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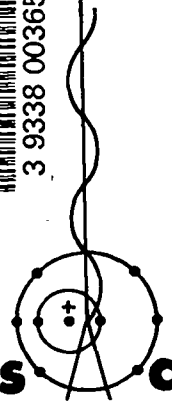

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REVIEW OF THERMAL EXPANSION AND DENSITY OF URANIUM AND PLUTONIUM CARBIDES

by

J. F. Andrew and T. W. Latimer

ABSTRACT

The published literature on linear thermal expansion and density of uranium and plutonium carbide nuclear fuels, including UC, PuC, (U, Pu)C, U_2C_3, Pu_2C_3, and $(U, Pu)_2C_3$, is critically reviewed. Recommended values are given in tabular form and additional experimental studies needed for completeness are outlined.

I. INTRODUCTION

This report is a critical review of the existing published information on linear thermal expansion and density of uranium and plutonium monocarbides, sesquicarbides and solid solution (U, Pu) mono- and sesquicarbides. Thermal expansion measurements were taken using dilatometry and x-ray diffraction lattice parameter measurements. Theoretical density values were calculated from x-ray lattice parameter work. The temperature dependence of the density was calculated from both bulk thermal expansion measurements and x-ray diffraction lattice parameters.

Experimental thermal expansion measurements are made by observing the difference in length at temperature T defined as L_T and the ambient length defined as L_o. The expansion data are generally plotted as per cent expansion $\frac{L_T - L_o}{L_o} \times 100$ versus temperature and the points thus obtained are fitted to a polynomial of the form $\frac{L_T - L_o}{L_o} = a + bT + cT^2 + dT^3 + \ldots$ etc., with constant coefficients a, b, c, d, etc., using a least squares technique. The instantaneous coefficient of linear thermal expansion is defined by

$$\alpha_i = \lim_{T \to T_i} \frac{L_i - L}{L_o(T_i - T)} = \frac{1}{L_o}\left(\frac{dL}{dT}\right)_{T = T_i}.$$

For practical applications the mean coefficient of linear thermal expansion between temperatures T_1 and T_2 is generally used,

$$\alpha_m = \frac{L_2 - L_1}{L_o(T_2 - T_1)}.$$

In most instances $L_1 = L_o$ and $T_1 = T_o$ where L_o and T_o are room temperature values.

The density values reported here were derived from x-ray diffraction results reported in the literature using the following relation:

$$\rho = \frac{nM}{N_o V} = \frac{1.6604\ nM}{V'},$$

where n = number of molecules per unit cell

n = 4 for UC, PuC and (U, Pu)C

n = 8 for U_2C_3, Pu_2C_3 and $(U, Pu)_2C_3$

M = gram formula weight

N_o = Avogadro's number, 6.02252×10^{23} molecules/mole

V = Volume of the unit cell in cm^3

V' = Volume of the unit cell in Å.

The average lattice parameters and standard deviations of the various compounds were derived from the unweighted mean of the values determined by the experimenters cited. The dependence of density on temperature was calculated from macroscopic thermal expansion measurements using the following equation:

$$\rho = \rho_o \Big/ \left[1 + 3\,\frac{\Delta L}{L_o} + 3\left(\frac{\Delta L}{L_o}\right)^2 + \left(\frac{\Delta L}{L_o}\right)^3 \right].$$

The values obtained were compared with the density calculated from the x-ray lattice parameter data at elevated temperature, where available.

II. URANIUM MONOCARBIDE

Single-phase uranium monocarbide has a narrow composition range at low temperature centered at 4.8 wt% carbon; however, a wide range of compositions on both sides of stoichiometry may be quenched in from high temperature. In hypostoichiometric uranium carbide, photomicrographs show that the uranium phase is found largely at the grain boundaries, becoming visibly continuous at ~4.3-4.4 wt% carbon. In hyperstoichiometric compositions, UC_2 or U_2C_3 or both are present depending on the temperature history of the specimen.

The most reliable thermal expansion study based on the use of sufficiently large samples and material characterization is that of Méndez-Peñalosa and Taylor[1] who used micrometer telescopes sighting on 150-mm-long arc-cast uranium carbide specimens with 99.3% theoretical density and with a carbon content varying from 4.35 wt% to 5.05 wt% (C/U = 0.89-1.08). He found that the dependence of the thermal expansion on composition in the above range is the same for temperatures below 800°C. Above 850°C the linear thermal expansion of the hypostoichiometric carbides increases rapidly and the specimens undergo a permanent deformation on cooling, probably due to the α-β transformation of uranium at 670°C and the β-γ transformation at 780°C. There were no significant differences in the expansion of specimens containing 4.7 to 5.05 wt% C. For those compositions he expressed the linear expansion, within 2%, by the equation:

$$\frac{L_T - L_o}{L_o} = -2.01 \times 10^{-4} + 1.004 \times 10^{-5} T + 1.17 \times 10^{-9} T^2$$

$$20 < T < 2000°C.$$

The results of Méndez-Peñalosa and Taylor[1] are given in Table I for an arc-cast 99.3% theoretical density uranium carbide with a carbon content of 4.9 wt%.

Stahl and Strasser[2] reported values of α_m about 10% higher than those of Table I for a 50-mm-long, arc-cast UC specimen (100% theoretical density) and about 15% lower than those of Table I for a sintered UC specimen (86% theoretical density). On the other hand, results of DeCrescente and Miller[3] for a 4.9 wt% C, 86% theoretical density, hot-pressed UC specimen, 50 mm long, were in good agreement with the data in Table I. Other thermal expansion measurements based on dilatometry have been reported in the literature by Secrest et al.,[4] Tripler et al.,[5] Kalish and Crane,[6] Meerson,[7] Chubb and Dickerson,[8] and Crane and Gordon.[9] Their results are, in general, within ± 10% of the data in Table I and show no systematic differences between arc-cast and sintered specimens.

TABLE I

THERMAL EXPANSION OF UC[a] FROM MÉNDEZ-PEÑALOSA AND TAYLOR[1]

Temperature	Expansion %	α_l	α_m
20°C	-	10.1×10^{-6}/°C	-
200	0.19	10.5	10.6×10^{-6}/°C
400	0.40	11.0	10.5
600	0.62	11.4	10.7
800	0.85	11.9	10.9
1000	1.10	12.4	11.2
1200	1.35	12.8	11.4
1400	1.61	13.3	11.7
1600	1.89	13.8	12.0
1800	2.17	14.3	12.2
2000	2.46	14.7	12.4

[a] Arc-cast, carbon content 4.9 wt%, 99.3% theoretical density.

TABLE II

TEMPERATURE DEPENDENCE OF THE THEORETICAL DENSITY OF $^{235}UC_{1.0}$ CALCULATED FROM THERMAL EXPANSION (MÉNDEZ-PEÑALOSA AND TAYLOR[1])

Temperature	Density (Mg/m^3)
20°C	13.61
200	13.53
400	13.45
600	13.36
800	13.27
1000	13.17
1200	13.07
1400	12.97
1600	12.87
1800	12.76
2000	12.65

Although the work of Méndez-Peñalosa and Taylor[1] has shown that the thermal expansion is independent of the carbon composition for dense UC below 800°C, there is no good work on the dependence of the thermal expansion on porosity, temperature history, impurity content, and method of fabrication.

The average lattice parameter of $UC_{1.00}$ was found to be 4.9600 ± 0.0010 Å using data reported by Ganguly and Vollath,[10] Leary et al.,[11] Magnier and Accary,[12] Williams et al.,[13] Wilson,[14] Laugier and Blum,[15] Benz and Farr,[16] Rundle et al.,[17] Boettcher and Schneider,[18] and Austin.[19] The theoretical densities of $^{238}UC_{1.00}$ and $^{235}UC_{1.00}$ derived from this lattice parameter are 13.61 ± 0.01 and 13.44 ± 0.01 Mg/m^3, respectively. The dependence of density on temperature obtained from the thermal expansion measurements of Méndez-Peñalosa and Taylor[1] is given in Table II. These values agree to better than ± 1% with those of the authors cited previously who obtained high-temperature x-ray measurements.

Both oxygen and nitrogen can be substituted for carbon in the UC structure. In general, substitution of nitrogen in any amount and oxygen in quantities over 1000-2000 ppm decreases the UC lattice parameter. Magnier et al.[20] reported lattice parameter increases in UC containing up to 7000 ppm oxygen; the maximum lattice parameter increase was 0.0016 Å at 2000 ppm oxygen. Anselin et al.[21] reported only a 0.0001 Å increase in the lattice parameter with the substitution of up to 10 at.% oxygen for carbon in the UC lattice. Brett et al.[22] reported an increase in the UC lattice parameter of 0.0005 Å in UC containing 1000 ppm oxygen and heat-treated in argon.

III. PLUTONIUM MONOCARBIDE

Plutonium carbide is a defect phase or nonstoichiometric compound and can exist with a carbon deficiency over a wide range of compositions. Various investigators[23,24,25,26] have found quenched and annealed single-phase compositions between $PuC_{0.66}$ and $PuC_{0.96}$. (See Appendix A, Table A-1 for conversion to wt% and at.%.) The Pu-C phase diagram recommended by the IAEA Panel on Thermodynamic Properties[27] shows single-phase monocarbide compositions at room temperature ranging from $PuC_{0.82}$ to $PuC_{0.90}$.

A reliable study of the thermal expansion of PuC at temperatures above 900°C has not been made. The best of the published data is that of Ogard et al.[28] for arc-cast $PuC_{0.85}$ over the temperature range 25-900°C using a quartz dilatometer and a specimen length of 25 mm. Ogard's results are expressed by the equation:

$$\frac{L_T - L_o}{L_o} = -4.0 \times 10^{-4} + 8.3 \times 10^{-6}\, T + 3.0 \times 10^{-9}\, T^2;$$

$$25 < T < 900°C.$$

The linear thermal expansion coefficients calculated from this equation are given in Table III. The tabulated data

TABLE III

THERMAL EXPANSION OF $PuC_{0.85}$[a] FROM OGARD et al.[28]

Temperature	Expansion %	α_l	α_m
25	-	8.5×10^{-6}/°C	-
200	0.138	9.5	7.9×10^{-6}/°C
400	0.340	10.7	9.1
600	0.566	11.9	9.8
800	0.816	13.1	10.5
900	0.950	13.7	10.9

[a] Arc-cast, carbon content 4.1 wt%, density unknown.

in the paper of Reshetnikov et al.[29] are unreliable because he does not report which coefficient α_i or α_m is given or the density of the specimen. The paper of Russell[30] gives (25-1000°C) $\alpha_m = 12.4 \times 10^{-6}/^{\circ}C$ for sintered $PuC_{0.96}$ (4.6 wt% C, density not reported) which is 12% higher than would be predicted from an extrapolation of the data of Ogard et al.[28] The higher results of Russell[30] may be due to a smaller sample size (< 20 mm) and a corresponding decrease in accuracy. Also Russell[30] used a composition outside the single-phase stability range.

The x-ray parameter measurement of Pallmer[31] for PuC of unknown composition gave (20-800°C) $\alpha_m = 10.8 \times 10^{-6}/^{\circ}C$ in good agreement with Ogard et al.[25] Rand and Street[32] reported (20-700°C) $\alpha_m = 10.6 \times 10^{-6}/^{\circ}C$ from x-ray lattice parameter measurements on $PuC_{0.84}$. However Pallmer[31] and Rand and Street[32] reported a linear temperature dependence of the lattice parameters which means that α_i and α_m are constant over the entire temperature range. This is surely not true.

The average lattice parameter of PuC was found to range from 4.956 ± 0.005 Å for carbon-poor compositions (40-45 at.% C) as measured by Chikalla,[24] Burnham et al.,[33] Rosen et al.,[25] and Kruger[26] to 4.9734 ± 0.0005 Å for carbon-rich (48-52 at.% C) compositions as measured by Chikalla,[24] Burnham et al.,[33] Rosen et al.,[25] and Kruger.[26] The theoretical density of $^{239}PuC_{0.90}$ derived from the lattice parameter for carbon-rich compositions is 13.49 ± 0.01 Mg/m³. The temperature dependence of the density of $PuC_{0.90}$ was calculated from the thermal expansion data of Ogard et al.[28] and is given in Table IV.

TABLE IV

TEMPERATURE DEPENDENCE OF THE THEORETICAL DENSITY OF $PuC_{0.90}$ CALCULATED FROM THE THERMAL EXPANSION DATA OF OGARD et al.[28]

Temperature	Density (Mg/m³)
25°C	13.49
200	13.43
400	13.35
600	13.26
800	13.17
900	13.11

TABLE V

THERMAL EXPANSION OF $(U_{0.95}Pu_{0.05})C_{0.98}$ + 0.1 wt% Ni FROM STAHL AND STRASSER[2]

Temperature	Expansion %	α_m
200°C	0.150	$8.6 \times 10^{-6}/^{\circ}C$
400	0.382	10.2
600	0.627	10.9
800	0.883	11.4
1000	1.221	11.9
1200	1.422	12.1
1400	1.678	12.2

(25°C) $\alpha_i = 8.8 \times 10^{-6}/^{\circ}C$, (1000°C) $\alpha_i = 14.6 \times 10^{-6}/^{\circ}C$ (Ogard et al.[25])

The available information on thermal expansion and density of PuC is far from complete. The temperature range of the measurements extends only to 1000°C and the compositions studied do not include the entire single-phase region. In addition, most specimens were not well characterized.

IV. URANIUM-PLUTONIUM MONOCARBIDE

The monocarbides of uranium and plutonium form a continuous series of solid solutions. In addition, oxygen and nitrogen impurities can substitute for carbon atoms in the (U, Pu)C lattice. The $\frac{C+O+N}{U+Pu}$ atomic ratio that yields a single-phase (U, Pu)C composition according to experimenters at LASL[34,35,36] is between 0.98 and 1.00.

The most reliable thermal expansion measurements, based on the use of sufficiently large samples and material characterization, are those of Stahl and Strasser[2] on sintered $(U_{0.95}Pu_{0.05})C_{0.98}$, $(U_{0.95}Pu_{0.05})C_{0.98}$ + 0.1 wt% Ni, $(U_{0.8}Pu_{0.2})C_{0.95}$ and $(U_{0.8}Pu_{0.2})C_{0.95}$ + 0.1 wt% Ni (oxygen content 2000-4000 ppm), using an alumina dilatometer with an inductance pickup and a 50-mm-long specimen. Within experimental error of 5%, the four compositions listed above gave identical thermal expansion coefficients even though the latter three compositions contained an unknown small amount of the sesquicarbide phase. Table V gives Stahl and Strasser's[2] results for sintered $(U_{0.95}Pu_{0.05})C_{0.98}$ + 0.1 wt% Ni with a density of 13.2 Mg/m³. These results agree within 5% with those of Ogard et al.[28] on $(U_{0.87}Pu_{0.13})C$ using a 25-mm-long

TABLE VI

TEMPERATURE DEPENDENCE OF THE THEORETICAL DENSITY OF $(^{235}U_{0.8}Pu_{0.2})C_{0.99}$ CALCULATED FROM THERMAL EXPANSION DATA OF STAHL AND STRASSER[2]

Temperature	Density (Mg/m^3)
25°C	13.46
200	13.40
400	13.31
600	13.21
800	13.11
1000	12.98
1200	12.90
1400	12.81

specimen of unknown density and with those of Bocker et al.[37] on $(U_{0.8}Pu_{0.2})C_{0.95}$ (experimental technique not given). Bocker et al.[37] also reported measurements on (U, Pu)C with several atomic per cent Zr, Ti, and Mo, which were 10% lower than the values in Table V at 1000°C.

The experimental values for the coefficient of thermal expansion reported in the literature for mixed monocarbides are probably accurate to ± 5%. This could be improved to ± 2% or better by using longer specimens and more care in the fabrication and heat treatment to insure single-phase material. The effect of stoichiometry, density, and impurity content on thermal expansion should also be investigated.

The average lattice parameter of $(U_{0.8}Pu_{0.2})C$ was found to be 4.9639 ± 0.0015 Å using $(U_{0.8}Pu_{0.2})C$ data by Ganguly and Vollath,[10] Leary et al.,[11] Brett et al.,[22] Rosen et al.,[25] Stahl et al.,[38] and LASL progress reports[34,35,39] and, in addition, $(U_{0.85}Pu_{0.15})C$ data by Brett et al.[22] and previously unpublished data of United Nuclear Corporation (see Appendix B, Table B-I). Ganguly and Vollath[10] studied compositions between $(U_{0.85}Pu_{0.15})C$ and $(U_{0.70}Pu_{0.30})C$ and found an increase of 0.0006 Å in the lattice parameter for each 5 at.% substitution of Pu for U. The (U,Pu)C compositions used to determine the lattice parameter included a relatively wide range of oxygen and nitrogen. No systematic variation of lattice parameter as a result of these impurities was found. For the calculation of the theoretical density of uranium-plutonium monocarbide, a $\frac{C}{U+Pu}$ ratio of 0.99 was used. The calculated theoretical densities of $(U_{0.8}Pu_{0.2})C_{0.99}$ of some isotopic compositions of interest are as follows:

0.7% ^{235}U, 99.3% ^{238}U 88-94% ^{239}Pu, 6-12% ^{240}Pu	13.58 ± 0.01 Mg/m^3
93% ^{235}U, 7% ^{238}U 88-94% ^{239}Pu, 6-12% ^{240}Pu .	13.46 ± 0.01 Mg/m^3

The temperature dependence of the density calculated from the expansion measurements of Stahl and Strasser[2] is given in Table VI. There are no high temperature x-ray measurements in the literature on (U, Pu)C for density comparison.

V. URANIUM SESQUICARBIDE

Uranium sesquicarbide is a stoichiometric compound and can be prepared by arc-casting a mixture of the elements containing 7.02 wt% carbon. The most reliable thermal expansion results for U_2C_3 in the literature based on the use of sufficiently large samples and material characterization are those of Méndez-Peñalosa and Taylor[40] over the temperature range 20-1700°C using a 127-mm specimen length and optical sighting on the ends with a micrometer telescope. He expressed the thermal expansion, within 2%, by the equation:

$$\frac{L_T - L_o}{L_o} = 12.6 \times 10^{-4} + 1.077 \times 10^{-5} T - 1.69 \times 10^{-9} T^2 + 1.55 \times 10^{-12} T^3 \qquad 20 < T < 1700°C .$$

The thermal expansion coefficients calculated from the above equation are given in Table VII.

The x-ray lattice parameter measurements of Wilson[14] give a linear variation with temperature in the range 1000-1800°C and mean thermal expansion coefficients 10 to 15% lower than those in Table VII; however, his data might be inaccurate since it does not extrapolate to a reasonable value at room temperature. The x-ray measurements of Norreys et al.[41] are more consistent

TABLE VII

THERMAL EXPANSION OF U_2C_3[a] FROM MÉNDEZ-PEÑALOSA AND TAYLOR[40]

Temperature	Expansion %	α_l	α_m
20°C	-	10.7×10^{-6}/°C	-
200	0.184	10.3	10.2×10^{-6}/°C
400	0.388	10.2	10.2
600	0.593	10.4	10.2
800	0.807	11.0	10.3
1000	1.037	12.0	10.6
1200	1.291	13.4	10.9
1400	1.576	15.2	11.4
1600	1.899	17.3	12.0
1700	2.078	18.5	12.4

[a] Arc-cast, carbon content 7.0 wt%, heat treatment 6 hr in vacuum, 1.33 mPa (10^{-5} torr) at 1600°C. Density unknown.

than Wilson's[14] and give a mean expansion coefficient at 1000°C of 10.5×10^{-6}/°C, in excellent agreement with the data in Table VII. Rough and Chubb[42] report values within a few percent of the data of Table VII but do not discuss the experimental technique used.

In all the above thermal expansion work, the specimen density was not given and the impurity content was not well established. More experiments are needed to study the effect of temperature history on the microstructure and thermal expansion coefficients.

The lattice parameter of U_2C_3 was found to be 8.088 Å by Ganguly and Vollath,[10] Benz and Farr,[16] Bowman et al.,[43] Dalton,[44] and Leary et al.[45] Slightly higher values of 8.089 Å and 8.090 Å were reported by Wilson[14] and Hennecke and Toussaint,[46] respectively. The theoretical densities of $^{238}U_2C_3$ and $^{235}U_2C_3$ derived from a lattice parameter of 8.088 ± 0.001 Å are 12.86 ± 0.01 Mg/m³ and 12.70 ± 0.01 Mg/m³, respectively. The temperature dependence of the density calculated from the thermal expansion data of Méndez-Peñalosa and Taylor[40] (Table VII) is given in Table VIII. The density values calculated from x-ray parameter measurements at elevated temperature[14,16] agree with the data in Table VIII to better than ± 1%.

VI. PLUTONIUM SESQUICARBIDE

Plutonium sesquicarbide can exist as a single-phase compound with a composition range of approximately $PuC_{1.45}$-$PuC_{1.50}$.[27,47] However, dilatometric thermal expansion measurements have not been reported on single-phase Pu_2C_3. The available thermal expansion data on Pu_2C_3 comes entirely from x-ray lattice parameter measurements. The most reliable work based on material characterization and equipment calibration is that of Green and Leary[48] who reported the temperature dependence of the lattice parameter of a plutonium carbide with a C/Pu atomic ratio of 2.2, which is a mixture of Pu_2C_3 + C. Their results are expressed by the equation:

$$\Delta a/a_o = (1.29 \pm 0.02) \times 10^{-5} (T - 25)$$

$$+ (2.07 \pm 0.14) \times 10^{-8} (T - 25)^2;$$

$$25 < T < 1650°C$$

and tabulated in Table IX. Rand and Street[49] reported x-ray lattice parameter measurements on $PuC_{1.44}$ (which was reported to be single phase) giving (20-1000°C)α_m = 16.2×10^{-6}/°C, 10% higher than Green and Leary's[48] value. There is no apparent explanation for these higher values. Pallmer[31] reported x-ray lattice parameter measurements on a mixture of PuC and Pu_2C_3, giving

TABLE VIII

TEMPERATURE DEPENDENCE OF THE THEORETICAL DENSITY OF $^{238}U_2C_3$ CALCULATED FROM THE THERMAL EXPANSION DATA OF MÉNDEZ-PEÑALOSA[40]

Temperature	Density (Mg/m³)
20°C	12.85
200	12.78
400	12.70
600	12.62
800	12.54
1000	12.46
1200	12.36
1400	12.26
1600	12.14
1700	12.08

TABLE IX

THERMAL EXPANSION OF Pu_2C_3 FROM GREEN AND LEARY[48]

Temperature	Expansion %	α_l	α_m
25° C	0	$12.9 \times 10^{-6}/C^4$	-
200	0.232	13.6	$13.3 \times 10^{-6}/C$
400	0.513	14.4	13.7
600	0.810	15.3	14.1
800	1.124	16.1	14.5
1000	1.455	16.9	14.9
1200	1.802	17.8	15.3
1400	2.165	18.6	15.7
1600	2.545	19.4	16.2

(20-800°C)$\alpha_m = 14.8 \times 10^{-6}$/°C, only 2% higher than the value of Green and Leary.[48]

There is a need for dilatometric measurements of thermal expansion for stoichiometric Pu_2C_3 to compare with the x-ray studies.

The average lattice parameter of Pu_2C_3 was found to be 8.132 ± 0.002 Å using data reported by Mulford et al.,[23] Chikalla,[24] Dalton,[44] Leary et al.,[45] Green and Leary,[48] and Rand and Street.[49] The theoretical density of $^{239}Pu_2C_3$ derived from this lattice parameter is 12.70 ± 0.01 Mg/m^3. The temperature dependence of the density shown in Table X is calculated from the x-ray lattice expansion data reported by Green and Leary[48] (Table IX).

TABLE X

TEMPERATURE DEPENDENCE OF THE THEORETICAL DENSITY OF Pu_2C_3 CALCULATED FROM THE X-RAY LATTICE PARAMETER DATA OF GREEN AND LEARY[48]

Temperature	Density (Mg/m^3)
25° C	12.70
200	12.61
400	12.51
600	12.40
800	12.28
1000	12.16
1200	12.04
1400	11.91
1600	11.78

TABLE XI

THERMAL EXPANSION OF $(U_{0.65}Pu_{0.35})_2C_3$ FROM GREEN AND WALTERS[50]

Temperature	Expansion %	α_l	α_m
25° C	0	9.6×10^{-6}/°C	
200	0.172	10.1	9.8×10^{-6}/°C
400	0.381	10.8	10.2
600	0.603	11.4	10.5
800	0.838	12.1	10.8
1000	1.087	12.8	11.2
1200	1.349	13.4	11.5
1400	1.624	14.1	11.8
1600	1.912	14.7	12.1
1700	2.061	15.1	12.3

VII. URANIUM-PLUTONIUM SESQUICARBIDE

The U_2C_3-Pu_2C_3 system forms a series of solid solutions. The only thermal expansion measurements in the literature are those of Green and Walters[50] who reported the temperature dependence of the x-ray lattice parameter of $(U_{0.65}Pu_{0.35})_2C_3$. The composition measured had an overall $\frac{C}{U+Pu}$ atomic ratio of 2.1 which was a mixture of $(U_{0.65}Pu_{0.35})_2C_3$ + C. Their results are expressed by the equation:

$$\Delta a/a_o = (9.54 \pm 0.21 \times 10^{-6}) \quad (T - 25)$$

$$+ (1.65 \pm 0.12 \times 10^{-9}) \quad (T - 25)^2$$

$$25 < T < 1700°C$$

and tabulated in Table XI.

The average lattice parameter of $(U_{0.8}Pu_{0.2})_2C_3$ was found to be 8.096 ± 0.002 Å by Ganguly and Vollath,[10] Dalton,[44] and Leary et al.,[45] all of whom studied compositions of approximately 60 at.% C and of varying Pu/U ratios. The effect of the substitution of Pu for U in compositions between $(U_{0.85}Pu_{0.15})_2C_3$ and $(U_{0.70}Pu_{0.30})_2C_3$ was an increase of 0.0012 to 0.0020 Å in the lattice parameter for each 5 at.% substitution of Pu for U. The average lattice parameter of $(U, Pu)_2C_3$ in $(U_{0.85}Pu_{0.15})$ carbide compositions containing 5-20 vol% $(U, Pu)_2C_3$ was 8.095 ± 0.001 Å using unpublished data of United Nuclear

Corporation (see Appendix B, Table B-I). The average lattice parameter of $(U, Pu)_2C_3$ in $(U_{0.8}Pu_{0.2})$ carbide compositions containing 5-45 vol% $(U, Pu)_2C_3$ was 8.096 ± 0.001 Å using data by Stahl et al.[38] and LASL progress reports.[39] The actual Pu/U ratio in the $(U, Pu)_2C_3$ phase in (U, Pu)C + $(U, Pu)_2C_3$ mixtures has been reported by Anselin et al.,[21] Potter and Roberts,[51] and Latimer[52] to be enriched in Pu compared to the (U, Pu)C phase. However, the recommended lattice parameter of 8.096 ± 0.002 Å for $(U_{0.8}Pu_{0.2})_2C_3$ is believed to be sufficiently accurate for the determination of the $(U, Pu)_2C_3$ density for (U, Pu)C + $(U, Pu)_2C_3$ mixtures having an overall $\frac{Pu}{U+Pu}$ atomic ratio of 0.2. The theoretical densities of $(U_{0.8}Pu_{0.2})_2C_3$ of some isotopic compositions of interest are as follows:

0.7% ^{235}U, 99.3% ^{238}U
88-94% ^{239}Pu, 6-12% ^{240}Pu 12.83 ± 0.01 Mg/m^3

93% ^{235}U, 7% ^{238}U
88-94% ^{239}Pu, 6-12% ^{240}Pu 12.72 ± 0.01 Mg/m^3.

The temperature dependence of the density of $(U_{0.8}Pu_{0.2})_2C_3$ calculated from the x-ray lattice parameter measurements of $(U_{0.65}Pu_{0.35})_2C_3$ at elevated temperatures by Green and Walters[50] is given in Table XII. There are no dilatometric expansion measurements on $(U, Pu)_2C_3$ for comparison with the above x-ray results.

TABLE XII

TEMPERATURE DEPENDENCE OF THE THEORETICAL DENSITY OF $(^{235}U_{0.9}{}^{239}Pu_{0.2})_2C_3$ CALCULATED FROM THE X-RAY LATTICE PARAMETER DATA OF GREEN AND WALTERS[50]

Temperature	Density (Mg/m^3)
25°C	12.72
200	12.65
400	12.58
600	12.49
800	12.41
1000	12.31
1200	12.22
1400	12.12
1600	12.02
1700	11.96

VIII. SUMMARY

Table XIII gives the recommended values for the coefficients of linear thermal expansion of uranium and plutonium carbides obtained from this review of the literature. It was difficult to assess the accuracy of the experimental measurements reported because the use of standard calibration specimens, such as platinum, was rarely reported. In addition, many of the experiments were carried out on specimens which were not well characterized. For these reasons, it was estimated that the values given in Table XIII are accurate, at best, to about ± 5%. Coefficients of linear thermal expansion for uranium and plutonium monocarbides and sesquicarbides were not determined for temperatures near their solidus temperatures. Maximum temperatures for which thermal expansion measurements were reported were 500-1000°C less than the solidus temperatures of the monocarbides and 400-700°C less than the solidus temperatures of the sesquicarbides.

Table XIV gives the recommended values for the theoretical densities obtained from this review of the literature. The recommended lattice parameters for the various monocarbide and sesquicarbide compounds are believed to be sufficiently accurate to allow their theoretical densities to be determined to within ± 0.01 Mg/m^3 in

TABLE XIII

RECOMMENDED VALUES FOR THE COEFFICIENTS OF LINEAR THERMAL EXPANSION ($10^{-6}/°C$) OF URANIUM AND PLUTONIUM CARBIDES[a]

	$(25°C)\alpha_i$	$(1000°C)\alpha_i$	$(25\text{-}1000°C)\alpha_m$
UC	10.1	12.4	11.2
PuC	8.5	13.7[b]	10.8[b]
(U, Pu)C	8.8	14.6	11.9
U_2C_3	10.7	12.0	10.6
Pu_2C_3	12.9	16.9	14.9
$(U, Pu)_2C_3$	9.6	12.8	11.2

[a] Values at other temperatures can be found in the various sections of this report.

[b] Data for T = 900°C.

TABLE XIV

RECOMMENDED VALUES FOR THE LATTICE PARAMETERS AND THEORETICAL DENSITIES[a] OF URANIUM AND PLUTONIUM CARBIDES

Compound	Lattice Parameter (Å)	Density (Mg/m^3) Isotopic Composition 0.7% ^{235}U 99.3% ^{238}U	93% ^{235}U 7% ^{238}U	88-94% ^{239}Pu 6-12% ^{240}Pu
UC	4.9600	13.61	13.46	-
$PuC_{0.90}$	4.9734	-	-	13.49
$(U_{0.8}Pu_{0.2})C_{0.99}$	4.9639	13.58	13.46	-
U_2C_3	8.088	12.85	12.72	-
Pu_2C_3	8.132	-	-	12.70
$(U_{0.8}Pu_{0.2})_2C_3$	8.096	12.83	12.72	-

[a] Calculated from the equation for density on page 1.

cases where the chemical and isotopic compositions are well known. In cases when higher precision for the theoretical density is required, the lattice parameter of the compound being studied should be determined by x-ray diffraction.

IX. CONCLUSIONS

1. Although coefficients of linear thermal expansion for uranium carbides have been measured by a number of investigators, relatively little thermal expansion data are available for plutonium-containing carbides.
2. There is a need for thermal expansion data on (U, Pu)C and (U, Pu)C + $(U, Pu)_2C_3$ compositions of interest as fast reactor fuels. These data are needed (1) to determine the maximum centerline fuel temperatures in helium-bonded carbide fuel elements which are strongly influenced by the initial hot fuel-cladding gap and (2) for thermal and mechanical analyses of carbide fuel elements during transient conditions. For analyses of transient overpower tests, the thermal expansion measurements should extend to temperatures approaching the melting point of the (U, Pu) carbides.
3. Although small variations in the x-ray lattice parameters of uranium and plutonium mono- and sesquicarbides were found among the various investigators, the theoretical densities derived from an average of the reported values are believed to be within 0.01 Mg/m^3 of the actual values if the chemical and isotopic contents are well known.

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APPENDIX A

CONVERSION TABLES

TABLE A-I

CONVERSION TABLES OF Wt% → At. % → ATOM RATIO FOR U-C AND Pu-C

^{238}U-C			^{239}Pu-C		
wt% C	at. % C	C/U	wt% C	at. % C	C/Pu
4.3	47.1	0.89	3.2	39.7	0.66
4.4	47.7	0.91	3.3	40.5	0.68
4.5	48.3	0.93	3.4	41.2	0.70
4.6	48.9	0.96	3.5	41.9	0.72
4.7	49.4	0.98	3.6	42.7	0.74
4.8	50.0	1.00	3.7	43.4	0.77
4.9	50.5	1.02	3.8	44.1	0.79
5.0	51.1	1.04	3.9	44.8	0.81
5.1	51.6	1.07	4.0	45.4	0.83
5.2	52.1	1.09	4.1	46.0	0.85
			4.2	46.6	0.87
			4.3	47.2	0.89
			4.4	47.8	0.92
			4.5	48.4	0.94
			4.6	49.0	0.96
			4.7	49.6	0.98
			4.8	50.1	1.00

APPENDIX B

LATTICE PARAMETERS

The following are lattice parameters determined by Gulf United Nuclear Fuels Corporation, Elmsford, New York for ($U_{0.85}Pu_{0.15}$) carbide fuels used in irradiation experiments. These experiments are now under the direction of Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

TABLE B-I

(U, Pu)C AND $(U, Pu)_2C_3$ LATTICE PARAMETERS FOR CARBIDE FUELS WITH A $\frac{Pu}{U+Pu}$ ATOMIC RATIO OF 0.15

Series No.	Compound[a]	Fuel Type[b]	wt. % O_2	wt. % N_2	Average ao (Å)
1300	MC	S	0.15	0.22	4.9656 ± 0.0004
1300	MC	H	0.30	0.11	4.9642 ± 0.0016
	M_2C_3				8.0943 ± 0.0006
1930, 1960	MC	S	0.11	0.03	4.9649 ± 0.0019
1930, 1960	MC	H	0.28	0.02	4.9656 ± 0.0002
	M_2C_3				8.0959 ± 0.0009
1950	MC	S	0.30	0.01	4.9640 ± 0.0020
1950	MC	H	0.44	0.02	4.9652 ± 0.0003
	M_2C_3				8.0951 ± 0.0005
5100	MC	S	0.25	0.04	4.9638 ± 0.0012
5100	MC	H	0.28	0.03	4.9643 ± 0.0005
	M_2C_3				8.0936 ± 0.0013

[a] M = (U, Pu).

[b] S = Stoichiometric (U, Pu)C.

H = Hyperstoichiometric (U, Pu)C.