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Chemical Vapor Deposition of Group IVB, VB, and VIB Elements With Nonmetals

A Literature Review

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

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CONTENTS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	min	minute
° C	degree Celsius	mL	milliliter
cm	centimeter	mm	millimeter
eV	electron volt	μm	micrometer
hr	hour	mole	gram mole of material
Hz	hertz, reciprocal second	pct	percent
kcal	kilocalorie	sec	second
kg	kilogram	torr	millimeter of Hg pressure
mA	milliampere		

CHEMICAL VAPOR DEPOSITION OF GROUP IVB, VB, AND VIB ELEMENTS WITH NONMETALS

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 on the nonmetal binary and ternary compounds of the group IVB, VB, and VIB elements, with emphasis directed to the following nonmetals: B, C, N, O, and Si. This review examines each of these binary and selected ternary compounds of the group IVB, VB, and VIB elements as coatings and gives some of their preparative methods, uses, and properties. A total of 259 references were found for these compounds of the nine elements. This review was utilized in the Bureau's research to provide abrasion-, erosion-, and corrosion-resistant coatings in order to conserve critical metals and protect various metallic surfaces in metallurgical, mining, and energy conversion systems.

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INTRODUCTION

Chemical vapor deposition (CVD) can be defined as a system in which one or more gaseous substances react on a heated substrate to form a compound or an element. CVD coatings have assumed a vital role in expanding the horizons of materials conservation; CVD coatings have a significant influence on material properties, providing improved corrosion resistance, electrical contact resistance, reflectivity, color, abrasion resistance, erosion resistance, and solderability, or a decrease in the coefficient of friction. Preparation of semiconductor and superconductor materials relies heavily on CVD technology. Using CVD coatings can reduce the use of critical and strategic materials--while retaining improvements in desired material performance--in a wide variety of applications.

CVD research by the Bureau of Mines has been conducted to minimize the consumption of strategic and critical materials in the manufacture of erosion-, abrasion-, and corrosion-resistant components used in metallurgical, mining, and energy conversion systems. Test results were recently reported for one CVD-coated ball valve seat prepared during previous Bureau research (205).[3]

The Bureau, a pioneer in the preparation of CVD tungsten, is reviewing the literature relating to the deposition of abrasion-, erosion-, and corrosion-resistant coatings of the group IVB, VB, and VIB elements and compounds. A literature review of the group IVB, VB, and VIB elements was published in 1979 (133). This present review brings together many of the references that have appeared since about 1966 on the binary and selected ternary compounds of the group IVB, VB, and VIB elements with B, C, N, O, and Si.

Several CVD reviews have been published that give some of the deposition techniques, as well as the properties of the deposited metals and some of the binary compounds. One such article, by Archer (5), concerns a few metals and some metalloids. Broszeit and Gabriel (31) have reviewed CVD techniques for protective coating and treatment for tools and structural parts. Perry and Archer (162-163) have surveyed wear-resistant coatings and some techniques of CVD. Yee (258) has made quite an extensive review of the use of CVD for protective coatings.

In addition to the review articles, there have been eight international conferences on CVD (21-23, 42, 61, 197, 203, 252), which will not be covered in general here.

In this review, the CVD literature will be considered for each group IVB, VB, and VIB metal, by periodic family, followed in each section by discussion of some of the methods of preparation, uses, and properties of the nonmetal deposits.

GROUP IVB METALS (Ti, Zr, Hf)

TITANIUM BORIDE

Titanium diboride (TiB_2) is usually deposited by the reaction of $TiCl_4$ with BCl_3 and H_2 at temperatures varying from 850° to 1,400° C and near 1 atm total pressure (130, 167, 225). Pierson and Randich have shown that TiB_2 can be deposited on Ta and stainless steels at temperatures of 850° to 1,100° C, yielding surfaces with good erosion resistance and Knoop hardness of about 3,300 kg mm^{-2} (175). Takahashi, Sugiyama, and Suzuki grew TiB_2 fibers using a gas mixture of $TiCl_4$, BCl_3, H_2, and Ar in an alternating current (ac) discharge (232). Under these conditions, the reaction could be accomplished at the lower temperatures of 300° to 700° C. Maximum growth was obtained at 400° C and discharge currents of 0.4 to 0.6 mA. Other investigators studied the growth of TiB_2 whiskers on quartz (146). They found that if small

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

amounts of Au, Pt, or Pd were painted onto the substrates, the whisker growth was improved. Some single crystals of TiB_2 grown on Ta wire were demonstrated (212); however, the addition of HCl was essential, as well as temperatures of 1,700° to 1,900° C. Several investigators studied the formation of TiB_2 on graphite substrates (18, 178-179, 237).

Besmann and Spear have published thermodynamic (16) and kinetic (17) studies of the CVD of TiB_2. Their results indicated that $TiCl_3$, as well as $HBCl_2$ and HCl, was also present (16). They obtained a simple linear rate expression that was used to calculate an activation energy of 40±12 kcal $mole^{-1}$ (15, 17) for the deposition. Randich and Gerlach have published a method for calculating the phase diagram for the Ti-B-Cl-H system (188-189).

Pierson and Randich (176-177) investigated the interaction of TiB_2 with the substrate. They found the substrate should not be deformed or transformed at temperatures up to 1,100° C, nor should it react with the byproducts of the reaction, in particular HCl. There was in some cases a thermal expansion difference that had to be corrected by the use of an interlayer of Ni or Cu. The substrates that could be used were Mo, W, Ta, Kovar, and high-Cr steels, as well as WC and TiC. These investigators found that a boride interlayer, usually M_3B or M_2B, was formed, possibly by diffusion. Here M could be a pure metal or an alloy. Ultrasound was employed to prepare thick films of TiB_2 on low carbon steel (220). Pierson and Mullendore have reported the preparation of TiB_2 using B_2H_6 instead of BCl_3 (174). Dense and adherent coatings were obtained using B_2H_6 with $TiCl_4$ and H_2 at 600° to 900° C on graphite substrates.

Bonetti, Comte, and Hintermann (28) used metal borohydride compounds to boronize metals. In this process, $Ti(BH_4)_3$ was produced in situ by the reaction of $TiCl_4$ with $LiBH_4$ in an air-free system at low temperatures. The thermal decomposition of $Ti(BH_4)_3$ at temperatures of 300° to 500° C yielded yellow metallic deposits, which were not found to be suitable at the present stage of this technology (28).

Good wear-resistant coatings of titanium boronitride ($TiB_{2\pm x}N_y$) have recently been reported (170-171). These coatings were produced by the action of $TiCl_4$ and BCl_3 with N_2 and H_2 at 1,150° to 1,450° C and pressures of 10 to 20 torr (171). The cubic boronitrides with an atomic ratio B/(B + N) of less than 0.75 had microhardness values up to 2,600 kg mm^{-2} (170).

ZIRCONIUM BORIDE

Whiskers of zirconium boride (ZrB_2) were formed on quartz substrates at temperatures of 1,000° to 1,200° C from a mixture of $ZrCl_4$, BCl_3, H_2, and Ar (145). Randich synthesized some alloy borides of the form (Ti, Zr)B_2 (185-186). These gave Vickers hardness values of approximately 3,700 kg mm^{-2} for (Ti, Zr)B_2 and 2,200 kg mm^{-2} for ZrB_2. These alloys were prepared by the H_2 reduction of the metal chloride and BCl_3 in the temperature range 800° to 1,100° C, with graphite as the substrate. Takahashi and Kamiya (224) studied the system $Ti_{1-x}Zr_xB_2$, where x = 1 to 0. They found that increasing the temperature increased the deposition rate, but the rate was not dependent on total flow rate. The temperature range was 900° to 1,400° C, and dense uniform deposits resulted when the metal halide partial pressures were high compared with the partial pressure of BCl_3.

TITANIUM CARBIDE

Titanium carbide (TiC) formation technology is far more advanced than that for TiB_2. Titanium carbide can be formed by the H_2 reduction of $TiCl_4$ on graphite at 1,000° to 1,900° C (50) or by the action of H_2 on a mixture of $TiCl_4$ and a suitable hydrocarbon at temperatures ranging from 850° to 1,350° C (228, 230, 233). The hydrocarbon can be propane (228, 233), methane (46), isopentane (230), and ethane, or ethene (230). Even carbon tetrachloride (CCl_4) can be used as the source of C (38, 152, 190).

Toulene (138, 180) and benzene (139) have been employed to coat steel as well as several hard alloys with TiC. Several patents have been granted for processes to coat manufactured objects (137), gun barrels (253), and even composite substrates (209). Two patents are concerned with codepositing TiC with ductile metals such as Co and Ni (38, 253), which is accomplished by introducing $CoCl_2$ or $NiCl_2$ as vapors with a carrier gas such as Ar or He.

Pearce and Marek (161) have given experimental and thermodynamic data to indicate that C needs to be present to reduce $TiCl_4$ with H_2 efficiently. This was also experimentally verified by Aggour, Fitzer, and Schlichting (1).

There have been several thermodynamic equilibrium treatments involving the Ti-Cl-H-C system over several temperature ranges (14, 43, 113, 127). In addition to these equilibrium treatments, there have been several rate studies reported (107, 208, 211). Kato, Yasunaga, and Tamari reported a growth rate of 1.2×10^{-4} cm sec^{-1} for TiC grown from the reduction of $TiCl_4$ and methane with H_2 at 1,360° C (107). The TiC whiskers grown on graphite were in the [111] direction. Stjernberg, Gass, and Hintermann (208) have reported that the rate of deposition of TiC is proportional to the methane concentration and inversely proportional to the HCl concentration at high HCl concentrations. They used the Langmuir-Hinshelwood mechanism to explain their experimental data. Subrahmanyam, Lahiri, and Abraham (211) have shown that the observed rate of formation of TiC from a mixture of $TiCl_4$, toluene, and H_2 is really a combination of a chemical reaction rate and a diffusion-controlled rate. When large flow rates are used, a plot of the logarithm of deposition rate versus the reciprocal of the absolute temperature produces a linear plot, compared with low flow rates, which give a nonlinear plot. This nonlinearity is due to diffusion rates. A thermodynamic approach has been published concerning the deposition of nonstoichiometric carbides of Ti (245).

Titanium carbide has been vapor-deposited onto cemented carbide substrates (65, 122, 210, 240) and onto sintered hard carbide substrates (121). In one case, the interface between the CVD TiC and cemented carbide substrate (204) was examined by scanning electron microscopy as well as Auger electron spectroscopy. There was evidence of C loss from the substrate during the formation of the TiC coating. Lee and Richman (122) found that the presence of air or water in the coating system changed the growth rate as well as the coating structure because of the fine particles of TiO_2 that were formed. Karp, Filip, and Gibas (103) found that TiC growth occurred in the [111] direction on sintered carbide substrates.

The wear resistance of steels has been improved by coating with TiC (44, 93, 165). There is a review article without references by Yamakishi (256) on the TiC treatment of steel, and an article on the industrial applications of TiC coatings on steel (166). Several patents have been granted (41, 79, 140, 182, 215) that are concerned with the deposition of TiC or the apparatus for its deposition.

TiC and TiN coatings reduce friction (75, 183) or strengthen the surface (202) and are also used as decorative coatings (200). Schintlmeister and Pacher (198-199) have discussed several of these applications and have predicted a great future for these coatings. Bonetti (27) has given some hardness values as well as thermal expansion coefficients for TiC on various cemented carbide substrates.

The use of lasers (3, 131) and of plasmas (48-49) for the deposition of TiC has been applied with success. The future of laser chemical vapor deposition (LCVD) seems secure because improved control of heating and cooling rates can be obtained and cleaner surfaces are exposed to the coating process.

ZIRCONIUM CARBIDE

Zirconium carbide (ZrC) is usually formed by the reduction of an appropriate zirconium halide with H_2 and a suitable hydrocarbon. This can be done at temperatures of 800° to 1,200° C (229, 236). Using methane, $ZrCl_4$, and H_2, Tamari and Kato (236) found that ZrC grew preferentially in the [100] direction with side planes generally $\{100\}$. The halide can be generated in situ by the action of a halogenation agent such as methylene chloride upon Zr sponge at 600° C (191), or it can be obtained by the sublimation of $ZrCl_4$ at 210° to 310° C (235). In one method, $ZrCl_4$ was fed into a fluidized-bed reactor as a fine powder (86). Ikawa and Iwamoto (98) employed methyl iodide vapor on Zr sponge to produce ZrI_4. The methyl iodide was reacted with the Zr at 400° to 800° C, and then ZrC was formed at temperatures above 1,000° C in a separate reaction zone (97, 99) or by addition of H_2 at 1,100° C (98). Recently, Ikawa (95) produced ZrC by first reacting Br_2 with Zr sponge at 600° C and then reacting methane and H_2 at approximately 1,400° C with the $ZrBr_4$. The effect of the gas composition on the deposition of ZrC has been reported (156).

Most of the ZrC obtained by CVD methods is produced from $ZrCl_4$ reacting with H_2 and methane, as is evidenced by several investigations (39, 96, 184, 196, 250). Samoilenko and Pereselentseva (196) deposited ZrC on W wire at temperatures of 1,300° to 1,500° C and obtained good growth rates with an activation energy of 21 kcal $mole^{-1}$. Ikawa (96) found that for good ZrC formation both H_2 and the hydrocarbon must be present.

Ambartsumyan and Babich (4) found that ZrC formed on graphite by the reaction of $ZrCl_4$ and H_2 obeys the rate equation:

$$V = 4.30 \times 10^3 \exp(-1660/T) \ \mu m \ min^{-1}$$

Some of the main uses of CVD ZrC are as coatings for cutting tools (112, 255) and for ThO_2 spheres (85) and as reactor fuel particles (54, 157).

HAFNIUM CARBIDE

Hafnium carbide (HfC) is produced by CVD from the chloride or the iodide with a H_2 and hydrocarbon mixture. Hertz, Spitz, and Besson (70-71) studied the conditions for forming HfC from $HfCl_4$, H_2, and methane. They found that stoichiometric HfC could be deposited (70) at temperatures of 1,200° to 1,500° C and at methane-to-$HfCl_4$ ratios of 0.25 to 4.5. Hertz, Spitz, and Besson (72) have reported that a maximum deposition rate of approximately 350 μm hr^{-1} at 1,500° C could be obtained when the H_2-to-methane ratio was approximately 30 and the methane-to-$HfCl_4$ ratio was approximately 2. The presence of free C lowered the coating adherence (71). In general, a large excess of H_2 is employed to yield hard adhesive coatings (69). At least two U.S. patents (29, 62) concerning HfC have been granted, of which one is for coating SiC fibers that are used to reinforce certain composites (62).

There have been at least five Japanese patents (56-58, 77-78) that report the preparation of HfC from the action of HfI_4 with a suitable hydrocarbon. In these methods, I_2 and Hf are reacted first to form HfI_4 at 200° to 600° C; care is required to prevent the decomposition of the HfI_4 (57). The hydrocarbon, propane or butane (56), and the HfI_4 are then reacted on the substrate at temperatures of 800° to 1,250° C (58). These patents were for HfC coatings on cutting tools.

TITANIUM CARBONITRIDE

Since both TiC and TiN offer good corrosion, abrasion, and erosion protection, it would seem that titanium carbonitride (TiC_xN_{1-x}) might offer better protection. With this idea in mind, several investigators have studied the carbonitride system (40, 172-173, 198). Denker (40) studied the mechanical, chemical, and electrical properties of monocarbides, mononitrides, and monoxides of several cubic systems. It was Denker's evaluation of the materials that predicted the carbonitrides would be useful as coating materials, particularly for the element Ti.

Titanium carbonitrides are prepared by the action of $TiCl_4$ with H_2, N_2, and methane at approximately 900° C (37, 195, 201, 206-207). Instead of methane, ethane, propane (25), chlorobenzene, pyridine (251), or CCl_4 (154) can be used. Takahashi and Itoh (219) used an ultrasonic field to form carbonitride films 30 to 120 µm thick. Reactants of propane or methane along with H_2, N_2, and $TiCl_4$ were used to produce the carbonitride films. The investigators found the Vickers microhardness increased from 1,850 to 3,600 kg mm^{-2} as x changed from 0 to 1 in the formula TiC_xN_{1-x}. They also found that films produced in an ultrasonic field were more adherent than those produced without it.

Bitzer and Lohmann (19-20) patented a process for preparing diffusion coatings at 800° to 1,400° C, using suitable organic compounds such as cyanuryl chloride, acetonitrile, propionitrile, or tetracyanoethylene as the source of C and N. In these cases, the substrate was Ti or Ti alloy and Ar was the carrier gas for the organic compound. Bloom (24) employed trimethyl amine along with $TiCl_4$ and H_2 at 550° to 750° C to form carbonitride coatings on steel. Yaws and Wakefield (257) have reported on a scaled-up system that used the amine and $TiCl_4$ at temperatures of 600° to 700° C.

TITANIUM NITRIDE

Titanium nitride (TiN) is generally deposited by the action of H_2 and N_2 with $TiCl_4$ at temperatures ranging from 700° to 1,400° C (2, 104-105, 216). Kato and Tamari (104) studied the crystal growth of TiN on graphite, and found the growth rate nearly proportional to the square root of the H_2 partial pressure. They also found the TiN to grow in the [111] direction preferentially. High frequency discharge conditions have been used to obtain TiN as a powder (241). Peterson (168) has reported on the role of the partial pressure of $TiCl_4$ in the production of TiN. He found that low $TiCl_4$ partial pressures produced columnar grains, whereas higher partial pressures resulted in randomly oriented grains. In addition, the lower partial pressure resulted in a faster coating rate.

One Japanese patent (100) involves the coating of W or Mo alloys with TiN. Sadahiro, Cho, and Yamaya (194) studied the effect of temperature and gas composition on the deposition of TiN onto cemented carbides. Okamoto and Umezawa investigated the coating of mild steel with TiN, TiC, or Ti (158). They found Vickers hardnesses of 1,600 to 1,800 kg mm^{-2} for the TiN coatings and 1,800 to 3,600 kg mm^{-2} for the TiC coatings. Takahashi and Itoh (218) obtained TiN coatings with Vickers hardnesses of 1,600 to 2,000 kg mm^{-2} when the deposition was conducted in an ultrasonic field. In addition, the film had a strong <200> orientation. Some investigators who studied the growth rate of TiN on Mo wire have suggested that the mechanism of growth was surface controlled in the early stages (142). The linear growths were on (100) planes and were cubic single crystals. The CVD temperatures used in this study were between 1,600° and 2,200° C, with a gas flow ratio of $2N_2$ to $TiCl_4$ of 0.7 to 1.0.

Kagawa (101) investigated the deposition of TiN using $TiBr_4$ instead of $TiCl_4$. When N_2 was used as the carrier gas, the substrate temperatures needed to be greater than 1,260° C, but slightly lower temperatures could be employed when a mixture of H_2 and N_2 was the carrier gas. Bojarski, Wokulaska, and Wokulska (26) grew TiN whiskers on W substrates by the reaction of $TiCl_4$ with N_2 and H_2 at temperatures from 1,200° to 1,450° C. The crystal growth was found to be in the [001] direction with well-formed pyramid cube tips.

Some organometallic compounds have been utilized with the object of producing good deposits at lower temperatures. One such compound was the liquid titanium tetrakis (dimethylamide), $Ti[N(CH_3)_2]_4$ (213). However, a temperature of 800° C was necessary for good TiN formation because lower temperatures were not sufficient for the Ti and N to interact and combine. When titanium tetrakis (diethylamide) was decomposed at 10^{-2} torr and 350° to 650° C on ceramic substrates, a phase that was shown to be Ti(CN) was formed (120). During the decomposition, H_2, methane, ethane, and ethene were formed. The thermal decomposition of metal coordination compounds of Ti with 2,2'-bipyridine (bipy) has been patented (34). When O_2 and N_2 were introduced with the $Ti(bipy)_3$ compound, TiN was said to be deposited. The compound was sublimed at 250° to 400° C at 10^{-4} to 10^{-6} torr and then decomposed on the substrate at about 500° C. Hintermann (74) has reported on the coating of bearing surfaces with TiC or Ti(CN) for use in places where high wear resistance is needed.

Deposition of TiN on steel substrates has been accomplished by the action of a radio frequency discharge upon a mixture of $TiCl_4$ with N_2 or with an N_2 and H_2 mixture (116). Lower temperatures of 850° to 950° C could be used.

ZIRCONIUM AND HAFNIUM NITRIDES

Zirconium nitride (ZrN) is usually deposited by the CVD process at temperatures of 950° to 1,300° C from the gas mixture of $ZrCl_4$, H_2, and N_2 (51, 141, 221). The best conditions were those in which the N_2-to-$ZrCl_4$ ratio was greater than 1 and in which there was at least 40 mole pct H_2 in the gas mixture (221). Whiskers were grown at the higher temperatures and were usually in the <100> orientation (141, 221). If various impurities are coated on the substrate, whisker growth can be improved. The most effective impurities are the metals Ni, Pd, Pt, Fe, and Mn (106, 144). Kato and Tamari (106) found the growth direction <100> to generally occur. In a study of the kinetics of ZrN formation from the gas phase, the reaction rate was found to change from first order to zero order in $ZrCl_4$ with increasing $ZrCl_4$ concentration, and an activation energy of 39 kcal $mole^{-1}$ was calculated (52). There have been at least two thermodynamic studies reported (114, 246).

Hafnium nitride (HfN) can be prepared in the same manner as is ZrN, except that $HfCl_4$ is generated in situ by the reaction of HCl upon Hf at 700° C (63-64). It is quite likely that the lower chlorides of Hf are also formed (64). In addition to coating W wires (63), HfN has been used to coat carbide tools for machining steel (192).

MISCELLANEOUS COMPOUNDS

There are several types of compounds formed by CVD of the group IVB metals in addition to those discussed above, in particular the silicides, oxides, and sulfides. The production of TiSi or $TiSi_2$ has been achieved by the reaction of $TiCl_4$ with $SiCl_4$, using H_2 gas in excess (117-118, 153). In most cases, a graphite substrate was employed at temperatures of 900° to 1,300° C. Some thermodynamic calculations have been reported (117). One German patent is listed (59) that describes the use of lower temperatures in a vacuum apparatus. Nickl, Schweitzer, and Luxenberg studied the system Ti-Si-C up to temperatures of 1,200° C using $TiCl_4$, $SiCl_4$, CCl_4, and H_2 (155). They reported that the ternary phases Ti_3SiC_2 or $Ti_5Si_3C_x$ were deposited at normal pressures.

At a temperature of 150° C, thin films of TiO_2 can be produced by the CVD process involving H_2O vapor and tetraisopropyl titanate (53, 66). Powdered TiO_2 as anatase was produced by the vapor phase reaction of O_2 with $TiCl_4$ by Suyama and Kato (214). Thin films of TiO_2 were produced by the vapor pyrolysis of ethyl titanate on glass substrates a at a temperature of 445° C (234). Titanium oxycarbide ($TiO_{0.5}C_{0.5}$) was produced by reacting $TiCl_4$, H_2, CO_2, CO, and methane in a reaction tube (111). The oxycarbide was used to increase cemented carbide tool life. Films of ZrO_2 and HfO_2 were prepared by the thermal decomposition of Zr or Hf β-diketonate compounds in the gas phase with O_2 (13).

Crystals and whiskers of TiS_2 (143) and ZrS_2 (149) were produced by the vapor deposition of $TiCl_4$ or $ZrCl_4$ reacting with H_2S on quartz substrates. The normal temperature was 400° to 850° C for TiS_2 and 800° C for ZrS_2. In addition, Motojima, Takahashi, and Sugiyama (150) formed zirconium phosphide (ZrP) whiskers at 900° to 1,300° C with a mixture of $ZrCl_4$, PCl_3, and H_2.

A general summary of some of the reactions for the preparation of the group IVB metal compounds is given in table 1.

TABLE 1. - Some CVD reactions for group IVB elements

Reaction	Vaporization temperature, °C	Substrate temperature, °C
$TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10HCl$	25- 60	850-1,400
$ZrCl_4 + 2BCl_3 + 5H_2 \rightarrow ZrB_2 + 10HCl$	200-250	900-1,300
$TiCl_4 + CH_4 \xrightarrow{H_2} TiC + 4HCl$	25- 60	850-1,360
$TiCl_4 + CCl_4 + 4H_2 \rightarrow TiC + 8HCl$	25- 60	1,200-1,600
$3TiCl_4 + C_3H_8 + 2H_2 \rightarrow 3TiC + 12HCl$	25- 60	850-1,000
$Zr + 2CH_2Cl_2 \rightarrow ZrCl_4$ + pyrolysis products	[1]210-310	NAp
$ZrCl_4 + CH_4 \xrightarrow{H_2} ZrC + 4HCl$	200-250	800-1,200
$Zr + 2Br_2 \rightarrow ZrBr_4$	[1]600	NAp
$ZrBr_4 + CH_4 \xrightarrow{H_2} ZrC + 4HBr$	NAp	~1,400
$HfCl_4 + CH_4 \xrightarrow{H_2} HfC + 4HCl$	300	1,200-1,500
$Hf + 2I_2 \rightarrow HfI_4$	[1]200-600	NAp
$3HfI_4 + C_3H_8 \rightarrow 3HfC + 8HI + 2I_2$	NAp	800-1,250
$2TiCl_4 + 2CH_4 + N_2 \xrightarrow{H_2} 2Ti(CN) + 8HCl$	25- 60	~900
$2TiCl_4 + 4H_2 + N_2 \rightarrow 2TiN + 8HCl$	25- 60	700-1,400
$2ZrCl_4 + 4H_2 + N_2 \rightarrow 2ZrN + 8HCl$	NAp	950-1,300
$2Hf + 2xHCl \rightarrow 2HfCl_x + xH_2$[2]	[1]700	NAp
$2HfCl_4 + N_2 + 4H_2 \rightarrow 2HfN + 8HCl$	NAp	900-1,300

NAp Not applicable. [1]In situ. [2]Here x = 2, 3, 4.

GROUP VB METALS [V, Nb(Cb), Ta]

MISCELLANEOUS VANADIUM COMPOUNDS

There are few CVD processes for the element V in the literature. Vanadium carbide (VC) was produced by the gas phase reaction of VCl_2 with methane at 1,050° to 1,150° C (47) for the treatment of low carbon metal working tools. The VCl_2 was usually prepared in situ by the action of Cl_2 or HCl upon V or ferrovanadium (162). In addition, Kieffer, Fister, and Heidler (109) deposited a titanium-vanadium nitride [(Ti,V)N] coating on cemented carbides at 1,100° C, using a mixture of $TiCl_4$, VCl_4, N_2, and H_2. Fine VN powder was produced by the action of VCl_4 with NH_3, H_2, and N_2 at 700° to 1,200° C (80). There is a published process to form thin films of V_2O_5 by the CVD reaction of $VOCl_3$ with H_2O vapor at room temperature (134, 217).

NIOBIUM AND TANTALUM BORIDES

Niobium diboride (NbB_2) was prepared by the reaction of $NbCl_5$ and BCl_3 with H_2 at temperatures of 950° to 1,200° C (148). The $NbCl_5$ and BCl_3 were prepared in situ by the action of Cl_2 on Nb foil and B_4C at 500° and 800° C, respectively (148). In a similar manner, Motojima and Sugiyama (147) deposited TaB_2 on quartz substrates at temperatures between 900° and 1,300° C. In this process, $TaCl_5$ was prepared by chlorination of Ta sponge at 500° C, and BCl_3 was prepared from B_4C at 800° C. These investigators found that the flow rates were low and quite critical for diboride formation and that the reaction was quite dependent upon the HCl concentration.

Armas (8) conducted a thermodynamic investigation to determine if TaB_2 and NbB_2 could be vapor-deposited in the absence of H_2. By using $NbBr_5$ or $TaBr_5$ with BBr_3, Armas and Combescure (10) deposited NbB_2 and TaB_2 in the temperature range 1,000° to 1,700° C at pressures from 10^{-2} to 2 torr. Good hexagonal crystals were produced at 1,400° C and a pressure of 2.5×10^{-2} torr (12). Armas, Combescure, and Trombe (11) also employed a solar furnace to produce similar results. Randich (187) vapor-deposited TaB_2 onto several substrates at temperatures of 500° to 1,000° C, using $TaCl_5$ and B_2H_6 with good success. The coating hardness was found to be temperature dependent with values around 2,500 kg mm^{-2} produced at temperatures above 600° C.

NIOBIUM AND TANTALUM CARBIDES

Niobium carbide (NbC) is generally vapor-deposited at temperatures of 900° to 1,200° C from the reaction of $NbCl_5$ with methane (32, 55). Coatings of NbC on steel yielded a hardness of 2,900 kg mm^{-2} when a methane-to-$NbCl_5$ gas ratio of 0.5:1 was used (136). Hydrogen was also used to reduce a mixture of $NbCl_5$ and CCl_4 at temperatures of 1,200° to 1,600° C (129, 169). Several patents have been granted for processes that react the metal halide with methane (135, 151) or CCl_4 (242). Tantalum carbide (TaC) can be prepared by the reduction of $TaCl_5$ and CCl_4 with H_2 at temperatures of 850° to 1,300° C (242). Takahashi and Sugiyama (226) employed an ac discharge to produce TaC from a mixture of $TaCl_5$, H_2, and propylene at temperatures of 400° to 600° C. Thick-wall tubes (up to 2.5 mm thick) of NbC were deposited on graphite tubes using $NbCl_5$ and methane (32). There was also a continuous CVD process reported for coating W filaments with TaC (67). The ac discharge method was also employed to produce fibrous NbC and NbN at temperatures of 300° to 700° C, using $NbCl_5$, H_2, and propane or N_2 (231).

NIOBIUM AND TANTALUM NITRIDES

Niobium nitride (NbN) can be prepared by the vapor deposition of a mixture of $NbCl_5$, N_2, and H_2 at substrate temperatures of 800° to 1,300° C (110). Recently, the growth parameters and crystal morphology were investigated (223). The investigators found that a gas mixture with an N_2-to-$NbCl_5$ ratio greater than 45 and with an H_2 flow rate of 3.5 mL sec^{-1} at 1,350° C produced the single nitride phase of NbN. At lower temperatures other phases were obtained. The phases Nb_2N and Nb_4N_3 were also identified along with NbN. The NbN crystal growth was preferentially in the <111> orientation (223). Instead of N_2, NH_3 or hydrazine can be used to produce Nb_2N or NbN as a fine powder using an H_2 plasma source (33). Use of NbF_5 instead of $NbCl_5$ was shown to produce NbN on a Mo substrate at about 900° C (193). The source of nitrogen in this case was N_2, and in addition, a large excess of both H_2 and N_2 was needed.

Tantalum nitride (TaN) was also vapor-deposited from the gas phase mixture of $TaCl_5$, N_2, and H_2 at temperatures of 700° to 1,300° C (73, 222). The substrates were cemented carbides (73) and Si (222). Both Ta_2N and TaN were found in the films produced. The Vickers microhardness values ranged from 1,200 to 2,200 kg mm^{-2} (222). Ammonia has been employed as the N source at temperatures of 700° to 1,300° C at atmospheric pressure (119). The major portion of the TaN produced was of the face-centered cubic variety.

Both TaN and NbN were deposited at temperatures of 300° to 500° C by thermally decomposing tantalum or niobium pentakis (dimethylamide) (213). Use of N_2 or H_2 as the carrier gas was found to be satisfactory. The decomposition product was identified as NbN, but the TaN was not completely identified.

MISCELLANEOUS COMPOUNDS

Several binary Nb superconducting compounds have been prepared by conventional CVD. Among these are Nb_3Ge (30), Nb_3Ga (247), Nb_3Sn (7, 244), and recently, Nb_3Si (160, 254). In general, the chlorides of Nb and the corresponding binary element are produced in situ at temperatures of 250° to 350° C (30, 160). These compounds are not covered in this review, as their major use is in the electronics industry. Tietjin (239) has published a review that addresses this area, and there is also a book by Vossen and Werner (249) concerning the production of thin films.

The reaction of $NbCl_5$ with $SiCl_4$ in the presence of H_2 was difficult to control (160), as generally Nb_5Si_3 and metallic Nb were formed instead of Nb_3Si. Both $NbSi_2$ and $TaSi_2$ were deposited by the action of $NbCl_5$ or $TaCl_5$ with $SiCl_4$ and H_2 at temperatures of 700° to 1,400° C (108). The disilicides as coatings were reported to have good oxidation resistance properties up to temperatures of 1,700° C (108).

In addition to the compounds mentioned, films of Ta_2O_5 have been produced for semiconductor devices (102), as well as thin films of $LiNbO_3$ for optical devices (36). A summary of the reactions and conditions for the group VB metal compounds is given in table 2.

GROUP VIB METALS (Cr, Mo, W)

CHROMIUM CARBIDE

The formation of chromium carbide (Cr_3C_2 or Cr_7C_3) onto steel is usually accomplished by gas chromizing (258). The steel parts with about 1 pct C are treated with $CrCl_2$ and H_2 at 900° to 1,000° C, with some methane added to aid in the carbide formation (45). The parts can be hardened to Vickers hardness values of 3,800 to 4,200 kg mm^{-2}. In addition to the chromizing process, carbide coatings can be produced by the decomposition or pyrolysis of organometallic compounds of Cr. One such process used dicumene chromium at 450° to 650° C to produce Cr_7C_3 coatings on stainless steel turbine blades (60). Another process involved the decomposition of chromium bis(ethylbenzene) in a vacuum at

TABLE 2. - Some CVD reactions for group VB elements

Reaction	Vaporization temperature, °C	Substrate temperature, °C
$V + 2HCl \rightarrow VCl_2 + H_2$[1].....................	[2]~900-1,000	NAp
$VCl_2 + CH_4 \rightarrow VC + 2HCl + H_2$..............	NAp	1,050-1,150
$2VCl_4 + 2NH_3 + H_2 \rightarrow 2VN + 8HCl$...........	~400	700-1,200
$2Nb + 5Cl_2 \rightarrow 2NbCl_5$......................	[2]500	NAp
$B_4C + 8Cl_2 \rightarrow 4BCl_3 + CCl_4$................	[2]800	NAp
$2NbCl_5 + 4BCl_3 + 11H_2 \rightarrow 2NbB_2 + 22HCl$....	NAp	950-1,200
$2Ta + 5Cl_2 \rightarrow 2TaCl_5$......................	[2]500	NAp
$B_4C + 8Cl_2 \rightarrow 4BCl_3 + CCl_4$................	[2]800	NAp
$2TaCl_5 + 4BCl_3 + 11H_2 \rightarrow 2TaB_2 + 22HCl$....	200- 300	900-1,300
$2TaCl_5 + 2B_2H_6 \rightarrow 2TaB_2 + 10HCl + H_2$......	200- 300	500-1,000
$2NbCl_5 + 2CH_4 \rightarrow 2NbC + 8HCl + Cl_2$........	200- 300	900-1,200
$2NbCl_5 + 2CCl_4 + 9H_2 \rightarrow 2NbC + 18HCl$......	200- 300	1,200-1,600
$2TaCl_5 + 2CCl_4 + 9H_2 \rightarrow 2TaC + 18HCl$......	200- 300	850-1,300
$6NbCl_5 + 7H_2 + 2C_3H_8 \rightarrow 6NbC + 30HCl$[3].....	200- 300	300- 800
$2NbCl_5 + 5H_2 + N_2 \rightarrow 2NbN + 10HCl$[3]........	200- 300	300- 800
$2NbCl_5 + N_2 + 5H_2 \rightarrow 2NbN + 10HCl$.........	200- 300	800-2,300
$2TaCl_5 + N_2 + 5H_2 \rightarrow 2TaN + 10HCl$.........	200- 300	700-2,300

NAp Not applicable.

[1] The partial pressure of VCl_2 varies directly as P^2_{HCl}/P_{H_2} when both HCl and H_2 are present.

[2] In situ.

[3] An ac discharge of 0.05 to 3.0 mA and 60 Hz frequency.

substrate temperatures 300° to 350° C (126). Some care must be employed to prevent deposition of the metal along with the metal carbide (133). There have been several articles that discuss the wear-resistant coating of Cr_7C_3 on steel (90-92), as well as corrosion-resistant Cr_7C_3 coatings on bearings and some cutting tools (76, 164).

MOLYBDENUM CARBIDE

Molybdenum carbide (Mo_2C) can best be deposited on steel at temperatures of 400° to 1,000° C by the reaction of MoF_6 with benzene and H_2 (258). Recently, Hojo, Tajika, and Kato produced Mo_2C as a fine powder by the reaction of $MoCl_4$, H_2, and methane at 800° to 1,400° C (83-84).

In this process, the $MoCl_4$ was produced in situ at 500° to 600° C from the action of Cl_2 on Mo. Films of Mo_2C can be deposited on glass from the thermal decomposition of $Mo(CO)_6$ (248). At a pressure of 10^{-3} torr and temperatures of 170° to 350° C, the deposition rate of Mo_2C was increased by using 600-eV electrons at 3 to 5 mA cm^{-2}. Microspheres have been coated with Mo_2C by the pyrolysis of $Mo(CO)_6$ for use as laser fusion targets (132). Even an ac discharge method has been employed to produce Mo_2C or W_2C from a mixture of isobutane, H_2, and the respective metal chloride at 360° to 480° C at atmospheric pressure (227).

TUNGSTEN CARBIDE

There have been more CVD processes developed for the production of tungsten carbide (WC) than for Mo_2C. One of the earliest methods involved the pyrolysis of $W(CO)_6$, at temperatures of 900° to 1,100° C, using an inert carrier gas (94). The thermodynamics of the decomposition of $W(CO)_6$ has been reported by Komorova, Lavrin, and Imris (115), who used the experimental data of others to show that the WC and W_2C came from the decomposition steps and not by a recombination reaction. Coatings of WC have been deposited on different substrates such as tools and costume jewelry by the reaction of WF_6 with H_2 and a suitable hydrocarbon. The hydrocarbon can be ethene (159), benzene (35, 123), toluene (6), or xylene (6). At temperatures up to 550° C, W_2C can be obtained from benzene, toluene, or xylene (6).

A mixture of H_2 and CO has also been employed with WF_6 at a temperature of 925° C and 300 torr (88-89, 238). Instead of WF_6, WCl_6 can be used with H_2 and methane to form WC coatings on cemented carbide tool tips (243) or ultrafine WC powder (81-82). The WC powders are produced at temperatures of 1,000° to 1,400° C (81). Wear-resistant coatings of WC were applied to substrates of Cu, Cu alloys, and Al (259), as well as to forms for molds for molding elastomers (181). A controlled nucleation process that gives the surface improved wear properties was developed (87).

MOLYBDENUM AND TUNGSTEN BORIDES AND SILICIDES

Armas, in addition to depositing the borides of Nb and Ta, also studied the vapor deposition of Mo and W borides (8-10). Deposition was accomplished by the thermal decomposition of a mixture of $MoCl_5$ or WCl_6 with BBr_3, using concentrated solar radiation as the heat source. The borides are of three composition types: M_2B, MB, and M_2B_5 (M = Mo or W). One patent for electrical contact layers has reported that Mo and W borides were deposited from a mixture of BCl_3 and H_2 with the respective metal chloride at 1,800° to 2,000° C (68). The method of Armas (8-10) can be used at temperatures of 1,400° to 1,600° C, without H_2; however, BBr_3 is more expensive than BCl_3.

Molybdenum disilicide ($MoSi_2$) has been reported as being deposited from a mixture of $MoCl_5$, $SiCl_4$, and H_2, using Ar to control the deposition rate (128). The deposition of tungsten silicide (WSi_2) was accomplished by the reaction of WF_6 with SiH_4 at substrate temperatures of 600° to 800° C (124-125), and the best fine-grained structure was obtained at 800° C. By carefully controlling the ratio of the two flow rates, WSi_2 can be formed without the species, W, Si, and W_5Si_3.

A summary of some representative equations with conditions for the preparation of the group VIB metal compounds is given in table 3.

TABLE 3. - Some CVD reactions for group VIB elements

Reaction	Vaporization temperature, °C	Substrate temperature, °C
$7Cr[C_6H_5CH(CH_3)_2]_2 \rightarrow Cr_7C_3$ + pyrolysis products	~195	450- 650
$12MoF_6 + C_6H_6 + 33H_2 \rightarrow 6Mo_2C + 72HF$	35- 50	400-1,000
$Mo + 2Cl_2 \rightarrow MoCl_4$	[1] 500-600	NAp
$2MoCl_4 + CH_4 + 2H_2 \rightarrow Mo_2C + 8HCl$	NAp	800-1,000
$2Mo(CO)_6 \rightarrow Mo_2C + 10CO + CO_2$	25-100	900-1,000
$2W(CO)_6 \rightarrow W_2C + 10CO + CO_2$	~144	650- 900
$2WF_6 + C_2H_6 + 3H_2 \rightarrow 2WC + 12HF$	18- 35	400- 900
$12WF_6 + C_6H_6 + 33H_2 \rightarrow 6W_2C + 72HF$	18- 35	400- 900
$WF_6 + CO + 4H_2 \rightarrow WC + H_2O + 6HF$[2]	18- 35	925
$2MoCl_5 + 2BBr_3 \rightarrow 2MoB + 5Cl_2 + 3Br_2$[3]	300	1,400-1,600
$4MoCl_5 + 2BBr_3 \rightarrow 2Mo_2B + 10Cl_2 + 3Br_2$[3]	300	1,000-1,700
$2WCl_6 + 2BBr_3 \rightarrow 2WB + 6Cl_2 + 3Br_2$[3]	140-150	1,400-1,600
$4WCl_6 + 2BBr_3 \rightarrow 2W_2B + 12Cl_2 + 3Br_2$[3]	140-150	1,000-1,700
$2MoCl_5 + 4SiCl_4 + 13H_2 \rightarrow 2MoSi_2 + 26HCl$	~160	700-1,400
$WF_6 + 2SiH_4 \rightarrow WSi_2 + 6HF + H_2$	18- 35	600- 800

NAp Not applicable. [1] In situ. [2] Low pressure of 300 torr.
[3] Low pressure of 10^{-2} to 2 torr and use of solar furnace.

CONCLUSIONS

Risks of periodic shortages of critical and strategic materials continue to exist as virtually all of the Western World is dependent on imports of critical mineral raw materials. Critical materials can be conserved through the use of alloys with lower strategic metal content and improved abrasion, erosion, and corrosion resistance on the surface. Concentrating the critical materials on substrate surfaces by chemical vapor deposition (CVD) can provide their needed properties although the materials are not present in the substrates. In addition, synergistic effects can result from combining coating and substrate properties. Through selective use of coatings on low-grade substrates, it may also be possible to reduce costs while conserving critical materials. The thin-film CVD coatings that were reviewed have a potential to reduce usage of critical materials while retaining or improving the desired performance (resistance to erosion, abrasion, and corrosion) of lower alloy components used in metallurgical, mining, and energy conversion systems.

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