Chemical vapour deposition of tantalum diboride

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Tantalum diboride (TaB_2) was deposited on a quartz substrate from a gas mixture of $TaCl_5$, BCl_3, H_2, and Ar at a temperature between 900 and 1300° C. When the atomic ratio (B/Ta) in source gas was held above 1.0 at 1000° C, TaB_2 with a composition of between $TaB_{1.90}$ and $TaB_{1.95}$ was obtained in a single phase. The deposits grew to grain crystals with an increase in temperature and with an increase in the atomic ratio (B/Ta) in the source gas. The mass transfer of $TaCl_5$ was supposed to be the rate-determining step. The Vickers microhardness values for the coating deposited at 1100° C from a source gas with atomic ratio (B/Ta) above 1.0 were 3500 to 4100 kg mm^{-2}. Dispersing Ni or Pd on the substrate as an impurity, woolly crystals of up to 100 μm in length were grown in 30 min at 1050° C, and the growth mechanism was thought to be that of tip-VLS.

1. Introduction
In the system Ta—B, five borides are known; Ta_2B, Ta_3B_2, TaB, Ta_3B_4, and TaB_2. Among these borides, the diboride (hexagonal of AlB_2-type) is interesting as a material for refractory (m.p. 3100 to 3200° C), wear-resistant, metallic conductant, and oxidation resistant [1] applications. Tantalum diboride has been synthesized by molten-salt electrolysis [2], borothermal [3, 4], and magnesiothermal [5] reaction, direct union of the elements, plasma-spray [6] reactions, self-propagating reactions [7], and chemical vapour depositions [8–12]. Single crystals of the boride have been grown by the floating zone technique [13] and by chemical vapour transport [14].

In this work, the parameters affecting the deposition of a single phase of tantalum diboride from a gas mixture of tantalum pentachloride, boron trichloride, hydrogen and argon were examined. The woolly crystals grown due to the impurity effect were also investigated.

2. Experimental
2.1. Materials
Commercial tantalum sponge (purity 99.9% minimum), boron carbide (B_4C), and liquefied chlorine were used without further purification. Hydrogen and argon were dehydrated by passing through concentrated sulphuric acid. Tantalum pentachloride and boron trichloride were prepared *in situ* by chlorination of tantalum sponge and boron carbide at 500 and 800° C, respectively, in which the flow rate of respective chlorides was calculated from the flow rates of chlorine assuming the quantitative chlorination,

$$Ta + \tfrac{5}{2} Cl_2 \longrightarrow TaCl_5,$$

$$\text{and } B_4C + 6 Cl_2 \longrightarrow 4 BCl_3 + C.$$
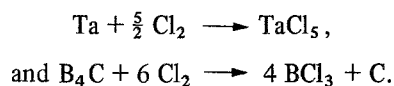
2.2. Deposition procedure
The apparatus is analogous to that used in previous experiment on the deposition of niobium diboride [15]. A tubular quartz substrate (7 mm i.d. and 90 mm in length) was held along the centre axis of a quartz tube (23 mm i.d.), which was heated from the outside so that the temperature at the middle point between the inner wall of the reaction tube and the surface of the substrate was 600° C in order to keep tantalum pentachloride in the vapour phase. A SiC resistor was inserted into the substrate tube, and the substrate temperature was measured by optical pyrometry, and controlled manually to a given temperature. The two streams of the chlorides were mixed just before the reaction zone.

For woolly crystal growth, aqueous solutions of metal salts were painted onto a substrate, dried in air, and decomposed or reduced to fine particles of the metals in the reaction tube.

2.3. Examination of the deposits

The appearance of the surface and the cross-section of the deposits was observed by SEM, and the crystallographic structure of the deposits was determined using an X-ray diffractometer. Micro-hardness on the cross-section of the polycrystalline layer of the deposits was measured by a Vickers microhardness tester (Akashi, MVK-C) with a load of 50 g. The atomic ratio (B/Ta) in the deposits was determined by an oxidation method. In the preliminary experiment, it was confirmed that boron oxide (B_2O_3) vaporized completely after 10 h in an air flow at 1200° C, while tantalum pentoxide was unaffected. Therefore, a collection of polycrystalline deposits (W_d) was oxidized to tantalum pentoxide ($W_{Ta_2O_5}$) in 20 h at 1200° C in an air flow, and the atomic ratio (B/Ta) in the deposits was calculated from the following equation;

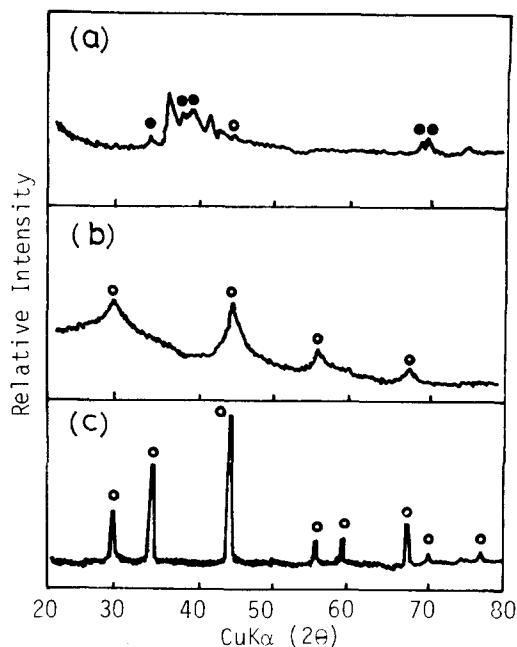$$(B/Ta) = 20.43\,(W_d/W_{Ta_2O_5}) - 16.74.$$

To etch the deposits, concentrated hydrofluoric acid was used at room temperature for 2 to 30 min.

3. Results and discussion
3.1. Conditions for deposition of single phase tantalum diboride

X-ray diffraction diagrams of the deposits are shown in Fig. 1, in which (a), (b) and (c) correspond to the diagrams of the samples deposited at 800, 950 and 1200° C, respectively. In Fig. 1a, diffraction peaks of the metal and lower borides of tantalum can be seen. With the increase of deposition temperature, the peaks change to those of tantalum diboride, and sharpen as a result of crystallization, as shown in Fig. 1c.

On the other hand, when the atomic ratio (B/Ta) in the source gas was increased from 0.5 to 16 at 1100° C, X-ray diffraction diagrams of deposits varied as shown in Fig. 2. With the
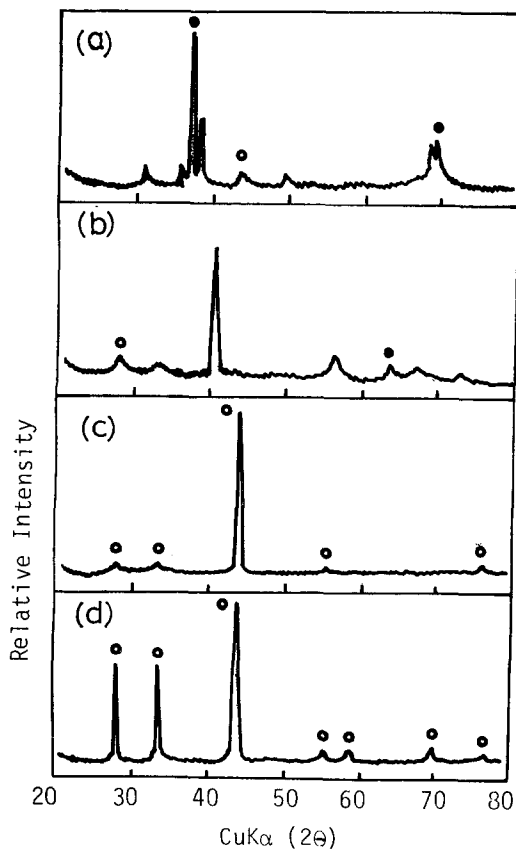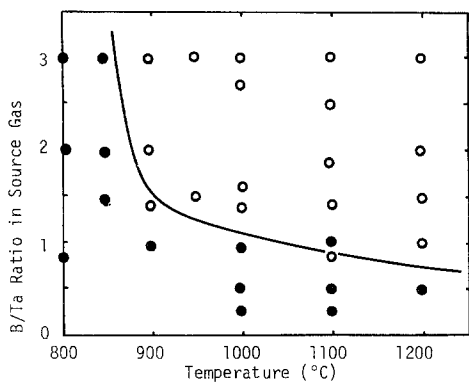

Figure 1 Effect of temperature on X-ray diffraction profiles of deposits, with a B/Ta ratio in the source gas of 3. Temperature: (a) 800° C; (b) 950° C; (c) 1200° C. (o) TaB$_2$; (●) Ta.

Figure 2 The effect of the ratio B/Ta in the source gas on the X-ray diffraction profiles of deposits. Temperature: 1100° C; B/Ta ratio in source gas: (a) 0.5; (b) 1.0; (c) 1.4; (d) 16. (o) TaB$_2$; (●) Ta.

Figure 3 Effect of temperature and B/Ta ratio in the source gas on the deposition of TaB_2. (○) TaB_2 single phase (not etched by conc. HF for 30 min at room temperature); (●) mixed phases of Ta and unidentified compounds (easily etched by conc. HF for 2 min at room temperature).

Figure 4 Effect of B/Ta ratio in the source gas on the B/Ta ratio in the deposits. Temperature: 1000° C.

increase of the atomic ratio (B/Ta) in the source gas, the deposits become a single phase of tantalum diboride.
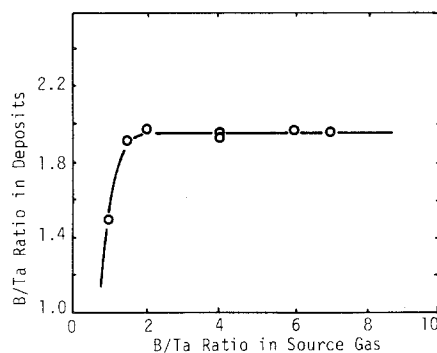
Besides the results from the X-ray diffraction diagram, the outstanding resistance of tantalum diboride against attack by concentrated hydrofluoric acid also helps us to discriminate between tantalum diboride and the lower tantalum borides or tantalum metal.

From the results of X-ray diffraction and the etching test, the deposition of tantalum diboride in single phase can be summarized as in Fig. 3, in which open circles show that deposits consisted of single-phase tantalum diboride.

It was found that the atomic ratio (H/Cl) in the source gas also affected the phase relation of the deposits. When the ratio (H/Cl) was below unity, mixed phases of tantalum diboride and unidentified compounds were formed.

3.2. The relationship between the atomic ratios (B/Ta) in the source gas and the deposits

At 1000° C, the atomic ratio (B/Ta) in the deposits increases with an increase of the ratio (B/Ta) in the source gas, and reaches 1.90 with a ratio in the source gas of 1.5. In the range of the ratio (B/Ta) in the source gas (2 to 7), the (B/Ta) ratio in the deposits remained near 1.95, as shown in Fig. 4. The homogeneity range of tantalum diboride extends from $TaB_{1.78}$ to $TaB_{2.57}$ [16] or from $TaB_{1.81}$ to $TaB_{2.02}$ at 927° C [17]. In the present work, the ratio (B/Ta) in the deposits of single-phase tantalum diboride varied only in a narrow range 1.90 to 1.95, and tantalum diboride within this range seems to be most stable thermodynamically, although there are few data on the tantalum–boron system compounds.

The lattice constants of the deposits obtained from the vapour with (B/Ta) ratio of 3 in the source gas at 1200° C were $a = 3.094$ Å and $c = 3.229$ Å, which are in good agreement with those in the literature of $a = 3.097$ Å and $c = 3.225$ Å ($TaB_{1.97}$) [18].

3.3. Variations of the appearance of deposits with the substrate temperature and with the atomic ratio (B/Ta) in the source gas

The surface appearance of the deposits varied with increase in deposition temperature, as shown in Fig. 5. Below 1000° C, the deposits were microcrystalline and adhered to the quartz substrate, although micro-cracks were observed. With increase in deposition temperature, the grains became larger, and the deposits were easily exfoliated.

Fig. 6 shows the surface appearance of deposits grown at 1100° C from a source gas of various atomic ratios (B/Ta). With increase of the ratio (B/Ta) in the source gas, grain growth was enhanced and hexagonal crystallites were formed, analogous to the tendency with temperature increase.

3.4. Woolly crystal growth in the presence of metallic impurities

Some impurity metals are expected to be liquid forming agents, and the presence of a liquid drop on the tip of a whisker or woolly crystal accelerates further growth of the crystallite along the axis VLS mechanism). Gold, platinum, palladium, iron,
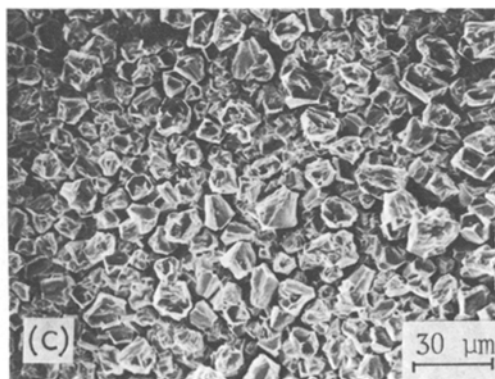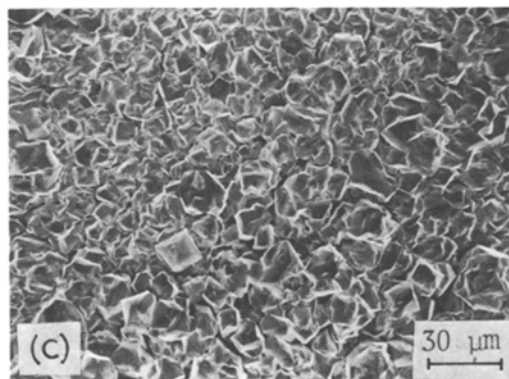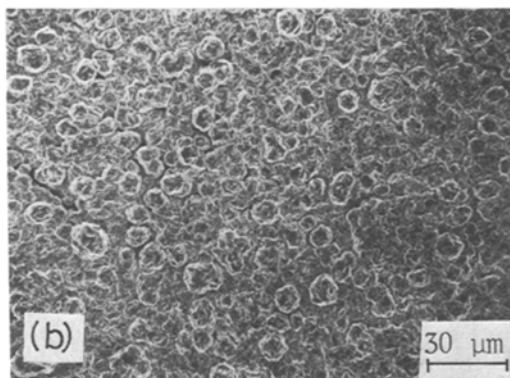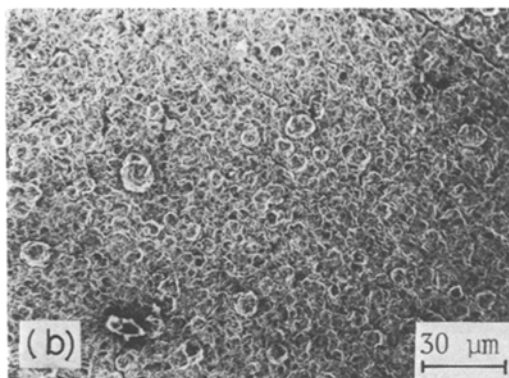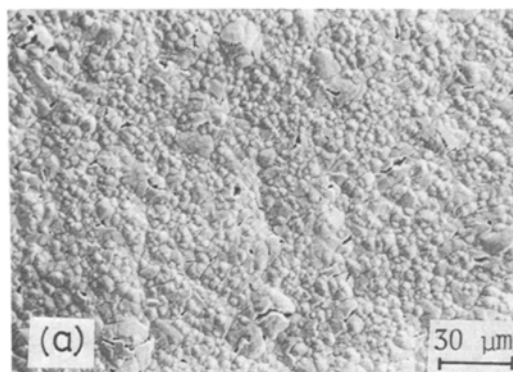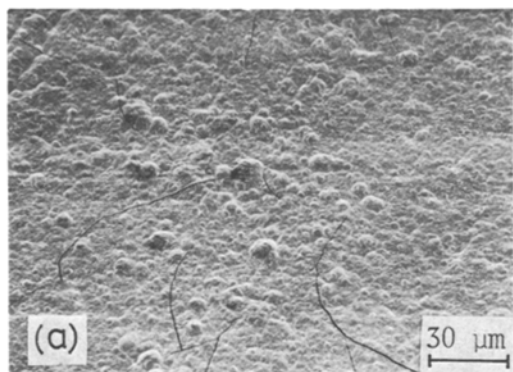
Figure 5 Surface appearance of deposits (influence of temperature) with a ratio B/Ta of 3 in the source gas, and a reaction time of 15 min. Temperature: (a) 900° C; (b) 1100° C; (c) 1300° C.

Figure 6 Surface appearance of deposits (influence of B/Ta ratio in source gas). Temperature: 1100° C; reaction time: 15 min; B/Ta ratio in the source gas: (a) 1, (b) 3; (c) 14.

cobalt, nickel, and chromium were used as impurity metals. Woolly crystals of tantalum diboride grew only under a very low chloride flow rates, such as $0.004 \, cm^3 \, sec^{-1}$ for tantalum pentachloride and $0.021 \, cm^3 \, sec^{-1}$ for boron trichloride at 1050° C. Of the impurity metals, nickel and palladium were the most effective in growing woolly crystals $100 \, \mu m$ in length and

0.1 to $2 \, \mu m$ in thickness, as shown in Fig. 7a. The X-ray diffraction diagram of the woolly crystals was similar to that cited in the Powder Data File, as expected from their curled shape.

On the tip of a woolly crystal grown with nickel impurity, a cap-like deposit can be seen in Fig. 7b, and the growth mechanism is supposed to be that of tip-VLS.
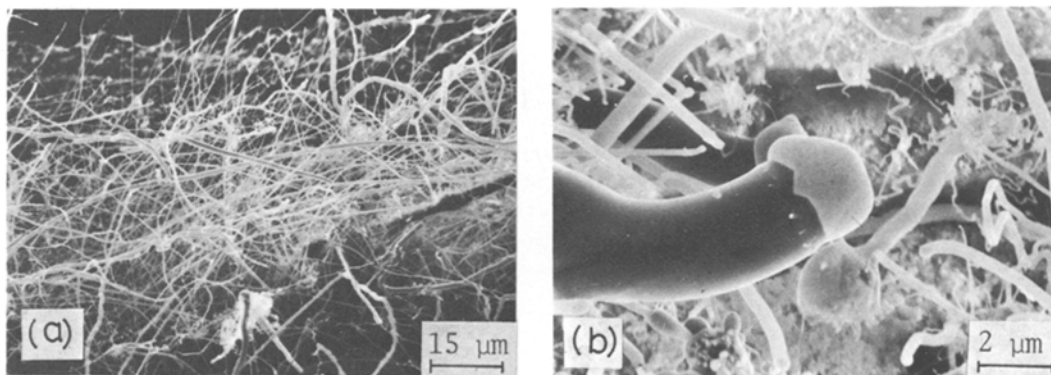
Figure 7 Woolly crystals. Temperature: $1050°$ C; BCl_3 flow rate: $0.021\,ml\,sec^{-1}$; $TaCl_5$ flow rate: $0.004\,ml\,sec^{-1}$; reaction time: 30 min; impurity: Ni. (a) Appearance under low magnification; (b) the tip of a woolly crystal.

3.5. The factors affecting the deposition rate

When the atomic ratio (B/Ta) in the source gas was 3, the deposition rate varied with temperature as shown in Fig. 8. The deposition rate had a plateau extending from 900 to $1000°$ C, and increased with chloride concentration. The decrease of the rate above $1200°$ C may arise from the deficiency of tantalum pentachloride in the vapour phase caused by tantalum diboride deposition on the inner wall of the reaction tube.

Fig. 9 shows the effect of the ratio (B/Ta) in the source gas on the deposition rate, in which the two curves correspond to total flow rates of chlorides $(TaCl_5 + BCl_3)$ of $0.2\,cm^3\,sec^{-1}$ and $0.4\,cm^3\,sec^{-1}$. An increase of boron trichloride concentration in the source gas decreases the deposition rate, while the morphology changes as was described in connection with Fig. 6.
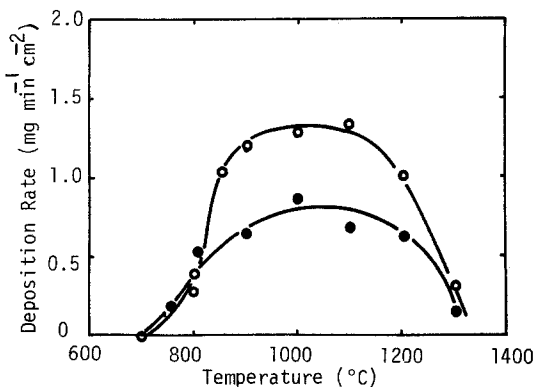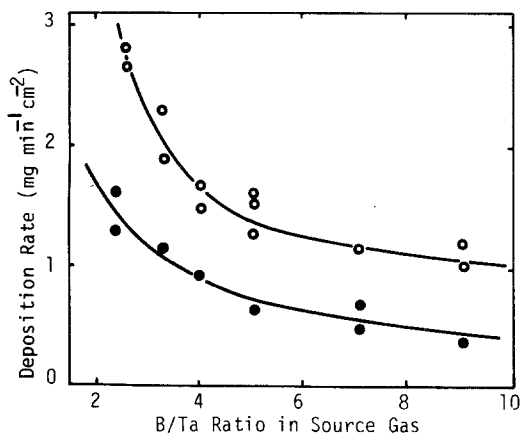

Figure 9 Effect of B/Ta ratio in the source gas on deposition rate. Temperature: $1000°$ C; $(TaCl_5 + BCl_3)$ flow rate: (●) $0.2\,ml\,sec^{-1}$; (o) $0.4\,ml\,sec^{-1}$.

Figure 8 Effect of temperature on deposition rate. (o) $TaCl_5$ flow rate: $0.06\,ml\,sec^{-1}$; BCl_3 flow rate: $0.18\,ml\,sec^{-1}$. (●) $TaCl_5$ flow rate: $0.03\,ml\,sec^{-1}$; BCl_3 flow rate: $0.09\,ml\,sec^{-1}$.

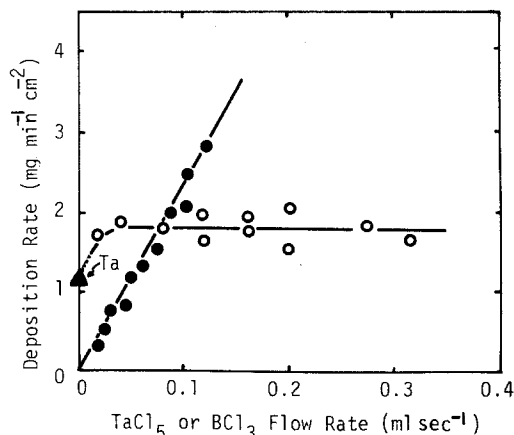*Figure 10* Effect of flow rate of halides on deposition rate. (●) Effect of $TaCl_5$ flow rate on deposition rate. Temperature: $1000°$ C; BCl_3 flow rate: $0.14\,ml\,sec^{-1}$. (o) Effect of BCl_3 flow rate on deposition rate. Temperature: 1000 to $1100°$ C; $TaCl_5$ flow rate: $0.04\,ml\,sec^{-1}$.

Under a constant flow rate of $0.04\,\text{cm}^3\,\text{sec}^{-1}$ of tantalum pentachloride, the deposition rate increased with increase in the flow rate of boron trichloride and became saturated above a flow rate of boron trichloride of $0.02\,\text{cm}^3\,\text{sec}^{-1}$ (open circles in Fig. 10, in which the deposition rate on the ordinate corresponds to that of tantalum metal). On the other hand, under a constant flow rate $0.14\,\text{cm}^3\,\text{sec}^{-1}$ of boron trichloride, the deposition rate increased linearly with increase of flow rate of tantalum pentachloride (closed circles in Fig. 10). These results shown in Figs. 9 and 10 suggest the rate-determining step of deposition to be that of mass transfer of tantalum pentachloride.

When the atomic ratio (H/Cl) in the source gas was increased, the deposition rate increased with the ratio (H/Cl), and became saturated above the ratio 1 to 1.5. Therefore, hydrogen reduction of the chlorides may be regarded as nearly quantitative.

3.6. Vickers microhardness
From Fig. 3, the single phase of tantalum diboride can be expected to be formed at 1000° C from a source gas with a ratio (B/Ta) above unity. Measured microhardness on a cross-section of a polycrystalline layer of the deposit indicated a clear correspondence with the phase relation as shown in Fig. 11. Gilman [19] reported the microhardness of tantalum diboride to be
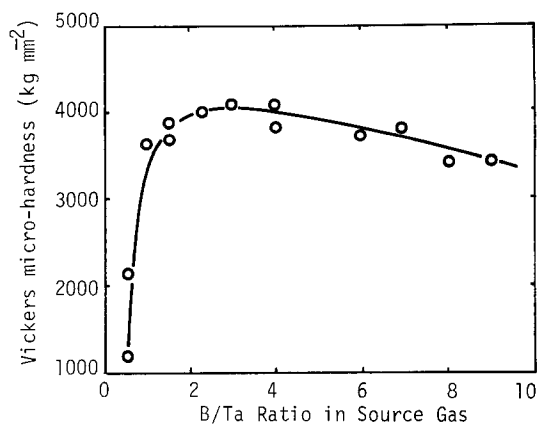
$2500\,\text{kg}\,\text{mm}^{-2}$. The hardness value measured in the present experiment was 3500 to $4100\,\text{kg}\,\text{mm}^{-2}$, and was considerably larger than that reported by Gilman. It seems that tantalum diboride may be a promising wear-resistant material.

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Figure 11 Effect of B/Ta ratio in the source gas on the microhardness of deposits. Temperature: 1100° C.