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DETERMINATION OF PHASE EQUILIBRIA IN THE
SYSTEM BeO-ThO₂

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

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ABSTRACT

Studies of the BeO-ThO₂ system indicate that eutectic reaction occurs between 70 and 74 mole percent BeO at a temperature of about 2150°C. The limits of solid solubility of BeO in ThO₂ at 2760°C as indicated by ceramographic inspection is less than 1.0 mole percent BeO. Solid solubility studies of ThO₂ in BeO at temperatures in excess of 2300°C indicate that the extent of solid solubility is less than 0.25 mole percent ThO₂.

I. INTRODUCTION

This is the second quarterly progress report on the project to establish the phase relationships in the BeO-ThO₂ system. The main objectives of this program are the establishment of the eutectic temperature and composition and the limits of solid solubility. Fusion point analysis coupled with ceramographic techniques is being used to determine the reaction temperatures. Ceramographic inspection of specimens of known composition is being used to determine the phases present. X-ray diffraction is used to support the ceramographic inspections. The work period covered in this report is from December 1, 1964 to March 1, 1965, and is being conducted under Contract AT(11-1)-1092, Task G.

II. EXPERIMENTAL PROCEDURES

The general procedure for preparing specimens consisted of first dry pressing 1/4 inch diameter pellets from blended powders of the desired composition. These pellets were then sintered at 1750°C (3180°F) for a period of 50 hours or longer depending upon the composition. The BeO has a 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 sintered pellets were then used for the subsequent investigations. Generally, portions of the pellets were either melted or heat treated in a tungsten filament furnace at the desired temperature. Weights were recorded prior to and after each heat treatment to insure no drastic compositional change occurs.

Ceramographic examinations of the specimens were used to determine the phases present. X-ray diffraction will be used for the solid solubility determinations, when the ceramographic inspections reveal that only one phase is present. However, the objective of obtaining a single phase as determined by ceramographic inspection, has not been attained at the present time.

III. RESULTS AND DISCUSSION

The objectives of the experiments conducted during the report period were to (1) determine the eutectic composition, (2) determine the solid solubility of ThO_2 in BeO and (3) determine the solid solubility of BeO in ThO_2 . None of these objectives has been realized at the present time. The compositional limits of these reactions have been narrowed by the investigations.

Several experiments have been conducted to determine the composition of the eutectic reaction. Previously reported work indicated that the eutectic occurs at a composition close to 70 m/o BeO (18.1 w/o). Specimens were prepared from 66 m/o BeO (15.52 w/o) to 74 m/o BeO (21.24 w/o) by first sintering 1/4-inch dry pressed pellets at 1750°C (3180°F) for 50 hours and then melting the specimens at 2400°C (4350°F) in the filament furnace and quenching to room temperature. Ceramographic examination of these specimens indicated that some primary ThO_2 was present in the specimens containing 66, 67 and 68 m/o BeO (15.52, 16.18, and 16.74 w/o). The ThO_2 in some instances was segregated indicating that the density difference between the ThO_2 and the eutectic allowed some of the ThO_2 to settle through the melt without reacting.

At compositions in excess of 69 m/o BeO (17.4 w/o), the microstructures were very similar in appearance. On quenching, a dendritic structure was formed which could not be resolved into its components, i. e., whether the eutectic was the sole component or if BeO was also present. Specimens were then heat treated at 1700°C (3090°F) for fifty hours after receiving the same preparation as described above. In these specimens, the extremely fine eutectic structure did exhibit grain growth and the individual components of the eutectic portion of the specimens could be resolved in some instances. At a composition of 74 m/o BeO (21.24 w/o), the basic species of the dendrites were BeO , indicating the phases present were BeO and eutectic. The additional heat treatment at 1700°C (3090°F) had resulted in too much grain growth to determine what phases were originally present in the specimens containing 71 to 73 m/o BeO (18.88 to 20.39 w/o BeO). ThO_2 and eutectic were the apparent phases in the specimens containing 66 to 69 and 71 m/o BeO (15.21 to 17.40 and 18.88 w/o). Some segregation did occur in these specimens so no definite conclusions can be made at this time. The specimen containing 70 m/o BeO (18.10 w/o) fractured into fine particles during the additional heat

treatment and was lost. At the present time, the apparent composition of the eutectic would be slightly in excess of 70 m/o BeO (18.10 w/o) but less than 74 m/o BeO (21.24 w/o). Additional experiments will be required to determine the eutectic composition.

The experiments for determining the solid solubility of ThO₂ in BeO were conducted using specimens that had been sintered for 24 hours at 1750°C (3180°F). The first series of specimens containing 1, 2, and 3 m/o ThO₂ (9.64, 17.72 and 24.6 w/o) was melted, after which individual specimens of each composition were held at temperatures of 2500°, 2400° and 2350°C (4530°, 4350° and 4260°F), for three minutes and then quenched. Another series of specimens was melted and the temperature lowered to 1700°C (3090°F), held for 3 minutes and quenched. This series was transferred to a molybdenum wound furnace and heat treated for 24 hours at 1700°C (3090°F) and then quenched. Ceramographic inspections indicated that ThO₂ was present in all of these specimens.

Specimens at composition levels of 0.25, 0.50 and 0.75 m/o ThO₂ (2.58, 5.04 and 7.39 w/o) were sintered at 1750°C (3180°F) for 24 hours. Individual portions of each of these specimens were melted, heat treated at temperatures of 2500°, 2400° and 2300°C (4530°, 4350° and 4260°F) and then quenched. A great deal of difficulty was encountered in preparing these specimens for ceramographic examination, since the specimens were very friable and tended to fracture at the grain boundaries which was the actual area of interest. After repeated efforts, some of the specimens were prepared adequately to determine the phases present. In the specimens containing 0.25 and 0.50 m/o ThO₂, (2.58 and 5.04 w/o) the eutectic was detected at the grain boundaries in the specimens quenched from all three temperatures. The specimens containing 0.75 m/o ThO₂ (7.39 w/o) had very slight traces of the eutectic composition in the specimens quenched from 2500° and 2300°C (4530° and 4260°F). No adequately prepared specimen was prepared from the specimens quenched from 2400°C (4350°F).

The results to date indicate that in the temperature range of 2300°C (4530°F) and greater, a two phase region still exists at a composition of 99.75 m/o BeO-0.25 m/o ThO₂ which would be composed of liquid and BeO. The region below the eutectic temperature at this composition is still being investigated. It must be pointed out that the above composition on a weight percent basis still contains 2.58 percent ThO₂, which is a considerable amount of BeO. Specimens are currently being prepared that contain down to 0.05 m/o ThO₂ which amounts to 0.525 w/o ThO₂.

In determining the solid solubility of BeO in ThO₂, specimens at 1, 2, 3 and 4 a/o BeO (0.096, 0.193, 0.292 and 0.393 w/o) were first pelletized from blended powder and then sintered for 150 hours at 1750°C (3180°F). After sintering, portions of the specimens were heat treated at 2760°C (5000°F) for periods of 1 and 3 minutes and then quenched to room temperature. Weight losses during these heat treatments were less than 1% with one exception in which the loss was 6 %. This particular specimen was excluded from the final analysis.

Ceramographic examinations were made of all of these specimens. The specimens held for three minutes at 2760°C (5000°F) had developed a fairly large grain structure as would be anticipated. In all cases, there was evidence of a eutectic phase at some point in the grain boundaries, with the amount slightly decreasing as the composition approached 1 a/o BeO (0.096 w/o). The structures were typical of a sintered material with some porosity present. However, the fact that very minute traces of a eutectic phase were present does indicate that the solubility of BeO in ThO₂ at 2760°C (5000°F) is less than 1 a/o BeO (0.096 w/o).

IV. FUTURE WORK

Additional experiments will be conducted to determine the eutectic composition. After this composition has been determined, a more accurate determination of the eutectic temperature can be made using specimens of the eutectic composition for the actual temperature studies. Further investigations will be conducted to determine the limits of solid solubility. Procedures for chemical analysis on the BeO-ThO₂ are underway and will be used on those specimens that actually are pertinent to the compositional limits of the system.

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