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Pressure Dependence of UO_2 Melting Measured by Double-Pulse Laser Heating[1]

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The melting point of uranium dioxide was measured as a function of isostatic pressure in an autoclave filled with helium up to 0.25 GPa. Containerless laser surface-heating was applied to measure the melting point by thermal arrest measurements during sample cooling. Precise control of the cooling rate, aimed at a precise determination of the freezing plateau, was obtained with a two-pulse method, where two Nd:YAG high power laser pulses are mixed within the same optical fiber and then focused on the sample surface. Calibration of the power of the two pulses permits the measurement of the melting point with very low uncertainty (0.5%). The measured melting slope of UO_2 is 170 and 200 $K \cdot GPa^{-1}$, a value which is markedly higher than that predicted by the Clausius–Clapeyron equation, which expresses this slope in terms of the enthalpy of fusion and the melting expansion. Possible reasons for this discrepancy are discussed.

KEY WORDS: high pressure; laser heating; melting point; spectral pyrometry; uranium oxide.

1. INTRODUCTION

The high-temperature thermodynamic properties of uranium dioxide are still a subject of investigation. The existence in the U-O phase diagram of a wide solid solution domain of the fcc structured $UO_{2\pm x}$ entails a number of questions regarding the oxygen solubility in solid and liquid and the shape of the solidus-liquidus curve, whose determination represents a very difficult experimental problem. The noncongruence of sublimation of the

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hyperstoichiometric oxide (UO_3 (g) is the dominant vapor component) makes it almost impossible to produce chemical equilibrium conditions in classical melting experiments. In this context, melting by laser heating in a high-pressure autoclave presents substantial advantages as it allows us to minimize surface vaporization effects and, by varying the buffer gas pressure, to study the behavior of the melting point in the *T*-*P* phase diagram.

The determination of the melting line in refractory compounds entails a number of experimental difficulties since conspicuous melting point variations occur only over pressure intervals of the order of several GPa, conditions under which pyrometric measurements are not viable and the melting temperature must be deduced from indirect considerations. On the other hand, at moderate pressures, where pyrometry is still usefully applicable, temperature variations of a few degrees have to be detected, which requires precise instruments in conjunction with very accurate calibration procedures. The work reported here deals with measurements in the 0.1 GPa range, where these latter problems are faced.

Results were obtained on high-pressure melting of near-stoichiometric uranium dioxide, in a range of the O/U ratio not very far from that of the congruent melting composition, which is included in the interval $1.99 < [O]/[U] < 2.00$.

The recommended value of the melting temperature of $UO_{2.00}$ at ambient pressure is $T_f = 3120 \pm 30$ K [1–3]. Its dependence on pressure was not measured until the end of the 1990s, since only recently melting point measurements could be carried out with a pyrometric precision sufficient to observe the systematic variation of T_f at moderately high pressures [1, 4]. In these experiments, the specimen was held in a small autoclave, where a laser beam was used to heat its surface to above the melting point; the laser was then switched off, letting the surface cool naturally to the freezing arrest point. The surface temperature was measured by a high-speed pyrometer. In previous work [1], the variation of the melting temperature with pressure for uranium dioxide, tungsten and graphite were compared with the values predicted by the Clausius–Clapeyron equation. While the two last studies presented a melting slope in agreement with the theoretical predictions—confirming the adequacy of the experimental method adopted—in UO_2 the measured melting slope was found to be approximately four times larger than that calculated. The reason for this discrepancy was attributed to the poor control on the cooling rate. In fact, this was apparently too rapid, and the measurements were affected by freezing undercooling phenomena. Moreover, at pressures below 0.01 GPa, slight—but in this context effective—changes in the O/U ratio in the molten layer of UO_2 could have led to lower freezing points.

In order to improve these measurements, a new method was developed, where two superimposed pulsed Nd:YAG laser beams were mixed within the same optical fiber and then focused on the sample surface. The pulse with the higher power peak was used to heat the sample above the melting point; the other one, less powerful, but of longer duration, was used to control the cooling rate on the sample surface. By enabling a much better definition of the freezing plateau, the two-pulse method permits us to obtain melting point measurements of high precision.

Furthermore, during the reported experiments it could be realized that an inert gas pressure of not less than 0.1 GPa was necessary in order to reduce the evaporation rate from the liquid to acceptable values. Thus, because of the absence of any contact between the molten pool and extraneous containment materials, invariance of the initial chemical composition during melting was much better handled here than in preceding experiments.

2. EXPERIMENTAL

2.1. Laser and Pyrometer System

Two pulsed Nd-YAG laser beams were mixed through a suitable optical system in the same fiber and then focused onto the sample surface after reflection on a YAG dichroic mirror.

The conditioning pulse basically prevented the temperature from decreasing too fast after application of the second power pulse, and allowed very good control of the extent of the freezing plateau. The pulse thermograms were measured and recorded by a high-speed (10 μs), two-channel (540 and 644 nm) pyrometer. The pyrometer output was proportional to the inverse of the brightness temperature over a sufficiently wide temperature range. Reference 5 contains a detailed description of the instrument as well as of the calibrating procedure. A Nicolet transient digitizer processed the pyrometer output signal as well as the laser pulse power profile. The brightness temperatures measured in the two channels were independently converted into real temperatures by using the measured transmissivity of the optical setup and urania emissivity. For molten and solid urania emissivities the values recommended in Ref. 2 were used.

2.2. High Pressure Vessel

The experimental setup is shown schematically in Fig. 1. The sample was mounted in the middle of a gas-filled high-pressure stainless steel vessel (maximum pressure: 0.4 GPa) with a thick sapphire window at the top. A second, thinner sapphire window was mounted 1 mm above the sample surface to reduce the convection flow in the gas. Helium was chosen as a buffer gas since it possesses the best optical properties at high pressures. A suitable gas-inlet system permitted setting the oxygen partial pressure inside the vessel up to 0.25% of the total pressure, within a precision of ~ 0.001 MPa. Alternatively, oxygen could be "rinsed off" with helium at high pressure, in order to establish a residual $p(O_2)$ of approximately 10 Pa. The highest pressure attainable with the available compressor could be varied up to 0.25 GPa. In the performed experiments, the applied pressure was not less than 10 MPa, in order to avoid vaporization effects, which, at lower pressure, were shown to markedly affect the measured melting-point slope. Note, however, that a disturbing (though smaller) evaporation from the surface was still taking place during the pulses even at higher pressures. A reduction of the oxygen losses was therefore attempted by inserting a proper oxygen partial pressure in the autoclave buffer gas. Yet, due to the nonequilibrium conditions of the system, a compensation of the slightly noncongruent vaporization of the sample could only be adjusted by empirical trials. The adequacy of these conditions did eventually represent a key issue in the interpretation of the results.

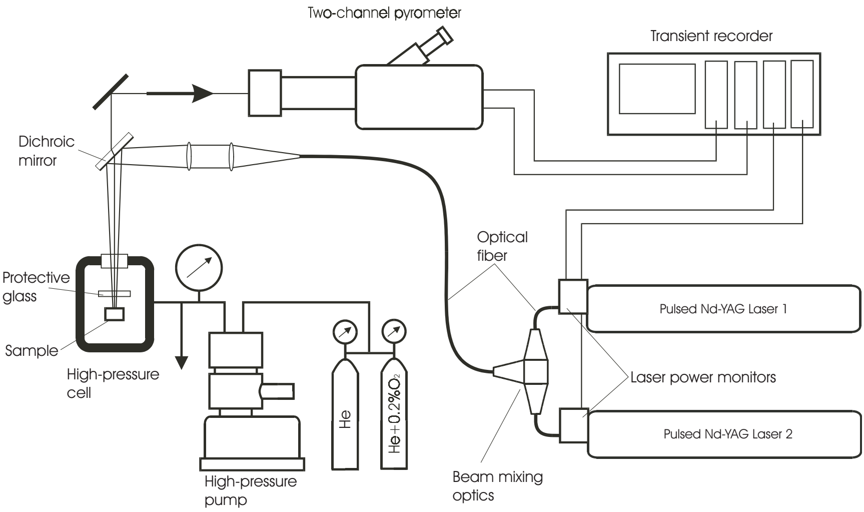

Fig. 1. Schematic of the experimental apparatus.

2.3. Samples

The samples used were nuclear grade UO_2 sintered pellets (95% of the theoretical density) manufactured by KWU-Siemens. Such pellets are cylinders of 8.3 mm in diameter, and of 12 mm in height. Each pellet was cut into three parts of approximately 4 mm in height to fit into the sample holder, and subsequently baked in an oven for 2 hours at 400°C under a flow of Ar 94%:$H_2$6% atmosphere to eliminate oil residues of the cutting process.

Thermogravimetric measurements by STA (simultaneous thermal analysis) and electro-motive force (EMF) analysis [6, 7] were performed to check the deviations from stoichiometry before and after the melting experiments. While the $[O]/[U]$ analysis of the starting material could reach a precision of better than 0.1%, that of detached samples of the refrozen layer was far less precise ($[O]/[U] = 2.000 \pm 0.005$).

Figure 2 shows two scanning electron micrographs of the sample surface after subsequent shots. In the refrozen area, the isotropic network of cracks, as well as the occurrence of columnar grain growth only in the axial direction, indicates that the liquid freezing process was homogeneous, and that no large radial temperature gradients were present in the spot. On the other hand, a steep drop of the temperature at the boundary of the

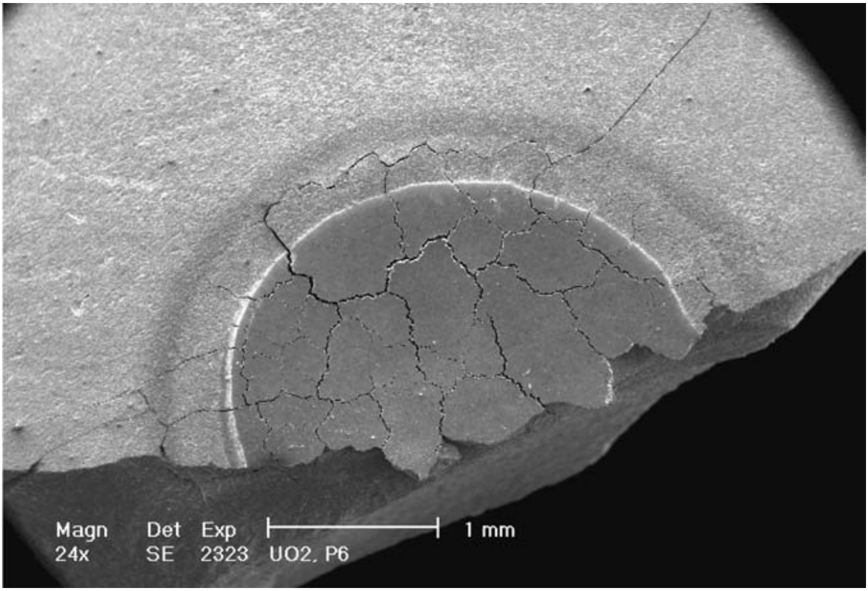

Fig. 2. SEM photograph of a UO_2 specimen after several melting/freezing experiments.

molten pool is revealed by the halos visible near the edges of the refrozen zone, indicating solid recrystallization with porosity coarsening, an effect occurring at approximately 2000 K. The power profile across the laser spot was measured to be effectively constant within a circle of 3 mm diameter.

3. RESULTS

Figure 3 shows two (one for each channel) standard thermograms, $T = T(t)$, plotted together with the power *vs.* time history of the laser beam impinging on the sample surface. The agreement of the signals of the two channels was very good. No inflection upon melting could be noticed during the heating stage. A slight slope decrease of $T(t)$ was always detected at temperatures significantly above the melting point, due to evaporation from the sample molten surface.

When the stronger power pulse was stopped, the surface cooled to the freezing thermal arrest point (visible in Fig. 3). Both the duration and intensity of the two laser pulses were adjusted to determine the prefixed maximum temperature, as well as the time duration in which the surface was maintained above the melting temperature. These parameters, along

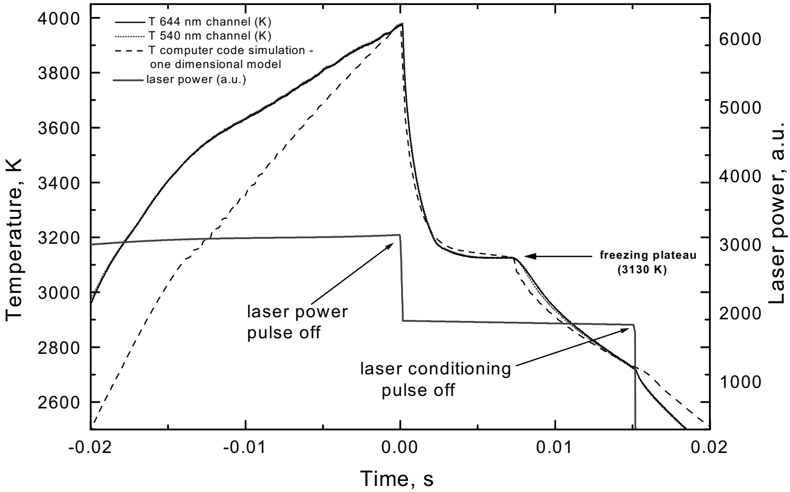

Fig. 3. Experimental thermograms (solid line for the 644 nm red pyrometer channel, dotted line for the 540 nm green pyrometer channel), comparison with the simulation (dashed line), and laser profile (solid black line).

with the buffer-gas pressure, controlled the amount of mass melted and the cooling rate, and hence the shape and extent of the freezing plateau. The curves were compared with theoretical calculations made with a one-dimensional model (see Fig. 3). This was an adequate approximation, since the power density was very homogeneous across the laser spot. The agreement with the experimental curves was satisfactory in the cooling stage down to the freezing arrest point; while in the ascending flank of the pulse, the measured temperature was always higher than predicted. Since the deposited power and the energy balance were checked with different standards of well know heat capacity, this discrepancy was likely caused by pyrometric perturbations due to gas convection or to a transitory decrease in the thermal conductance across the heated layer.

Over one hundred melting point measurements were performed at pressures from 10 MPa to 0.25 GPa. The regression line representing the freezing point variation with pressure for the 644 nm channel is shown in Fig. 4. Fitting was made on distinct sets of experiments performed at eleven different pressures. The average value measured at each pressure was taken with its standard error as the weighting factor. The fitted slope of the melting line was $S_f = 201.2\ \mathrm{K \cdot GPa^{-1}}$ (regression coefficient $=0.98$), and the extrapolated melting temperature at atmospheric pressure was 3133 K,

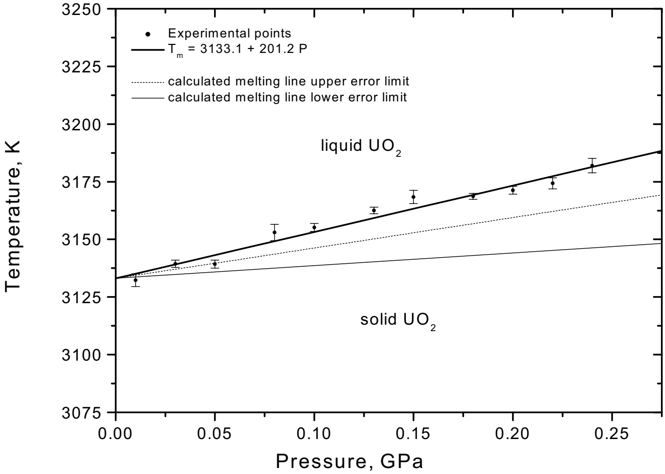

Fig. 4. Melting point dependence on pressure: pyrometer 644 nm channel average experimental melting points at each pressure with the standard error and regression line calculated with the indicated standard errors as weighting factors. The limit melting lines calculated on the basis of literature data reported in Ref. 2 are also displayed.

in agreement with the value recommended in Refs. 1–3. For the 540 nm channel the results were slightly different: $S_f = 174.2\ \mathrm{K \cdot GPa^{-1}}$ and $T_f = 3128\ \mathrm{K}$.

The samples were submitted to measurement cycling over the whole pressure range, with oxygen partial pressures varying from 10^{-5} to 0.05 MPa. The good reproducibility of the melting points (with $< 1\%$ error, due to the temperature scale definition) proved that the order-of-magnitude variation of T_f with pressure could not be ascribed to the measured changes in the O/M ratio during the pulse.

4. DISCUSSION

The measured average slope of the melting line, S_f, was first compared with that predicted by the Clausius–Clapeyron equation:

$$\left(\frac{dT_f}{dP}\right) = \frac{T_f \Delta v_f}{\Delta H_f} \tag{1}$$

In the *P*-*T* state diagram of a chemical invariant, Eq. (1) defines the slope of the line of coexistence of the solid and liquid phases under equilibrium conditions. Δv_f is the specific volume change upon melting, T_f is the melting temperature, and ΔH_f is the latent heat of fusion. In reported experiments all studies were aimed at creating conditions under which Eq. (1) could be reasonably satisfied.

Values of the pertinent thermodynamic quantities have been recently published in Refs. 2 and 3, the latest critical review papers on UO_2 thermophysical properties. The standard melting point of nominally stoichiometric $UO_{2.00}$ is $T_f = 3130 \pm 20\ \mathrm{K}$, a value very close to that obtained in our laboratory with a lower uncertainty than that given in Ref. 3. For Δv_f the value $(8.26 \pm 3.3) \times 10^{-6}\ \mathrm{m^3 \cdot kg^{-1}}$ was calculated from the density values recommended in Refs. 2 and 3. For ΔH_f, the value of $277.1 \pm 3.7\ \mathrm{kJ \cdot kg^{-1}}$ recommended in Refs. 3 and 8 was preferred to the lower value proposed in Ref. 2. The value reported in Ref. 8 is, in fact, based on enthalpy data near the melting point, rather than being extrapolated from fitting of several enthalpy and thermal capacity databases over a wider temperature range.

By substituting the chosen values in the right hand side of Eq. (1), one calculates a melting line slope of $93.3 \pm 38.4\ \mathrm{K \cdot GPa^{-1}}$. The experimental melting line slope ($174.2 < S_f < 201.2\ \mathrm{K \cdot GPa^{-1}}$) is closer to the one predicted by the Clausius–Clapeyron equation than the previous value of

$S_f = 401.2\ K \cdot GPa^{-1}$ reported in Ref. 1. Yet, the disagreement is still too large if compared with the uncertainty of the values of ΔH_f and Δv_f, whose expected variation with pressure cannot be so large to be responsible for such a change in the melting slope. It seems reasonable instead to attribute the disagreement to a possible, slight change of the O/U ratio, during the melting/freezing experiments carried out at pressures below 0.1 GPa. At pressures of up to the order of 10 MPa, a dramatic evaporation from the liquid surface was taking place, as evidenced by deposits left on the adjacent protective window. This evaporation was leading to a chemical reduction of the sample surface, and, consequently, to a lowering of the melting point. According to the liquidus/solidus data reported in Ref. 9, a deviation in the [O]/[U] ratio of 0.005 units—the present accuracy of our chemical analyses—from the value of 2.00 would result in a melting point decrease of approximately 10 K. An error of this order of magnitude on the average melting temperatures measured at pressures lower than 0.1 GPa can explain the disagreement of the measured S_f slope with the expected value of dT_f/dP. On the other hand, lower deviations from stoichiometry cannot be kept under control, and are below the detection limit of the presently available analysis. More sensitive chemical analysis of refrozen specimens (EMF measurements can reach a precision in the [O]/[U] ratio of better than 1×10^{-3} units) will make it possible to apply first-order corrections to the measured melting point. However, inspection of the variation of the calculated melting slope by fitting subsets of points measured above increasingly higher pressures, in spite of a larger uncertainty, reveal a continuous decrease of S_f. Additional measurements will be therefore carried out up to pressures of 0.4 MPa in order to reduce further the perturbing variations of the sample stoichiometry.

5. SUMMARY

A two-pulse laser method was applied to high-pressure melting measurements in stoichiometric uranium dioxide. The measured melting slope (dT_f/dP) was higher than that calculated with the Clausius–Clapeyron equation, although the extrapolated melting temperature at atmospheric pressure was within the uncertainty interval of the recommended value. Further analyses aimed at determining the O/U ratio in the low-pressure molten samples are planned, in conjunction with measurements at higher pressures. These will lead to a better understanding of the results and, eventually, to applications to the more problematic hyperstoichiometric uranium oxides. Finally, the main objective of this investigation, i.e., to supplement the missing thermodynamic data of the UO_{2+x} liquidus/solidus parameters with melting measurements at high pressure, appears to be achievable.

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