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Chemical vapour deposition of TiB_2 protective layers on a brass plate

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A brass plate was coated with TiB_2 layers from a gas mixture of $TiCl_4$, BCl_3, H_2 and argon. The lowest deposition temperature was very low, 530° C, which is 70° C lower than for a copper plate and 150 to 250° C lower than for other substrates. The corrosion resistivities of the brass plate against 12 N HCl, 16 N HNO_3, 36 N H_2SO_4 and sea water, as well as the abrasion resistivity against whirled sea sand, were improved outstandingly by coating with the TiB_2 layers.

1. Introduction

Titanium diboride (TiB_2) is a representative of fine ceramic compounds having excellent mechanical and chemical characteristics such as superhardness affording good wear and abrasion resistance, high resistance against corrosion or attack by molten metals, and good electrical and thermal conductivities. Recently, it has been suggested that a key technology for the development of the oceans is the development of effective strong protective coatings to the structural materials involved in ocean environments, in which materials suffer from severe corrosion and abrasion by sea-water and sea-sand and from the growth of shellfish.

Copper or copper alloys are considered not to encourage the growth of shellfish, but to have poor stabilities against corrosion and abrasion.

TiB_2 protective layers have been most conveniently obtained by the chemical vapour deposition (CVD) process using the gas mixtures $TiCl_4$–BCl_3–H_2 [1–4], $TiCl_4$–BBr_3–H_2 [5, 6] and $TiCl_4$–B_2H_6–H_2 [7, 8]. TiB_2 layers have also obtained by the titanization of boron fibres [9, 10] and by ion plating [11]. We have reported on TiB_2, TaB and TaB_2 coatings on a copper plate and on its corrosion and abrasion resistivities against acid solutions, sea water and whirled sea sands [3, 4, 12].

In this work, a brass plate was coated with TiB_2 layers in the temperature range 530 to 800° C, and its corrosion and abrasion resistivities were examined.

2. Experimental procedures

A vertical reaction tube (quartz, 21 mm i.d. and 350 mm long), in the central part of which the brass plate was hung using a tungsten hook, was heated from the outside. The brass plate (5 mm × 5 mm × 0.2 mm) was abraded by emery papers sequentially and degreased with acetone ultrasonically and dried. Commercial titanium tetrachloride was saturated into hydrogen using a circulation-type saturator at a given temperature. Boron trichloride was prepared *in situ* by the chlorination of boron carbide (B_4C) at 800° C using argon as a carrier gas. The gas mixture of titanium tetrachloride, boron trichloride, hydrogen and argon was introduced into the lower inlet of the reaction tube, and purged from the upper outlet. The TiB_2-coated brass plate (hereafter called the coated plate) was immersed in concentrated acid solutions or sea water at a given temperature, and the weight decrease caused by corrosion was measured at intervals. Furthermore, the coated plate was immersed and fixed in 500 ml of deionized water containing sea-sand (50 g, 20 to 30 mesh) which was stirred violently by a screw at about 400 r.p.m., and the weight decrease caused by sea-sand abrasion was measured at intervals. The surface of the coated plate was set vertically to the direction of revolution of the water.

3. Results and discussion

3.1. Deposition parameters

3.1.1. Effect of source gas flow ratio

The effect of the source gas flow ratio ($BCl_3/TiCl_4$) on the deposition of TiB_2 layers on the brass plate was examined in the reaction temperature range 700 to 800° C and a total flow rate of titanium tetrachloride and boron trichloride of $0.4\,ml\,sec^{-1}$. The maximum deposition rate (thickness) of TiB_2 layers was obtained at a ratio (B/Ti) of 2 to 3, and the thickness decreased steeply above or below these ratios.

3.1.2. Effect of reaction temperature

An appreciable weight gain of the brass plate indicating deposition of TiB_2 layers was observed at a reaction temperature as low as 600° C. The lowest deposition temperature at which the characteristic colours of the brass plate disappeared completely to the tarnished silver colours of TiB_2 layers was very low, about 530° C, which is 70° C lower than that for a copper plate and 150 to 250° C lower than for other substrates. Deposition temperatures of the TiB_2 layers as low as the 530 to 600° C obtained in this work have not been reported, and are very important for industrial applications. This lowering effect of the deposition temperature of TiB_2 layers may be attributable to the high promotional effect on the nucleation of TiB_2 crystallites and/or to some catalytic activity for surface reactions on the brass plate at the initial stage of

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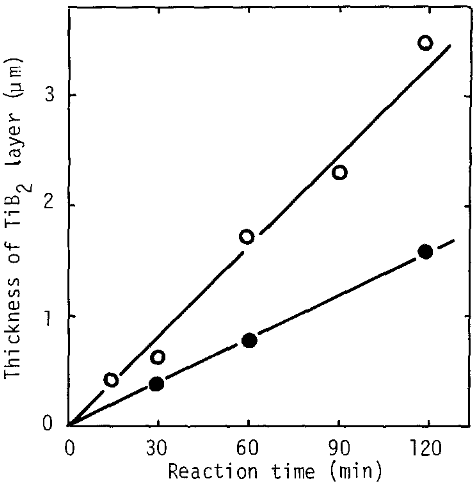

Figure 1 Effect of reaction time on the thickness of the TiB_2 layer. Reaction temperature (●) 600° C, (○) 700° C. Total gas flow rate $2.0\,ml\,sec^{-1}$, $TiCl_4$ $0.14\,ml\,sec^{-1}$, BCl_3 $0.26\,ml\,sec^{-1}$, argon $0.4\,ml\,sec^{-1}$.

deposition. The thickness of the TiB_2 layers increased linearly with increasing reaction time; the growth rates were 0.8 and $1.6\,\mu m\,h^{-1}$ for reaction temperatures of 600 and 700° C, respectively (Fig. 1).

3.2. Identification and morphology

The deposited layers obtained at 600° C were amorphous and could not be identified as the TiB_2 phase by X-ray diffraction. However, the results obtained by electron probe microanalysis (EPMA) showed that the titanium element was present in these layers with the same peak ratios as in crystalline TiB_2 layers. TiB_2 layers obtained above 700° C were partly crystallized.

The surface appearances of a TiB_2 layer obtained at 700° C for 30 min is shown in Fig. 2. It can be seen that the surface of the TiB_2 layer was relatively dense, except for the formation of some wrinkles. The TiB_2 was in general a single layer with uniform thickness, and had a good adherency with the substrate as can be seen in Fig. 3. However, the formation of an apparent intermediate layer with a uniform thickness of about 1/5 that of the TiB_2 layer was observed sometimes at the boundary between the TiB_2 (outer) layer and the substrate, as can be seen in Fig. 4. No apparent differences in composition between the intermediate layer and the outer TiB_2 layer were observed by EPMA, and copper or zinc elements were not detected. These intermediate layers were also observed in the case of TiB_2 coatings on a phosphor-bronze plate [13].

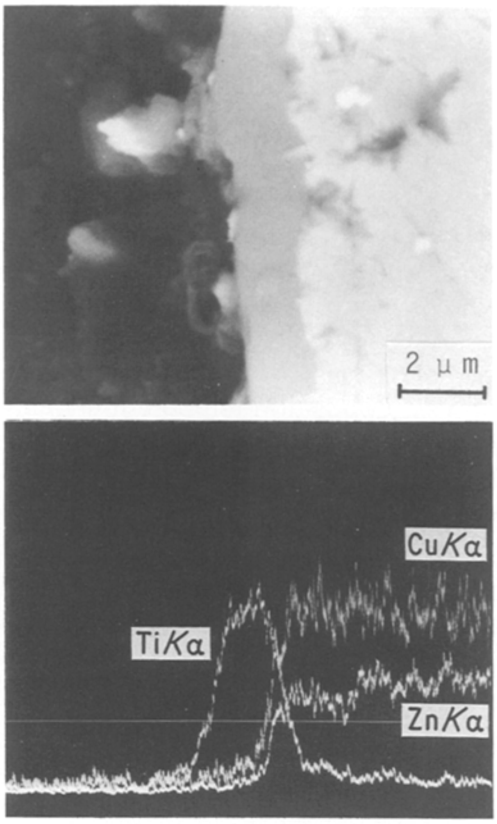

Figure 3 Appearance of polished cross-section of TiB_2-coated brass plate and its EPMA. Reaction temperature 700° C.

3.3. Corrosion resistivities of the coated plate against concentrated acid solutions and sea-water

3.3.1. 12 N HCl

The effect of the immersion time in 12 N HCl solutions maintained at 60° C is shown in Fig. 5, with a bare brass plate as a reference sample. The weight of the coated plate immersed in 12 N HCl decreased linearly with increasing immersion time, but the rate of decrease

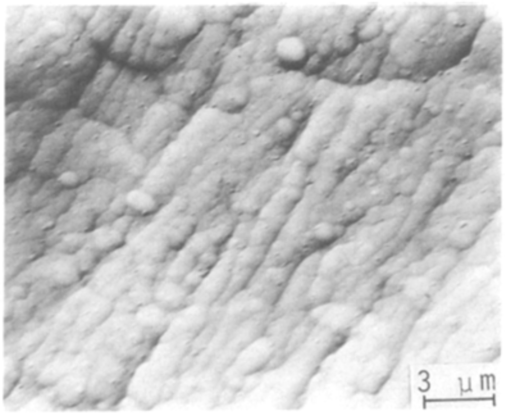

Figure 2 Surface appearance of the TiB_2 layer. Reaction temperature 700° C, reaction time 60 min.

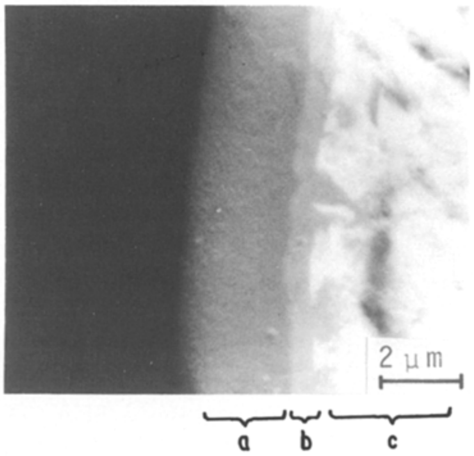

Figure 4 Polished cross-section of TiB_2 layers. Reaction temperature 700° C. (a) TiB_2 layer, (b) intermediate layer, (c) brass plate.

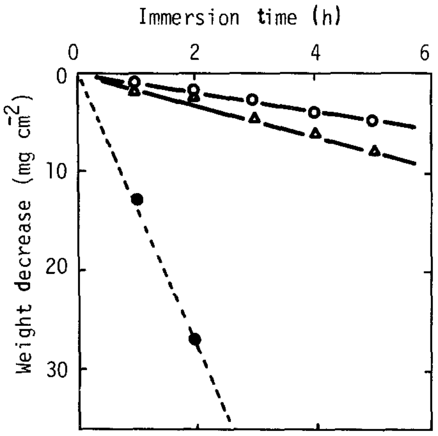

Figure 5 The weight decrease with increasing immersion time in 12 N HCl of TiB_2-coated brass plate. Reaction temperature 700° C, temperature of 12 N HCl 60° C. Thickness of the TiB_2 layers: (△) 1.6 μm, (○) 2.4 μm. (●) Bare brass plate.

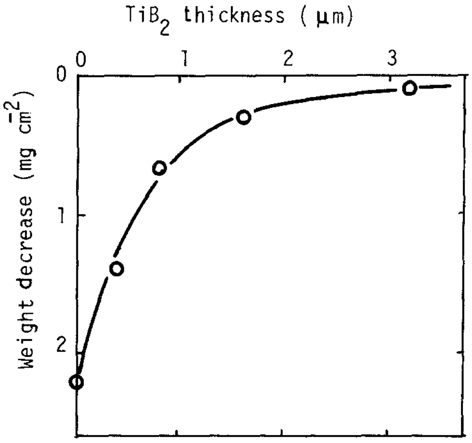

Figure 7 Effect of the thickness of the TiB_2 layer on the weight decrease of a TiB_2-coated brass plate immersed in 36 N H_2SO_4. Immersion time 2 h, temperature of 36 N H_2SO_4 60° C.

was much smaller than that of the bare brass plate: 1/16 for a thickness of the TiB_2 layer of 2.4 μm and 1/8 for 1.4 μm. The effects of the thickness of the TiB_2 layer on the weight decrease of the coated plate immersed in 12 N HCl are shown in Fig. 6, in relation to the immersion time. The weight decrease of the coated plate fell steeply with increasing thickness of the TiB_2 layer and attained a constant value at a thickness of about 2 μm, irrespective of the immersion time. Many corroded holes were observed in thin TiB_2 layers (below 2 μm) after 5 h of immersion time. It may be considered that corrosion of the brass plate through pinholes present in the TiB_2 layers is the main reason for the large weight decrease for the thinner TiB_2 layers.

3.3.2. 36 N H_2SO_4

Fig. 7 shows the effect of the thickness of the TiB_2 layer on the weight decrease of coated plates immersed in 36 N H_2SO_4 maintained at 60° C for 2 h. The weight decrease of the coated plate reduced with increasing thickness of the TiB_2 layer and attained a nearly constant value at a thickness of about 2 to 3 μm. The appearance and colour of the surfaces of thick TiB_2 layers (above 2 μm) did not change at all, while thin layers (below 1 μm) changed to black in colour followed by flaking.

3.3.3. 16 N HNO_3

The effect of the thickness of the TiB_2 layer on the weight decrease of coated plates immersed in 16 N HNO_3 at 20° C is shown in Fig. 8. It can be seen that the effect of the thickness of the TiB_2 layer on the weight decrease is similar to those for 12 N HCl or 36 N H_2SO_4.

3.3.4. Sea-water

The weight decrease of coated plates immersed in sea-water is shown in Fig. 9, together with those for the bare brass, copper and iron plates as reference samples. The weight decrease of a coated plate with a TiB_2 layer of 3.2 μm thickness after 50 h of immersion was smaller than that of a bare brass plate, and was 0.1 mg cm^{-2}.

3.3.5. Corrosion mechanism

Blaauw [14] has reported that the density of pinholes present in the Si_3N_4 layers obtained by plasma CVD was reduced exponentially with increasing thickness of the layer. It may be considered that a similar relationship is found also in the coatings obtained by other processes. Thus, if the corrosion resistivity of the

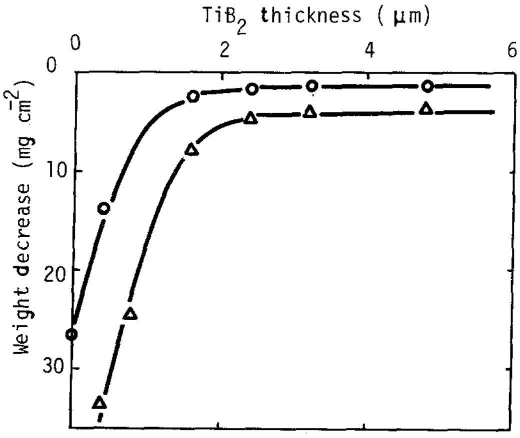

Figure 6 Effect of the thickness of the TiB_2 layer on the weight decrease of a TiB_2-coated brass plate immersed in 12 N HCl. Reaction temperature 700° C, temperature of 12 N HCl 60° C. Immersion time (○) 2 h, (△) 5 h.

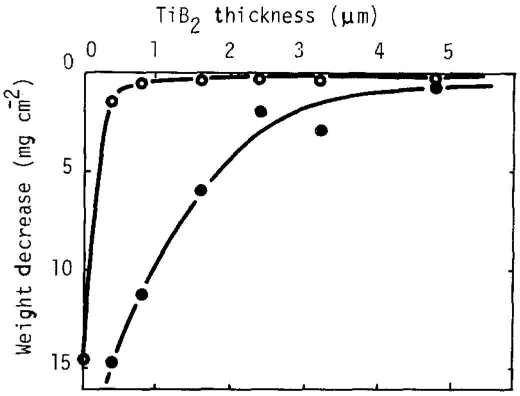

Figure 8 Effect of the thickness of the TiB_2 layer on the weight decrease of a TiB_2-coated brass plate immersed in 16 N HNO_3. Reaction temperature 700° C, temperature of 16 N HNO_3 20° C. Immersion time (○) 1 h, (●) 2 h.

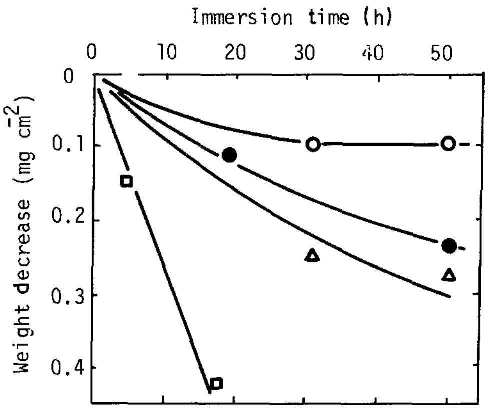

Figure 9 The weight decrease with increasing immersion time in sea-water of a TiB_2-coated brass plate. Reaction temperature 700° C, temperature of sea-water 30° C. Thickness of TiB_2 layers: (●) 0.8 μm, (○) 3.2 μm, (□) Bare iron plate, (△) bare brass plate.

coated layer itself against corrosive solutions is very excellent, the observed weight decrease of the coated plate may be caused mainly by the corrosion of the substrate through surface defects such as pinholes, and the weight decreases exponentially with increasing thickness of the coated layer with attainment of a constant value of zero at a thickness above a certain value. Thus, TiB_2 layers with a thickness of 2 to 5 μm obtained on the brass plate will be almost pinhole-free, and the constant weight decrease observed at 2 to 5 μm thickness is mainly caused by corrosion of the TiB_2 layer itself.

3.4. Abrasion resistivity against sea-sand

The weight decrease of coated plates exposed to whirled sea sand in water is shown in Fig. 10. The weight of the bare brass, iron or copper plates decreased linearly with increasing exposure time except for the initial stage of the exposure time. On the other hand, that of the coated plates reached a constant value depending on the thickness of the TiB_2 layer after about 50 h exposure. The weight decrease observed in the initial stage of the exposure time is probably attributable to preferential abrasion of the tips of nodules or projections. The above results suggests that a TiB_2-coated brass plate has an extremely high abrasion resistivity. A mirror-like surface of the TiB_2 layer was attained after an exposure time of 30 to 50 h.

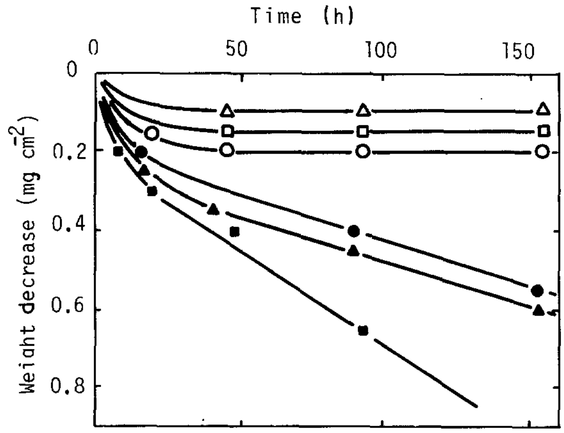

Figure 10 The weight decrease with increasing exposure time in whirled sea sand of a TiB_2-coated brass plate. Reaction temperature 700° C, thickness of TiB_2 layers (○) 0.8 μm, (□) 1.6 μm, (△) 3.2 μm. (■) Bare brass plate, (▲) bare iron plate, (●) bare copper plate. Sea-sand 20 to 30 mesh, revolution rate about 400 r.p.m.

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