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Chemical Vapor Deposition of Group IVB, VB, and VIB Elements, A Literature Review

By H. O. McDonald and J. B. Stephenson

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CHEMICAL VAPOR DEPOSITION OF GROUP IVB, VB, AND VIB ELEMENTS, A LITERATURE REVIEW

by

H. O. McDonald[1] and J. B. Stephenson[2]

ABSTRACT

The Bureau of Mines reviewed the chemical vapor deposition (CVD) literature of the group IVB, VB, and VIB elements. This review was utilized in the Bureau's research to provide erosion-, abrasion-, and corrosion-resistant coatings for valve components used in coal gasification units. This report attempts to bring together the many CVD references that have been published since 1966. Each of the group IVB, VB, and VIB metal coatings were reviewed, and some of their preparation methods, uses, and properties are given. A total of 160 references were found for the nine elements. Isotope separation, stronger steels, solar absorbers, alloys, superconductors, optical fibers, and coatings to increase the life of materials are some of the new uses for CVD.

INTRODUCTION

Chemical vapor deposition (CVD) may be defined as "the formation of coatings or thick deposits by chemical reactions of gaseous precursors at a heated substrate" (14).[3] CVD processes offer alternatives to the search for improved or new materials because coatings or free-standing shapes can be deposited in a highly pure, dense, and nonporous form. The CVD process also has a higher throwing power than that of electrodeposition and vacuum evaporation, sputtering, or ion plating. Currently CVD is largely used in the semiconductor industry to provide materials having a specified grain structure and orientation. The future holds much promise for CVD to provide wear- and corrosion-resistant coatings for low-alloy or carbon steels because of the scarcity of materials (Cr, Ni, Co) available to form stainless steels and other corrosion- and wear-resistant alloys.

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

CVD research by the Bureau of Mines was initiated to extend the "useful life of steel" under an interagency agreement with the U.S. Energy Research and Development Administration (now the Department of Energy). The objective was to provide erosion-, abrasion-, and corrosion-resistant CVD coatings for valve components used in coal gasification units. The Bureau of Mines, a pioneer in the preparation of CVD tungsten, has been reviewing the literature relating to the deposition of the group IVB, VB, and VIB elements in its search for suitable wear-resistant coatings. This publication attempts to bring together the many CVD references that have appeared since, "Vapor Deposition" by Powell, Oxley, and Blocher was published in 1966 (116).

Several CVD reviews have been published. Holzl (68-69) has published two reviews in which pyrolysis and reduction techniques are given. A literature search of Mo, W, and Re as coatings has been reported by Kadner (79). Pyrolytic tungsten obtained from tungsten halides has been reviewed by Emyashev and Slavgorodskaya (43). Hintermann and Gass (62), Schroff (129), Blocher (15-16), and Beguin (7) have published CVD review articles. Two recent review articles, one concerning the deposition of metals on nonmetallic surfaces (126) and one concerning the deposition of semiconductors (143) for electronic materials, recently have been published.

In addition to the review articles, there have been five international conferences on chemical vapor deposition (17-18, 53, 129, 152). Two of the published Plansee Seminars (9-10) also have pertinent information on chemical vapor deposition problems and techniques, with the main emphasis on molybdenum.

The CVD literature will be considered for each group IVB, VB, and VIB metal by periodic family, followed by some of the methods, uses, and properties of the deposits.

GROUP IVB METALS (Ti, Zr, Hf)

Titanium

Titanium is usually deposited by the van Arkel process (146), which is the thermal decomposition of TiI_4 at 1,200° to 1,400° C (80, 85). The iodide is vaporized at 160° to 250° C and carried by a flow of argon to the hot substrate. The reduction of $TiCl_4$ with hydrogen on iron at 950° to 1,200° C is another common deposition method (116, p. 320). However, equilibrium product calculations by Yean and Riter (160) show that titanium formation is not very favorable by the use of hydrogen alone in the reduction of $TiCl_4$. Reduction of $TiCl_4$ by iron has been proven by Kidin, Andryushechkin, Ragimov (84) at temperatures higher than 950° C. Their results indicate that the titanium layer was actually a solid solution of titanium in α-iron. Lower chlorides of titanium are formed also during the hydrogen reduction of $TiCl_4$ on steel (76). One recent patent (34) involves the deposition of titanium from the tetrachloride on a tubular substrate of columbium or tantalum at 1,200° to 1,500° C. Another patent (151) describes the formation of Cr-Ti alloys on refractory metals by the use of $TiCl_4$ on Ti and Cr metals. The lower chlorides formed, possibly $CrCl_2$ and $TiCl_3$, at 800° C then are reduced by hydrogen at 1,370° C. An alloy composition of 45 pct Ti and 55 pct Cr was reported to have been formed by this method.

Shelton and Holt (135) have produced alloys of titanium and zirconium by use of the van Arkel iodide process at 1,300° C. Titanium and zirconium metal-sponge were mixed together with iodine to produce the tetraiodides. At 240° to 355° C, the triiodides are formed by the reaction of the excess metal sponge with the tetraiodides. The amount of titanium in the alloy will decrease from 87 wt-pct to 35 wt-pct as the vaporizer temperature is increased to 355° C.

Zirconium and Hafnium

Most of the references involving CVD reactions of zirconium and hafnium concern the formation of refractory compounds; hence only a few references involving the deposition of the pure metals can be given. Both zirconium and hafnium have been deposited by the techniques used for titanium. According to van Arkel and deBoer (147), zirconium can be deposited from the ladle at temperatures of 1,200° to 1,450° C; slightly higher temperatures are needed to deposit hafnium from the iodide. The solid iodides are usually vaporized at temperatures of 250° to 300° C for ZrI_4 and about 400° C for HfI_4.

The reduction of zirconium or hafnium chloride by hydrogen is questionable. Early investigators reported and patented the hydrogen reduction of $ZrCl_4$, but later work revealed these deposits to have been zirconium carbides or nitrides. These zirconium compounds were formed because of impurities in the hydrogen. When ultrapure hydrogen is employed, no metal deposition occurs (116, p. 329). Zirconium was deposited at 800° to 1,000° C by a displacement reaction involving the metal substrate, hydrogen, and $ZrCl_4$ (116, p. 329).

A fairly detailed study of an adapted van Arkel method for producing zirconium coatings was published by Sale (123), who proposed a mechanism to explain the iodide process. The process probably involves the disproportionation of ZrI_2 as well as the thermal decomposition of ZrI_4. A thermodynamic analysis of the van Arkel iodide process has been published (134). Some representative CVD equations for the group IVB metals are given in table 1.

TABLE 1. - Some CVD reactions for group IVB metals

Reaction	Vaporization temperature, ° C	Substrate temperature, ° C
$TiI_4 \rightarrow Ti + 2I_2$	160-250	1,200-1,400
*$TiCl_4 + 2H_2 \xrightarrow{Fe} Ti + 4HCl$	25- 60	950-1,200
$ZrI_4 \rightarrow Zr + 2I_2$	250-350	1,200-1,400
*$ZrCl_4 + 2H_2 \xrightarrow{Fe} Zr + 4HCl$	200-250	800-1,000
$HfI_4 \rightarrow Hf + 2I_2$	~400	1,100-1,400

*A displacement reaction with metal substrate--here Fe is the substrate.

GROUP VB METALS (V, Cb, Ta)

Vanadium

Vanadium is probably best deposited by the decomposition of vanadium diiodide. The higher iodides of vanadium usually are not suitable because they decompose before volatilization. The vanadium diiodide was vaporized at 700° to 1,000° C and deposited on substrates at 1,000° to 1,200° C (42, 82, 146, p 511-514). Hydrogen reduction of other vanadium halides generally yields vanadium. Federer (47), however, has found that the hydrogen reduction of vanadium pentafluoride results in the formation of vanadium trifluoride rather than vanadium. The hydrogen reduction of vanadium tetrachloride is possible (47), provided substrate temperatures are high enough (1,000° to 1,200° C) and flow rates carefully controlled. Lower chlorides of vanadium were deposited indicating that the process probably proceeds via a lower chloride of vanadium. Val and Accary (145) have proposed that VCl_2 is an intermediate in the reduction of VCl_4 by hydrogen.

Vanadium hexacarbonyl (155) was cited in a patent which involves the pyrolysis of the organometallic compound on a heated substrate. The organometallic compound was dissolved in a suitable solvent and atomized onto a metal substrate such as tantalum at 500° C. It would appear that other organometallic vanadium compounds could be used in the same way. In fact, alloy systems may be adaptable to this method.

Columbium and Tantalum

Columbium and tantalum are considered together because their chemical properties are so similar. Columbium or tantalum coatings can be obtained by thermally decomposing the respective iodide prepared in-situ (120). Recently, the thermal decomposition of CbI_3 and TaI_3 has been reported (117); in this work tantalum triiodide was vaporized at 250° to 300° C and tantalum was deposited upon substrates at 1,300° to 1,500° C, while columbium triiodide was vaporized at about 600° C and columbium was deposited at 1,300° to 1,600° C. Jerreat and Rawling (78) also have reported the deposition of Ta from TaI_5. The TaI_5 was vaporized at 650° C and Ta was deposited at 1,200° C with a transport rate of 350 mg/hr. The chlorides and bromides also can be thermally deposited, but higher temperatures are required.

Generally, Cb and Ta deposits are formed by the hydrogen reduction of $CbCl_5$ or $TaCl_5$ (115). The pentachlorides of Columbium or tantalum can be prepared by direct chlorination of the metal at 200° to 300° C or by the chlorination of a graphite-metal oxide mixture. The vaporized pentachlorides nominally are reduced by hydrogen at 900° to 1,200° C. Babich, Kurganov, and Strogonov (3-4) have conducted a study at atmospheric pressure of the metal deposition rates as a function of temperature and gas flow rates. The best results were obtained at 1,000° to 1,100° C; increased temperature resulted in increased grain size and roughness. Excess hydrogen caused an increase in the reduction, but since the reaction is exothermic, the temperature must be controlled carefully for proper grain size. Another deposition rate study has been published for the reaction of $TaCl_5$ and H_2 at 900° to 1,600° C on several

substrates, an activation energy of 12.3 kcal/mole was reported (96). Lorel and Pinteau (94) have reported on tantalum and columbium deposition at pressures of 5 to 30 torr. Two patents have been granted using $CbCl_5$ and $TaCl_5$ (99, 109) and hydrogen.

There are data concerning the reduction of vaporized TaF_5 and CbF_5 with hydrogen. A computer-assisted study was conducted (105) with the theoretical yield calculated as being obtained with a 2- to 5-fold excess of hydrogen and 7.4 to 16.4 vol-pct TaF_5 at 1,327° to 1,527° C. Temperatures of 1,027° to 1,227° C are needed for Cb deposition for the same concentration range of CbF_5. An earlier investigation on the hydrogen reduction of TaF_5 and CbF_5 suggested that successful coatings could be obtained from CbF_5, but at 550° C the pure metal was not produced from TaF_5 (22).

Tantalum and perhaps columbium are suggested as coatings for boilers and chemical plants working in marine environments (2), because tantalum is inert to attack by sea water and air up to 250° C. Tantalum coatings on steel by CVD can be made if an interlayer of Cr, Ti, or Zr is first applied (2). Table 2 gives a summary of the CVD reactions for the group VB metals.

TABLE 2. - Some CVD reactions for group VB metals

Reaction	Vaporization temperature, ° C	Substrate temperature, ° C
$VI_2 \rightarrow V + I_2$	700-1,000	1,000-1,200
$VCl_4 + 2H_2 \rightarrow V + 4HCl$	50- 100	1,000-1,200
$2CbI_3 \rightarrow 2Cb + 3I_2$	~600	1,300-1,600
$2CbCl_5 + 5H_2 \rightarrow 2Cb + 10HCl$	200- 300	900-1,200
$2TaI_3 \rightarrow 2Ta + 3I_2$	250- 300	1,300-1,500
$2TaI_5 \rightarrow 2Ta + 5I_2$	·650	>1,200
$2TaCl_5 + 5H_2 \rightarrow 2Ta + 10HCl$	200- 300	900-1,200

GROUP VIB METALS (Cr, Mo, W)

Chromium

Chromium can be readily electrodeposited, but since CVD coatings have been found to be less prone to peeling and less porous, several CVD methods have been developed and investigated. One of the earliest of the CVD methods is that of Koopman, deBoer, and van Arkel (86), which involves the decomposition of CrI_2. In this method, CrI_2 is carried by a carrier gas at about 800° C, or a carrier gas is passed over iodine at 130° C and then over chromium at 800° C; then chromium is finally deposited on a substrate at a somewhat higher temperature by thermal decomposition. Good fine-grained deposits can be obtained at atmospheric pressure up to substrate temperatures of 1,400° C (116, p. 290). Hydrogen has also been used to reduce CrI_2 (148), and high-purity chromium was obtained by this method.

The method most often used for obtaining chromium coatings is called the chromizing process. This process employs either the hydrogen reduction or a metal displacement of chromous chloride. This method has been discussed in detail by Powell, Oxley, and Blocher (116, p. 290) and thus will be mentioned only briefly here. There are several processes used. On one extreme H_2 and HCl gas are passed over $CrCl_2$ at 850° to 900° C and then carried to a substrate heated at 1,000° to 1,200° C. In another chromizing technique, powdered chromium or ferrochromium is chlorinated in situ at 800° to 1,000° C and transported to the substrate where it is reduced or decomposed. Usually iron or steel is the substrate and the reaction may be represented as

$$CrCl_2 + Fe \rightarrow Cr + FeCl_2 .$$

This reaction is done at atmospheric pressure and 900° to 1,200° C (114).

Chromizing processes that utilize H_2 reduction (150) can be represented as

$$2HCl_{(g)} + Cr_{(s)} \rightarrow CrCl_{2\,(g)} + H_{2\,(g)} \text{ at } 900° \text{ C}$$

and

$$H_{2\,(g)} + CrCl_{2\,(g)} \rightarrow Cr_{(s)} + 2HCl_{(g)} \text{ at } \sim 1{,}200° \text{ C}.$$

The latter reaction, which is the reverse of the former, is accomplished by using excess hydrogen and a substrate of higher temperature than 900° C. Chromium may be pyrolytically produced at temperatures greater than 900° C from $CrCl_3$ (98), or by the hydrogen reduction of $CrCl_3$ formed in situ (122). In the latter method, the $CrCl_3$ is formed at 950° C and carried by hydrogen to the substrate, at ≥1,000° C, where deposition occurs. This same chromizing process also can be accomplished by use of a HBr-H_2 mixture upon chromium or ferrochromium (72). A fairly detailed paper by Hudson (72) presents some equilibrium data for both the HCl-H_2 and the HBr-H_2 processes, along with some experimental data.

Recently, several organometallic compounds of chromium have been employed for CVD coatings. These are of interest because lower deposition temperatures can be used in some cases; however, they are generally more expensive and care must be taken to avoid intermediate decomposition products which can affect purity and coating properties. Some typical organometallic chromium compounds that have been used are chromium hexacarbonyl, $Cr(CO)_6$; dicumene chromium, $Cr[C_6H_5CH(CH_3)_2]_2$; bis(ethylbenzene) chromium, $Cr(C_2H_5C_6H_5)_2$; (mesitylene) tricarbonylchromium, $Cr(CH_3)_3C_6H_3(CO)_3$; bis(benzene) chromium, $Cr(C_6H_6)_2$, and other aromatic derivatives (37, 41, 56). The use of dicumene chromium (97) has been patented, as has that of dibenzenechromium (110). Dicumene chromium has been used to form semiconductor devices (1), and to coat uranium dioxide (128). Chromium hexacarbonyl has been employed for chromium formation, but purer deposits are obtained from dicumene chromium (127). The metal-to-carbon bond in chromium hexacarbonyl is stronger than the metal-to-carbon bond in dicumene chromium because the conditions for strong sigma, σ, bonding are available and it is possibile for metal-to-carbonyl pi, π, bonding to occur.

Dicumene chromium does not have the right geometry to form strong σ bonds, and hence the resulting bonds are weak. The reported enthalpy of formation for $Cr(CO)_6$ is -234.2±0.4 kcal/mole (112), compared with 21±8 kcal/mole for $Cr(C_6H_6)_2$ (50). The enthalpy of formation for dicumene chromium should be similar to that for $Cr(C_6H_6)_2$. Since chromium hexacarbonyl decomposes less readily than dicumene chromium, coatings made from the carbonyl contain more carbide impurities. A kinetic study of the thermal decomposition of the carbonyl has been reported (131) and is first order with an activation energy of 4.25 kcal/mole. Carbide formation has been suppressed by using HI as a catalyst in the decomposition of bis(ethylbenzene) chromium (13).

Molybdenum

Molybdenum can be deposited by the thermal decomposition or hydrogen reduction of either the pentachloride or the pentabromide (116, p. 302). The deposition of molybdenum by the hydrogen reduction of the pentachloride was reported by Childs, Cline, Kisner, and Wulff (29). The most adherent molybdenum coatings were obtained on nickel at 950° C and low pressures. Wlodek and Wulff have further investigated the adhesion of vapor-deposited molybdenum from the chloride (157). Adherent molybdenum coatings could not be formed on iron or steel substrates without first applying the electroplated nickel interfacial layer. Molybdenum has been coated successfully on a heated wire at 20 to 200 torr and 700° to 1,300° C by the hydrogen reduction of the pentachloride (113). More recently, molybdenum has been coated onto vanadium by the hydrogen reduction of $MoCl_5$ at temperatures above 750° C and reaction pressures below 50 torr (51). It was found necessary to have a nickel interlayer in order to form adherent coatings.

Very pure tungsten and molybdenum have been prepared by the thermal decomposition of tungsten hexachloride or molybdenum pentachloride (57). This was accomplished in vacuum at temperatures of 1,500° to 2,000° C. Weise (154) has found that single crystals can be formed by the thermal decomposition of the tungsten or molybdenum chloride; by controlling the experimental conditions, he was able to prepare crystals having preferred oriented faces. This has been investigated further by Evstyukhin, Abanin, Mel'nikov, and Perlovich (44), who obtained their best results at higher substrate temperatures, up to 1,430° C, and at pressures of 10^{-5} to 10^{-6} torr. The substrate used was molybdenum foil. Chizhikov, Kreingauz, and Pluzhnikova (30) have codeposited tungsten and molybdenum alloys by the thermal decomposotion of their chlorides. Adherent coatings were obtained on tungsten and molybdenum substrates at 1,600° C. Molybdenum also has been deposited onto single-crystal silicon substrates by the decomposition of molybdenum pentachloride (27).

Molybdenum can be deposited also by the hydrogen reduction of the hexafluoride. Shroff and Delval (137) have investigated the reaction from 600° to 1,100° C at partial pressures of 5 to 760 torr and with hydrogen-to-hexafluoride ratios of 1 to 60. They found that a H_2-to-MoF_6 ratio of 3 or greater coupled with a partial pressure of 300 torr and 700° C gave a good deposition rate. These investigators also examined the structure of the deposits as well as substrate adherence on several surfaces. At least two

patents have been reported (35, 70) using MoF_6 and H_2. A rather extensive adherence study has been reported by Federer and Poteat (49). Substrates that form stable fluorides at the deposition temperatures usually result in nonadherent coatings. This was examined thermodynamically as well as experimentally by Gabe (52) and by Bryant and Meier (25).

Molybdenum can be deposited also from the hexacarbonyl by pyrolysis and by reduction with hydrogen. The techniques involved in the pyrolysis of molybdenum carbonyl as well as chromium and tungsten carbonyl have been reported by Lander and Germer (91-92). Kaplan and d'Heurle (81) have investigated the formation of thin films produced by the hydrogen reduction of $Mo(CO)_6$ or $W(CO)_6$ at reduced pressures. When hydrogen is used as the carrier gas, the best results are obtained with an $Mo(CO)_6$ vapor pressure of 0.02 torr with H_2 at 2.0 torr and the deposition temperature range of 350° to 600° C (130). Several investigators (77, 121) have investigated the use of carbon dioxide as compared to hydrogen as a carrier gas in the reduction of molybdenum carbonyl. Boyes (20) has reported on a field-ion microscopy study of molybdenum films obtained by the thermal pyrolysis of $Mo(CO)_6$. The kinetics of the thermal decomposition of $Mo(CO)_6$ at 134.5° to 159° C and at 341° to 409° C have been studied using the statistical method (5), the investigators report activation energies of 28.8 kcal/mole at 134.5° to 159° C and of 6.3 kcal/mole at 341° to 409° C. Other investigators (8, 90) have investigated the effect of concentration of $Mo(CO)_6$ vapors and temperature in the preparation of molybdenum metal powder. They found that the bulk densities of the powders could be varied from 0.05 to 2.5 g/cm^3.

Tungsten

Tungsten is similar to molybdenum except that most of the reduction reactions are more easily accomplished. There is more interest in vapor-depositing tungsten because of its high melting point and density. The deposition of tungsten is accomplished by methods ranging from the thermal decomposition of WCl_6, the deBoer process, to the hydrogen reduction of complex organometallic tungsten compounds. The thermal decomposition of WCl_6 at low pressures requires substrate temperatures of 1,500° C or higher (89), whereas the use of hydrogen as a reducing agent can result in tungsten being formed at atmospheric pressures and temperatures of 500° to 600° C (103). Shroff (136) deposited W by an in situ method; Cl_2 is reacted with W at 850° to 900° C, and the resulting chloride decomposed at 950° to 1,100° C. A method for depositing tungsten foil on copper was developed using WCl_6 and hydrogen at 750° to 1,000° C (83). The deposition efficiency can be from 40 pct to as high as 80 pct under these conditions (116, p. 323). Generally high hydrogen-to-tungsten hexachloride ratios and substrate temperatures at 750° to 800° C are required for good adherency. Pinteau (111) has investigated the deposition of tungsten on Al_2O_3 substrates at 800° to 1,000° C using WCl_6 and hydrogen. The preferred crystal orientation was that of the [*100*] plane parallel to the substrate surface. Hudson, Tagami, and Yang (71) have reported that tungsten can be deposited with good reproducibility in the [*110*] crystal orientation by the hydrogen reduction of tungsten hexachloride. This preferred [*110*] orientation is of considerable interest because it has a higher work function than the other orientations. In many cases, removal of

hydrogen by vacuum-annealing the coated substrate at 1,200° C results in improved adhesion of the tungsten coating (95). Hydrogen reduction of tungsten hexachloride in a vacuum furnace at 2,700° to 3,300° C has resulted in producing tungsten whiskers having a higher tensile strength than commercial tungsten filaments (139). Korolev, Stolyarov, Emel'yanov and Mosalkov (88) employed a cyclic process to improve the quality of the tungsten coating of the substrate. This was accomplished by alternating the periods of hydrogen reduction of WCl_6 with periods of inert gas treatment at the same temperature as the reduction conditions. Recently a detailed study of the effect of dopants, such as K, Al, and Si, upon the rate of reduction of WCl_6 by hydrogen was reported (158, 159). The deposition rate was slower when dopants were added; in addition, the deposition rate decreased when the H_2-to-WCl_6 ratio was increased at constant temperature. The results were explained by assuming that the gas-phase diffusion of reactants was the rate-controlling step in the deposition process.

A patent utilizing the hydrogen reduction of tungsten hexachloride to produce tungsten-coated glass fibers having good electrical resistance was granted (19). Tungsten also has been deposited on silicon substrates for use as semiconductor devices by Melliar-Smith, Adams, Kaiser, and Kushner (104). Adherent deposits were obtained from hydrogen reduction of the hexachloride and hexafluoride of tungsten, using a pressure range from vacuum to atmospheric.

Recently the use of tungsten hexafluoride has been shown to be quite attractive (107), and there have been a number of investigations to support this thesis. McKnight (102) extols the use of tungsten hexafluoride in vapor-phase forming processes and indicates that CVD tungsten can be used to protect molybdenum from carbiding. Tungsten coats also can be used to prevent hydriding of materials such as Cb, Ta, and Ti. Although tungsten is a good high-temperature material, it is subject to high-temperature oxidation, which may be alleviated by a coating of tungsten silicide. Heestand and Leitten, (61) were granted a patent for forming tungsten tubing by the hydrogen reduction of tungsten hexafluoride.

Several papers deal with the process variables involved in hydrogen reduction of tungsten hexafluoride, including flow rates (12) and pressure (63) for rapid and optimal deposition rates. The fastest rates were obtained at atmospheric pressure and 800° C using a H_2-to-WF_6 ratio of 1.5 or greater. A statistical study of the efficiency on deposition of tungsten as a function of temperature, pressure, and flow rates at a constant reaction time has been published by Patterson, Robinson, and Hebble (108).

Tungsten deposited by the hydrogen reduction of tungsten hexafluoride has been compared with tungsten obtained by the thermal decomposition method in regard to grain orientation, yields, surface aspects, and quality of deposits (118). The possibility of trapped gases has been investigated both for the thermal process (125) and for the reduction process (46). The investigators found bubble formation when the samples were annealed; however, if the deposition temperature was close to 0.3 of the melting point of the metal deposited, no bubbles were formed on annealing. In the hydrogen reduction of WF_6, the

interaction of the substrate has been investigated partially also (23, 25). Several investigators have studied the kinetics of the hydrogen reduction of tungsten hexafluoride, however, the mechanism is still not well understood. Haskell (58) has applied rate theory, assuming the rate step as the desorption of the hydrogen halide. Haskell and Byrne (59) have reported on a mechanism for growth of tungsten utilizing X-ray and transport data. Some effects of additives on the deposition rate of CVD tungsten from the hexafluoride have been reported also (73); these studies indicated that O_2 and H_2O poisoned the surface and hence reduced the rate of deposition, while HF had no effect. Hoertel (64) has reported the effects of additives in regards to the grain size and microstructure of CVD-produced tungsten from the hydrogen reduction of WF_6. Hoertel found that the addition of 2 vol-pct butane or 4 vol-pct propane to the H_2 and WF_6 mixture produced deposits with fine grain size and a corresponding increase in microhardness. Golovanov, Krasovskii, Pleshakov, and Turner (55) have studied the kinetics of the reaction, $WF_6 + 3H_2 \rightarrow W + 6HF$, when H_2O, N_2, CO_2, and Ar were added. Their results indicate that the deposition rate is dependent on the pressure of WF_6 and weakly dependent on the pressure of H_2. The additives did not change the nature of the experimental curves. Both the report by Cheung (28) and the thesis by Huggins (75) suggest mechanisms for the kinetic deposition process. Bryant and Meier (26) have investigated the kinetics of the hydrogen reduction of tungsten hexafluoride, and they calculate an activation energy of 7.3 kcal/mole, assuming desorption of HF from the surface as the rate step. McCarty, Reith, and Simon (101) have suggested that tungsten pentafluoride could be a reactive intermediate in the reduction of WF_6.

The coefficient of expansion and the electrical resistivity of tungsten have been utilized in silicon semiconductor devices (100, 133). CVD tungsten has been used to join stainless steel alloys (93); however, there are problems with surface oxide. CVD tungsten has been evaluated for mechanical properties at high temperatures (31-32), and Farrell (45) has measured the creep properties in vacuum. The use of the hydrogen reduction of tungsten hexafluoride to produce coatings is given in two Soviet patents (33, 55) and one German patent (36). A laser beam has been used for the heat source to deposit tungsten from a WF_6 and H_2 mixture (11). Haskell and Iman (60) have measured the erosion and heat transfer properties of tungsten-coated steel.

In addition to some thermodynamic calculation studies by Wahl and Batzies (149), there have been some interesting studies involving preferred grain orientation in tungsten produced by chemical vapor deposition (24). Bryant (24) has compared the strength and temperature stability of these preferred grain types. Different orientations are produced when tungsten is deposited from the hexafluoride as opposed to the hexachloride (24, 59).

Tungsten can be vapor-deposited also by thermal decomposition of tungsten hexacarbonyl (91-92). Ward, Coon, and Oxley (153) have reported the optimum conditions for reducing the hexacarbonyl using hydrogen and steam or carbon dioxide. The carbonyl method has resulted in several coating uses, such as on porcelain and iron (106), as well as a patent for coating wire (87). Some thermodynamic as well as kinetic studies using tungsten hexacarbonyl have been reported (6, 140-142, 144), but more work must be done to clarify this area.

Some other organometallic tungsten compounds, such as mesitylene tungsten tricarbonyl, $W(CO)_3[(CH_3)_3C_6H_3]$, and hexa(trifluorophosphine) tungsten, $W(PF_3)_6$, have been used in CVD processes (138, 155). Some CVD reactions for the group VIB metals may be found in table 3.

TABLE 3. - Some CVD reactions for group VIB metals

Reaction	Vaporization temperature, ° C	Substrate temperature, ° C
$CrI_2 \rightarrow Cr + I_2$	800	>800 up to >1,000
$2CrI_3 \rightarrow 2Cr + 3I_2$	~600	>900
$Cr + 2HCl \rightarrow CrCl_2 + H_2$ $CrCl_2 + H_2 \rightarrow Cr + 2HCl$	(1)	(1)
$*2CrCl_3 + 3H_2 \rightarrow 2Cr + 6HCl$	950	>1,000
$**Cr[C_6H_5CH(CH_3)_2]_2 \xrightarrow{HI} Cr + 2C_6H_5CH(CH_3)_2$	~195	400- 600
$2MoCl_5 \rightarrow Mo + 5Cl_2$	~300	1,500-2,000
$2MoCl_5 + 5H_2 \rightarrow 2Mo + 10HCl$	300	>750
$MoF_6 + H_2 \rightarrow Mo + 6HF$	35- 50	600-1,100
$\neq Mo(CO)_6 \rightarrow Mo + 6CO$	25-100	350- 600
$\neq\neq WCl_6 \rightarrow W + 3Cl_2$	140-150	>1,500
$WCl_6 + 3H_2 \rightarrow W + 6HCl$	350-450	500- 600
$WF_6 + 3H_2 \rightarrow W + 6HF$	18- 35	400-1,100
$\neq W(CO)_6 \rightarrow W + 6CO$	25-100	350- 600

[1] 1st reaction, 2d reaction } formed at 900° C; on substrate ~1,200° C.
*$CrCl_3$ is actually formed in situ and carried by H_2 to substrate.
**HI is a catalyst that suppresses carbide formation.
≠Partial pressures of $Mo(CO)_6$ and $W(CO)_6$ are ~0.02 torr and ~0.10 torr, respectively, with H_2 as carrier gas at 2.0 torr.
≠≠Low pressure ~10^{-4} torr.

Several alloys have been produced by chemical vapor deposition techniques, particularly in the rhenium-tungsten system. Donaldson, Hoertel, and Cochran (39, 65) had some success using the hexafluorides of Re and W; however, the alloy composition was nonuniform. Roberts (119) and Federer (48) also have reported on this system. An intensive investigation by Huegel and Holman has been reported (66-67, 74). Codeposits of rhenium and tungsten are difficult

to control owing to the large difference in the reduction temperature of the corresponding hexafluorides. Brenner and Anderson (21) have produced rhenium-tungsten coatings using some oxychlororhenium compounds, ReO_3Cl or $ReOCl_4$, with WF_6 instead of ReF_6; however, only about 6 pct Re is incorporated into the alloy system.

In addition to rhenium, there have been attempts to alloy tungsten with cobalt (38) and with molybdenum (40).

CONCLUSIONS

Alloy systems are of interest as high-temperature coatings that are also resistant to oxidation and/or corrosion. These alloy systems are much needed in today's technology. Higher processing temperatures will be needed for applications such as coal gasification, and the need for oxidation-resistant surfaces will be even greater. Metals such as chromium are in short supply; they may be conserved by vapor-depositing them on metals that are not so scarce, thus conserving our natural resources.

Basic research on CVD processes may lead to determining how one might produce preferred orientation in materials not yet studied. The result could be materials having improved electrical properties as well as higher mechanical strength. There have even been suggestions that CVD may be used for isotope separation (132) because an 0.8-pct C^{12}-to-C^{13} enrichment ratio has been reported in carbon deposition from $C_{12}H_{26}$.

The amount of literature dealing with CVD processes continues to grow at an ever-increasing pace. New developments such as the use of CVD for isotope separation, the development of stronger steels by CVD, the production of solar absorbers, and the preparation of alloys and superconductors, optical fibers, and coatings to increase the life of materials are just a few of the areas where CVD is expanding its horizons.

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