LOW TEMPERATURE PYROLYSIS PRODUCTS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN HEXACARBONYLS

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Abstract—The Group 6 metal hexacarbonyls have often been investigated as precursors in chemical vapour deposition processes. The solid products, obtained by thermal decomposition of the vapours of the compounds below 300°C, have been re-examined. Under these conditions, all three carbonyls produce a metallic phase with a face-centred cubic structure, distinct from the body-centred cubic structure of the pure metals. Microanalysis shows that the materials contain roughly equimolar amounts of carbon and oxygen. Pyrolysis of ¹⁸O-labelled Mo(CO)₆ has demonstrated that the oxygen derives from the CO ligand of the precursors. Evidence that the pyrolysis products are insterstial oxycarbides is presented; their response to annealing treatment is described.

The importance of thin films of chromium, molybdenum and tungsten in microelectronics and other technologies has motivated many investigations of chemical vapour deposition processes using the metal carbonyls, $M(CO)_6$, as precursor compounds. In the first such study,¹ it was found that face-centred cubic (fcc) materials formed when $Mo(CO)_6$ and $W(CO)_6$ were pyrolysed below 500°C. Higher temperatures and other precautions were necessary to obtain the body-centred cubic pure metals. The fcc materials were originally formulated as carbides, but chemical analyses carried out on the pyrolysis products of $Mo(CO)_6^2$ and $W(CO)_6^3$ showed the materials contained oxygen. Recently, a similar fcc phase has been prepared by the decomposition of $Cr(CO)_6$ in a corona discharge.⁴ The fcc materials, obtained by pyrolysis of the three $M(CO)_6$ complexes below 300°C, have been re-investigated. A fuller appraisal of their chemical nature and probable mechanism of formation than in previous work has been possible.

The pyrolysis products were prepared by subliming the carbonyl up a Pyrex tube under dynamic

vacuum, and allowing pyrolysis to occur in a heated portion of the tube. The tubes were 3 mm internal diameter and sealed at their lower end. The carbonyls (Aldrich) were sublimed before use. Each pyrolysis run used roughly 20-30 mg of carbonyl, which was initially placed in the bottom of the tube. The samples of $Cr(CO)_6$ and $Mo(CO)_6$ were held at 50°C, and W(CO)₆ at 60°C. The pyrolysis zone was heated by a tubular resistance furnace, 75 mm long. In all cases, the temperature at the centre of the furnace was 300°C. Heavy deposition of solid material from $Cr(CO)_6$ and $Mo(CO)_6$ onto the tube wall began at ~ 150°C, and at ~ 230°C in the case of $W(CO)_6$. The dark, metallic deposits were poorly adherent, and all analyses were performed on loose flakes of material detached from the tubes. The equilibrium vapour pressures of the carbonyls under the conditions used⁵ are much higher than the ultimate vacuum of ~ 0.05 torr obtainable in the pyrolysis apparatus. Allowing for the production of CO on decomposition, it is apparent that the pyrolysis products formed under a flux of CO sufficient to eliminate the possibility of oxidation by residual oxygen in the apparatus. The actual CO pressure during pyrolysis was at least 0.2-0.3 torr.

Qualitative analyses of the pyrolysis products

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were obtained by laser ionization mass analysis (LIMA) using a Cambridge LIMA 2A system. Positive ion LIMA spectra of the pyrolysis products all showed strong M⁺, C⁺ and O⁺ peaks. No polyatomic ions such as CO⁺ were detected. These results provided initial evidence that the materials were oxycarbides. Confirmation of the origin of the oxygen was sought by pyrolysing a sample of 50% ¹⁸O-labelled $Mo(CO)_6$. This was prepared by reacting cycloheptatriene molybdenum tricarbonyl⁶ with C¹⁸O (Alfa) in 1,2-dichloroethane solution. LIMA showed that the ¹⁶O/¹⁸O ratio in the pyrolysis product was 1.1+0.1, confirming that 91-100% of the oxygen in the material originated from the CO ligand of the precursor. The mechanism of incorporation of carbon and oxygen into the pyrolysis products will be considered below.

Quantitative analyses were made by conventional chemical methods, and the results are summarized in Table 1. Carbon analyses were performed by combustion with an iron oxide additive in a Carlo Erba 1130 instrument. Samples of Cr_3C_2 (Johnson Matthey), Mo_2C and WC (both Alfa) were used as standards. Oxygen analyses were made by Pascher Laboratories, Remagen, using a Balzers Exhalograph EAO-202 instrument. The results indicated approximately equimolar amounts of oxygen and carbon in each of the pyrolysis products. Very similar analytical data were obtained by Vogt³ for the low temperature pyrolysis products of W(CO)₆.

Scanning electron microscopy (SEM) was used to confirm that the materials had dense, locally uniform microstructures, consisting of grains 50– 200 nm in size. These observations helped support the supposition that the products were chemically homogeneous, with bulk compositions reflecting the analytical data.

X-ray powder diffraction patterns were recorded using Cu- K_{α} radiation. The materials each consisted of a single fcc phase, with the approximate lattice parameters listed in Table 1. Diffuse diffraction peaks, consistent with the particle size broadening expected from 25 nm particles,⁷ were observed. Since the actual grain sizes observed by SEM were somewhat larger, disorder in the materials was

Table 1. Analytical data for the pyrolysis products

Precursor	Element weight (%)		Deduced	Lattice parameter
	С	0	composition	(Å)
Cr(CO) ₆	9.55	12.0	$CrC_{0.52}O_{0.49}$	4.14
Mo(CO) ₆	4.33	5.47	MoC _{0.38} O _{0.36}	4.19
W(CO) ₆	2.44	2.93	WC _{0.39} O _{0.36}	4.17

probably responsible. Pure molybdenum and tungsten have been claimed to crystallize in the fcc structure, but only in the form of extremely thin films, below the thicknesses encountered here.⁸ In view of the analytical data, it is likely the pyrolysis products are non-stoichiometric interstitial phases, with the carbon and oxygen atoms occupying octahedral interstices in an fcc lattice of metal atoms, presumably in a random fashion. This suggestion has been made previously,^{1,2} but will be briefly reviewed.

To investigate their thermal stability, samples of the oxycarbides were annealed in evacuated silica ampoules at 600°C for 24 h, and examined by Xray powder diffraction. The fcc material obtained from $Cr(CO)_6$ was entirely transformed into Cr_3C_2 , Cr_2O_3 and an unidentified phase. The Mo(CO)_6 pyrolysis product was partially converted into α -Mo₂C, MoO₂ and molybdenum metal, while the W(CO)_6 pyrolysis product remained unchanged.

The B1(NaCl) structure described above is one of the types adopted by the so-called Hägg phases, discussed by Toth.9 The molybdenum and tungsten carbides, α -MoC_{1-x} and α -WC_{1-x}, have this structure. The atomic radius of chromium is slightly too small to allow interstitial carbides to form, and phases such as Cr_3C_2 have more complicated structures. In formulating the pyrolysis products as interstitial phases of this sort, a further novel feature is their relatively large oxygen content. The composition of the Cr(CO)₆ pyrolysis product is very close to the idealized composition, $CrC_{0.50}O_{0.50}$, expected for full occupation of the octahedral interstices. In the other two oxycarbides, vacancies must be present. The metal lattices in these materials are rather dilated, particularly in the $Cr(CO)_6$ pyrolysis product. Here, the distance between neighbouring metal atoms is 2.93 Å, which is considerably more than twice the normal radius of a 12-coordinate chromium atom, 1.267 Å.⁹ It might be anticipated that the fcc phase would possess limited stability, as shown by the annealing experiments.

In the discussion above, it has been assumed that the pyrolysis products are oxycarbides, containing no undissociated CO. The distance between the carbon and oxygen atoms on adjacent interstitial sites will be ~ 2.95 Å, much too far to allow any direct bonding to be retained. The best evidence that the materials contain no undissociated CO is the lack of any CO⁺ or CO⁻ peaks in their LIMA spectra. Furthermore, their IR spectra, recorded in KBr discs, showed no v(CO) absorptions. Vogt obtained X-ray photoelectron spectra for the fcc tungsten oxycarbide,³ but definite conclusions could not be reached about the chemical state of the constituent atoms. It is known, however, that in the β -state of chemisorbed CO on molybdenum and tungsten surfaces, the C-O bond is greatly weakened, with both atoms involved in bonding to the surface.¹⁰ Desorption of β -CO from tungsten occurs only above $\sim 700^{\circ}$ C.¹¹ A recent study of the adsorption of CO on a chromium (110) surface showed that at -150°C CO preferentially bonded in a "side-on" fashion, with v(CO) appearing in the 1150–1330 cm^{-1} range, and dissociation occurred above -100° C.¹² These findings provide some precedent for the surface dissociation of CO which must occur during synthesis of the oxycarbides. The deposition of carbon in the material could also be accompanied by the production of CO_2 , as considered by Kaplan and d'Heurle.¹³ This process is clearly not very important here, and it is uncertain whether the slight excess of carbon over oxygen observed in the materials is significant. A study of the gaseous thermal decomposition products of Mo(CO)₆ and $W(CO)_6$ by mass spectrometry showed that the CO^+/CO_2^+ ratio was always above 50.¹⁴

It is likely that the pyrolysis products described closely resemble those obtained in previous work, under somewhat different sets of conditions. Their compositions were not always investigated in great detail, particularly when film deposition rates and electrical properties were of principal interest.^{13,15,16} The presence of hydrogen as a background gas clearly did not prevent the incorporation of carbon and oxygen into the pyrolysis products.^{2,3} Auger electron spectroscopy (AES) indicated that films produced by the photo-assisted decomposition of $Mo(CO)_6$ had a composition close to the pyrolysis products discussed here.¹⁶ Electron diffraction and AES also showed that similar materials can be obtained by the decomposition of $Cr(CO)_6^4$ and $Mo(CO)_6^{17}$ in a corona discharge. Hence, the results described are likely to be relevant to a range of low temperature chemical vapour deposition techniques.

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