350. *The Growth of Titanium Nitride on Hot Filaments.*

By F. H. Pollard and P. Woodward.

The conditions for the deposition of titanium nitride on hot filaments in a continuous-flow process have been studied, using the decomposition of halide in the presence of nitrogen and hydrogen. Optimum conditions for the deposition are : filament temperature $\simeq$ 1450°, total reaction pressure 30—40 cm. Hg, titanium chloride at 36° (vapour pressure $\simeq$ 17 mm.), and a gaseous mixture of equal quantities of nitrogen and hydrogen. The rate of flow is unimportant. The effect of the various factors on the nature of the deposit is discussed.

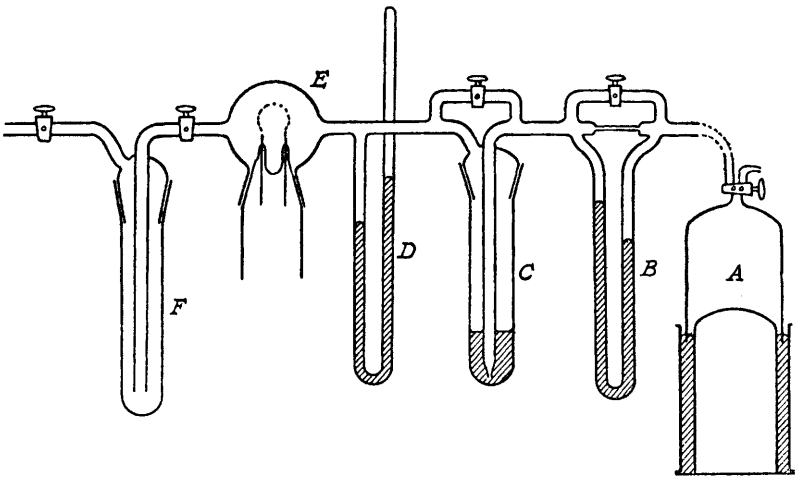
Previous work on the nitrides, carbides, and borides of the transition elements has been summarised by Becker (*Physikal. Z.*, 1933, **34**, 185; " Hochschmelzende Hartstoffe und ihre Technische Anwendung," Verlag Chemie, Berlin, 1935), but the most recent development has been given by Moers (*Z. anorg. Chem.*, 1931, **198**, 243), in which a crystalline product is grown

on a hot filament from the gaseous phase. For example, to form a nitride, a volatile halide of the metal can be reduced in presence of nitrogen. This technique has also been applied in the production of high-melting metals by Van Arkel (*Metallwirts.*, 1934, **13**, 405), and the production of pure boron by Laubengayer, Hurd, Newkirk, and Hoard (*J. Amer. Chem. Soc.*, 1943, **65**, 1924).

Experimental.

A continuous-flow method was found most suitable for the investigation of a reaction with so many variable factors, and the apparatus in its final form is illustrated in Fig. 1. The gasholder *A* contains any desired mixture of nitrogen and hydrogen at a pressure slightly greater than atmospheric. This can be pumped through the apparatus at a rate measured by the difference in pressure across the capillary in the manometer *B*, with butyl phthalate as the manometric liquid. The gases then bubble through the trap *C* containing titanium tetrachloride surrounded by a water-bath at a known temperature; it is assumed that the rate of flow is sufficiently slow for saturation to occur. The mixture then passes into the reaction vessel *E* containing the heated filament. The total pressure in *E* is measured by the mercury manometer *D*, the surface of the mercury being protected by a thin film of butyl phthalate. Reaction occurs on the hot filament, but owing to the extensive decomposition of the tetrachloride into lower chlorides on the vessel walls, it is impossible to measure the temperature of the filament with an optical pyrometer. It is therefore necessary to estimate this temperature by means of the current through the filament, and a calibration must be carried out previously under similar conditions, but in absence of titanium chloride vapour. It is unfortunate that extremely accurate control is not possible by this method, since the formation of the deposit is markedly dependent on the filament temperature.

Fig. 1.



In any experiment, the pressure and rate of flow are adjusted as necessary, the titanium chloride by-pass tap being kept open until steady conditions are reached. This tap is then closed, forcing the gases to bubble through the liquid, and the duration of the experiment is measured from this point.

The pressure indicated by the flowmeter *B* is not an absolute measure of the quantity of gas passing per unit time; this value depends also upon the total pressure in the reaction vessel. The Poiseuille formula shows that the quantity of gas flowing through a capillary under isothermal conditions is proportional to $p_2^2 - p_1^2$, where p_1 and p_2 are the pressures at the two ends of the capillary. Hence a constant value of $(p_2 - p_1)$ will give a constant rate of flow only if $(p_2 + p_1)$ is also constant. Thus, the rates of flow for two reactions are the same only if the total time is the same. This consideration applies when comparing reactions at different pressures.

The filaments are of tungsten or tantalum of various thicknesses. Fine tantalum wire can be spot-welded directly on to the thick tungsten leads, but tungsten filaments require a short nickel bridge. A.C. at low voltage is used for heating, currents up to 30 amps. being obtained from a Variac transformer. After adjusting the voltage to give the required initial current (and temperature), no further adjustments are made, but since nitrides of this type are good conductors, deposition of nitride causes a reduction of resistance in the filament and consequent increase in current. Thus, it is possible to estimate the rate of growth from the rate of increase of current under constant voltage. The total increase of current is not, however, an accurate measure of the quantity of nitride produced, since the actual increase will depend upon the crystalline structure of the deposit. Of two wires, coated with equal quantities of nitride, one having few large crystals and the other having many small ones, the former will have a smaller "effective" diameter than the latter—see Fig. 2, in which (*b*) would give a larger current increase than (*a*). All samples are therefore weighed to estimate the quantity of nitride produced.

Exit gases from the reaction are passed through a liquid-air trap *F* and a soda–lime tube to remove hydrogen chloride as completely as possible.

Experimental Results.—The variables investigated were: (1) The proportion of nitrogen to hydrogen in the gaseous mixture used. (2) The rate of flow of gases through the apparatus. (3) The temperature

of the titanium chloride bath, *i.e.*, the concentration of $TiCl_4$ vapour in the reaction mixture. (4) The total pressure in the reactions vessel. (5) The temperature of the filament. (6) The nature of the filament.

Initial Conditions.—A few preliminary experiments indicated that a deposit of nitride as well-formed, golden-yellow, cubic crystals can be obtained by using a total reaction pressure of 40 cm., a rate of flow of 4·5 cm. pressure of butyl phthalate, a titanium chloride bath at 18°, and a filament of tungsten, diameter 0·25 mm., length 2·5 cm., with an initial current of about 10 amps. These being used as the initial conditions, various modifications could be effected, and resulting differences in the product observed.

Effect of the N : H *Ratio.*—Experiments using mixtures of 3 : 1, 1 : 1 and 1 : 3 (N : H) revealed that, in general, equal volumes of nitrogen and hydrogen give the largest yield. Moreover, using this mixture, the yield is not affected by the position or orientation of the filament.

FIG. 2.

The Effect of Temperature of the Filament.—Experiments were carried out with the same initial conditions, but using a gaseous mixture of equal volumes of hydrogen and nitrogen. The filament temperature was first calibrated by means of an optical pyrometer, and a series of experiments was then carried out with different starting currents. The results are collected in the following table. There is a

	Initial current, amps.	Approx. initial temp.	Final current, amps.	Yield, mg.	Nature of deposit.
(1)	8	1050°	9	8	Dark purple and grey; microcrystalline
(2)	9	1250	18	30	Multicoloured small crystals; nitride crystal structure
(3)	10	1450	17½	27	Bronze yellow; fairly large crystals
(4)	11	1600	13½	4	Deposit at sides of bow only

narrow optimum range of temperature within which the nitride can be produced. If the temperature is lower than this value the crystals are black, and probably consist of pure metal. With an increase in temperature, the crystals become larger until an upper limit is reached, above which no deposit at all is obtained.

The multicoloured exterior which is sometimes obtained is probably due to a coating of lower chlorides of titanium deposited during the final pumping-out of the reaction vessel. The coloured layer can be removed with hot water, and breakage of a sample reveals a completely yellow cross-section except for the tungsten core.

A pointed filament (in place of the usual bow shape) gave a deposit only in the region away from the point. This is caused by the critical temperature being exceeded in the locality of the point. Apart from exceptional temperature effects of this kind, however, the shape does not markedly alter the nature of the deposit.

Effect of the Concentration of Titanium Chloride Vapour.—Results are summarised in the following table. It would appear that 36° is about the optimum temperature for the titanium chloride, equal

Temp. of $TiCl_4$ bath.	Initial current, amps.	Final current, amps.	Increase, amps.	Yield, mg.
0°	9½	<10	<½	Very small
10	9½	15	5½	18
18	9½	18½	9	29
29·5°	9½	18½	9	34
36	9½	22½	13	53
39	9½	18½	9	36

volumes of nitrogen and hydrogen being used. The size of the crystals deposited can be regulated by a judicious adjustment of the starting temperature. Higher relative concentrations of titanium chloride were not investigated because of the enormous amount of wall deposit produced.

Effect of the Rate of Flow and Total Reaction Pressure.—It was found that variation of the rate of flow by a factor of 3 produced no appreciable change, either in the amount of the deposit or in its characteristics. There is no doubt, however, that a pressure of 30—40 cm. is much more favourable for deposition than a pressure of about an atmosphere. The following table gives data to illustrate these facts.

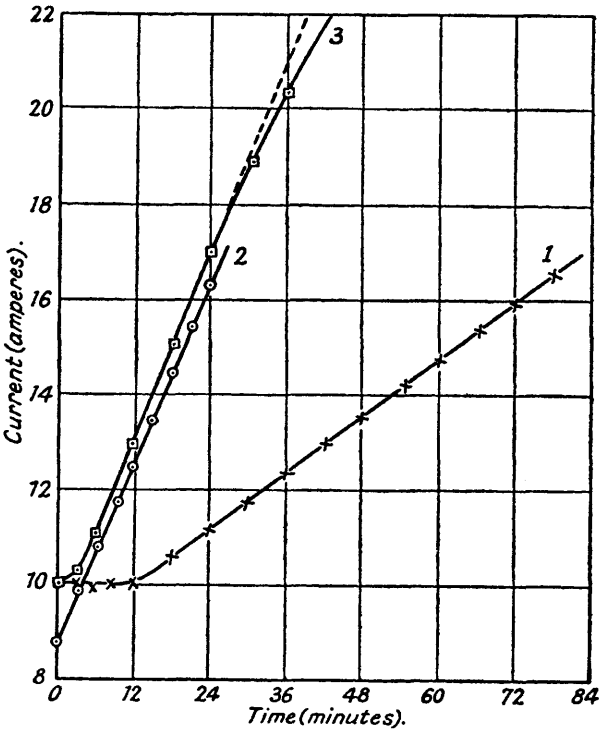
Analysis.—A sample of golden-yellow crystals analysed colorimetrically (by oxidation with hydrogen peroxide to the pertitanate) showed a titanium content agreeing with TiN within the limits of the method (about 2%). Titanium nitride is dissolved by fused potassium hydrogen sulphate.

Effect of the Nature of the Filament.—Two variables were investigated : (*a*) the chemical nature of the filament, (*b*) its physical condition. (*a*) Tungsten and tantalum filaments were used—tungsten in thicknesses of 0·2—0·35 mm., tantalum 0·2 mm. only. The qualitative result was the same in all cases, although the induction period before deposition begins tends to be longer for tantalum than for tungsten. In general, also, thin wires give a more even deposit than thick ones. (*b*) It was found that " aged "

Total press., cm. Hg.	Rate of flow.*	Current increase, amps.	Yield, mg.	Duration of expt., mins.
50	3·0	4·7	17	51
,,	4·5	4·4	18	35
,,	6·0	4·3	~16	25
,,	7·8	3·3	14	20
40	2·0	9·5	37	100
30	3·0	9·6	40	75
,,	6·2	11·3	44	40
,,	10·5	12·2	44	25
76	1·5	2·5	12	60
,,	3·0	2·7	13	40
,,	4·5	2·5	13	25
,,	6·0	2·5	14	15

* In cm. of butyl phthalate.

FIG. 3.



Variation of current with time.

	Press, cm.	$N_2 : H_2$.	Flow, cm.	$TiCl_4$.
1	40	1 : 1	2·3	21°
2	30	1 : 1	10·5	36
3	30	1 : 1	6·2	36

filaments (Langmuir, *Physical Rev.*, 1923, **22**, 374) tend to give a much more coherent and continuous layer of nitride than filaments which had not been so treated, but in no case could single-crystal coatings of nitride be produced. The currents necessary to produce any given temperature in a vacuum were calculated, Langmuir's tables being used with suitable corrections for end losses (Jones and Langmuir, *Gen. Elect. Rev.*, 1927, **30**, 311; Langmuir, Maclane, and Blodgett, *Physical Rev.*, 1930, **35**, 478). Electrical heating with A.C. can be considered equivalent to non-electrical heating (Johnson, *ibid.*, 1938, **54**, 459).

Discussion.—The rôle of the filament. Fig. 3 shows current–time curves during deposition under constant voltage. The induction period is probably controlled by the state of the filament, which may not only require cleaning but also etching (Taylor and Langmuir, *ibid.*, 1933, **44**, 423) to give a spacing more nearly equal to that of titanium nitride. Single-crystal filaments are said to give " einkrystalline " deposits (Fischvoigt and Koref, *Z. techn. Physik*, 1925, **6**, 296), but we have been unable to confirm this.

The linear increase indicates a constant rate of deposition of titanium and nitrogen, and the fall-off from linearity is explained by the critical temperature effect.

Mechanism. A likely mechanism is that the tetrachloride in presence of hydrogen is decomposed to the metallic state, and that nitride formation occurs simultaneously. Formation of complexes with ammonia, as described by Brager (*Acta Physicochim. U.R.S.S.*, **1939**, **10**, 593; **1941**, **14**, 297) at lower temperatures, seems improbable here. Preliminary experiments indicate that titanium nitride is unstable in a vacuum at 1500° and this is probably the cause of the critical temperature effect.

THE UNIVERSITY, BRISTOL.

[*Received, December 22nd*, 1947.]