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Experimental and Numerical Optimization of the U-Zr-C Ternary Phase Diagram

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Abstract

The U-Zr-C ternary phase diagram is optimized using melting point and vapor pressure data recently measured at Los Alamos National Laboratory and by graphical and numerical curve fitting of self-consistent thermodynamic and phase diagram data reported in the literature. The system is described from 2473 K to 3693 K using isothermal ternary phase diagrams. The solidus and liquidus curves of the $U_xZr_{1-x}C_y$ solid solution were estimated from combined thermodynamic and adjusted phase diagram data. From the solidus and liquidus curves for the solid solution, the reversible heat transferred from the solid to the liquid phase for UC and ZrC were calculated to be 150 and 324 kJ/mol, respectively; and the maximum in the excess free energy for mixing was determined to be on the order of 1100 J/mol at 56% ZrC.

I. Introduction

The uranium-zirconium-carbon (U-Zr-C) system is of importance due to the potential application of $(U_yZr_{1-y})C_x$ solid solutions or $(U_yZr_{1-y})C_x + C$ composite materials in nuclear thermal propulsion. In particular, these may be materials of choice for the manned mission to Mars.¹ Some advanced nuclear rocket design concepts assume fuel operating temperatures in excess of 2800 K. The $(U_yZr_{1-y})C_x$ and $(U_yZr_{1-y})C_x + C$ systems are attractive for such applications because of their excellent nuclear properties and thermal stability. Although vaporization or corrosion behavior of nuclear fuels may be the most important life-limiting factor during nuclear thermal reactor operation, melting behavior is an important reactor design criteria.

Numerous investigators have experimentally determined portions of the binary and ternary phase diagrams in the system U-Zr-C. Unfortunately a great many of the studies are in disagreement and no effort has been made to optimize the ternary diagram. The general lack of agreement and inconsistencies between laboratories appears to be due in part to deficiencies in materials characterization and in part to the difficulties associated with measuring these very high temperatures.

This communication attempts to resolve the U-Zr-C ternary phase diagram, in isothermal sections, using recent experimental melting point and vapor pressure data measured in our laboratories combined with the most self-consistent phase diagram and thermodynamic data in the literature.²⁻²⁵ The presentation (and final paper) will provide practical details for understanding the U-Zr-C phase diagram and how we should use it for nuclear thermal propulsion system designs.

II. Experimental Procedures*

Specimens of UC_x , $U_xZr_{1-x}C_y$, $U_xZr_{1-x}C_y + C$, $U_xZr_{1-x}C_y + UC_{2-n}$, and $U_xZr_{1-x}C_y + C + UC_2$, were prepared and melted inductively. The temperatures at melting were

* Note to reviewers: further details on the experimental procedures and a full account of our experimental results will be presented in the final paper. The optimized diagrams shown in the final paper may also be slightly changed depending on the results of new measurements made prior to our final submission.

determined by sighting in on a black body cavity. Selected specimens were also heated to $\approx 1800^\circ\text{C}$ and vapor pressures were measured using mass spectroscopy.

III. Methods of Modelling and Graphical Projections

The U-Zr-C isothermal phase diagrams were developed using a combination of thermodynamic data and self-consistent phase diagram data. Using enthalpies of fusion and optimal curve fitting routines, mathematical equations were formulated to describe the various composition versus temperature relations representing the phase boundaries in the system. Appendix A describes the thermodynamic basis for the curve fitting routines for the binary compounds. Equations describing the binary systems Zr-C and U-C were first developed in order to establish the boundary conditions for the ternary system.

The pseudobinary phase diagram ZrC-UC₂ has been well developed^{2,4,7} and was used to define the ternary eutectic and the boundaries of the three-phase regions on the carbon-rich side of the phase diagram. Table 1 describes the various temperatures and compositions which were used as boundary conditions. During multiple linear regression routines, the mathematical expressions were forced through the data that are shown in table 1. Table 2 describes the values for the enthalpies of fusion which were used in determining the shape of solidus and liquidus curves. The data for the pure metals and UC₂ were not used in the curve fitting but are shown for comparison.

The 1973 K data of Nickel *et al.*²¹ were used to describe the shape of the carbon-poor side of the (U_yZr_{1-y})C_x solidus line as it is projected into the ternary coordinate system. The representative equation is shown in appendix B (equation B.10). The shape of the carbon-poor side of the (U_yZr_{1-y})C_x solidus line was estimated at higher temperatures by forcing the curve through the carbon-poor solidus lines for UC and ZrC, while maintaining the general shape of the curve described by equation B.10.

There is a limited amount of data which describes the solidus and liquidus curves of the (U_yZr_{1-y})C_x solid solution. From lattice parameter measurements, it is known that UC and ZrC form a nearly ideal solution.⁴ The data of Tosdale¹⁷ and Brownlee¹⁶ appear to describe the general shape of the solidus and liquidus curves, respectively. However, their data for the end members UC and ZrC, in particular, are inconsistent with values reported in the literature. In order to get a best estimate of the shape of these curves, it was assumed that the temperature measurements of Tosdale and Brownlee were subject to systematic errors which were a linear function of temperature. It was also assumed that the specimens which they studied had compositions along a straight line between UC_{1.00} and ZrC_{0.81}, which correspond to our estimates of the compositions at the maximum congruent melting points of the binary systems. Figure 1 shows the adjusted data of Tosdale and Brownlee based on these assumptions. The adjusted curves shown in figure 1 appear to be reasonable estimates of what is expected for the near-ideal solution behavior of UC-ZrC. The equations which describe these curves are presented in appendix B. Using relationships described by Wagner²⁷ and the curves for the (U_yZr_{1-y})C_x liquidus and solidus (equations B.8 and B.9), the slopes were calculated near the end points using the equations:

$$\frac{dT}{dx_L} = - \frac{(x_L - x_S)T}{(1-x_S)\Psi_{UC} + x_S\Psi_{ZrC}} \cdot \frac{\partial^2 \Delta G_L}{\partial^2 x_L} \quad (1)$$

and

$$\frac{dT}{dx_S} = - \frac{(x_L - x_S)T}{(1-x_L)\Psi_{UC} + x_L\Psi_{ZrC}} \cdot \frac{\partial^2 \Delta G_S}{\partial^2 x_S} \quad (2)$$

where G_L and G_S are the molar free energies for the liquid and solid phases, respectively, and the terms Ψ_{UC} and Ψ_{ZrC} represent heat supplied to the system from the reversible transfer of one mole of UC and ZrC, respectively, from the solid to the liquid phase. The molar free energy of formation can be related to the excess molar free energy of formation, G^{Ex} , through the following equation:

$$\frac{\partial^2 \Delta G}{\partial^2 x} = \frac{RT}{x(1-x)} + \frac{\partial^2 G^{Ex}}{\partial^2 x} \quad (3)$$

Substituting equation 3 appropriately into equations 1 and 2 and rearranging we obtain the following equations (for $x_L^{ZrC} < x_S^{ZrC} < 1$) which represent the liquidus and solidus curves, respectively:**

$$\Psi_{UC} \approx 3.932RT^2 \cdot \frac{dx_L^{ZrC}}{dT} \quad (4)$$

and

$$\Psi_{UC} \approx 0.7977RT^2 \cdot \frac{dx_S^{ZrC}}{dT} \quad (5)$$

Similarly, (for $x_L^{UC} < x_S^{UC} < 1$) we obtain the following equations which represent the liquidus and solidus curves, respectively:†

$$\Psi_{ZrC} \approx 7.313RT^2 \cdot \frac{dx_L^{ZrC}}{dT} \quad (6)$$

and

$$\Psi_{ZrC} \approx 0.8797RT^2 \cdot \frac{dx_S^{ZrC}}{dT} \quad (7)$$

From equations (4) through (6) we get two independent estimates each of Ψ_{UC} and Ψ_{ZrC} . In the case of equations (4) and (5), Ψ_{UC} was determined to be 149 and 151 kJ/mol, respectively, at $x_S^{ZrC} = 0$ and $T = 2798$ K. In the case of equations (6) and (7), Ψ_{ZrC} was determined to be 333 and 314 kJ/mol, respectively, at $x_S^{ZrC} = 1$ and $T = 3693$ K. These calculations suggest that the adjusted solidus temperature data of Tosdale and liquidus temperature data of Brownlee are self-consistent. Through graphical integration of equations (2) and (3), the excess free energy for the solid solution, G_{SS}^{Ex} , was found to go through a maximum at $x_S^{ZrC} = 0.56$ and may be expressed as follows:

$$G_{SS}^{Ex} = 0.045RT \quad (8)$$

** From the ratio of the slopes of the data shown in figure 1 (equations B.8 and B.9) it was determined that $x_S^{ZrC} = 4.943x_L^{ZrC}$ at $x_S^{ZrC} = 0$. Thus, this substitution has been made in (4) and (5) in order to avoid otherwise indeterminate equations.

† From the ratio of the slopes of the data shown in figure 1 (equations B.8 and B.9) it was determined that $(1 - x_S^{ZrC}) = 0.1203(1 - x_L^{ZrC})$ at $x_S^{ZrC} = 1$. Thus, this substitution has been made in (6) and (7) in order to avoid otherwise indeterminate equations.

Therefore, at 3000K, G_{SS}^{Ex} equals 1120 J/mol, which is a reasonable value for a material which exhibits near-ideal solution behavior.

IV. The U-Zr-C Ternary Phase Diagram

The mathematical expressions which were derived to define the various phase boundaries in the U-Zr-C system are shown in appendix B. Figures 2 through 6 show the optimized ternary phase diagrams from 2473 to 3693 K. At 2473 K (figure 2) four phases exist: liquid (L), carbon (C), uranium dicarbide (UC_2), and $(U_yZr_{1-y})C_x$ solid solution (SS). The carbon-rich portion of the diagram consists of three two-phase regions and a three-phase region of C, UC_2 , and $(U_yZr_{1-y})C_x$. In accordance with Gibb's phase rule, the boundaries of the three-phase region must be straight lines in an isothermal ternary coordinate system since there are only three degrees of freedom. The lines extend from carbon and the β - $UC_2 + C$ eutectic to a point along the $(U_yZr_{1-y})C_x$ solid solution; this point corresponds to the $C + UC_2 + (U_yZr_{1-y})C_x$ solvus line as defined by the ZrC- UC_2 pseudo-binary diagram.^{2,4,7}

Liquid begins to form on the carbon-rich side of the diagram at 2673 K, which is the temperature corresponding to the minimum congruent melting point of the UC- UC_2 solid solution. As the temperature is increased to 2753 K (figure 3) which is the congruent melting point of $UC_{1.88}$, a significant amount of liquid phase extends into the carbon-rich portion of the diagram. There is a particularly important two-phase region consisting of C and $(U_yZr_{1-y})C_x$ extending from pure carbon to a point along the $(U_yZr_{1-y})C_x$ solid solution; this point corresponds to the $L + C + (U_yZr_{1-y})C_x$ solidus line as defined by the ZrC- UC_2 pseudo-binary diagram. As the temperature is increased further to 2873 K (figure 4) the only liquid-free regions remaining are the $(U_yZr_{1-y})C_x$ solid solution and the $C + (U_yZr_{1-y})C_x$ two-phase region, which has narrowed considerably. At 3273 K (figure 5) the only liquid-free region remaining is the $(U_yZr_{1-y})C_x$ solid solution. And at 3693 K (figure 6) ZrC₈₁ melts congruently and liquid therefore covers the entire ternary diagram.

V. Conclusions

The U-Zr-C ternary phase diagram was described in isothermal sections from 2473 to 3693 K. This system is of particular importance due to its potential application in nuclear thermal propulsion. At temperatures which are more useful in a reactor (>2800 K), there are two regions in the phase diagram which are free of liquid and potentially suitable fuel choices, i.e., the single phase $(U_yZr_{1-y})C_x$ solid solution region and the two phase region of carbon plus solid solution. As the temperature is increased, the $C + SS$ region narrows and the single phase SS region retreats toward the composition ZrC₈₁. Therefore, higher operating temperatures necessarily demand lower uranium concentrations. The potential use temperature of a $(U_yZr_{1-y})C_x$ single phase material is significantly greater than that of the two phase material.

Appendix A

Curve fitting of the solidus and liquidus
phase boundaries for the binary compounds

In optimizing the solidus and liquidus curves of the U-C and Zr-C binary phase diagrams it was found that a model proposed by Wagner,²⁷ which approximates the phase boundaries in the vicinity of the maxima and minima as parabolae with a common horizontal tangent, gave excellent fit for the binary compounds. In fitting the solidus and liquidus curves for the binary compounds, the following curve fitting parameters were defined:

$$\tau = T - T^* \quad (\text{A.1})$$

$$\xi = x_C^L - x^* \quad (\text{A.2})$$

$$\eta = x_C^S - x^* \quad (\text{A.3})$$

$$\alpha = \frac{\xi^2}{T} = \frac{2\Delta H_{\text{fus}}}{T^*} \cdot \frac{\Delta G_S''}{\Delta G_L'' - \Delta G_S''} \quad (\text{A.4})$$

$$\beta = \frac{\eta^2}{T} = \frac{2\Delta H_{\text{fus}}}{T^*} \cdot \frac{\Delta G_L''}{\Delta G_L'' - \Delta G_S''} \quad (\text{A.5})$$

where x^* is the mole fraction of carbon at the melting point T^* , x_C is the mole fraction of carbon at the temperature of interest, T , the superscripts L and S represent liquidus and solidus respectively, the subscripts L and S represent liquid and solid respectively, ΔH_{fus} is the heat of fusion (see table 2), and $\Delta G''$ is the second derivative of the free energy of formation versus composition equation:

$$\Delta G'' = \frac{\partial^2 \Delta G_f}{\partial^2 x_C} \quad (\text{A.6})$$

Note that the terms α and β in equations A.4 and A.5 represent curve fitting parameters for the liquidus and solidus curves, respectively. The shapes of the solidus and liquidus curves are obtained by fitting experimental data to the respective polynomial equations, as follows:

$$x_C = x^* \pm \sqrt{|\beta\tau|} \left[1 + A|\tau| + B|\tau|^2 + C|\tau|^3 + \dots \right]^{1/2} \quad (\text{A.7})$$

or

$$x_C = x^* \pm \sqrt{|\alpha\tau|} \left[1 + A|\tau| + B|\tau|^2 + C|\tau|^3 + \dots \right]^{1/2} \quad (\text{A.8})$$

where the coefficients A, B, C... are curve fitting coefficients. The coefficients may be different on either side of the liquidus or solidus curves, i.e., the $\pm$ symbols do not imply the liquidus and solidus curves are symmetrical about x^* .

In the case of ZrC, for example, ΔG_f was calculated using the activity functions of Storms²⁸ and the following relationship:

$$\Delta G_f(\text{ZrC}) = RT[(1 - x_C)\ln a_{\text{Zr}} + x_C \ln a_{\text{C}}] \quad (\text{A.9})$$

By fitting equation A.9 to a fourth-order polynomial equation at $T = 3693$ K, and taking the second derivative we obtain:

$$\Delta G_S'' = \frac{\partial^2 \Delta G_f}{\partial^2 x_C} = 5.0509 \cdot 10^7 - 2.4654 \cdot 10^8 x_C + 3.1109 \cdot 10^8 x_C^2 \quad [\text{J/mol}] \quad (\text{A.10})$$

Zirconium carbide melts congruently at $T^* = 3693$ K at the composition $x^* = 0.4475$. From equation A.10, $\Delta G_S'' = 2480$ kJ/mol for $\text{Zr}_{.5525}\text{C}_{.4475}$. And the estimated molar enthalpy of formation is 43.9 kJ/mol. The dimensionless coefficient β was determined to

be $-1.733 \cdot 10^{-5}$ from the intercept of the fitted regression function of η^2/τ versus τ using phase diagram data. Knowing the parameters described above, α and $\Delta G_L''$ were determined by rearranging equations A.4 and A.5 to the following forms:

$$\alpha = \beta \left[1 - \frac{2\Delta H_{fus}}{\beta T^* \Delta G_S''} \right]^2 = -4.036 \cdot 10^{-5} \text{ at } T^* \quad (\text{A.11})$$

and

$$\Delta G_L'' = \frac{\Delta G_S''}{1 - \frac{2\Delta H_{fus}}{\beta T^* \Delta G_S''}} = 1626 \text{ kJ/mol at } T^* \quad (\text{A.12})$$

The curve fitting routines of α and β versus τ were used to estimate the shape of the liquidus and solidus curves respectively, the results of which are summarized in appendix B.

In the U-C system there was not adequate free energy versus composition relationships or data to accurately estimate $\Delta G_S''$ or $\Delta G_L''$ at the melting point. However, extrapolation of the solidus and liquidus phase diagram data gave estimates of α and β of $-2.531 \cdot 10^{-5}$ and $-4.619 \cdot 10^{-6}$, respectively. Therefore, given α , β , ΔH_{fus} , and T^* , $\Delta G_S''$ and $\Delta G_L''$ were estimated from the following relationships:

$$\Delta G_L'' = \left| \frac{2\Delta H_{fus}}{T^*(\sqrt{\alpha\beta} - |\alpha|)} \right| \quad (\text{A.13})$$

and

$$\Delta G_S'' = \left| \frac{2\Delta H_{fus}}{T^*(|\beta| - \sqrt{\alpha\beta})} \right| \quad (\text{A.14})$$

For $U_{0.5}C_{0.5}$, $\Delta G_L''$ and $\Delta G_S''$ were estimated to be 1634 and 3687 kJ/mol, respectively. The results of curve fitting routines to give the shape of the liquidus and solidus curves are summarized in appendix B.

Appendix B

Optimized mathematical descriptions of the phase boundaries in the systems U-C, Zr-C, and U-Zr-C used in generating the isothermal ternary phase diagrams.

Zr_{1-x}C_x solidus phase boundaries §

$$x_C = 0.4475 + \sqrt{\Delta} [1.733 \cdot 10^{-5} - 1.719 \cdot 10^{-7}\Delta + 9.251 \cdot 10^{-10}\Delta^2 - 2.728 \cdot 10^{-12}\Delta^3 + 3.649 \cdot 10^{-15}\Delta^4 - 1.873 \cdot 10^{-18}\Delta^5]^{1/2} \quad (\text{B.1})$$

$$x_C = 0.4475 - \sqrt{\Delta} [1.734 \cdot 10^{-5} - 4.056 \cdot 10^{-8}\Delta + 8.232 \cdot 10^{-11}\Delta^2 - 9.057 \cdot 10^{-14}\Delta^3 + 4.763 \cdot 10^{-17}\Delta^4 - 9.541 \cdot 10^{-21}\Delta^5]^{1/2} \quad (\text{B.2})$$

§ See appendix A for a discussion of the methods used for calculating these phase boundaries.

Zr_{1-x}C_x liquidus phase boundaries §

$$x_C = 0.4475 - \sqrt{\Delta} [3.888 \cdot 10^{-5} - 1.700 \cdot 10^{-7} \Delta + 7.868 \cdot 10^{-10} \Delta^2 - 1.065 \cdot 10^{-12} \Delta^3 + 6.530 \cdot 10^{-16} \Delta^4 - 1.502 \cdot 10^{-19} \Delta^5]^{1/2} \quad (B.3)$$

$$x_C = 0.4475 + \sqrt{\Delta} [4.036 \cdot 10^{-5} + 5.432 \cdot 10^{-8} \Delta] \quad (B.4)$$

U_{1-x}C_x solidus phase boundary for x_C < 0.5 §

$$x_C = 0.5 - \sqrt{\Delta} [4.620 \cdot 10^{-6} - 2.724 \cdot 10^{-9} \Delta - 2.063 \cdot 10^{-11} \Delta^2 + 3.740 \cdot 10^{-14} \Delta^3 - 2.4042 \cdot 10^{-17} \Delta^4 + 5.460 \cdot 10^{-21} \Delta^5]^{1/2} \quad (B.5)$$

U_{1-x}C_x liquidus phase boundary for x_C < 0.5 §

$$x_C = 0.5 - \sqrt{\Delta} [2.531 \cdot 10^{-5} + 1.458 \cdot 10^{-7} \Delta + 5.215 \cdot 10^{-11} \Delta^2 - 4.870 \cdot 10^{-4} \Delta^3 + 2.996 \cdot 10^{-8} \Delta^4 - 6.477 \cdot 10^{-21} \Delta^5]^{1/2} \quad (B.6)$$

Zr_{1-x}C_x/Zr_{1-x}C_x + C phase boundary (after Storms ²⁷)

$$x_C = 0.50052 + 1.8208 \cdot 10^{-6} T - 1.3603 \cdot 10^{-9} T^2 \quad (B.7)$$

(UC_{1.00})_{1-x}(ZrC_{.81})_x solid solution solidus phase boundary †

$$x_{ZrC_{.81}} = 4.7161 \cdot 10^4 T^{-1} - 4.014 \cdot 10^8 T^{-2} + 1.313 \cdot 10^{12} T^{-3} - 1.564 \cdot 10^{15} T^{-4} \quad (B.8)$$

(UC_{1.00})_{1-x}(ZrC_{.81})_x solid solution liquidus phase boundary †

$$x_{ZrC_{.81}} = 1.0975 \cdot 10^6 T^{-1} - 1.2259 \cdot 10^{10} T^{-2} + 5.1144 \cdot 10^{13} T^{-3} - 9.429 \cdot 10^{16} T^{-4} + 6.464 \cdot 10^{19} T^{-5} \quad (B.9)$$

Minimum (U_yZr_{1-y})C_x carbon concentration at the 1973 K solidus †

$$x_C = 0.3655 - 107.43X + 49.395X^2 - 22.811X^3 + 5.8078 X^4 + 108.427 \ln(1+X) \quad (B.10)$$

In equations B.1 through B.8, Δ is equal to (T*-T), where T* is the maximum congruent melting point, T is the temperature in degrees Kelvin, x or y represent mole fraction, and X is the mole fraction of uranium on a metal basis.

† See text for a discussion of the assumptions used in estimating these phase boundaries.

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Table 1. Temperatures and corresponding compositions used in generating the isothermal phase diagrams.

<u>Description</u>	<u>Composition</u>	<u>Temperature, K</u>
ZrC maximum congruent melting point	ZrC _{0.81}	3693
ZrC+C eutectic	ZrC _{1.86}	3123
β -Zr+ZrC eutectic	ZrC _{0.03}	2093
UC maximum congruent melting point	UC _{1.00}	2798
β -UC ₂ maximum congruent melting point	UC _{1.88}	2753
UC-UC ₂ solid solution minimum congruent melting point	UC _{1.53}	2673
β -UC ₂ + C eutectic	UC _{1.93}	2723
γ -U + UC eutectic	UC _{0.01}	1390
β -UC ₂ + C + (U _y Zr _{1-y})C _x solid solution ternary eutectic	U _{0.79} Zr _{0.21} C _{1.94}	2683
C solid-liquid-vapor triple point	C _{1.00}	4130

Table 2. Estimated Heats of Fusion in the U-Zr-C System.

Compound	ΔH_{fus} (kJ/mol)
ZrC	79.5
UC	59.8
UC ₂	113
C	34.4
β -Zr	20.9
γ -U	12.6

Figure 1. Adjusted solidus and liquidus temperature data for the $(U_yZr_{1-y})C_x$ solid solution.

Figure 2. Isothermal ternary phase diagram of the system U-Zr-C at 2473K.

Figure 3. Isothermal ternary phase diagram of the system U-Zr-C at 2753K.

Figure 4. Isothermal ternary phase diagram of the system U-Zr-C at 2873K.

Figure 5. Isothermal ternary phase diagram of the system U-Zr-C at 3273K.

Figure 6. Isothermal ternary phase diagram of the system U-Zr-C at 3693K.