

The Unexpected Formation of MB₂ Layers (M = Refractory Metal) on Metal Surfaces

Wibke Friedhoff,^{[a],‡} Edgar Milke,^[a] and Michael Binnewies*^[a]

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The reactions between refractory metals (Ti, Zr, V, Nb, Ta, Mo, W) and BCl₃ vapour at high temperatures have been studied. For this purpose, the metal wires were heated up by an electrical current in a BCl₃ atmosphere for a couple of hours. Optical and X-ray diffraction methods were used to analyze the solid products, whereas mass spectrometry was used to study the gas phase composition. In the reactions

with Ti, Zr, V, Nb and Ta, we observed the formation of MB₂ layers on the metal surfaces. Molybdenum reacted with formation of MoB, with tungsten no reaction was observed at all. This is contrary to the thermodynamic expectations. The mechanism of the coating process is discussed from a thermodynamic viewpoint.

Introduction

Borides of several transition metals, especially refractory metal diborides, MB₂, are under discussion for application in high-temperature processes.^[1–3] For example, TiB₂, ZrB₂ and CrB₂ are used in turbine blades, high-temperature furnaces or rocket nozzles. Several of these diborides have high specific electrical conductivities and chemical resistivity against molten salts, molten metals and oxygen. Because of this, they are ideal materials for high-temperature chemistry, especially high-temperature electrochemistry, and in particular as cathode materials in aluminium electrolysis.

These materials are difficult to prepare and difficult to process and shape, as a result of their hardness and high melting points. Bulk metal borides are usually prepared from the elements by solid-state reaction at very high temperatures, even though this method has a lot of disadvantages.^[4] The main problems are low reaction rates, side reactions and reactions with the crucible material. Therefore, alternative preparation methods at lower temperatures have been developed by using molten metals as solvents.^[5–7]

For some applications, these diborides are used as coatings on different substrates. Up to now several techniques are available to build up such coatings. Different techniques are used to form thin films of refractory metal diborides like TiB₂. Thin layers mostly used as diffusion barrier for semiconductor applications can be prepared by different CVD methods.^[8–16] An alternative method of formation of refractory metal boride thin films is the PLD technique.^[17] The typical thickness of layers formed by these techniques

is between 10 and 50 nm. Somewhat thicker layers can be formed by sputtering (500 nm)^[18] and electrodeposition.^[19–23]

We report here on a simple *chemical* process to coat refractory metals with layers of metal diborides by using chemical reactions at the solid/gas interface. The layer thickness is in the magnitude of up to some hundred μm . The thermodynamic background of the processes will be discussed.

Results and Discussion

Spirally wound metal wires were heated by an electrical current up to high temperatures of 2000 K and exposed to a static atmosphere of boron chloride, [$p(\text{BCl}_3) \approx 1 \text{ bar}$]. Typically, the reaction was performed for a couple of hours. The wires had a diameter of 0.5–1 mm and a length of about 10 cm. The temperature was measured pyrometrically. A sketch of the specific reaction apparatus is shown in Figure 1. These experiments are a little similar to the old experiments of Moers in 1931. He reduced gaseous BBr₃ with hydrogen on the surfaces of hot metal wires and described the formation of metal borides, but no further information about the composition of these borides has been given.^[24] In parallel experiments, we investigated the reactions between the metals and boron chloride by mass spectrometry in order to gather information on the composition of the gas phase. For this purpose, a spirally wound metal wire (outer diameter about 4 mm) was placed in a quartz tube and heated by an electrical current. BCl₃ ($p < 1 \text{ mbar}$) was passed over the wire, and the gaseous reaction products were detected by a specifically equipped mass spectrometer,^[25] whereas the solid products were analyzed by optical methods, that is, by electron microscopy and X-ray powder diffraction.

[a] Institut für Anorganische Chemie,
Callinstr. 9, 30167 Hannover, Germany
Fax: +49-511-762-2254

E-mail: michael.binnewies@aca.uni-hannover.de
[‡] Current address: An der Questenhorst 2, 30173 Hannover,
Germany

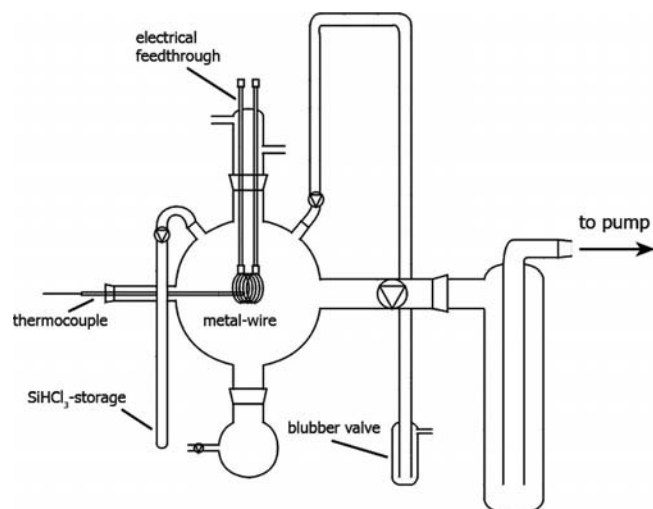
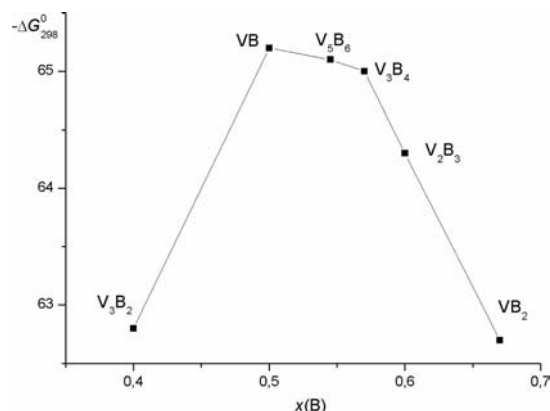


Figure 1. Schematic representation of the apparatus.

The reactions were carried out with the elements Ti, Zr, V, Nb, Ta, Mo and W in a BCl₃ atmosphere. With Ti, Zr, V, Nb and Ta, we observed the formation of MB₂ layers on the surface of the metals. Molybdenum formed a MoB layer, but tungsten did not react under these conditions at all. The formation of VB₂ will be discussed in detail from a thermodynamic viewpoint. We selected this system in contrast to the other ones, because the thermodynamic data for all relevant borides, V₃B₂, VB, V₅B₆, V₃B₄, V₂B₃ and VB₂, are available in critical compilations of thermochemical data.^[26,27] The plot of the Gibbs energies of these borides versus composition shows clearly the consistency of the

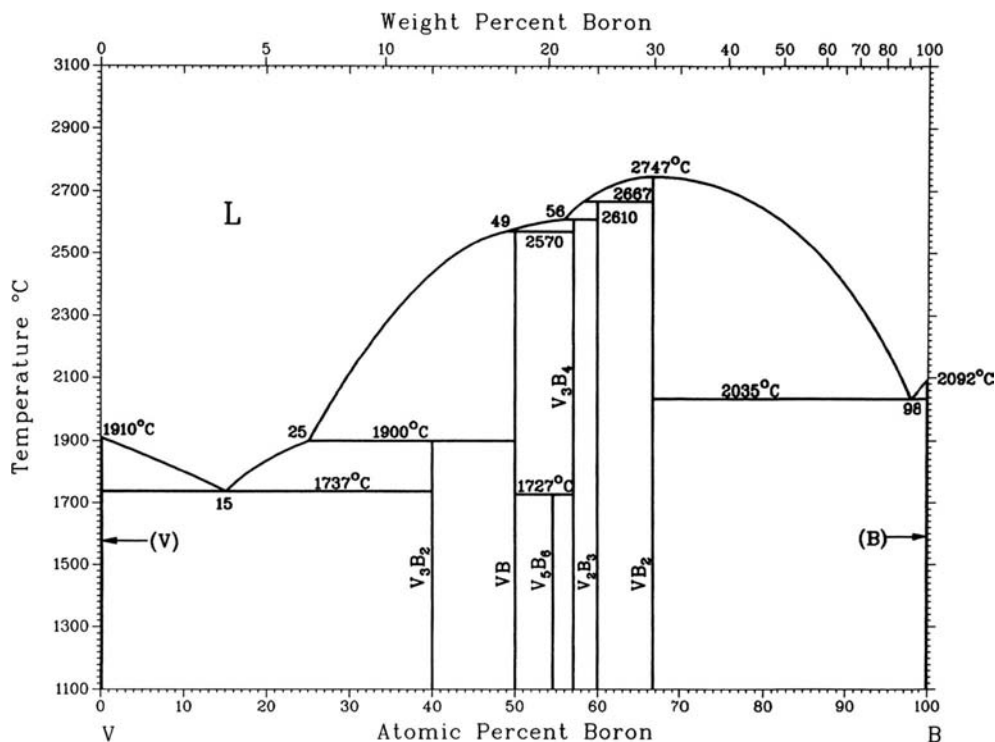
data set under discussion here (Figure 2). Discussions on the consistency of thermodynamic data sets of solid compounds in binary systems are given in ref.^[28,29]

Figure 2. Gibbs energies of vanadium borides in kJ/atom⁻¹.

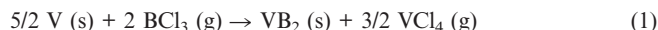
The systems Ti/B, Zr/B, Nb/B, Ta/B, Mo/B and W/B will be reviewed much more briefly, because up to now these systems have not been characterized from a thermodynamic viewpoint. The observations and conclusions for these systems are similar to those in the vanadium system.

The V/BCl₃ System

Figure 3 shows the experimentally determined phase diagram of the V/B system.^[30] There are six vanadium borides from V₃B₂ to VB₂. We exposed a vanadium wire (*d* = 1 mm)

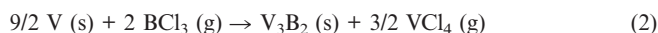
Figure 3. Vanadium/boron phase diagram.^[30] Reprinted with permission of ASM International.

to a BCl_3 atmosphere at 1200 °C for one hour. During this time, a layer of VB_2 ($d = 0.22$ mm) was formed. The following ions were found in a mass spectrometric investigation: $\text{Cl}^+(25)$, $\text{HCl}^+(100)$, $\text{BCl}^+(6)$, $\text{BCl}_2^+(55)$, $\text{BCl}_3^+(17)$, $\text{V}^+(1.1)$, $\text{VCl}^+(1.4)$, $\text{VCl}_2^+(4.3)$, $\text{VCl}_3^+(3.8)$, $\text{VCl}_4^+(1.2)$. This indicates the presence of HCl , BCl_3 , VCl_4 (and probably VCl_3) in the gas phase. Additionally, the formation of solid VCl_3 could be proven by means of X-ray powder diffraction measurements. Obviously, vanadium reacts with gaseous boron chloride with formation of a layer of VB_2 on the metal core. Reaction (1) seems to be favoured from a thermodynamic viewpoint, because of the negative Gibbs energy.



$$\Delta_R G_{1500}^0 = -112.5 \text{ kJ mol}^{-1}$$

Nevertheless, the formation of VB_2 as a coating in contact with vanadium metal is unexpected, because vanadium and vanadium diboride cannot coexist in a thermodynamic equilibrium. In addition, VB_2 exhibits the lowest thermodynamic stability among the vanadium borides, as shown in Figure 2. Therefore, the question arises: *What is the reason for the formation of VB_2 instead of V_3B_2 ?* To answer this question we consider a possible step-by-step reaction course. The reaction of vanadium with boron chloride with formation of solid boron and gaseous vanadium(IV) chloride is strongly endergonic ($\Delta_R G_{1500}^0 = 222.7 \text{ kJ mol}^{-1}$) and cannot occur. Therefore, in a first step one would expect the reaction given in Equation (2).



$$\Delta_R G_{1500}^0 = -202.6 \text{ kJ mol}^{-1}$$

From a thermodynamic point of view, reaction (2) is possible. In addition, V_3B_2 is the only boride phase that is predicted to be able to coexist with metallic vanadium. The step-by-step formation of boron-richer borides by reaction of a boron-poorer boride with gaseous boron chloride is endergonic in all cases. This is shown by the two reactions given in Equations (3) and (4).



$$\Delta_R G_{1500}^0 = 30.3 \text{ kJ mol}^{-1}, K = 0.09$$

$$\Delta_R G_{1500}^0 = 24.2 \text{ kJ mol}^{-1}, K = 0.14$$

Nevertheless, such reactions are possible. The reasons for this are the experimental conditions: gaseous vanadium chloride, which is formed during the reactions, is continuously removed from the equilibria by condensation within the reaction vessel. Therefore, equilibria like (3) or (4) are shifted to the sides of the reaction products, and so the boron-richer boride VB_2 can be formed step by step. In an alternative route, VB_2 may be formed in one reaction step between the metal and the boron-rich gas phase. In both cases, the result is a nonequilibrium situation: vanadium in contact with VB_2 . This becomes possible, because the veloc-

ity of the thermodynamically favoured solid–solid reaction between these two high-melting solids [Equation (5)] is expected to be very low.



$$\Delta_R G_{1500}^0 = -125.9 \text{ kJ mol}^{-1}$$

In the Ti/BCl_3 system, we have observed the formation of the boron-richer boride TiB_2 in addition to the boron-poorest boride TiB . This is one indication for a step-by-step reaction course (see below).

The Nb/BCl₃ System

The following phases are known in the phase diagram of Nb/B: Nb_3B_2 , NbB , Nb_5B_6 , Nb_3B_4 and NbB_2 .^[30] We exposed a niobium wire ($d = 1$ mm) to a BCl_3 atmosphere at 1500 °C for three hours. During this period of time, a layer of NbB_2 ($d = 0.4$ mm) was formed. In addition, a small amount of a yellow condensate, probably NbCl_5 , was found in the reaction vessel. The following ions were found in a mass spectrometric investigation: $\text{Cl}^+(28)$, $\text{HCl}^+(100)$, $\text{BCl}^+(1)$, $\text{BCl}_2^+(9)$, $\text{BCl}_3^+(4)$, $\text{Nb}^+(0.4)$, $\text{NbO}^+(0.5)^+$. This indicates the presence of HCl , BCl_3 and very small amounts of unidentified gaseous niobium species. Figure 4 shows an edge of a fracture of the wire after the reaction. Only a little bit of the niobium metal remained at the core of the wire after the reaction time. In the end, a porous wire of NbB_2 is formed by this method in a “shape-controlling synthesis”.^[32]

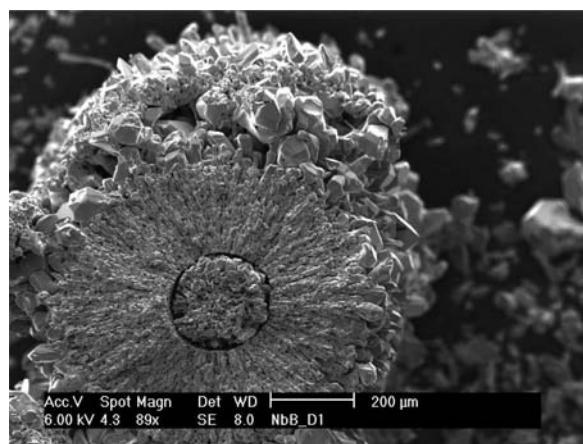


Figure 4. NbB_2 layer on a niobium wire.

The Ta/BCl₃ System

The following phases are known in the phase diagram of Ta/B: Ta_2B , Ta_3B_2 , TaB , Ta_3B_4 and TaB_2 .^[30] We exposed a tantalum wire ($d = 0.5$ mm) to a BCl_3 atmosphere at 1400 °C for 1.8 h. During this period of time, a layer of TaB_2 ($d = 0.09$ mm) was formed. In addition, a small amount of a yellow condensate, probably TaCl_5 , was found in the reaction vessel. No gaseous tantalum species could

be identified by means of mass spectrometric investigations. Figure 5 shows the polished face of a wire after the reaction. It is clearly visible that the layer is much more compact than that obtained as a result of the reaction of niobium with BCl₃.

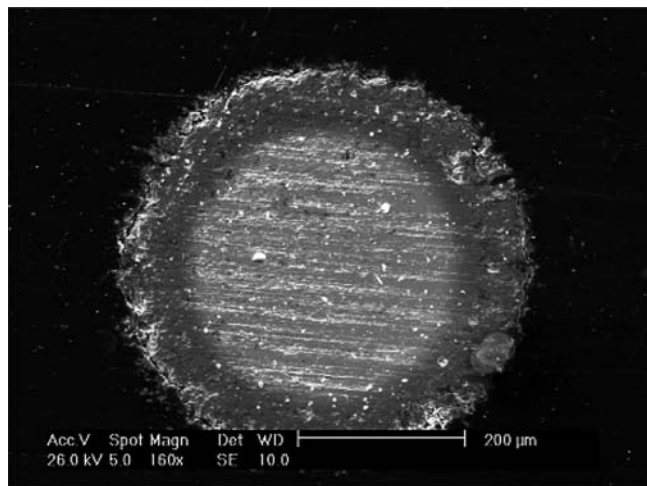
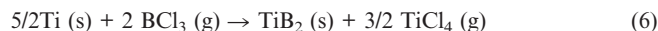


Figure 5. Polished face of a tantalum wire coated with TaB₂.

The Ti/BCl₃ System

The following phases are known in the phase diagram of Ti/B: TiB, Ti₃B₄ and TiB₂.^[30] We exposed titanium wire (*d* = 0.5 mm) to a BCl₃ atmosphere at 1200 °C for two hours. During this time, a layer of titanium borides (*d* = 0.07 mm), which could be identified as TiB₂, was formed in addition to TiB. Furthermore, a violet condensate, probably TiCl₃, was found in the reaction vessel. The presence of TiB among the products indicates the step-by-step formation of boron-rich metal borides. The following ions were found in a mass spectrometric investigation: Cl⁺(23), HCl⁺(100), BCl⁺(8), BCl₂⁺(88), BCl₃⁺(34), Ti⁺(5), TiCl⁺(6), TiCl₂⁺(17), TiCl₃⁺(13), TiCl₄⁺(2). This indicates the presence of HCl, BCl₃ and titanium chlorides (TiCl₃, TiCl₄). The reaction [Equation (6)] between titanium and boron chloride is a lot more exergonic than the reactions discussed above, but the overall reaction behaviour is very similar.



$$\Delta_R G^\circ_{1500} = -509.8\text{ kJ mol}^{-1}$$

The Zr/BCl₃ System

The following phases are listed in the phase diagram of Zr/B: ZrB₂ and ZrB₁₂.^[30] We exposed a zirconium wire (*d* = 1.1 mm) to a BCl₃ atmosphere at 1300 °C for 75 min. During this time, a thin layer of ZrB₂ (*d* = 0.05 mm) was formed. As an example, the X-ray powder diffraction diagram of ZrB₂ is given in Figure 6. In addition, a colourless condensate, probably ZrCl₄, was found in the reaction vessel. The following ions were found in a mass spectrometric investigation: Cl⁺(22), HCl⁺(100), BCl⁺(7), BCl₂⁺(50),

BCl₃⁺(11), Zr⁺(12.5), ZrCl⁺(1.3), ZrCl₂⁺(2), ZrCl₃⁺(6.4), ZrCl₄⁺(2.3). This indicates the presence of HCl, BCl₃ and ZrCl₄. The reaction [Equation (7)] between zirconium and boron chloride has the highest exergonic potential, but the thickness of the resulting layer is the lowest of all discussed here.

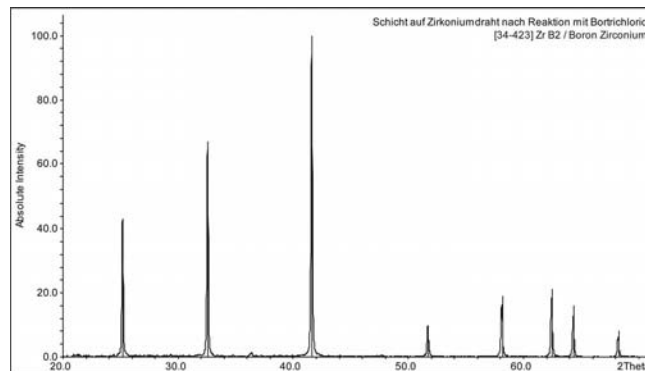
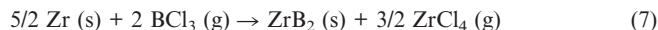


Figure 6. Powder diffraction diagram of ZrB₂.



$$\Delta_R G^\circ_{1500} = -686.3\text{ kJ mol}^{-1}$$

A boride that is able to coexist with the metal was formed only in the case of zirconium.

The Mo/BCl₃ and W/BCl₃ Systems

The following phases are listed in the phase diagram of Mo/B: Mo₂B, MoB, MoB₂, Mo₂B₅ and MoB₄.^[30] (recently published structural investigations on “MoB₂” and “Mo₂B₅”; see ref.^[31]). We exposed a molybdenum wire (*d* = 0.5 mm) to a BCl₃ atmosphere at 1500 °C for 30 min. During this time, a nonporous thin layer of MoB (*d* = 0.09 mm), particularly adhering on the surface of the metal, was formed (Figure 7). Mass spectrometric investigation did not show any species including molybdenum and chlorine.

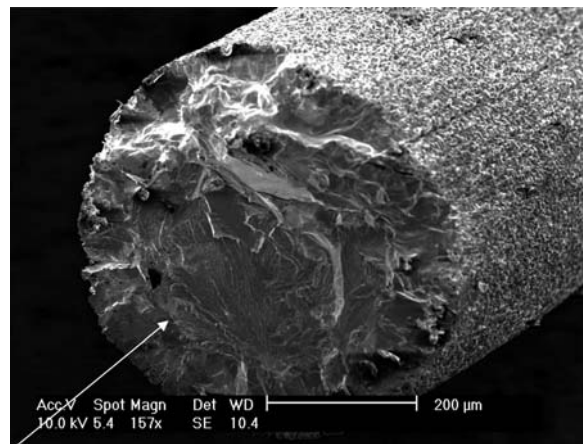


Figure 7. Fracture edge of a molybdenum wire coated with MoB (the arrowhead indicates the phase boundary between Mo and MoB).

In the system W/BCl₃ we could not observe any reaction even at temperatures up to 1800 °C.

Conclusions

Our experiments have shown that some refractory metals react with boron chloride at high temperatures usually with formation of diboride layers on the surface of the metals and volatile metal chlorides. In the cases of strongly exergonic reactions, the metal chlorides could be observed by means of mass spectrometry. If the boride layers are compact, practical applications seem to be possible. From a thermodynamic viewpoint, the formation of boron-rich metal borides in contact with the metals is unexpected (with the exception of ZrB₂). The boron-rich borides are yet formed, due to the high reaction velocity of the solid–gas reactions between a metal-rich boride and gaseous boron chloride compared to the low reaction velocity of a solid–solid reaction between the metal and a boron-rich boride. Furthermore, the reactions between metals and boron chloride have proven as a suitable method to prepare single-phase boron-rich borides by an alternative route.

Experimental Section

Chemicals: The chemicals used were vanadium (99.5%), zirconium (99.5%) and tungsten (99.95%) from Haines & Maassen Metallhandelsgesellschaft mbH, niobium (99.9%), titanium (99.6%) and molybdenum (99.97%) from Goodfellow GmbH Germany, tantalum (99.95%) from Strem Chemicals and boron(III) chloride (> 99.9%) from Merck

Experimental Procedure: The metal wires were contacted with the electrical feedthrough. After this, the apparatus was evacuated with a vacuum pump. In the next step, the apparatus was filled with BCl₃ vapour; the valve between the storage vessel and the reaction chamber was open during the experiment. The vapour pressure of BCl₃ at room temperature is almost 1 bar. The wire was heated up and kept at the reaction temperature for the reaction time. Wire temperatures were measured with a pyrometer (Infratherm IS 5, IMPAC Electronic, Frankfurt). Powder diffraction measurements were carried out by using a Stadi P, Cu-K_α (Stoe, Darmstadt) diffractometer. The scanning electron microscopy analyses were performed with an XL 30, Philips (Eindhoven) instrument.

Acknowledgments

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