UNIVERSITY OF DENVER
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DETERMINATION OF PHASE EQUILIBRIA IN THE SYSTEM BeO-ThO_2

Third Quarterly Report
Contract AT(11-1)-1092, Task G

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I. INTRODUCTION

The purpose of this program is to establish the phase relationships in the BeO-ThO₂ system. The main objectives are to establish the eutectic composition and temperature and limits of solid solubility. Fusion point techniques are being used for determining the reaction temperatures. Ceramographic inspection of the specimens are used to verify results. The solid solubility determinations are being conducted primarily by ceramographic inspections with X-ray diffraction being used to confirm the results. The work period covered is from March 1, 1965 to June 1, 1965, and is being conducted under Contract AT(11-1)-1092, Task G.

II. EXPERIMENTAL PROCEDURES

All of the specimens for this study are prepared by dry-pressing 1/4-inch diameter pellets from thoroughly blended powders. These pellets are sintered at 1750°C (3180°F) for 50 hours or longer depending upon the composition. Generally, the pellets with 50 m/o BeO or more are adequately sintered after 50 hours for further tests. The high ThO₂ content pellets require longer sintering times to partially react the specimens. The BeO has a nominal purity of 99.95% BeO with the principal impurities being 100 ppm Fe and 350 ppm Cr. The ThO₂ is optical grade with a purity of 99.99% ThO₂.

Small portions of the partially reacted pellets are then used for solubility limits and eutectic temperature determinations. Melted specimens are used for those samples containing in excess of 60 m/o BeO whereas high temperature heat treatments are used for the high ThO₂ content specimens. Melting is accomplished using a tungsten filament furnace. Weights are recorded before and after each operation to insure compositional limits are maintained.

Ceramographic inspections are used throughout this investigation to determine the structure and phases present. X-ray diffraction is used in the solid solubility studies, but is not as accurate a method of determining the phases present as the ceramographic inspection. X-ray diffraction is not capable of detecting small amounts of BeO in the presence of ThO₂. However X-ray diffraction does detect ThO₂ in the presence of BeO within the limits of the studies conducted to date.

III. RESULTS AND DISCUSSION

The objective of this study is to establish (1) the eutectic composition and temperature, (2) the solubility of ThO_2 in BeO and (3) the solubility of BeO in ThO_2 . During this report period, the eutectic composition was established at 70 m/o BeO (18.1 w/o) and a temperature of $2155^\circ\text{C} \pm 5^\circ$. A solubility of BeO in ThO_2 of less than 0.25 m/o BeO (0.024 w/o) was indicated at temperatures close to the eutectic. The solubility of ThO_2 in BeO is less than 0.05 m/o ThO_2 (0.525 w/o ThO_2) at temperatures approaching the eutectic.

For the eutectic composition studies, specimens were prepared at one mol percent increments from 66 to 74 m/o BeO (15.52 to 21.24 w/o BeO). These specimens were dry pressed from thoroughly blended powders and given an initial sintering treatment at 1750°C (3180°F) for 50 hours. Portions of the sintered pellets were then melted at 2500°C (4532°F) in a tungsten filament furnace. Lower melting temperatures resulted in segregation of the components. After melting, the specimens were rapidly cooled to room temperature and prepared for ceramographic examination. This examination indicated that this particular method did not give distinguishable microstructures.

The specimens that had been melted were then given an additional heat treatment at 1750°C (3180°F) to allow grain growth to proceed. Times at temperature of 24 to 48 hours were used. After grain growth and coalescence, the individual components of the microstructure could be resolved. Ceramographic inspection indicated that the eutectic occurred at a composition of 70 m/o (18.1 w/o BeO). At compositions of less than 70 m/o BeO , a primary dendritic structure of ThO_2 existed, which was surrounded by eutectic material. A primary BeO dendritic structure with surrounding areas of eutectic was present at compositions with more than 70 m/o BeO .

In the next series of tests, the eutectic temperature was determined using specimens of the eutectic composition. Sintered specimens were heat treated at progressively higher temperatures for a period of 3 to 5 minutes. The starting temperature was 2100°C (3820°F) and 10°C temperature intervals were used. Duplicate specimens were used for these tests. The first indication of melting in these tests occurred at 2160°C (3920°F). Ceramographic examinations confirmed these results. 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). After heat treatment, the specimens were then examined ceramographically for evidence of melting. This examination indicated that melting did not start until a temperature of 2155°C (3911°F) was attained. Slight evidence of melting occurred in one of the specimens heat treated at 2150°C (3902°F). However, at these temperatures, an experimental error of 5°C can be encountered. The conclusion from these experiments was that the eutectic temperature was 2155°C ± 5°.

For the determination of the solubility of ThO₂ in BeO, compositional levels of 0.2, 0.15, 0.10 and 0.05 m/o ThO₂ (2.07, 1.56, 1.05 and 0.53 w/o) were used. The specimens were first sintered for 50 hours at 1750°C (3180°F) to prevent segregation on melting. Portions of the sintered specimens were melted at 2500°C after which the temperature was slowly lowered to the preselected heat treatment temperatures. Heat treatments were conducted at temperatures of 2350°C (4260°F), 2250°C (4080°F) and 2160°C (3920°F) for a period of ten minutes after which the specimens were quenched to room temperature. The maximum solubility would be anticipated at the eutectic temperature.

Ceramographic examinations indicated that all of the specimens were still in the two-phase region, BeO plus liquid, since a slight trace of the eutectic composition was present in all of these specimens. X-ray diffraction confirmed these results with small amounts of ThO₂ being present in the X-ray patterns. Specimens are currently being prepared with 0.04 to 0.005 m/o ThO₂ (0.42 to 0.05 w/o).

In the ThO₂-rich portion of the system specimens containing 0.75, 0.50 and 0.25 m/o BeO (0.072, 0.048 and 0.024 w/o) were prepared. The specimens were partially reacted by sintering at 1700°C (3180°F) for 50 hours. Portions of these specimens were then heated to 2600°C (4710°F) and held for five minutes and then quenched to room temperature. Ceramographic inspection of these specimens indicated that a liquid phase was present at the ThO₂ grain boundaries. In subsequent heat treatments the specimens were first heated to 2600°C (4710°F) and then the temperature was slowly reduced to temperature levels of 2350°C (4260°F) and 2250°C (4080°F) and held at temperature for five minutes followed by rapidly cooling to room temperature. Ceramographic examinations again indicated that a liquid phase was present in all of these specimens. The apparent limit of solubility of BeO in ThO₂ is less than 0.25 m/o BeO (0.024 w/o). Additional time at temperature will be required to confirm this observation.

IV. FUTURE WORK

The studies to determine the solubility of BeO in ThO₂ and ThO₂ in BeO will be continued. These experiments will be conducted close to the eutectic temperature, since the greatest amount of solid solubility would be anticipated in this region. After the limits of solid solubility have been determined at the eutectic temperature, this study will be extended to include lower temperatures.

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