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MELTING POINTS
OF
HYPOSTOICHIOMETRIC URANIUM DIOXIDE

By

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JUNE, 1966

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INTRODUCTION

Recent interest in the properties of hypostoichiometric UO_2 and high temperature U- UO_2 phase relationships⁽¹⁻³⁾ has motivated further melting point studies of nonstoichiometric UO_2 .

The reported melting point for UO_2 varies between 2174 °C and 2880 °C⁽⁴⁻¹⁵⁾ with most recent values between 2750 °C and 2880 °C. However, most melting point data are reported for nearly stoichiometric compositions. Christensen⁽¹¹⁾ reported a 2400 °C melting point for hyperstoichiometric $\text{UO}_{2.15}$. Duncan et al.⁽¹³⁾ indicated that the melting point for $\text{UO}_{1.96}$ was approximately 100 °C higher than the melting point for $\text{UO}_{2.0}$. Conversely, Latta and Fryxell⁽¹⁵⁾ recently reported that the melting points for nonstoichiometric $\text{UO}_{2.003}$ to $\text{UO}_{1.75}$ decreased with decreasing O:U ratio.

This note reports the melting points for hypostoichiometric $\text{UO}_{2.00}$ to $\text{UO}_{1.67}$. The melting points decrease below 2.00 agreeing in general with the results of Latta and Fryxell.⁽¹⁵⁾ However, the melting

point of $\text{UO}_{2.00}$ is lower than that reported by Latta and Fryxell, and the melting points of the most hypostoichiometric UO_{2-x} are higher. The data also suggest a possible maximum in the melting point at a stoichiometry less than 2.00.

EXPERIMENTAL TECHNIQUE

Fabrication of Hypostoichiometric Oxide

Uranium dioxide cylinders with large axial holes were filled with uranium metal⁽²⁾ and were encapsulated in tungsten crucibles. These crucibles were heated for 10 to 240 minutes at 1600 °C to 2500 °C in 10^{-5} torr vacuum. After cooling, each cylinder was examined ceramographically; and the O:U ratio of the originally stoichiometric UO_2 was determined gravimetrically by oxidation to U_3O_8 .

The microstructure of the hypostoichiometric UO_2 consisted of two-phase polycrystalline UO_2 with uranium metal uniformly dispersed in the grain boundaries. The final O:U ratios of the samples were controlled by varying the heating temperature: the higher the temperature, the lower the O:U ratio.⁽¹⁻²⁾

Melting Point Determinations

Melting points were determined in purified inert atmospheres* using an electric tungsten "V" filament furnace.⁽¹¹⁾ Small, 10-25 mg samples of the oxide were placed in the bottom of the filament. Specimen melting was observed using a long working distance microscope, and simultaneously, filament temperatures were measured using an optical brightness pyrometer. The time required to measure a single melting point was less than 5 seconds. The system was calibrated using materials of known melting points (Al_2O_3 , Cu, Nb, Mo, Pt, Ni). Three to ten measurements were made of each specimen. Precision of the temperature measurements is within $\pm 25^\circ\text{C}$, and standard mean deviations are less than $\pm 25^\circ\text{C}$ (Table I).

TABLE I. Melting Points of Hypostoichiometric Uranium Dioxide

O:U Ratio	Melting Point $^\circ\text{C}$	Mean Deviation	Number of Samples
2.002	2790	± 17	3
2.001	2804	± 13	9
1.922	2792	± 9	10
1.917	2735	± 25	4
1.889	2744	± 19	3
1.878	2703	± 22	4
1.871	2716	± 28	3
1.868	2746	± 8	3
1.841	2701	± 21	6
1.823	2721	± 12	3
1.803	2681	± 8	3
1.794	2698	± 17	3
1.792	2627	± 22	8
1.780	2603	± 17	10
1.778	2664	± 25	3
1.735	2648	± 24	7
1.713	2568	± 27	7
1.686	2533	± 31	5

* The argon and 8% hydrogen-argon contained less than 1 ppm O_2 and less than 5 ppm H_2O .

DATA AND RESULTS

The melting point of hypostoichiometric UO_{2-x} decreases with decreasing O:U ratio between 2.00 and 1.67.

The melting point for stoichiometric UO_2 agrees with that (2805°C) reported by Hausner,⁽¹⁴⁾ but is lower than the 2880°C melting point reported by Latta and Fryxell.⁽¹⁵⁾ The reason for these differences is not apparent. The variation cannot be attributed solely to the different techniques since Hausner⁽¹⁴⁾ and Latta and Fryxell⁽¹⁶⁾ employed a similar thermal arrest method.

The melting point values reported here at O:U ratios less than 2.00 vary from those reported by Latta and Fryxell. Although both show a significant decrease in the melting point for UO_{2-x} , their values are higher near $\text{UO}_{2.00}$ and lower for the lower O:U ratios.

FIGURE 1. Melting Points of Hypostoichiometric Uranium Dioxide

Samples with O:U ratios substantially less than 2.00 melted at lower temperatures during the initial melting point determination than during subsequent remelting. For example, the initial melting point of a $\text{UO}_{1.71}$ sample was 2550 °C. The second and third melting points of the same sample were 2600 °C and 2660 °C, respectively. After heating near 2500 °C for approximately three minutes, the sample melted at 2790 °C. Only the initial melting point for each sample is reported.

The melting point changes resulting during melting and heating are undoubtedly caused by O:U ratio changes occurring during melting. Although a purified argon or 8% hydrogen-argon atmosphere was used during the melting point determinations, the oxygen partial pressure was still sufficiently large to increase the O:U ratio during heating.⁽³⁾

This compositional variation during the melting point determinations suggests that the actual melting points in the very low substoichiometric oxide may be lower than those reported because a small, but finite time was required to measure the melting point.

The portion of the melting point curve near stoichiometry remains uncertain. Although not shown conclusively, a maximum in the melting point curve possibly exists between $\text{UO}_{2.00}$ and $\text{UO}_{1.93}$. Compounds which dissociate at high temperatures need not exhibit a maximum melting point at the stoichiometric composition of the compound.⁽¹⁶⁾ The maximum in the liquidus curve possesses a horizontal tangent. The sharpness of the maximum gives some indication of the degree of dissociation: the sharper the maxima, the less the degree of dissociation. Since the slope of the UO_{2+x} liquidus is greater than the slope of the UO_{2-x} liquidus, the maximum, if it occurs, should occur at a hypostoichiometric composition.⁽¹⁶⁾

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