

the original belief, the brittle cracking advance does not occur during one stress cycle but is spread over about 100 cycles, the crack slowing down gradually to its original velocity. The dark bands on the fracture surface were examined under the microscope to see if evidence of the progress of the crack could be obtained, but the surface was too rough to show fatigue striations.

A possible explanation of this behaviour is that the cracking noise is heard when brittle fracture occurs in a small area of the surface which does not extend across the full width of the specimen (small isolated areas of brittle fracture can be seen on the surfaces shown in Fig. 1). The area of brittle fracture then spreads rapidly across the specimen during subsequent cycling until, when the crack front is back to its minimum length, the conditions for slow crack growth again occur. The specimen finally fails completely during one stress cycle when brittle fracture occurs across the full width of the specimen.

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¹ Pearson, S., *Royal Aircraft Establishment Tech. Rep. No. 66204* (1966).

² Gilbey, D. M., and Pearson, S., *Royal Aircraft Establishment Tech. Rep. No. 66402* (1966).

High Temperature Structure of Plutonium Dicarbid

THE presence of a dicarbid in the Pu-C system was originally reported by Drummond¹. Mulford and Ellinger² showed that the compound was unstable below $\sim 1,750^\circ\text{C}$, and that it decomposed to form PuC_2 and carbon. These workers were unable to index the X-ray diffraction pattern obtained at room temperature from alloys quenched from the molten state. Chackraburty and Jayadevan³ indexed diffraction lines from a sample of PuO_2 and carbon quenched from the reaction temperature of $2,200^\circ\text{C}$ as arising from a body centred tetragonal phase isomorphous with UC_2 and deduced that this was also the high temperature structure. Tetragonal structures have also been found in quenched materials by J. A. Leary and J. G. Reavis (private communication), who also reported that the formation temperature of PuC_2 was $1,650^\circ\text{C}$. As part of a study of the phase relationships in the UC_2 - PuC_2 system it was necessary to determine the high temperature structure of PuC_2 . The apparatus used was a high temperature diffractometer⁴ attached to a conventional Philips X-ray goniometer using $\text{Cu } K_\alpha$ radiation.

The sample was prepared by arc-melting mixtures of plutonium and carbon to give alloys containing nominally 67 atomic per cent C. The buttons thus formed were crushed, milled and pressed into a disk of diameter 0.5 in. and sintered at $1,650^\circ\text{C}$, just below the transformation temperature, and then hand ground to a thickness of 0.04 in. on silicon carbide paper. The sample was heated in the diffractometer to an indicated surface temperature of $1,500^\circ\text{C}$, in a vacuum of $< 5 \times 10^{-6}$ torr, and scanned at $0.5^\circ (2\theta) \text{ min}^{-1}$. The only phase present was body centred cubic (bcc) Pu_2C_3 with $a = 8.340 \text{ \AA}$; the graphite present did not give a diffraction pattern. High purity helium was fed into the chamber to a pressure of 10 torr before increasing the temperature in steps of $\sim 50^\circ\text{C}$. The specimen was held at each temperature for 30 min before commencing the scan. When the sample temperature was raised to $1,710^\circ\text{C}$ the line intensity of the bcc Pu_2C_3 pattern diminished, and a new set of diffraction peaks appeared.

The 2θ values, d values and peak heights found at $1,710^\circ\text{C}$ are shown in Table 1; reflexions were not detected at 2θ angles greater than 75° , probably because of thermal vibration of the lattice. The structure of PuC_2 was face

Table 1. X-RAY DATA FOR PuC_2 OBTAINED AT $1,710^\circ\text{C}$

Relative peak heights	2θ observed (degrees)	d observed	d calculated	hkl	a observed (\AA)
20	26.12	3.4086	3.4221	211	8.349
100*	27.12	3.2852	3.2912	111	5.690
16	30.17	2.9596	2.9636	220	8.371
80	31.36	2.8500	2.8503	200	5.700
7	33.72	2.6557	2.6508	310	8.398
11	40.09	2.2472	2.2403	321	8.408
53	44.93	2.0157	2.0154	220	5.701
11	51.04	1.7878	1.7871	332	8.386
53	53.24	1.7190	1.7188	311	5.701
27	55.86	1.6445	1.6456	222	5.697
13	65.42	1.4254	1.4251	400	5.702
11	68.07	1.3762			
27	72.11	1.3087	1.3078	331	5.704
24	74.22	1.2766	1.2747	420	5.709

* Not obtained during the first scan at $1,710^\circ\text{C}$.

centred cubic (fcc) although a residual pattern of bcc Pu_2C_3 was still present. In particular, peak 211 of the bcc phase had not diminished and peak 111 of the fcc phase was absent on the first scan. A second scan of the low angles at $\sim 1,730^\circ\text{C}$ showed that the 211 peak (bcc) had shrunk and peak 111 of the fcc phase had appeared, suggesting that the reaction $\text{Pu}_2\text{C}_3 + \text{C}$ proceeds slowly at this temperature. The lattice parameter of PuC_2 at $1,710^\circ\text{C}$ is $5.70 \pm 0.01 \text{ \AA}$. It is not possible on a high temperature diffractometer to measure or compare line intensities accurately enough to determine the space group of PuC_2 , and the determination of the carbon position can only be achieved by high temperature neutron diffraction. The tetragonal cell observed by Chackraburty³ and by J. A. Leary and J. G. Reavis (private communication) is almost certainly a metastable phase formed by a martensitic transformation on quenching fcc PuC_2 . This produces a phase similar to the structure obtained on quenching UC_2 from high temperature.

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¹ Drummond, J. L., McDonald, B. J., Ockenden, H. M., and Welsh, G. A., *J. Chem. Soc.*, 4785 (1957).

² Mulford, R. N. R., Ellinger, F. H., Hendrix, G. S., and Albrecht, E. D., *Plutonium 1960*, 310 (Cleaver-Hume Press, London, 1960).

³ Chackraburty, D. M., and Jayadevan, N. C., *Acta Cryst.*, 18, 811 (1965).

⁴ Harper, E. A., *AERE-R 5695*.

Matrix Property of Vibrational Overlap Integrals

In this communication I shall point out a matrix multiplication property possessed by arrays of vibrational overlap integrals of diatomic molecular band systems. Consider any three electronic states L, M, N between which the $L \leftrightarrow M$, $L \leftrightarrow N$ and $M \leftrightarrow N$ transitions are allowed. Each of the wavefunctions ψ_l associated with vibrational levels l of L , and each of the wavefunctions ψ_n associated with the vibrational levels n of N , may be represented by an eigenfunction expansion of the wavefunctions ψ_m of the levels m of M as follows:

$$\psi_l(r) = \sum_m (l,m) \psi_m(r) \quad (1a)$$

$$\psi_n(r) = \sum_m (n,m) \psi_m(r) \quad (1b)$$

$$\text{where} \quad (a,b) = \int \psi_a(r) \psi_b(r) dr \quad (1c)$$

is the vibrational overlap integral, r is the internuclear separation and (a,b) is the Franck-Condon factor q_{ab} .

The overlap integral (l,n) can be constructed from equations (1a) and (1b) through