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The structure of evaporated tungsten films. By R. L. MOSS and I. WOODWARD, *Department of Chemistry, The Queen's University of Belfast, England*

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While tungsten as a bulk metal crystallizes with the body-centred cubic structure (type A2) two further modifications have been reported, namely, face-centred cubic (type A1) occurring in evaporated tungsten films deposited in vacuo (Beeck, 1950) and that known as β -tungsten. The β -tungsten modification, found originally by electrolysis of melts (Hartmann, Ebert & Bretschneider, 1931; Burgers & van Liempt, 1931) is classified as type A15, the space group being $O_h^3-Pm\bar{3}n$ with 8 atoms in the unit cell: 2 in (a): 0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; and 6 in (c): $\pm(\frac{1}{4}, \frac{1}{2}, 0; \odot)$. This form of tungsten has also been found in films sputtered from tungsten electrodes on to the walls of a glass container (Petch, 1944), in films formed in some vacuum lamps (Rooksby, 1944) and in films deposited in an atmosphere of wet hydrogen on nickel sheet at 200–300 °C. (Charlton & Davis, 1955, 1956).

It has been suggested, however, that β -tungsten is an oxide of tungsten (Hägg & Schönberg, 1954; Charlton & Davis, 1955) though Mannela & Hougen (1956) and Millner *et al.* (1957) believe that their β -tungsten, formed by the reduction of the oxide, WO_3 , is a true allotropic form of the metal.

In the course of the X-ray examination of tungsten films deposited on glass in good vacua, Debye-Scherrer lines other than those due to b.c.c. tungsten were noted in certain instances, and identified as belonging to the A15 type structure. In our opinion, the formation of an oxide was precluded by the conditions under which such films were deposited. The effects of varying conditions of vacuum, substrate temperature, film thickness etc. on the structure type of the film deposited are reported below.

Films were prepared by evaporating from an axially placed wire (Tungsten Mfg. Co., Ltd., 'pure') on to the inner wall of a cylindrical 'Pyrex' vessel, held at a known temperature. Before evaporation, the glass vessel was continuously evacuated and baked at a temperature above 450 °C. for at least 2 hr. producing a vacuum of 10^{-5} – 10^{-6} mm. Hg. During the last 30 min. of this period, the tungsten filament was out-gassed at a temperature close to the evaporation point of the metal. Currents of > 5.0 a. through 0.2 mm. wire gave rise to a visible outgassing film on the glass. Generally powder photographs were taken of the tungsten film adhering to small fragments of the glass vessel mounted on a Unicam

(3 cm. radius) single crystal camera, using Cu $K\alpha$ radiation at a glancing angle of about 15°. In some cases, the metal film was scraped off its glass backing and mounted on a glass fibre.

The results obtained for films deposited in vacua of 10^{-5} – 10^{-6} mm. Hg. and weighing about 10 mg. (geometrical area, ~ 100 cm.²) are summarised in Table 1.

In films having the A15 structure lines for $\theta > 40^\circ$ were not sufficiently resolved for measurement. This was attributed partly to instrumental broadening and also to broadening due to small particle size. The lines observed were indexed on the basis of the A15 structure, $a = 5.046$ Å (cp. 5.038, Neuburger, 1933), a small amount of b.c.c. form being usually present in addition.

Some experiments were also carried out where deposition of the tungsten film was begun under poor vacuum conditions, 10^{-2} – 10^{-3} mm. Hg. Improvement of the vacuum to 10^{-4} – 10^{-5} mm. Hg. during the evaporation showed that gettering of the residual gas was occurring. Whether or not a strong outgassing film had been formed previously, the tungsten film subsequently deposited contained the A15 form.

While evaporation in a poor vacuum, say 10^{-2} mm. Hg. would be expected to produce some oxide, calculation shows that with a volume of 1 litre and a pressure of 10^{-5} mm. Hg. only about 0.01% of the total film deposited could be the low oxide, W_3O . Thus the occurrence of A15 tungsten, reported in Table 1 cannot be interpreted on the basis that it is an oxide.

Table 1 shows that the presence, (a)–(c), or absence, (d)–(g), of an outgassing film formed on the glass apparently controls the structure of the tungsten subsequently deposited. (Decrease in the substrate temperature appears to control, i.e. decrease, the small amount of b.c.c. present in predominantly A15 specimens). The absence of an outgassing film indicates that the temperature of the wire has not been high enough to cause evaporation from it and possibly has also been insufficient to outgas it completely. In this case, a minute amount of oxide will be formed initially on evaporating from the filament and it would appear from our experiments that its presence can induce the tungsten film to deposit in the A15 structure.

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Table 1. *Structure types for evaporated tungsten films*

	Outgassing film	Substrate temperature (°C.)	Structure type
(a)	+	–78	A2
(b)	+	0	A2
(c)	+	540	A2
(d)	–	–196	A15
(e)	–	–78	A15
(f)	–	–78*	A15
(g)	–	0	A15

* Film weight = 20 mg.

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Scale models of polypeptide chains with permanent connections between 'backbone' atoms.*

By WILLIAM W. SCHUELKE, LILLIAN CASLER and ROBERT B. COREY, *California Institute of Technology, Pasadena, California, U.S.A.*

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An earlier communication (Corey & Casler, 1958) described the recent use of small permanent magnets for hydrogen bonds in molecular models constructed of colored, rubber-like vinyl plastic. These models were originally developed (Corey & Pauling, 1953) several years ago for use in studies of the structures of amino acids, peptides, and related compounds. In many respects they resemble the Stuart-type models now commercially available, adjacent bonded atoms being held together by means of snap fasteners and double-ended brass studs. When used for constructing very large molecules, the weight of the models and the local strains that develop when they are handled sometimes cause the snap fasteners connecting bonded atoms to pull apart. This occurrence is especially frequent with representations of molecules of polypeptides and similar compounds that consist essentially of long chains of atoms. For such molecules it is highly desirable that the 'backbone' of the chain be constructed so that its adjacent atoms will not separate, even when subjected to considerable manipulative stress. This note describes models for representing a polypeptide or a linear carbon chain embodying this feature.

The device employed for joining adjacent atoms in the chain is shown in Fig. 1. It consists of a double-ended

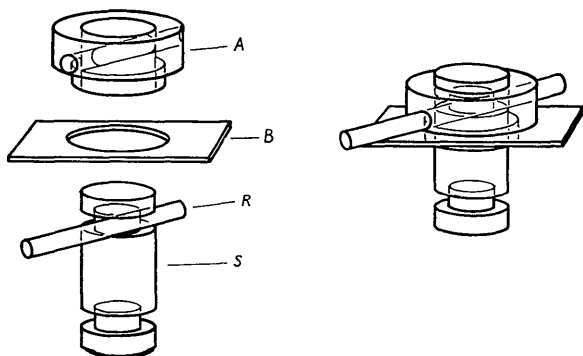


Fig. 1. An exploded view of the locking device for joining adjacent atoms of a chain. *S* is a double-ended stud that can be locked to the atom insert *A* by the insertion of a rod *R*. *B* is a backing plate that serves to anchor *A* firmly in the plastic atom.

aluminum stud *S* that can be locked into an aluminum insert *A* around which the plastic atom is cast. The stud *S* is locked into *A* by means of a round brass or steel rod

that passes through a hole in *A* so as to fit into a circular keyway in the stud. The assembly includes a backing plate *B* which serves to anchor the insert *A* firmly in the plastic atom.

Fig. 2 is a phantom drawing of a typical α -carbon atom. Two of the bonds—those connecting to adjacent amide groups in the chain—are made by means of the new stud fasteners; the other two—those connecting to a hydrogen atom and a side chain—are the usual snap fasteners. For the sake of clarity of the drawing, only one snap fastener, that on the front of the model, is shown.

Fig. 3 is an assembly drawing of a portion of a polypeptide chain showing the positions of the stud fasteners in the amide groups and the α -carbon atoms. The two snap fasteners on the α -carbon atoms are not shown.

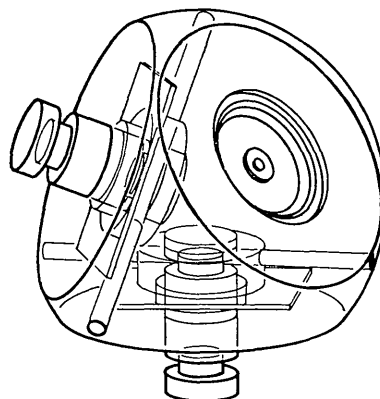


Fig. 2. A phantom drawing of a typical α -carbon atom, showing the two inserts and stud connectors that form the intra-chain bonds. One of the two snap fasteners is not shown in this drawing for the sake of clarity.

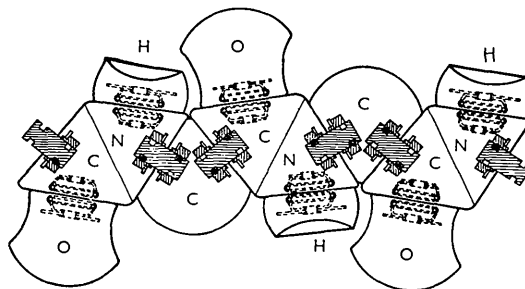


Fig. 3. An assembly drawing of a portion of a polypeptide chain showing the positions of the locked stud fasteners in the amide groups and the α -carbon atoms.

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