Thermodynamic analysis and experimental study of TiB$_2$ coatings by CVD

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Abstract. The coatings of titanium dibordie (TiB$_2$) on a high purity graphite substrate by chemical vapor deposition (CVD) was studied by using a gas mixture of TiCl$_4$, BCl$_3$ and H$_2$. The reaction thermodynamics and the influences of TiCl$_4$: BCl$_3$ flow ratio on the growth rate of TiB$_2$ are analyzed by using HSC software, X-ray diffraction, FESEM and EDS. The experimental results indicate that TiCl$_4$ is according to the theory of gradual dechlorinating in this reaction and a large excess of H$_2$ and TiCl$_4$ can improve the growth rate of TiB$_2$.

Introduction

The titanium dibordie (TiB$_2$) is a very useful ceramic materials. Particularly outstanding properties are the high temperature hardness, erosion resistance and chemical inertness [1]. Because of these properties, titanium diboride has been used in many field, such as the Evaporator boat in high vacuum metal coatings, the protection of weapons and armored vehicle [2].

Chemical vapor deposition is a major method for TiB$_2$ coatings. Chemical vapor deposition is most suitable for the production of technically pure dense titanium diboride in arbitrary sizes and shapes. Moers [3] in 1931, first reported the successful conditions under which the material was formed. CVD of TiB$_2$ by the hydrogen reduction of the halides of titanium and boron. It was not until the 1960's, however, that any further study of the CVD of the procedure diboride was reported [4-8]. Thermodynamic and kinetic analyses of the transport reactions of TiB$_2$ were recently published by Besmann and Spear [9,10]. H. O. Pierson AND A. W. Mullendore [11] had been studied of the chemical vapor deposition of titanium diboride on graphite using the reaction of TiCl$_4$ with B$_2$H$_6$ in hydrogen atmosphere.

The CVD system used in this experimental is similar in design to those employed by other researchers[9,10]. The overall reaction of the vapor deposition of TiB2 is as follow [12]:

$$TiCl_4\,(g) + 2BCl_3\,(g) + 5H_2\,(g) = TiB2\,(s) + 10HCl\,(g) \tag{1}$$

The condensed phase deposited on the high purity graphite substrate.

In this paper, thermodynamic of the reactions of TiB$_2$ are analyzed by HSC chemistry. Furthermore, the titanium diboride coatings are studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and EDS. Results of the growth rate relation in different TiCl$_4$: BCl$_3$ flow ratio are found. As will be shown, the under the same deposition temperature and vacuum degree, the growth rates and the morphologies depend to a large extent on the gas flow ratio of TiCl$_4$ and BCl$_3$. The thickness of deposited coatings using different TiCl$_4$: BCl$_3$ flow ratio are revealed on the high purity graphite substrate, while XRD and microstructure will be presented.

Experimental

The schematic diagram of the experimental apparatus is illustrated in fig. 1. Heat was supplied by a 380-V power. The temperature of deposition chamber was controlled by infrared thermometer. In order to obtain uniform TiB$_2$ coatings, the graphite substrate, was rotated by a rotary motor in the

deposition chamber. The $TiCl_4$ inlet lines are heated with heating tape to avoid the condensation of the reagent gases on the way. H_2, BCl_3 and $TiCl_4$ were mixed in a gas mixing chamber before importing the depositon chamber and there temperatures are lower than 773 K. Then the mixed gases entered the deposition chamber by airway. Most of exhaust gases are removed through a suction arrangement full of iron filing.
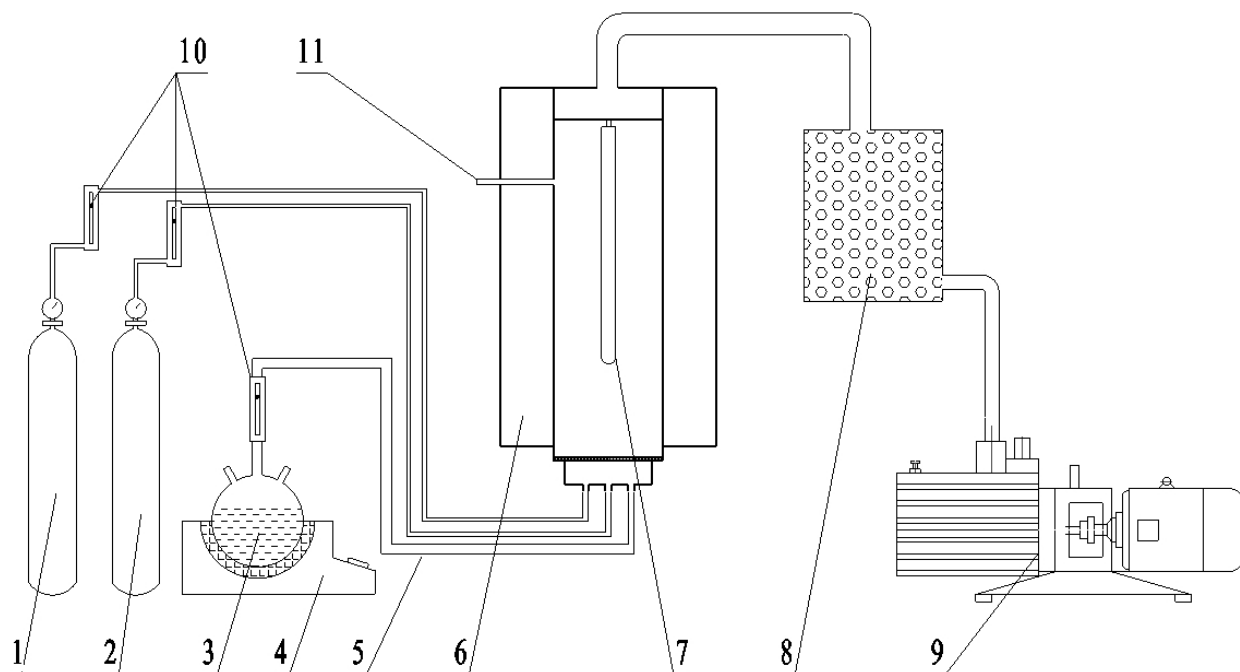

Fig. 1 Schematic diagram of the CVD reactor

(1) BCl3; (2) H2; (3) TiCl4; (4) temperature controller; (5) thermal insulation materials; (6) deposition chamber; (7) high purity graphite substrate; (8) iron filing; (9) vacuum pump; (10) gas flowmeter; (11) temperature control system.

In this experiment, the vacuum degree of deposition chamber was lower than 5×10-6 mTorr. The deposition temperature was kept at 1223 K, Metering accuracy was maintained at $\pm 1\%$. With these conditions, two different experiments were undertaken. The first group was deposited 3 hours with the molar ratio $TiCl_4$: BCl_3: H_2 =1: 2: 15, which the molar ratio of $TiCl_4$ to BCl_3 is the theoretical molar ratio. The second group was deposited 3 hours with the molar ratio $TiCl_4$: BCl_3: H_2 =2: 2: 15. Table 1 summarizes the field of deposition parameters.

Table 1 Field of deposition parameters

Parameters	Group 1	Group 2
Substrate	graphite	graphite
Deposition temperature	1223±1% [K]	1223±1% [K]
Vacuum degree	70 [mTorr]	70 [mTorr]
Temperature of H_2	288±1% [K]	288.15±1% [K]
Pressure of H_2	0.04 [MPa]	0.04 [MPa]
Flow rate of H_2	0.9 [m^3/h]	0.9 [m^3/h]
Temperature of $TiCl_4$	393±1% [K]	393±1% [K]
Pressure of $TiCl_4$	0.06 [MPa]	0.06 [MPa]
Flow rate of $TiCl_4$	0.055 [m^3/h]	0.11 [m^3/h]
Temperature of BCl_3	303±1% [K]	303±1% [K]
Pressure of BCl_3	0.06 [MPa]	0.06 [MPa]
Flow rate of BCl_3	0.085 [m^3/h]	0.085 [m^3/h]

The structure and morphology of the Titanium diboride coatings were investigated by using X-ray diffraction, field emission scanning electron microscopy (FESEM) and EDS.

Results and discussion

Thermodynamic analysis. The changes in free energy of formation of Reactions are shown in Fig. 2 as a function of temperature. The Gibbs free-energy values of the reactants and products were obtained from the HSC Chemistry (Outokumpu Technology Corporation). These sources are generally accurate and satisfactory for the thermodynamic calculations of most CVD reactions, they are often revised and expanded. As shown in fig. 2, under the deposition temperature of reaction (1223K), there is a subchloride formed such as $TiCl_3$. But there is no $TiCl_2$ at that temperature (1223K) because of ΔG_f ($TiCl_2$) > 0 (reaction of $TiCl_4 \rightarrow TiCl_2$ or $TiCl_3 \rightarrow TiCl_2$). Therefore, the reaction sequence of the reaction in the furnace is $TiCl_4 \rightarrow TiCl_3 \rightarrow TiB_2$ and $TiCl_4 \rightarrow TiB_2$.

Legend:
- $2TiCl_4 + H_2 = 2TiCl_3 + 2HCl$
- $TiCl_4 + H_2 = TiCl_2 + 2HCl$
- $2TiCl_3 + H_2 = 2TiCl_2 + 2HCl$
- $TiCl_4 + 2BCl_3 + 5H_2 = TiB_2 + 10HCl$
- $2TiCl_3 + 4BCl_3 + 9H_2 = 2TiB_2 + 18HCl$
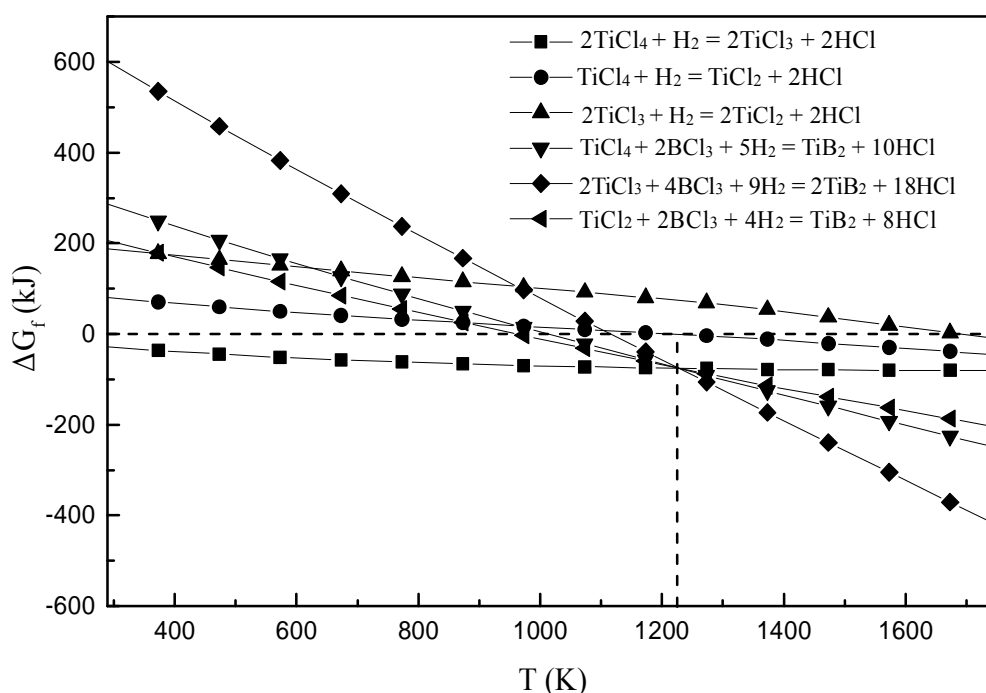- $TiCl_2 + 2BCl_3 + 4H_2 = TiB_2 + 8HCl$

Fig. 2 Changes in free energy of formation

Structure and morphology of the deposit. From the orientation characteristics of the deposited layers investigated by X-ray diffractometry, oriented growth was found to be related to the $TiCl_4/BCl_3$ gas ratio in the vapor. Fig. 3 shows that the TiB_2 coatings deposited at different $TiCl_4/BCl_3$ gas ratio have almost the same XRD patterns. At the same time, figs. 3a and 3b are typical diffractometer traces of deposits from group 1 and group 2, showing that in the deposits from group 1 only (100) lattice planes are more developed than group 2. However, all the lattice planes of the deposits from group 2 are closer to the standard date from PDF2-2004 ICDD NO. 01-085-2083 of TiB_2.
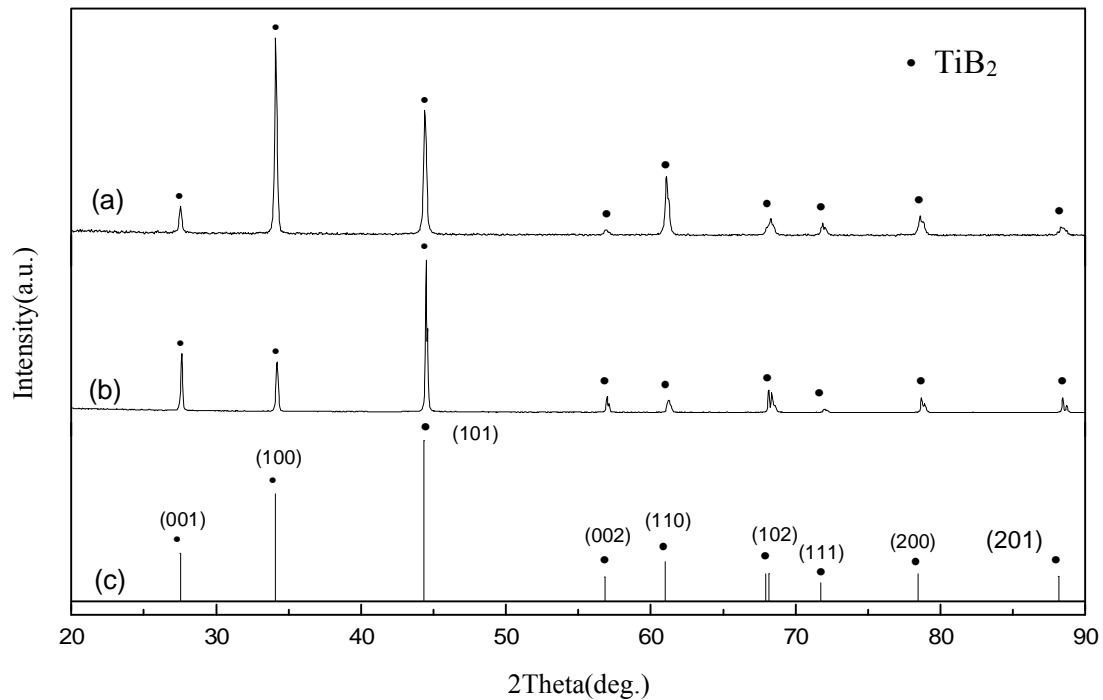
Fig. 3 X-ray diffraction patterns of the deposits.
(a) At flow rate of $TiCl_4$ 0.055m^3/h; (b) At flow rate of $TiCl_4$ 0.11m^3/h; (c) The standard date from PDF2-2004 ICDD NO. 01-085-2083

Fig. 4 (a) and (b) display that SEM micrographs and EDS patterns of the surface of the coatings deposited at the condition of group 1. Fig. 4 (a) and (b) display that SEM micrographs and EDS patterns of the surface of the coatings deposited at the condition of group 2. It is compare fig. 4 (a) with (c) showing the morphology of granular structure of the coatings deposited at the condition of group1 is more uneven than the group 2. The possible reasons are lack of $TiCl_4$ supply in the deposition chamber, which is caused by $TiCl_4$ is reduced by hydrogen producing $TiCl_3$ at the entrance of the mixed gases. The results of spot 1 and spot 2 in the table 2 evidence of a lack of titanium in the coatings deposited at the condition of group 1. The Ti/B ratio of spot 2 shown in table 2 approached to the stoichiometric value of TiB_2 coatings was deposited at the condition of group 2, because the sufficient $TiCl_4$ entered the deposition chamber for the reaction.

Table 2 The EDS analysis results of different regions of samples in fig. 4 (a) and (c)

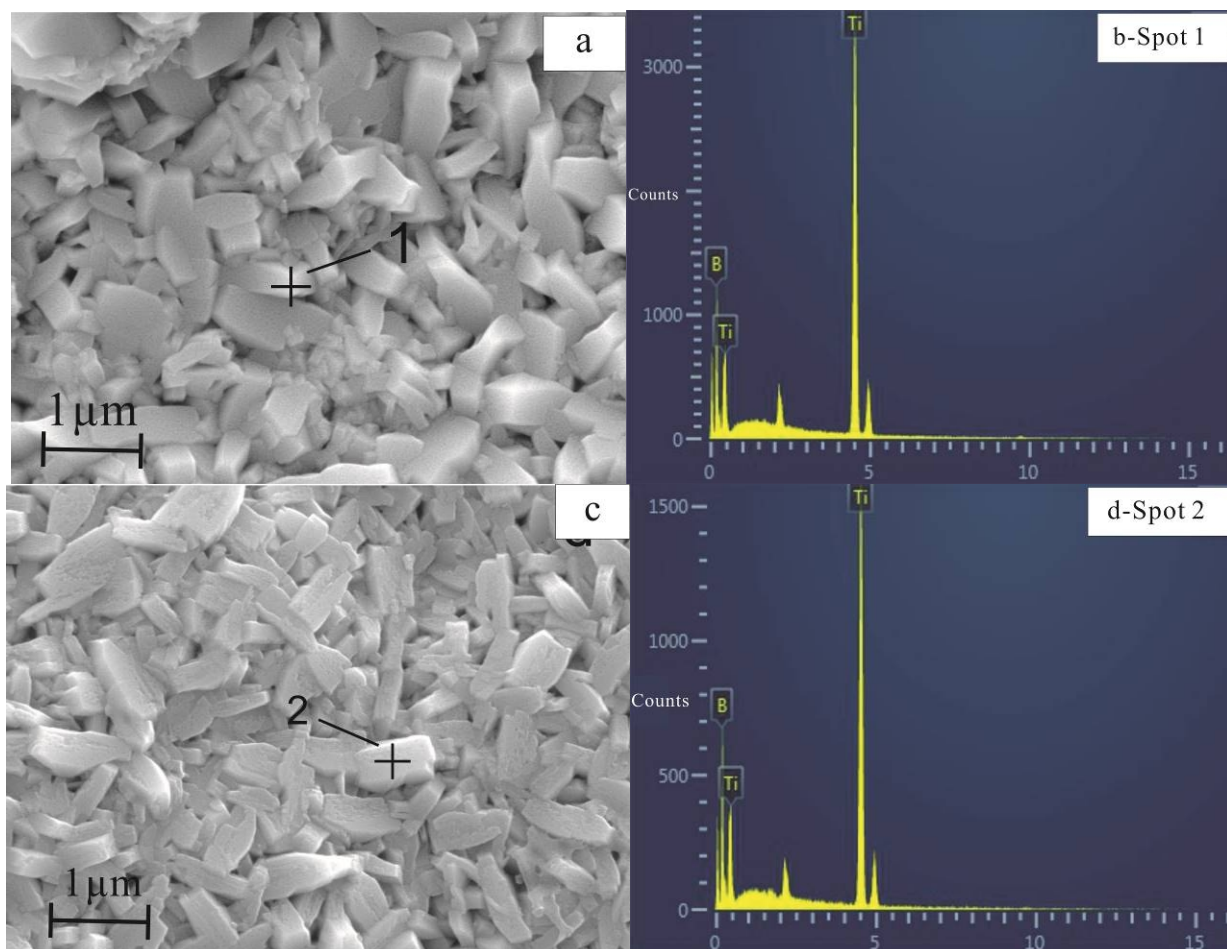| Spot No.	Element	wt.[%]	at. [%]	Ti/B atom ratio
1	B	37.68	72.84	0.37
	Ti	62.32	27.16	
2	B	32.86	68.46	0.46
	Ti	67.14	31.54	

Fig. 4. SEM micrographs and EDS results of the surface of TiB$_2$ coatings.
(a, b) and (c, d) are the microstructure of TiB$_2$ coatings deposited at flow rate of TiCl4 0.055m^3/h and 0.11m^3/h.

Fig. 5 (a) and (b) shows a typical cross section of a thick deposit obtained with condition of group 1 and group 2 for 3 hours by SEM micrographs. All deposition parameters are identical except the flow rate of TiCl$_4$ in the condition of group 1 and group 2. The rate of TiCl$_4$ in group 1 is 0.055m^3/h, and Ti/B is 1: 2. While the rate of group 2 is 0.11 m^3/h and Ti/B is 1: 1. Obviously, the Ti/B ratio in the group 1 is theoretical ratio, content of Ti in the group 2 is one time more than theory amount. As show in fig. 5(a), the thickness of the coatings deposited at Ti/B = 1: 2 for 3 hour have reached to 17 micron. The fig. 5(b) show the thickness of the coatings deposited at Ti/B = 1: 1 for 3 hour have reached to 22 micron. Thus, this indicates that it is not all TiCl$_4$ conversion to TiB$_2$. This result found evidence of a subchloride formed such as TiCl$_3$.
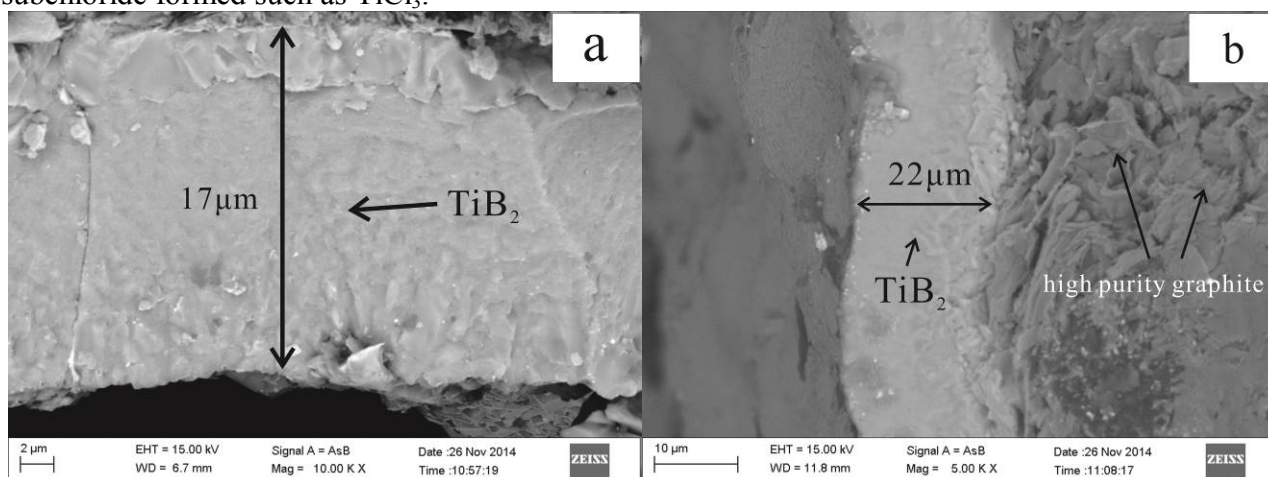

Fig. 5 SEM micrographs of the section of TiB$_2$ coatings.
(a) and (b) are the microstructure of TiB$_2$ coatings deposited at flow rate of TiCl$_4$ 0.055m^3/h and 0.11m^3/h.

Conclusion

TiB$_2$ coatings could be deposited on the high purity graphite by CVD. Under the deposition temperature of reaction (1223K), the reaction sequence of the reaction in the furnace is TiCl$_4$→TiCl$_3$→TiB$_2$ and TiCl$_4$→TiB$_2$. These coatings have basically uniform structure and composition with the condition of Ti: B = 1: 2 and Ti: B = 1: 1. But the deposition has higher growth ratio, when the flow ratio of TiCl$_4$ is the double of the theory amount.

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