An Analytical Representation of the Thermal Conductivity and Electrical Resistivity of $UC_{1\pm x}$, PuC_{1-x} , and $(U_yPu_{1-y})C_{1\pm x}$

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ABSTRACT

This report uses selected measurements from the literature to construct analytical expressions that describe the electrical and thermal conductivity of pure, high-density $UC_{1\pm x}$, PuC_{1-x} , and $(U_yPu_{1-y})C_{1\pm x}$ as a function of x , y , and temperature. The approach shows that many of the differences between the reported measurements can be resolved if the carbon content of the single-phase material is taken into account. Analytical expressions are also given that describe the temperature variation of the phase boundaries for these phases.

I. INTRODUCTION

Past studies of the actinide carbides have demonstrated that the thermal conductivity is a sensitive function of the purity (oxygen, nitrogen, and nickel being the principal elements of concern); the porosity, for which the shape of the pores is important; the presence of a second phase, which might be the metal, the dicarbide, or the sesquicarbide; and the temperature. Less attention has been given to the effect of changing the carbon content of the cubic lattice. This review will concentrate on the influence of the carbon concentration and demonstrate that the behavior of both binary systems as well as the ternary alloy is related through this variable. Indeed, many of the differences found in the literature can be resolved if the changing carbon concentration is taken into account. This is particularly important to an understanding of the UC phase.

Uranium carbide has a very narrow single-phase region at low temperatures, as shown in Fig. 1. Thus, almost all thermal conductivity studies of this phase have used material that was two phase at low temperatures and that became single phase at some higher temperature. Consequently, temperature affected the conductivity directly, as well as indirectly, by causing a change in the carbon concentration as the phase followed the phase boundary. In addition, this composition change is not necessarily a smooth function of temperature but depends on how effectively the two phases maintain equilibrium. Thus, depending on the thermal history, the conductivity values may show some hysteresis. Each of these effects has been observed occasionally in the reported measurements.

This report describes an attempt to fit many of the reported measurements of thermal and electrical conductivity, through the Lorentz equation, with a single expression that describes these properties as a function of composition and temperature. The Lorentz constant [$2.4 \times 10^{-8} (V/K)^2 = L_0$] is assumed to be independent of composition and temperature. The phonon contribution was made inversely proportional

to the square of the carbon atom vacancy concentration as was found from studies of the NbC and ZrC systems.^{1,2} In addition, temperature-induced vacancies, calculated from the behavior of the heat capacity, also were taken into account.

Only values obtained from high-density, high-purity samples for which the carbon concentration was reported were used in this review. Even these data would have been more useful had they been published in tabular form. Conductivity values, which were based on diffusivity measurements, were recalculated using the latest heat capacity³ and density information.⁴ When this correction was not possible, the data were ignored. Consequently, we did not analyze in detail all the data that have been published. For this the reader is referred to the excellent review by Lewis and Kerrisk.⁵

II. PHASE BOUNDARIES

To understand how the temperature affects a two-phase mixture containing mostly the cubic phase, one must know the phase boundary behavior of the cubic phase. Figure 1 shows the chosen shape of the single-phase fields of UC and PuC as a function of temperature, based on published information. These boundaries can be described by the following equations, where $X = C/M$ (M represents U or Pu) and T is the temperature (in kelvins):

$$UC + U_{(1)}: 1 - 0.1/\{\exp[9 \times 10^{-3}(1980 - T)] + 1\} + 2 \times 10^{-6}T = X_{(UC-U)} \quad (1)$$

$$UC + UC_2: 1 + 1/\exp[6 \times 10^{-3}(2525 - T)] = X_{(UC-UC_2)} \quad (2)$$

$$PuC + Pu_{(1)}: 0.61 + 0.259\{1 - 1/\exp[5.2 \times 10^{-3} \text{abs}(T - 907)]\} = X_{(PuC-Pu)} \quad (3)$$

$$PuC + Pu_2C_3: 0.96 - 5 \times 10^{-5}T = X_{(PuC-Pu_2C_3)} \quad (4)$$

Complete phase diagrams for the binary systems are given in Figs. 2 and 3.

Although the general behavior of the ternary system is known, the exact boundaries remain to be determined. Using the limited published information, we propose that the boundaries can be described by the following equations, where Y is the atom fraction plutonium in the (U,Pu)C phase and X is the C/M ratio in the binary and ternary systems:

$$MC + \text{metal}: Y^2X_{(PuC-Pu)} + (1 - Y^2)X_{(UC-U)} = X_{(PuUC-metal)} \quad (5)$$

$$MC + M_2C_3: Y^2X_{(PuC-Pu_2C_3)} + (1 - Y^2)X_{(UC-UC_2)} = X_{(PuUC-M_2C_3)} \quad (6)$$

Figures 4 and 5 show the consequences of these equations at 1000 K and 1873 K, respectively. Fortunately, the thermal conductivity behavior of the ternary compound and PuC is not very sensitive to their phase boundary composition. The same cannot be said for UC.

III. ELECTRICAL RESISTIVITY

We assume that the Lorentz equation ($\lambda_e = L_0T/\rho$, where ρ is the resistivity) applies to these compounds at all compositions and temperatures. However, PuC presents a problem that will be discussed shortly.

At room temperature, quenched UC has a resistivity minimum at UC_{1.0}.⁶ To connect these limited data to a composition in the PuC phase, we drew a smooth curve, as shown in Fig. 6, which would give a calculated thermal conductivity at MC_{0.9} that would agree with values measured for PuC.⁵ Next, a

temperature coefficient was introduced at $MC_{0.9}$ that agreed with thermal conductivity measurements for PuC^7 at low temperature and that was small at high temperature. In addition, a temperature coefficient was used at $MC_{1.0}$ that agreed with resistivity measurements for UC^6 . Based on this approach, the resistivity of UC and PuC is described by the following equation, where $X = C/M$:

$$151.6 - 70 \exp[-400(1 - X)^2] + 0.12(T - 300)/\{\exp[50(0.97 - X)] + 1\} \\ - 70/[\exp(0.0015T)] - 5 \times 10^{-8}(X - 0.9)(T - 300)^3 = \rho \text{ (}\mu\Omega \cdot \text{cm)} \quad (7)$$

The results from this equation are compared with some published information in Fig. 7.^{8,9} The dashed upward turn in resistivity above 1500 K describes the expected behavior of $UC_{1.11}(UC + U_2C_3)$ as the material dissolves carbon upon heating. We propose that the values reported by Grossman⁸ which are above the other measurements in this region are influenced by this effect. The proposed resistivity of hypothetical $MC_{0.9}$ is considerably lower than the measured behavior of $PuC_{0.9}$. This difference suggests that either the measured resistivity of PuC is much too large or the theoretical Lorentz constant does not apply to this phase. It is tempting to suggest that the radioactive decay of plutonium introduces sufficient defects in the lattice of PuC to abnormally increase its resistivity. This discrepancy, however, does not materially affect the approach taken in this review.

IV. THERMAL CONDUCTIVITY

A. Uranium Carbide

The work on UC falls into two categories. Samples have been either hypostoichiometric and contained uranium at room temperature, or they have been hyperstoichiometric and contained either UC_2 or U_2C_3 , depending on the heating history. Because most of the information has been obtained for hyperstoichiometric UC , the following analysis will be based mainly on this material using the data shown in Fig. 8.¹⁰⁻¹⁶

There are two regions—one at low temperatures (below 1100 K), and one at high temperatures (above 1500 K)—which we will discuss separately. At low temperatures and near the stoichiometric composition, heat is carried by phonons in addition to electrons. Consequently, we added an arbitrary phonon contribution to the electron conduction in order to fit the data in this region. Unfortunately, at low temperatures there is no assurance that the UC phase is in equilibrium at its phase boundary, with the result that the measured thermal conductivity values may represent a quenched-in composition that contains a nonequilibrium concentration of carbon atoms. In addition, the effect of a possible oxygen impurity is most pronounced in this temperature region. Thus, our proposed thermal conductivity in this region should be considered a lower limit. In addition, there may be some direct effects produced by the small amount of UC_2 or U_2C_3 present. We assume that a small, temperature-independent vacancy concentration remains at room temperature to prevent the equations from approaching infinity at low temperatures. We propose that the phonon contribution can be described by

$$8 \times 10^{-4}/\{T[1.154 \times 10^3 \exp(-18365/T) + (1 - X) + 6 \times 10^{-8}]\}^2 = C_p \text{ (W/m} \cdot \text{K)} \quad (8)$$

This equation includes the concentrations of thermally induced vacancies and chemical vacancies $(1 - X)$ as well as a small constant term. Based on the behavior of ZrC ,^{1,2} we assume the effect is inversely proportional to the temperature and the vacancy concentration squared. At high temperatures, the thermal conductivity of UC is described solely by the electrical resistivity combined with the Lorentz equation as follows:

$$2.4T/\rho = C_E \text{ (W/m} \cdot \text{K)} \quad (9)$$

The solid line in Fig. 8 describes the total conduction for $UC_{1.0}$, whereas the dotted line gives only the electron component. When the two-phase mixture ($UC + UC_2$) is examined at high temperatures, the composition can change with temperature as carbon is incorporated into the lattice as C_2 groups. According to the data of Wheeler,¹⁰ this additional carbon causes the thermal conductivity to decrease. The dashed line shows the proposed behavior of $UC_{1.08}$. The failure of the data from the $UC_{1.08}$ sample studied by Wheeler to follow this line possibly is caused by a failure of the sample to stay in equilibrium with the phase boundary composition.

When UC is mixed with free uranium, the UC phase can contain a small equilibrium concentration of carbon vacancies at low temperatures which cause a lowering of the thermal conductivity. As the temperature is increased, the equilibrium carbon vacancy concentration increases to produce an increasingly lower stoichiometry, as shown in Fig. 1. The rate of this change peaks near 1900 K. Using a sample of $UC_{0.96}$, Wheeler observed an abrupt increase in thermal conductivity near this temperature which, after repeated thermal cycling, gave the S-shaped curve labeled (1) in Fig. 9.^{17,18} We propose that the increase in thermal conductivity above 1900 K was caused by the changing position of the UC phase as excess uranium dissolved. Thus, at high temperatures, carbon atom vacancies appear to have an effect that is the reverse of their effect at low temperatures. This behavior was used to define the equation that describes the electrical resistivity in this region. If Eqs. (7) and (9) are solved using the temperature variation of the phase boundary composition [Eq. (1)], the resulting thermal conductivity is given by the solid line in Fig. 9. A dashed line shows the behavior of $UC_{0.96}$, which would become single phase above 1900 K. Because the sample studied by Wheeler¹⁰ was found to have lost uranium preferentially, owing to surface vaporization, the somewhat lower reported values are understandable.

The overall effect of temperature and composition is shown three dimensionally in Fig. 10. The region above the dashed line is the phonon contribution. Finally, Fig. 11 summarizes the thermal conductivity variation within the single-phase region at various high temperatures. The line labeled MELTING POINT describes the thermal conductivity at the melting temperatures of the indicated compositions.

B. Plutonium Carbide

Very few data are available for pure, high-density PuC. Consequently, the arc-cast sample of $PuC_{0.87}$ studied by Leary et al.⁷ was used as the basis for fixing both the conductivity and the temperature coefficient at this composition within the temperature range of the measurement (473 to 673 K). We assume that other compositions can be adequately described by combining Eqs. (7) and (9). The proposed variation with composition at 343 K and 1300 K is shown in Figs. 12 and 13, respectively.

C. Uranium-Plutonium Carbide

Conductivity of the ternary compound is affected by two composition variables, the C/M ratio and the U/Pu ratio. We assume that the C/M ratio affects the conductivity in exactly the same manner as we described for the binary systems. To determine the influence of the U/Pu ratio, one must first extract from the reported measurements the effect produced by the sometimes unreported C/M ratio.

The values reported at low temperatures, shown in Fig. 14,^{19,20} vary with plutonium content to a large extent because of a variation in the unreported C/M ratio. Consequently, this information is not very valuable in defining the effect produced by the added plutonium. On the other hand, Wheeler¹⁰ used hypostoichiometric material for which the C/M ratio was given. His results are shown in Fig. 13 for 1300 K and are compared with the behavior of hypostoichiometric UC in Fig. 15. Because a small amount of liquid metal would have been present in these samples at 1300 K, the somewhat excessive conductivity is to be expected. Nevertheless, the data suggest that the presence of 20% Pu has essentially no effect.

whereas 40% lowers the conductivity markedly compared with that of pure UC. Based on this work, we propose that the effect of added plutonium follows the equation

$$C_p + C_F - 8 \times 10^3 Y^2 (1 - Y)^2 = C_T (U, Pu, C) \quad (10)$$

Figure 15 describes the effect of the changing phase boundary composition as the temperature is changed for alloys containing 20% and 40% Pu.

The behavior of hyperstoichiometric material is described in Fig. 16²¹ and compared with several measurements. The temperature coefficient of 0.8 U + 0.2 Pu and 0.7 U + 0.3 Pu obtained by Leary et al.⁷ shows a serious discrepancy, and we cannot obtain agreement by any reasonable change in the equations used to describe these materials. The results of Lewis²¹ agree quite well with our analysis except above 1600 K where the carbide begins to take up carbon and become hyperstoichiometric, which causes a drop in thermal conductivity. It is not clear whether this difference is due to nonequilibrium conditions existing within their sample or to a characteristic of the ternary system. Clearly, additional studies are needed that take all the important variables into account.

V. SUMMARY

If the data are taken at face value, there is considerable scatter in the reported thermal conductivity values for UC, PuC, and (U,Pu)C. However, this scatter can be reduced markedly if the effect of carbon content is taken into account. Of interest is the carbon content of the single-phase material at its phase boundary, a quantity which is temperature dependent. Analytical expressions were developed in this report to describe the temperature-dependent behavior using published information. Although these expressions have no theoretical basis, they are sufficiently accurate to allow an understanding of the thermal conductivity behavior.

Thermal conductivity has two components, conduction caused by electrons and conduction caused by lattice vibrations (phonon). The thermal and electrical conductivities are related through the Lorentz equation. Based on published information, we developed an analytical expression which describes the electrical resistivity as a function of temperature and composition. Although the composition variation is known at room temperature, the variation at high temperatures is not known. Consequently, a composition variation was chosen that would fit the thermal conductivity at high temperatures after taking the changing phase boundary composition into account. We assume that this expression is smooth and continuous between UC and PuC. Unfortunately, the measured electrical and thermal conductivities of PuC are not consistent with the Lorentz equation. Thus, to preserve internal consistency, we calculated a resistivity from the measured thermal conductivity rather than using the measured electrical resistivity of PuC.

Phonon conduction is important only at relatively low temperatures and near the perfect lattice composition because lattice imperfections interfere with lattice vibrations. Experience with other carbide systems indicates that the phonon contribution changes inversely with temperature and with the square of the vacancy concentration. Vacancies were considered to arise from three sources: chemical (that is, MC_{1-x}), thermal, and intrinsic imperfections that are important only at low temperatures and at the stoichiometric composition. Using an equation that accounts for all three, we adjusted a single term to fit the conductivity in excess of that provided by the electrons. Although the resulting expression is complex, it does provide a smooth analytical description of the temperature and carbon content variation which we assume can be applied to the ternary system, (U,Pu)C_{1±x}.

When plutonium is dissolved in UC, the lattice is disrupted by the foreign atom, and in addition, both the low- and high-carbon boundaries move to a high vacancy content. These changes have an important effect on the phonon component. Consequently, at low temperatures there is a substantial reduction in

thermal conductivity that is nearly linear with plutonium content when M_2C_3 is present as the second phase. At high temperatures, where electron conduction dominates, the effect of added plutonium is very nonlinear. There is only a small effect at compositions up to 20 mol% Pu. Based on very limited data, we propose that this effect goes as the fifth power of the plutonium concentration. Because of the carbon composition effect, there is a significant difference between the behavior of $MC + M_2C_3$ and $MC + M$, where M is the sum of the plutonium and uranium content. In addition, because the M_2C_3 exists as isolated domains in the ternary alloy, carbon composition equilibrium may not be easily achieved and the expected reduction in thermal conductivity at high temperatures may not be realized for alloys that have been at temperature for only a short time.

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Fig. 3. Phase diagram of the Pu-C system.

Fig. 4. Proposed phase boundary compositions for the ternary compound in equilibrium with the metal or M₂C₃ at 1000 K.

Fig. 5. Proposed phase boundary compositions for the ternary compound in equilibrium with the metal or M₂C₃ at 1873 K.

Fig. 6. Electrical resistivity of UC_{1±x} at various temperatures.

Fig. 7. A comparison between the proposed electrical resistivity of UC and various measurements. The dashed line above 1300 K shows the proposed effect of the changing phase boundary. The C/U ratios for the samples are indicated.

Fig. 8. A comparison between the proposed behavior of hyperstoichiometric UC and the various measurements. The dotted curve below 1100 K follows the electron component. The dashed curve above 1500 K shows low $UC_{1.08}$ might behave. Studies done using diffusivity measurements are indicated by "d", whereas direct conductivity measurements are indicated by "D".

Fig. 9. A comparison between the proposed behavior of hypostoichiometric UC and the various measurements. The dashed curve above 1900 K describes the proposed behavior of $UC_{0.96}$. Studies done using diffusivity measurements are indicated by "d", whereas direct conductivity measurements are indicated by "D".

Fig. 10. A three dimensional representation of the thermal conductivity of UC as a function of composition and temperature. The dashed curve shows the limit of the electron component.

Fig. 11. The thermal conductivity of UC_{1+x} at various temperatures. The curve labeled MELTING POINT shows the conductivity of the composition at its respective melting point.

Fig. 12. A comparison between the proposed thermal conductivity at 343 K and various measurements. The dashed line is realized only in the ternary system. Direct conductivity measurements are indicated by "D".

Fig. 13. A comparison between the proposed thermal conductivity at 1300 K and various measurements.

Fig. 14. A comparison between the proposed thermal conductivity at 573 K and various measurements. The carbon content of samples studied by Leary et al. (1964) are unknown. Studies done using diffusivity measurements are indicated by "d", whereas direct conductivity measurements are indicated by "D".

Fig. 15. A comparison between the proposed behavior of UC and several ternary compositions in the hypostoichiometric region.

Fig. 16. A comparison between the proposed behavior of UC and several ternary compositions in the hyperstoichiometric region.