ThO₂. By extrapolation, their results indicated that a eutectic occurred in the BeO-ThO₂ binary at about 70 m/o BeO and 2200° C (3990° F). Reeve and Murray⁴ in their investigation of the ternary system BeO-UO₂-ThO₂ found no reaction other than the solid solution between UO₂ and ThO₂. In considering the BeO-UO₂-ThO₂ system as a quasi-binary with UO₂-ThO₂ solid solution and BeO as the components, the eutectic reaction was noted to occur between 60 and 80 w/o BeO and 2100° C (3810° F). Johnson⁵ melted a binary mixture of BeO and ThO₂ and observed that melting started at 2100° C (3810° F) and was complete at 1200° C (3990° F). The exact composition after melting was not determined. Lang et al.⁶, found some evidence of a stable high-temperature solid solution of BeO-Mg O-ThO₂, which when projected into the BeO-ThO₂ system would indicate a solid solubility of ThO₂ in BeO of about 20 m/o.

Smith, Cline, and Frechette⁷ determined that a high-temperature modification of BeO existed. In their first studies, this modification was found to occur at 2050° C (3720° F) and the high-temperature form was thought to be cubic with a lattice parameter of $a = 4.76\text{\AA}$. On the basis of recent observations and calculations Smith, Cline, and Austerman⁸, indexed the high-temperature BeO modifications as tetragonal.

The influence of the β to α BeO transformation on systems containing BeO has not been a research subject to date.

Figure 1. The Liquidus Curve for BeO-ThO₂ Determined by Wartenburg¹

Figure 2. The Liquidus Curve Determined by Geach and Harper.² (Original data given in weight percent)

IV. EXPERIMENTAL PROCEDURES

All of the specimens used in this study were prepared from 99.99% ThO₂ (optical grade) and 99.95% BeO. The principal impurities in the BeO were 100 ppm Fe and 350 ppm Cr. One-gram specimens were blended in a "wiggiebug" mixer. Pellets measuring 1/4-inch in diameter were dry-pressed from the blended powders. Dry-pressed pellets were subject to high volatilization rates during subsequent melting operations. To overcome the volatilization problem, the dry-pressed pellets were sintered at 1700° C (3090° F) in hydrogen for a period of at least 50 hours. Portions of the sintered pellets and a tungsten filament furnace with a gettered hydrogen atmosphere were used for melting and high-temperature studies. Specimen weights were checked after each step to insure that compositional limits were maintained. Quantitative spectrographic analysis was used to determine the true composition of several of the specimens used in the solid solubility studies.

Ceramographic inspections were conducted on all specimens after heat treatment. X-ray diffraction was the principal method for determining the solid solubility of ThO₂ in BeO. Since X-ray diffraction techniques were incapable of detecting small amounts of BeO, ceramographic inspections were used to determine the solid solubility of BeO in ThO₂.

An MRC high-temperature X-ray camera with a 5 mil rhenium filament was employed for the BeO phase inversion studies. Initial studies were conducted in a vacuum, but severe volatilization of the BeO occurred. The use of a helium atmosphere reduced the amount of BeO volatilization. A further reduction in BeO volatilization occurred when the specimen was first melted onto the rhenium heater in the filament furnace and then the heater and the specimen were transferred to the X-ray camera. Copper K α radiation was used for all diffraction studies.

Temperatures throughout this investigation were measured with a "Pyro" micro-optical pyrometer. This pyrometer was calibrated against known melting points of oxide ceramics.

V. RESULTS AND DISCUSSION

In the first series of experiments that were conducted, an attempt was made to establish the solidus temperature. Specimens from 20 to 99 m/o BeO (27.48 to 90.36 w/o) were heated in the tungsten filament furnace until the first visible signs of melting were detected. The temperatures were recorded and the specimens examined ceramographically to determine the degree of melting that had occurred. A great deal of scatter in the melting point data was obtained. The ceramographic inspections indicated that in several cases, the amount of melting that had occurred was in excess of that would be expected at or near the eutectic temperature. These inspections indicated that the eutectic composition was between 65 and 75 m/o BeO (14.96 and 22.13 w/o).

To determine the eutectic composition, specimens were prepared at one mole percent increments from 66 to 74 m/o BeO (15.52 to 21.24 w/o BeO). These specimens were melted at 2500° C (4532° F) in the tungsten filament furnace after receiving the initial sintering treatment. After melting, the power to the furnace was turned off to effect rapid cooling. A melting temperature of 2500° C (4532° F) was required to prevent segregation in the melt since at lower melting temperatures segregation was definitely a problem. The structure obtained could not be resolved into the individual components. Etching the specimens with either hot ammonium bifluoride-hydrofluoric acid or sulfuric acid etches did not resolve the structure.

The melted specimens were then heat treated for 24 to 48 hours at 1750° C (3180° F) to allow grain growth to proceed. After grain growth and coalescence, the individual components could be resolved. The eutectic occurred at a composition of 70 m/o BeO (18.1 w/o) which agrees with the results obtained by Von Wartenburg.¹ Reactions on either side of the eutectic composition were as expected, with a primary ThO₂ dendritic structure being present on the ThO₂ side and a primary BeO dendritic structure being present on the BeO side.

The eutectic temperature was determined by using specimens of the eutectic composition. Sintered specimens were heat treated at progressively higher temperatures for 3 to 5 minutes. After each heat treatment, the specimens were inspected ceramographically for any indication of melting. At least two specimens were used for each heat treatment. The starting temperature was 2100° C (3820° F) and 10° C temperature intervals were used. A temperature of 2160° C (3920° F) was required before any indication of melting was observed.

Specimens in quintuplicate were then heat treated for 5 minutes at temperatures of 2145° C (3893° F), 2150° C (3902° F), 2155° C (3911° F) and 2160° C (3920° F). The ceramographic examination indicated melting did not occur until a temperature of 2155° C (3911° F) was attained. Slight evidence of melting occurred in one specimen heat treated at 2150° C (3902° F). This temperature difference of 5° C was within the range of experimental error that would be expected at these temperatures. The eutectic temperature of 2155° C $\pm$ 5° (3911° F) is lower than that determined by Von Wartenburg¹ (2210° C), Geach² and Harper (2360° C) and Geller³ (2200° C) but higher than reported by Reeve and Murray⁴ (2100° C) and Johnson⁵ (2100° C). The phase diagram showing the eutectic reaction is shown in Figure 3. As shown in Figure 3, an area exists in which the liquidus and solidus are very close. The liquidus projection was made from the observations on the first group of experiments in which the main objective was to determine the eutectic temperature and composition.

In determining the solid solubility of ThO₂ in BeO, specimens containing 1.0 to 0.005 m/o ThO₂ (9.639 to 0.053%) were used. The solid solubility was determined both above and below the eutectic temperature. At one mole percent ThO₂ a considerable amount of eutectic material is still present at the grain boundaries as an inspection of Figure 4 indicates. Two phases were easily detected by ceramographic inspections to a composition of 0.05 m/o ThO₂ (0.525 w/o). X-ray diffraction indicated ThO₂ to be present which confirmed the results of the ceramographic examination.

In the heat treatments of specimens containing less than 0.05 m/o ThO₂, the specimens were first melted at a temperature of 2500° C (4532° F) slowly cooled to a preselected temperature for 10 minutes, and quenched to room temperature. The specimens for the 1500° C (2732° F) and 1780° C (3090° F) were given an additional heat treatment at these temperatures for a period of 800 hours. These specimens were tightly encapsulated in molybdenum foil to reduce volatilization. After heat treatment, the specimens were examined both ceramographically and by X-ray diffraction to determine if primary ThO₂ was present. Results of the solid-solubility studies of ThO₂ in BeO are presented in Table I.

The amount of solid solubility of ThO₂ in BeO is very small in most instances (less than 0.016 m/o ThO₂). A slight increase in solid solubility occurs close to the eutectic temperature (2160° C heat treatments) where between 0.03 and 0.016 m/o ThO₂ is soluble in BeO.

Figure 3. The BeO-ThO₂ System

250 X

Figure 4. Specimen Containing 1 m/o ThO₂ after Melting and Heat Treatment at 2300° C showing BeO (Matrix) and Eutectic (Grain Boundaries). (Dark Areas Are Voids)

Table I. Solid Solubility Studies of ThO₂ in BeO

<u>Heat Treatment Temperature, °C</u>	<u>Composition, m/o ThO₂</u>	<u>Phases Present</u>
2350°	0.04	BeO-ThO ₂
	0.03	BeO-ThO ₂
	0.016	BeO-ThO ₂
	0.012	BeO, BeO-ThO ₂
	0.005	BeO
2300°	0.04	BeO-ThO ₂
	0.03	BeO-ThO ₂
	0.016	BeO-ThO ₂
	0.012	BeO, BeO-ThO ₂
	0.005	BeO
2260°	0.04	BeO-ThO ₂
	0.03	BeO-ThO ₂
	0.016	BeO
	0.012	BeO
	0.005	BeO
2160°	0.04	BeO-ThO ₂
	0.03	BeO-ThO ₂
	0.016	BeO
	0.01	BeO
	0.005	BeO
1700°	0.04	BeO-ThO ₂
	0.03	BeO-ThO ₂
	0.016	BeO-ThO ₂
	0.012	BeO
	0.005	BeO
1500°	0.04	BeO-ThO ₂
	0.03	BeO-ThO ₂
	0.016	BeO-ThO ₂
	0.012	BeO
	0.005	BeO

The solid solubility studies of BeO in ThO₂ used specimens from 4.0 m/o to 0.1 m/o BeO (0.393 to 0.0095 w/o). After pre-sintering, these specimens were held at 2600° C (4711° F) for a period of 5 to 10 minutes followed by lowering the temperature to either 2500° C (4530° F) or 2250° C (4080° F) and holding the specimen at the lower temperature for a period of 5 to 10 minutes. The specimens were then rapidly cooled to room temperature. One series of specimens was also heat treated at 2600° C (4711° F) slowly cooled to 2160° C (3920° F) and rapidly cooled to room temperature followed by heat treating at 1700° C (3900° F) for 150 hours.

The ceramographic examinations indicated that two phases were present in all of the specimens heat treated at 1700° C (3090° F). At a temperature of 2250° C (4080° F) and 2500° C (4530° F), specimens containing 0.1 m/o BeO (0.0095 w/o) were single phase ThO₂. Two phases were present in specimens containing 0.25 m/o BeO (0.072 w/o) at temperatures of 2250° C (4080° F) and 2500° C (4530° F) indicating that this composition was a two-phase field of liquid plus solid. This examination indicates the solid solubility of BeO in ThO₂ in the solid state, is less than 0.1 m/o BeO (0.0095 w/o).

High-temperature X-ray diffraction was used to verify the existence of a phase inversion in BeO. In pure BeO, this inversion was detected between 2000° C (3630° F) and 2100° C (3810° F). The X-ray diffraction pattern was in general agreement with that obtained by Smith et al.⁸. A specimen containing 0.087 m/o ThO₂ (0.914 w/o) by analysis showed the BeO phase inversion between 2000° C (3630° F) and 2100° C (3810° F). Thoria was also present in the X-ray pattern obtained with this particular specimen. The exact position of the phase inversion in the two phase field BeO-ThO₂ could not be accurately determined, since specimen volatility in the high-temperature X-ray camera was too great to allow the necessary number of scans required. Therefore, the temperature of the β to α phase inversion shown in Figure 3, is not firmly established for the BeO-ThO₂ system.

A well defined substructure existed in specimens of pure BeO that had been melted at 2500° C (4530° F) and then quenched to room temperature (Figure 5). This substructure was attributed to the BeO β to α inversion, since no evidence of such a structure was present in sintered BeO. Additions of ThO₂ in the region of ThO₂ solid solubility (<0.03 m/o ThO₂) did not suppress the formation of this type of structure. Figure 6 is a photomicrograph of a specimen containing 0.016 m/o ThO₂ which was

500 X

Figure 5. Melted and Quenched Specimen of BeO Showing Sub-grain Structure

first melted at 2500°C (4530°F) by heat treating at 2350°C (4260°F) for three minutes and quenching to room temperature. A fine substructure is present in this specimen. Lowering the heat treatment temperature to 2260°C (4100°F), followed by quenching still results in a substructure being present (Figure 7), although there is some increase in structure size.

Prolonged heat treatment at temperatures below the inversion temperature results in grain growth of the crystallites. A typical structure is shown in Figure 8 of a specimen that had been melted and quenched and then heat treated for 800 hours at 1500°C (2730°F). The conclusion of these observations was that ThO_2 in solid solution has no effect on the BeO phase inversion.

500X

Figure 6. BeO Specimen with 0.016 m/o ThO₂. Heat Treated at 2350° C.

500X

Figure 7. BeO Specimen with 0.016 m/o ThO₂. Heat Treated at 2260°C.

500X

Figure 8. BeO Specimen with 0.016 m/o ThO₂. Heat Treated at 1500°C.

VI. CONCLUSIONS

The results of these studies indicate that a eutectic is present in the BeO-ThO₂ system at 70 m/o BeO (18.1 w/o) and a temperature of 2155° C ± 5° (3911° F). The solid solubility of ThO₂ in BeO is temperature dependent to some extent with less than 0.016 m/o ThO₂ (0.16 w/o) being soluble at temperatures below the eutectic temperature. At temperatures approaching the eutectic temperature a slight increase is noted in the solid solubility of ThO₂ in BeO but is still less than 0.03 m/o (0.32 w/o). Above the eutectic temperature a decrease in solid solubility of ThO₂ in BeO occurs as the melting point of BeO is approached. The solid solubility of BeO in ThO₂ is less than 0.1 m/o BeO (0.0095 w/o) in the solid state.

The BeO phase inversion between 2000° C (3630° F) and 2100° C (3810° F) was substantiated. This inversion occurs below the eutectic temperature in the BeO-ThO₂ system. Small additions of ThO₂ had no detectable effect on the temperature of the phase inversion, both within the region of ThO₂ solid solubility and also within the two phase region BeO plus ThO₂.

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