Short Communications

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Crystal chemistry of higher carbides of plutonium.

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Evidence of a higher carbide other than Pu_2C_3 and PuC was reported by Drummond, McDonald, Ockenden & Welch (1957) and by Mulford, Ellinger, Hendrix & Albrecht (1960). In the first case, plutonium dioxide was stated to have been mixed with carbon in the proper ratio and heated in a resistance furnace under inert atmosphere to about 2200 °C, and in the second case plutonium metal and graphite were melted in an arc furnace. In both cases X-ray diffraction patterns showed evidence of extra lines in addition to Pu_2C_3, but these could not be indexed. The reported patterns were different from each other. In the present work the method of preparation was similar to that described by Drummond *et al.* but the temperature range could be taken as high as 2800 °C under suitable conditions.

In each case plutonium dioxide, intimately mixed with carbon in the proper ratio for the reaction $PuO_2+4C \rightarrow PuC_2+2CO$ in a graphite crucible, was heated for 5–10 minutes in the furnace and cooled rapidly. Temperatures of preparation were between 2200 °C to 2600 °C. The carbon monoxide evolved during each reaction was removed by continuous evacuation. The chance of occluded oxygen in the system was likely to be small at such high temperatures. The patterns obtained from 20 preparations gave evidence of additional lines; lines due to oxides of plutonium could not be detected. The data are given in Table 1. The lines below 1·48 Å were measured by superposition of two or more films, as mostly the lines were too weak. The diffraction data in the Table could be conveniently explained on the basis of a mixture of (1) Pu_2C_3, (2) PuC_2, identified as a new phase isostructural with tetragonal UC_2, (3) carbon (graphite), and (4) a phase for which mostly weak lines were recorded. The spacings of the weak lines, correspond to the spacings of the strong lines of Mulford's data.

Depending on the temperature and period of heating of these preparations, the percentages of the carbide phases in the mixture were found to be changing. However, it was not possible to isolate the higher carbides in pure forms.

We could index PuC_2 lines with $a=b=3{\cdot}63$ and $c=6{\cdot}094$ Å, $Z=2$ and space group $I4/mmm$ (D_{4h}^{17}) having UC_2 or CaC_2 structure type. The Pu atoms are in (*a*) positions and carbon atoms in (*e*) positions. Plutonium to plutonium separations are, therefore,:

$$\mathrm{Pu}-8\mathrm{Pu}=3{\cdot}98\ \text{Å}$$
$$\mathrm{Pu}-4\mathrm{Pu}=3{\cdot}63\ \text{Å}$$

Following the method adopted by Sharma & Subramanian (1964) and checked in a few cases by conventional chemical methods for determining the carbon contents, the bound carbon and free carbon of some preparations were determined. While the samples had varying free carbon, the bound carbon in free carbides (total sample minus free carbon) were found to vary mostly from 9·2 % to 9·7 % and in one case as high as 10 % indicating the presence of another carbide phase with higher carbon content, since the theoretical values for bound carbon are 7·0 % and 9·1 % for Pu_2C_3 and PuC_2 respectively. Although the major constituent of the mixture was Pu_2C_3 as determined from X-ray analysis, yet it was observed that whenever

Table 1. *Analysis of the carbide phases* ($\lambda=1{\cdot}5418$ Å)

			Pu_2C_3		PuC_2	
Intensity	*d*	$q_o^2\times10^{-4}$	$q_c^2\times10^{-4}$	*hkl*	$q_c^2\times10^{-4}$	*hkl*
s(b)**	3·344 Å	530	540	211		
w*	3·205	578				
s−	3·119	611			610	101
mw	3·045	641			640	002
w−*	2·942	686				
mw	2·887	713	720	220		
s−*	2·565	903	900	310	900	110
mw−*	2·487	960				
w*	2·417	1018				
mw−*	2·167	1266	1260	321		
mw+	1·961	1545			1540	112
w*	1·813	1808			1800	200
mw−	1·769	1898			1890	103
w	1·729	1988	1980	332		
w	1·592	2343	2340	510 413		
mw*	1·561	2439			2440	202
w−	1·526	2552			2560	004
w(b)*	1·486	2690	2700	521		
w*	1·447	2838				
vw−	1·310	3463			3460	114
vvw	1·288	3582	3600	620	3600	220
vw−	1·269	3691			3690	213
vw	1·254	3781	3780	541		
vw	1·189	4202			4210	301
vw+	1·174	4311	4320	444		
vvw−	1·155	4454			4450	105
vw(b)	1·147	4513	4500	710	4500	310
vw(b)	1·107	4849	4860	633		
vvw(b)	1·086	5038	5040	642		
vvw	1·075	5146			5140	312
vvw(b)	1·067	5224	5220	730		
vvw(b)	1·031	5584	5580	732 651		

* The weak unindexed lines and the probable superimposed lines due to reflexions reported as *m* or *s* by Mulford (1960) are noted.

** Combined with graphite line. The *d* values of other graphite lines observed are: 2·13(*w*), 2·04(*w*), 1·67(*w*), 1·23(*w*+), 1·15(*w*−).

the value of bound carbon was higher the weak lines corresponding to Mulford's data reported in Table 1 appeared relatively stronger.

Further evidence of another new carbide phase was obtained on heating plutonium dioxide with carbon sufficient to produce PuC up to 1800 °C, mixing the product with excess carbon and finally heating it to 2400–2600 °C. Out of seven preparations, two identical patterns have been obtained which showed it to be mixture of carbon and the new phase. As the number of lines obtained was not great, no crystallographic deductions are suggested. The diffraction lines of this phase, the spacings of which are quite different from those reported in Table 1, was also detected in the preparations of higher carbides when PuO_2 and carbon were heated first to 1700 °C to 1800 °C for some time and then heated to 2300 °C to 2600 °C.

The X-ray diffraction patterns of all the preparations, loaded in silica capillaries of 0·20 to 0·28 mm internal bore, were taken in a 19 cm Unicam camera with copper radiation. An optical pyrometer was used for measuring the temperatures of the preparations.

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A special application of the crystal setter.

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In a note on the setting of crystals in X-ray diffraction work one of us described a method and a corresponding instrument for setting crystals (Kulpe, 1963). This instrument ('crystal setter') has been under trial for nearly two years in our Institute. It has proved fully satisfactory and is now used for all our routine setting. The setting procedure is simple, quick, and sufficiently accurate even for relatively big corrections (15° on each of two crossed arcs of the goniometer head).

In favourable cases it may be possible to obtain a set of lattice parameters starting from a single oscillation photograph, without the necessity of using more than one crystal or remounting the crystal on the goniometer head, by setting the crystal corresponding to three non-coplanar directions.

The 'layer lines' corresponding to such directions will in general not be recognizable without the help of the crystal setter. The recognizability is of course better if one of the lattice parameters is fairly large, but then adjustment in a direction corresponding to such a large translation period will be rather difficult. In the following an example of this kind is shown to demonstrate the possibility of obtaining three settings from one oscillation photograph (Fig. 1) and in order to indicate the accuracy obtainable in one or in two steps, respectively. A mica crystal was used.

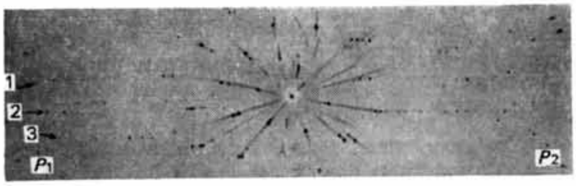

Fig. 1. 10° oscillation photograph of a mica crystal. The arrows 1,2,3 indicate rows of reflexions which may be adjusted as mis-set zero layer lines. P_1, P_2 are marking points.

In Fig. 1 P_1 and P_2 are marks which make it easy to put the film around the crystal setter in the correct position. The three arrows marked 1,2,3 indicate rows of reflexions which were then adjusted as equatorial layers. The photographs were taken with the plane of the lower arc of the goniometer head perpendicular to the X-ray beam. Copper radiation was used.

For the three marked rows the following corrections were read off from the arcs of the crystal setter:

1. $\alpha_\perp = 14{,}6°$ rhs 2. $\alpha_\perp = 6{,}3°$ lhs 3. $\alpha_\perp > 15{,}0°$ lhs
$\alpha_\parallel = 1{,}8°$ afc $\alpha_\parallel = 7{,}5°$ tc $\alpha_\parallel = 2{,}6°$ tc

(rhs = to the right hand side; lhs = to the left hand side afc = away from the collimator; tc = towards the collimator). In the third case the setting $\alpha_\perp$ exeeded the measuring range of the arc (± 15°). A second setting photograph enabled $\alpha_\perp$ to be determined to $\alpha_\perp = 16{,}6°$.

Figs. 2, 3, 4 show oscillation photographs obtained after the corresponding settings. The translation periods along

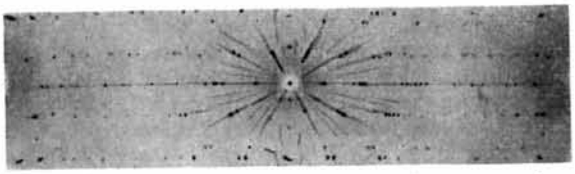

Fig. 2. Oscillation photograph according to case 1 (oscillation angle 10°).

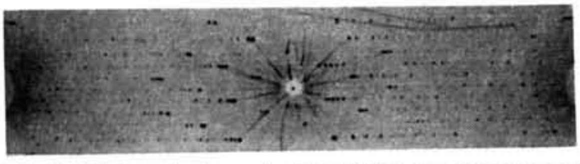

Fig. 3. Oscillation photograph after setting according to case 2: Ni filter, oscillation angle 90°.