Original Article

Investigation of mechanical properties and oxidation resistance of CVD TiB₂ ceramic coating on molybdenum

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Abstract

TiB₂ anti-oxidation ceramic coatings were successfully synthesised on a Mo substrate by using chemical vapor deposition (CVD). A scratch test was performed to measure the adhesion strength of the TiB₂ ceramic coatings to the Mo substrate. The results indicated good adhesion between the two materials; the adhesion strength was 125 mN. Furthermore, high-temperature oxidation tests indicated that the CVD TiB₂ ceramic coating protected the Mo substrate against oxidation up to 900 °C. Isothermal oxidation experiments revealed that the Mo substrate covered with a 13-µm-thick TiB₂ ceramic coating was protected against oxidation for a duration of 5 h. The oxidation kinetics followed a parabolic law for the first 2.5 h and a linear law in the next 2.5 h.

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1. Introduction

Mo is a useful metal with many excellent physical and chemical properties, such as corrosion resistance, good electrical and thermal conductivities, and a high melting point (2622 °C) [1,2]. Therefore, Mo and Mo alloys are widely used in the aerospace, metallurgy, nuclear, and energy industries, as well as in lighting technology, high-temperature furnace construction, sputtering targets, and high-performance electronics [3-5]. Nevertheless, the applicability of Mo is limited owing to its extremely poor resistance to oxidation at high temperatures. Mo is easily oxidised in air even at 427 °C [5].

To improve the oxidation resistance of Mo, various methods have been employed, such as anti-oxidation coating and the addition of anti-oxidation elements (Si, B, etc.). However, the addition of B and Si is limited by the low solubility and poor workability [6]. The oxidation-resistance coating method is widely used for Mo and Mo-based alloys. In previous studies, two major types of coating materials were used for obtaining anti-oxidation protective layers on the surface of Mo: 1) MoSi₂ [5] and MoSi₂-based composites, e.g., MoSi₂–SiO₂ [2], (Mo, W)Si₂–Si₃N₄ [7,8], MoSi₂+ X Sic [9], and Mo-Si-B [10-17], and 2) metals (alloys), e.g., Ir [18], W [19-21], and Ni-20Cr [4]. Some ceramic materials also exhibit excellent properties, such as high-temperature oxidation resistance, a high melting point, and high hardness. Titanium diboride (TiB₂), which is a candidate material for ultrahigh-temperature ceramics, is attracting increasing attention. It has superior properties, such as a high melting point (approximately 3100 °C [22]),

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high hardness (maximum 45 GPa [23]), good electrical and thermal conductivities, and chemical inertness [24]. Additionally, as a very important anti-oxidation ceramic material, TiB₂ can resist oxidation in air up to 1100 °C [25]. Thus, TiB₂ has been utilised for a protective coating for various applications. TiB₂ as a protective coating has been used for cemented carbide cutting tools [26], moulds, and other tools [27,28]. However, there has been little research on the TiB₂ ceramic as an anti-oxidation coating on the surface of Mo. In using a ceramic anti-oxidation coating, the major problem is poor adhesion between the ceramic coating and the metal substrate. However, the adhesion strength can be improved either via substrate surface treatment [29] or by increasing the substrate temperature [30]. Therefore, the TiB₂ ceramic can be considered as a protective layer to improve the oxidation resistance of Mo metal.

In discussions regarding the oxidation resistance of TiB₂ coatings for Mo, Mo-B-Si coatings are also mentioned owing to their similar composition and oxidation performance. Mo-B-Si coatings have exhibited excellent high-temperature oxidation resistance for Mo and Mo alloys [11,12,14,15,31,32], particularly in the temperature range of 1200–1700 °C [11,12,14]. However, the oxidation resistance of Mo-B-Si coatings is poor at temperatures below 1000 °C [31–34]. At temperature of 650–750 °C, pest oxidation of the coatings occurs [31,34]. Conversely, the TiB₂ ceramic exhibits good and reliable oxidation resistance below 1000 °C. Thus, it is of interest to examine the mechanical and oxidative properties of TiB₂ ceramic coatings on Mo substrates.

In our previous work [35], a high quality TiB₂ ceramic coating was successfully synthesized on metallic Mo by using a chemical vapor deposition (CVD) method, and the microstructure and morphology of the coatings on the Mo substrate have been examined. The objective of this study was to systematically investigate the effectiveness of a TiB₂ ceramic coating for improving the oxidation resistance of Mo. Firstly, the adhesion strength and microhardness of the coating were measured. Furthermore, the oxidation behaviour of the TiB₂ ceramic coatings on the Mo substrate was investigated. Oxidation tests were performed on the coatings from room temperature to 900 °C, which is the temperature required for Mo moulds in our future work.

### 2. Experimental method

#### 2.1. Materials

The experimental materials are from our previous work. The TiB₂ ceramic coatings were deposited on a sheet of metallic Mo using a gas mixture of H₂ + TiCl₄ + BCl₃ under 1000 °C by CVD. The overall chemical reaction is as follows.

\[
2\text{BCl}_3(g) + 5\text{H}_2(g) + \text{TiCl}_4(g) = 10\text{HCl}(g) + \text{TiB}_2(s)
\]

Within this work, the TiB₂ ceramic coating was deposited on Mo substrate using a conventional vertical CVD reactor. The experimental equipment was self-made in this study. The schematic design of the experimental CVD system is illustrated in Fig. 1. The graphite deposition chamber was heated with a graphite resistance heating element. The temperature was measured by a platinum-rhodium thermocouple and with a temperature controller (CKW-3100, BCHY, Beijing, China) to ± 5 °C. The TiCl₄ was heated to boiling point of 135 °C in a resistance furnace. TiCl₄, BCl₃ and H₂ were introduced into the bottom of the deposition chamber via stainless steel tubing, respectively. The TiCl₄ gas path was heated by conventional heating tapes to ensure that no condensation of the reagents occurred within the lines.

It is well known that the adhesion between ceramic coatings and metal substrates is poor. Many factors affect the adhesion strength. Among the most important factors are the surface characteristics of the substrate. A roughened surface can improve the adhesiveness of ceramic coatings [36,37]. Hence, the surfaces of the Mo substrates were roughened by 600 grit silicon carbide sandpaper to improve the adhesiveness of the TiB₂ ceramic coatings to the substrates. Then, the Mo substrates were ultrasonically cleaned with acetone for 30 min. Finally, the substrates were suspended in the centre of the deposition chamber by a Mo wire. A. J. Caputo et al. [38] reported that some properties of CVD TiB₂ depend on the deposition temperature. They found that TiB₂ coatings deposited at ≥900 °C exhibited very low erosion rates and that the coating hardness increased with the deposition temperature. Hence, we used a high deposition temperature (1000 °C) to obtain good coating properties. More detailed deposition conditions are presented in Table 1. The appearance and cross-section images of the materials we used in this work are shown in Fig. 2 [35].

#### 2.2. Mechanical-property test of TiB₂ ceramic coatings on Mo substrate

Adhesion measurements were performed according to a standard test method for evaluating the adhesion strength between a vapor deposition film and a substrate (JB/T 8554, People’s Republic of China Machinery Industry Standard (PRCMIS)). The scratch method was employed for testing the adhesion of the TiB₂ ceramic coatings to the Mo substrates. The adhesion strength was evaluated using a nanoscratch tester (TriboIndenter, Hysitron, Minneapolis, USA) with a diamond cube-corner stylus under a continuously increasing load. The load ranged from 0 to 250 mN, with a loading rate of 5 mN/s. Furthermore, a microhardness tester (FM-700, Future-tech, Kawasaki, Japan) was used to evaluate the microhardness of the TiB₂ ceramic coating.

### Table 1 – Deposition condition of TiB₂ coating by CVD.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Mo</th>
<th>molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition temperature</td>
<td>1000 °C</td>
<td></td>
</tr>
<tr>
<td>Deposition time</td>
<td>2 h</td>
<td></td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>40–50 kPa</td>
<td></td>
</tr>
<tr>
<td>Pressure of H₂</td>
<td>0.15 MPa</td>
<td></td>
</tr>
<tr>
<td>Flow rate of H₂</td>
<td>635 cm³/min</td>
<td></td>
</tr>
<tr>
<td>Temperature of TiCl₄</td>
<td>155 °C</td>
<td></td>
</tr>
<tr>
<td>Flow rate of TiCl₄</td>
<td>130 cm³/min</td>
<td></td>
</tr>
<tr>
<td>Flow rate of BCl₃</td>
<td>195 cm³/min</td>
<td></td>
</tr>
</tbody>
</table>
2.3. Oxidation test

To study the oxidation process of the specimens, oxidation experiments were performed in a tube furnace with a temperature accuracy of ±5 °C. These experiments were conducted in dry air at 300, 450, 600, 750, and 900 °C. Additionally, isothermal-oxidation tests were performed at 900 °C for 1, 2, 3, 4, and 5 h. Thermal analysis, thermogravimetry (TG), and differential scanning calorimetry (DSC) were performed to investigate the oxidation mechanisms. The tests were performed using a Netzsch STA449F3 thermoanalytical system (TG measurement error was 10⁻⁴ mg, temperature measurement error was <1 °C) at a constant heating rate of 10 °C/min in flowing air at a flow rate of 150 mL/min in the temperature range of 20–900 °C. The duration of the isothermal was 5 h at 900 °C. For comparison, thermogravimetric tests of uncoated Mo were also performed under the same oxidation conditions.

2.4. Characterisations of coating before and after oxidation

The phases of the coatings formed on the Mo substrate were examined using X-ray diffraction (XRD, X’ Pert Pro, PANalytical B.V., Almelo, Netherlands) at 40 mA and 40 kV with Cu Kα radiation (λ = 1.541 Å, step size = 0.0334°, integration time of 19.69 s/step, scan rate of 0.216° s⁻¹ from 5° to 90°). Scanning electron microscopy (SEM, Ultra Plus, Zeiss, Heidenheim, Germany) and energy-dispersive X-ray spectroscopy (EDS, X-Max 50, Oxford Instruments, Oxford, UK) were performed to investigate the microstructure, morphology, and composition of the coatings. XRD was also used to determine the phase composition of the oxidation products on the surface of the specimens after the oxidation experiments. The oxidation products were imaged and analysed using SEM, and their compositions were analysed using EDS.

3. Results and discussion

3.1. Mechanical properties of TiB₂ coatings

According to a standard method for testing the adhesion strength between a vapor deposition film and a substrate (JB/T 8554 from PRCMIS), scratch adhesion tests were performed by applying continuous loading from 0 to 250 mN with a 5-mN/s increase rate. The adhesive strength was assessed according
to the critical load, which was identified by an abrupt change in the coefficient of friction. To reduce the influence of the surface roughness in the evaluation of the coefficient of friction, the surface roughness must be <0.32 µm according to the test standard JB/T 8554. Hence, the coating was polished by 2000 grit silicon carbide sandpaper before the scratch tests. The surface roughness of the coating was measured using a three-dimensional laser scanning microscope (LEXT OLS4100, Olympus, Tokyo, Japan). The results of the roughness test indicated that after polishing, the average surface roughness was 0.26, which is 0.32 lower than the value specified by the test standard JB/T 8554. Fig. 3 shows the coefficient of friction plot for the scratch testing of the TiB₂ ceramic coating on a pure Mo substrate. Two turning points are observed in the coefficient of friction plot: the lower critical load and upper critical load, corresponding to the critical loads for failure of the coating. Before the lower critical load was reached, the coefficient of friction increased slowly and fluctuated slightly with the increasing load. At this stage, the coating exhibited good adhesion to the substrate and was polished by the indenter. Then, we observed an abrupt increase in the coefficient of friction over a short period of time, indicating that the coating began to crack and peel off. Therefore, the lower critical load was defined as the adhesion strength of the coating to the substrate. As the load continued to increase, an upper critical load was observed. Subsequently, the coating was removed from the substrate. Hence, the friction coefficient increased slowly with the increasing load. According to the results, as shown in Fig. 3, the adhesion strength of the TiB₂ ceramic coatings to the Mo substrate was approximately 125 mN. Q. L. Lv and J. Gao [39] reported that good adhesion of a Hf metal coating to a Mo substrate was achieved using ion-beam sputtering; the adhesion strength was approximately 120 mN. The adhesion of the as-prepared CVD TiB₂ coatings to the Mo substrate in the present study was as good as that of the previously reported Hf metal coating. Additionally, the TiB₂ coating exhibited high microhardness relatively to MoSi₂ coating on Mo substrate. The mean average microhardness value of the coating we obtained was 28 GPa and the maximum microhardness value was 30 GPa. But the MoSi₂ coating microhardness only have a mean value of 13 GPa [40]. Generally, the hardness values for TiB₂ films can vary between 25 and 36 GPa [27]. In our work, hardness of as-preparation TiB₂ coatings on Mo substrate is in accordance with the consistently range of TiB₂ hardness value [23,41–43].

3.2. TG and DSC of TiB₂ coated on Mo

Fig. 4 presents the weight-gain data obtained during continuous oxidation of Mo covered with the TiB₂ coating. For comparison, the data for a pure Mo specimen are also shown. The possible oxidation reactions are as follows.

\[
2\text{TiB}_2(s) + 5\text{O}_2(g) = 2\text{TiO}_2(s) + 2\text{B}_2\text{O}_3(l) \tag{2}
\]

\[
\text{B}_2\text{O}_3(l) = \text{B}_2\text{O}_3(g) \tag{3}
\]

\[
\text{Mo}(s) + 3\text{O}_2(g) = 2\text{MoO}_3(s) \tag{4}
\]

\[
3\text{MoO}_3(s) = \text{Mo}_3\text{O}_9(g) \tag{5}
\]

The weight gain of the pure Mo and the Mo covered with the TiB₂ coating started at 550 and 720 °C, respectively, in agreement with previously reported data for the oxidation of TiB₂ [44]. The rate of weight gain for the pure Mo specimen increased up to 790 °C; subsequently, the weight-gain rate remained high up to 850 °C, and then rapid weight loss occurred. These results can be explained by the fact that Mo is very easily oxidised at low temperatures in air, and its oxide (MoO₃) is easily volatilised according to reaction (5) [45]. However, the Mo covered with the TiB₂ coating exhibited entirely different weight-gain trends. Above 720 °C, the sample exhibited very slow weight gain up to the final temperature. This indicates that the TiB₂ functioned as a protective layer on
the surface of the pure Mo metal and improved the oxidation resistance of the Mo.

The thermal-analysis results for the TiB$_2$ coated on Mo in air are presented in Fig. 5. The heating rate was 10 °C/min in the heating segment up to 900 °C, and the duration of the isothermal oxidation was 5 h at 900 °C. According to the TG curve in Fig. 5, a very small weight gain (0.03%) occurred in the initial oxidation period up to 120 °C. Although this weight gain was negligible, it indicates the start of the oxidation, as supported by the DSC curve. The oxidation reaction was followed by reaction (2). Subsequently, the weight did not change until the temperature reached 400 °C, owing to the formation of low-viscosity B$_2$O$_3$ glass that functioned as an O barrier. When the oxidation temperature increased to 450 °C, the vaporisation of B$_2$O$_3$ (liquid) (see reaction (3)) occurred more vigorously, resulting in weight loss. When the temperature increased to 720 °C, slight weight gain occurred, because a large amount of B$_2$O$_3$ fluid covered the surface of the TiB$_2$ coating, preventing its further oxidation. Above this temperature, rapid weight gain occurred up to 900 °C because of the rapid vaporisation consumption of the B$_2$O$_3$ glass, causing part of the TiB$_2$ to be exposed in air, which led to further oxidation. Thereafter, isothermal oxidation occurred for 5 h. The weight-change rate of the specimen was dependent on the oxidation time. For the first 2.5 h, the weight-gain rate decreased with the oxidation time, and the oxidation kinetics of the specimen essentially followed a parabolic law. Then, the weight-gain rate increased, and the oxidation kinetics followed a linear law.

3.3. Phase and microstructure of oxide scales

To further examine the oxidation process of the TiB$_2$ ceramic coatings formed on Mo, samples prepared under identical conditions were oxidised at 300, 450, 600, 750, and 900 °C for 5 h. XRD was employed to identify the phases of the oxide scales, and their morphology was examined using SEM. The results are shown in Figs. 6 and 7, respectively. When the samples were exposed to air at temperatures of 300 and 450 °C for 5 h, only the peaks of TiB$_2$ were detected, as shown in Fig. 6. However, as shown in Fig. 5, the TG and DSC curves indicated that oxidation (reaction (2)) occurred at these two temperatures. It is considered that the phases of the reaction products were undetected because of their small amount. Indeed, the weight gain was only 0.03%, according to the foregoing TG data. At 600 °C, the TiO$_2$ peaks were observed, but the B$_2$O$_3$ peaks were absent. Additionally, the B$_2$O$_3$ peaks were absent at 750 and 900 °C, as shown in Fig. 6. This is because the B$_2$O$_3$ evaporated with the increasing temperature, as confirmed by the EDS mapping in Fig. 7. With the increasing temperature, the B content gradually decreased, and the O content increased. When the temperature increased to 900 °C, the TiB$_2$ peaks completely disappeared, and only TiO$_2$ peaks remained. After the total consumption of TiB$_2$ (T = 900 °C and 5-h oxidation time), important changes were observed, as shown in Fig. 6(e): high-crystallinity TiO$_2$ (crystallites) was formed on the surface. The XRD patterns (Fig. 6) and EDS mapping (Fig. 7(e)) indicated that Mo was present on the surface of the coating, suggesting that the TiB$_2$ coating (13 μm thick) lost its ability to protect the Mo substrate after 5 h of oxidation at 900 °C in air.

Furthermore, isothermal oxidation studies for the Mo substrate coated with the TiB$_2$ ceramic coating were performed in air at 900 °C for 1, 2, 3, 4, and 5 h. Fig. 8 presents the XRD patterns of Mo coated with TiB$_2$ oxidised in air at 900 °C for different durations. As shown, TiO$_2$ and B$_2$O$_3$ peaks were detected, as well as TiB$_2$ peaks, after 1 h of oxidation. Thus, both TiO$_2$ and B$_2$O$_3$ were formed on the surface after 1 h of oxidation. The intensity of the B$_2$O$_3$ peak was reduced after 2 h, and the B$_2$O$_3$ peak disappeared after 3 h. As described previously, the volatilisation of B$_2$O$_3$ increased with time, causing the disappearance of B$_2$O$_3$. After 2 h of oxidation, only the TiB$_2$ peak remained. After 5 h of oxidation, the TiB$_2$ peak disappeared, and a Mo peak was observed. Hence, when the sample was exposed to air for 5 h at 900 °C, the only phase on the surface was TiO$_2$.

Fig. 9 shows SEM images of the specimens after oxidation at 900 °C for various durations. As indicated by the SEM images of the as-prepared TiB$_2$ coating surface in our previous work [35], the coating typically exhibited a rod-like particle microstruc-
ture with a small gap. As shown in Fig. 9(a), a liquid phase filled the small gap. According to the results of the foregoing analysis, the liquid phase was $B_2O_3$. This is consistent with the EDS mapping results in Fig. 9(a). Comparing Fig. 9(a)–(c) reveals that the $B_2O_3$ content decreased with the exposure time. Fig. 9(d) and (e) indicate that crystalline TiO$_2$ was formed on the surface of the Mo substrate, supporting the foregoing XRD results and TG data.

Fig. 10 presents cross-sectional SEM images and element line scanning EDS analysis results for the oxidation of the TiB$_2$ coating at 900 °C for different durations. Oxide scales were formed after oxidation for 1, 2, 3, 4, and 5 h at 900 °C. As shown in Fig. 10(a)–(e), the TiB$_2$ coatings were generally oxidised with the increasing oxidation time, and there were obvious boundaries between the oxide layer and the unoxidised layer (TiB$_2$). For the five aforementioned oxidation durations, the thicknesses of the oxide scales were approximately 3, 6, 9, 10, and 13 µm, respectively. These results indicate that the oxidation rate was higher in the initial oxidation period than in the later stage, in accordance with the TG results shown in Fig. 5. The results of element line scanning EDS analysis indicated that the oxide scales mainly comprised O and Ti. The B content was lower in the oxide scales than in the TiB$_2$ coatings. This suggests that the $B_2O_3$ evaporated during the oxidation at 900 °C. The jagged concentration line profiles of B, Ti, and O for the oxide scales resulted from pores in the oxide scales. The
Fig. 9 – SEM images and EDS mapping of Mo coated with TiB$_2$ oxidised in air at 900 °C for different durations.

Fig. 10 – Cross-sectional SEM images and element line scanning EDS analyses of the TiB$_2$ coating after oxidation at 900 °C for different durations in air.
pores were due to the evaporation of B₂O₃ formed during the oxidation of the dense TiB₂ coating. Conversely, the smooth concentration line profiles indicate that the TiB₂ coatings were dense.

3.4. Oxidation mechanism

The foregoing results indicate that the CVD TiB₂ ceramic coating formed on the surface of the Mo metal protected the Mo substrate against oxidation up to 900 °C in air. B₂O₃ was formed in the process of oxidation, and the protection against the oxidation of the coating depended on the formation of B₂O₃. The oxidation process of the TiB₂ coating started at a low temperature (100 °C), as indicated by the TG data (Fig. 5). At this temperature, the surface of the coating with the rod-like TiB₂ phase was surrounded by low-viscosity B₂O₃ glass resulting from the slight oxidation of the TiB₂ coating (see Figs. 8(b) and 9(a)). The B₂O₃, as a protective layer, prevented the further access of O ions. Thus, the formation of the B₂O₃ layer prevented the further oxidation of the TiB₂ coating. However, the volatilisation of B₂O₃ became noticeable above 720 °C, resulting in rapid oxidation of the TiB₂ coating. A high oxidation rate was detected up to 900 °C through TG (Fig. 5). Isothermal oxidation studies (at 900 °C) revealed that the oxidation rate decreased with the oxidation time, owing to the formation of a new B₂O₃ layer. However, the oxidation kinetics of the sample exhibited different trends at isothermal temperature 900 °C duration of 5 h. For the first 2.5 h, the oxidation kinetics of the sample followed a parabolic law. For the next 2.5 h, the oxidation kinetics essentially followed a linear law. After oxidation for 5 h at 900 °C, XRD data (Fig. 8) and SEM (Fig. 9) images indicated the complete consumption of TiB₂ and the volatilisation of B₂O₃, and only a porous and non-protective TiO₂ crystal was observed on the Mo substrate.

4. Conclusions

To improve the oxidation resistance of Mo metal, a TiB₂ coating was synthesised on the surface of pure metallic Mo using CVD. According to the experimental results, the following conclusions are drawn.

1. The TiB₂ ceramic coating, as an anti-oxidation protective layer on the Mo metal, was successfully obtained on the pure Mo substrate via CVD. The as-deposited TiB₂ ceramic coating exhibited good adhesion to the Mo substrate and a high microhardness. These good mechanical properties of the coating were due to the roughened surface of the substrate and the high deposition temperature.

2. The weight gain of only 0.03% indicates that the TiB₂ coating exhibited high oxidation resistance during oxidation below 720 °C. The TiB₂ coatings also exhibited good oxidation resistance in the range of 720–900 °C; the weight gain increased to 0.4% but was far smaller than the 2.3% weight gain of pure Mo. In this temperature range, the oxidation resistance depended on the coating-layer thickness and oxidation time. At 900 °C, the 13-μm-thick TiB₂ layer protected the Mo substrate against oxidation for up to 5 h.

3. The oxidation mechanism of the TiB₂ coating was examined from room temperature to 900 °C. The oxidation process of the TiB₂ coating started at a low temperature (100 °C). The oxidation resistance of the TiB₂ coating depended on the state of the reaction product B₂O₃. Below 720 °C, B₂O₃ functioned as a low-viscosity diffusion barrier that covered the surface of the coating, preventing further ingress of O ions and thereby preventing further oxidation of the TiB₂. At 720–900 °C, the B₂O₃ glass was consumed by vaporisation, which slightly reduced the protective ability.

4. The oxidation kinetics of the sample exhibited different trends during oxidation for 5 h at 900 °C. For the first 2.5 h, the oxidation kinetics essentially followed a parabolic law. For the next 2.5 h, they followed a linear law.

Conflict of interest statement

The authors declared that they have no conflicts of interest to this work.

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