Journal of the Less-Common Metals, *141* (1988) 327 - 333

TiB_2 COATINGS ON PHOSPHOR BRONZE PLATES BY CVD AND THEIR PROPERTIES

SEIJI MOTOJIMA and HISASHI HOTTA

Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu 501-11 (Japan)

(Received October 12, 1987; in revised form January 11, 1988)

Summary

A phosphor bronze plate was coated with a thin layer of TiB_2 from a gas mixture of $TiCl_4$, BCl_3, H_2 and argon at temperatures of 580 - 850 °C. The oxidation and corrosion stabilities were examined. Uniform and adherent TiB_2 layers were obtained on the phosphor bronze plate in the temperature range of 600 - 700 °C. The deposition rates were 1.1 $\mu m\ h^{-1}$ and 2.2 $\mu m\ h^{-1}$ at temperatures of 700 °C and 750 °C respectively. TiB_2-coated phosphor bronze plates were stable to oxidation at temperatures below 600 °C and were slightly affected by 3.2 N HNO_3 at room temperature and concentrated HCl at 60 °C.

1. Introduction

Titanium diboride (TiB_2) has many excellent chemical and mechanical characteristics, such as high refraction and high resistance to abrasion, oxidation, corrosion and chemical attack. These characteristics make it a promising candidate for many chemical and engineering applications which involve high temperatures and severe abrasion or corrosion.

TiB_2 protective coating layers have been most conveniently obtained by a chemical vapour deposition (CVD) process using a gas mixture of $TiCl_4$–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 been obtained by the titanization of boron fibres [9, 10] and by ion plating [11].

We have previously reported the deposition of the TiB_2 coating onto the copper plate, and its corrosion resistance against acid solutions and seawater and its abrasion resistance against sea sand [3, 4].

In this work, we examined the CVD parameters for the deposition of TiB_2 protective layers onto the phosphor bronze plate, and examined the oxidation and corrosion stability.

0022-5088/88/$3.50

2. Experimental procedure

A vertical reaction tube (quartz, inner diameter 21 mm) — in the central part of which the substrate(phosphor bronze plate, 10 mm × 10 mm × 0.3 mm) was hung using tungsten wire — was heated from the outside. The phosphor bronze plate (96wt.% Cu, 4wt.% Sn, 0.02 - 0.04wt.% P) was polished by emery paper (1200), and was cleaned ultrasonically in acetone. Titanium tetrachloride was saturated into hydrogen gas using a circular saturator, and was introduced into the reaction zone from the lower inlet of the reaction tube. Boron trichloride was prepared *in situ* by the chlorination of boron carbide (B_4C) at 800 °C. The total gas flow rate was fixed at 3.1 ml s^{-1} and the total chloride flow rate ($TiCl_4$ + BCl_3) was 0.26 ml s^{-1}, unless otherwise described.

3. Results and discussion

3.1. Deposition parameters

The effects of the reaction temperature and source gas flow ratio (BCl_3–$TiCl_4$) on the deposition of TiB_2 layers are shown in Fig. 1. An appreciable weight increase was observed at reaction temperatures above 600 °C, and the weight increased steeply above 700 °C. The lowest deposition temperature at which the colour of the phosphor bronze plate disappeared to become the silver colour of TiB_2 deposits was about 580 °C — 40 °C lower than that on copper substrate [3].

This lowest deposition temperature is comparable with that of deposition from $TiCl_4$–B_2H_6–H_2 gas [7, 8]. The lowering of the deposition temperature may be caused by the higher catalytic activity of the substrate surface for the nucleation of TiB_2 crystallites, which is especially affected by the

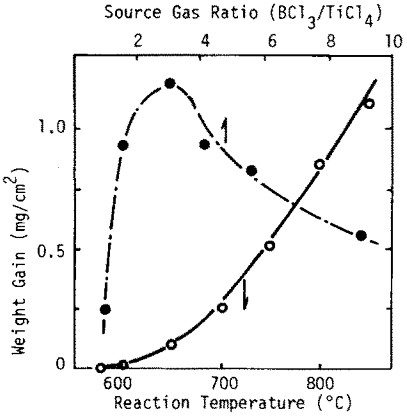


Fig. 1. Effect of the reaction temperature and source gas flow ratio (BCl_3–$TiCl_4$) on the weight gain: reaction time, 30 min; ●, reaction temperature 800 °C; ○, source gas flow ratio (BCl_3–$TiCl_4$) of 1.5.

presence of tin and/or phosphor as well as copper. The thickness of the TiB_2 layer increased linearly with increasing reaction temperature, and the growth rates were 1.1 $\mu m\ h^{-1}$, 2.2 $\mu m\ h^{-1}$ and 3.4 $\mu m\ h^{-1}$ at the reaction temperatures of 700 °C, 750 °C and 800 °C respectively. These values are considerably higher than that obtained for the gas system $TiCl_4$–BCl_3–H_2 using substrates of cemented carbides or nickel-bonded TiB_2 [2].

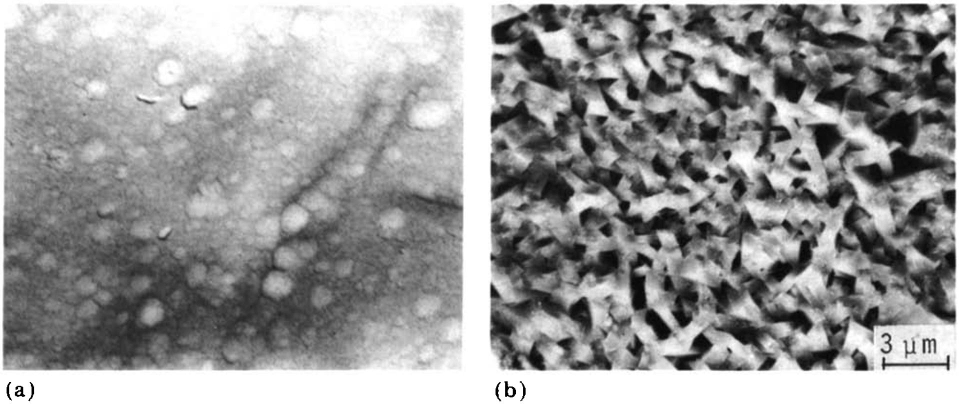
The maximum deposition rate was obtained at the source gas flow ratio (BCl_3–$TiCl_4$) of 2 - 3, below which it decreased steeply and above which it decreased gradually, as can be seen in Fig. 1.

The TiB_2 layers obtained at reaction temperatures below 750 °C were very fine and completely dense; appreciable grain growth or roughening of the surface was observed at a temperature of 850 °C (as seen in Fig. 2). There was good adhesion of the thin TiB_2 layers (less than 2 μm thick) with the substrate, despite the low reaction temperature of 600 - 700 °C. However, thick TiB_2 layers (more than 2 μm thick) were apt to form cracks or to peel off, probably because of a large difference in thermal expansion between the TiB_2 layers and the substrate, and because of the formation of brittle intermediate layers (perhaps TiB), as seen in Fig. 3. These intermediate layers could not be observed on the thin TiB_2 layers (less than 1 μm thick). For the copper substrate, no such intermediate layers were observed, and good adhesion was obtained for TiB_2 layers up to 10 μm thick [3].

Abnormal extrusion of the bulk of the substrate through the TiB_2 layers was observed rarely (as can be seen in Fig. 4). These defects, as well as pinholes, cracks or brittle intermediate layers, will degenerate characteristics such as oxidation and corrosion stabilities.

3.2. Stability to oxidation of the TiB_2-coated phosphor bronze plate

The phosphor bronze plate coated with TiB_2 layers was exposed to air at elevated temperatures; the weight gain is shown in Fig. 5, in comparison with that of the bare phosphor bronze plate. The bare phosphor bronze plate



(a) (b)

Fig. 2. Surface appearance of the TiB_2-coated layers. Reaction temperature: (a) 700 °C; (b) 850 °C; reaction time: 30 min, source gas flow ratio (BCl_3–$TiCl_4$) of 1.5.

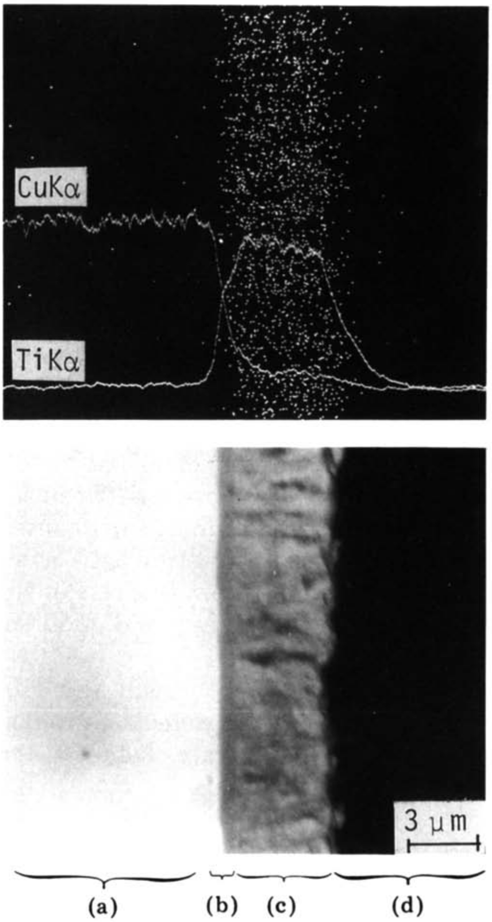


Fig. 3. Cross-section of the TiB_2-coated phosphor bronze plate (a) and the line profiles by electron probe microanalysis (b). Reaction temperature, 800 °C; reaction time, 90 min; (a) substrate; (b) intermediate layer; (c) TiB_2 layer; (d) resin.

was oxidized easily at temperatures above 450 ℃. However, TiB_2-coated phosphor bronze plates oxidized gradually with an increase in the oxidation temperature above 600 ℃; the weight gain increased steeply above 800 - 850 ℃. But the rate of weight increase of the TiB_2-coated phosphor bronze plate was less than that of the bare phosphor bronze plate, being about a quarter at 800 ℃. No weight increase or tarnishing reaction was observed below 600 ℃. The influence of the thickness of TiB_2 layers on the weight gain of the TiB_2-coated phosphor bronze plate when exposed to air at elevated temperatures is shown in Fig. 6. The weight gain decreased steeply with increasing thickness of the TiB_2 layers and reached a constant value which depended on the oxidation temperature: 1 μm at oxidation temperatures of 700 - 800 ℃ and more than 3 μm at 900 ℃. In the temperature range of

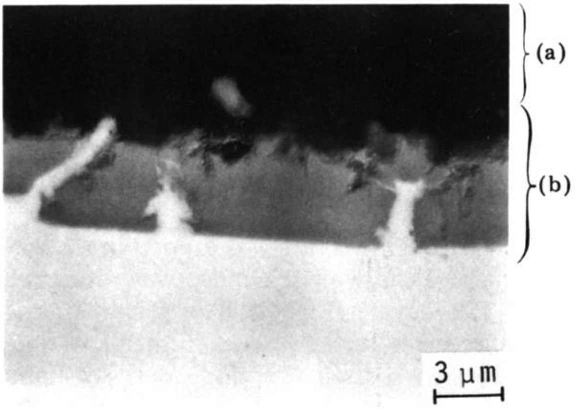
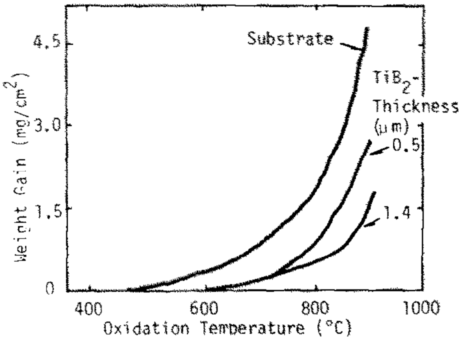


Fig. 4. Cross-section of the TiB_2-coated phosphor bronze plate. Reaction temperature, 800 °C; reaction time, 60 min; source gas flow ratio (BCl_3–$TiCl_4$) of 3; (a) TiB_2 layer; (b) substrate.



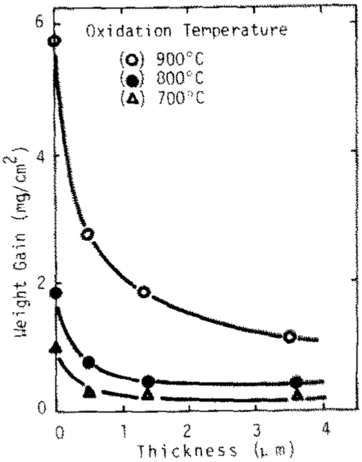


Fig. 5. Oxidation stability of the TiB_2-coated phosphor bronze plate exposed in air at elevated temperatures. Reaction temperature, 700 °C; increasing rate of the oxidation temperature, 18.2 °C min^{-1}; air flow rate, 1.0 ml s^{-1}.

Fig. 6. Effect of the thickness of TiB_2 layers on the weight gain of the coated plate exposed in air at elevated temperatures. Reaction temperature, 700 °C; increasing rate of the oxidation temperature; 18.2 °C min^{-1}; oxidation temperature: ○, 900 °C; ●, 800 °C; △, 700 °C.

600 - 700 °C, the oxidation of the TiB_2 layers obeyed the "parabolic law", which may be affected by the formation of dense and protective layers of TiO_2. However, at temperatures above 800 °C, the oxidation obeyed the initial "parabolic law" followed by the "linear law". The slight weight increase observed in the temperature range of 600 - 700 °C is considered to be caused mainly by the oxidation of the TiB_2 layer itself, whereas the steep weight increase observed above 800 °C is caused mainly by crack formation

on the TiB_2 layers followed by oxidation of the phosphor bronze plate itself. It may be concluded that the TiB_2 layer is stable to oxidation at temperatures below 700 °C in air and improves the oxidation stability of the phosphor bronze plate.

3.3. Stability to acid solutions of the TiB_2-coated phosphor bronze plate

3.3.1. 3.2 N HNO_3

A phosphor bronze plate coated with TiB_2 layers was dipped in a 3.2 N HNO_3 solution at room temperature, and the weight change was measured and plotted against the thickness of TiB_2 layers (Fig. 7). The weight of the TiB_2-coated phosphor bronze plate reduces linearly with immersion time with increasing thickness of the TiB_2 layers; then the slope decreases and reaches a constant value at a thickness above 3 μm, indicating that pinhole-free films are obtained at thicknesses above 3 μm. The weight decrease of the TiB_2-coated phosphor bronze plate (with TiB_2 layers 3.2 μm thick) was one-twentieth that of the bare phosphor bronze plate after 3 h of immersion. But TiB_2 layers could not act as a perfect protective layer against dilute nitric acid solution, because TiB_2 layer dissolve very slowly in this solution, as reported by Covino *et al.* [14].

3.3.2. Concentrated HCl

The weight change of the TiB_2-coated phosphor bronze plate dipped in concentrated HCl at a temperature of 60 °C is shown in Fig. 8. The weight of the coated plate decreased linearly with increasing immersion time, but the

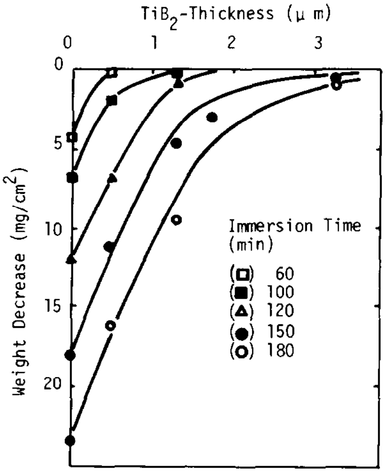


Fig. 7. Corrosion stability of the TiB_2-coated phosphor bronze plate to 3.2 N HNO_3. Reaction temperature 700 °C; source gas flow ratio (BCl_3–$TiCl_4$) of 1.5; immersion time in 3.2 N HNO_3 at 60 °C; □, 60 min; ■, 100 min; △, 120 min; ●, 150 min; ○, 180 min.

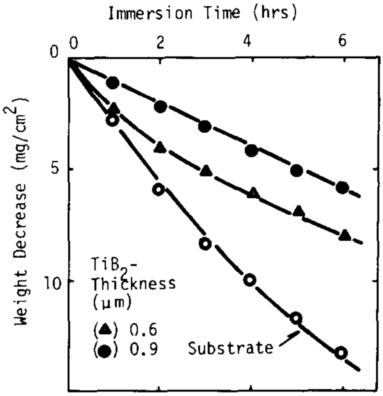


Fig. 8. Corrosion stability of the TiB_2-coated phosphor bronze plate to concentrated HCl. Reaction temperature, 700 °C, source gas flow ratio (BCl_3–$TiCl_4$) of 1.5; immersion temperature: 60 °C; ○, bare phosphor bronze plate: △, ●, TiB_2-coated phosphor bronze plate; thickness of TiB_2 layer: △, 0.6 μm; ○, 0.9 μm.

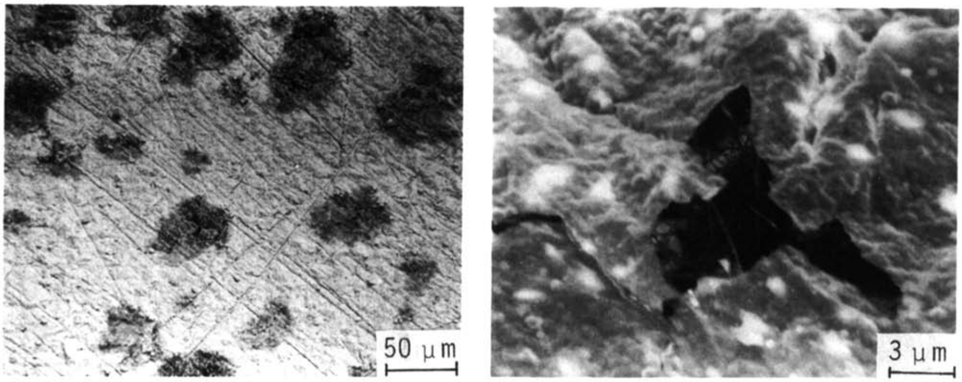


Fig. 9. Surface appearance of the TiB_2-coated phosphor bronze plates which were immersed in concentrated HCl for 9 h. Reaction temperature, 700 °C; source gas flow ratio (BCl_3–$TiCl_4$) of 1.5; thickness of TiB_2 layers, 0.6 μm.

rate was smaller than that of the bare plate: one-half for TiB_2 layers 0.9 μm thick. The weight reduction of the coated plate at a reaction temperature of 800 °C was considerably larger than that at 700 °C; the same weight decrease was observed for the coated plate with TiB_2 layers 0.9 μm thick at 700 °C and with layers 5.3 μm thick at 800 °C.

The surface appearance of the coated plate with TiB_2 layers 0.6 μm thick, immersed in concentrated HCl for 9 h at 60 °C, is shown in Fig. 9. The surface of these TiB_2-coated layers was tarnished in places and a central part of the tarnished layers was exfoliated. These tarnished spots were formed by the dissolution of the substrate through pinholes in the thin TiB_2 layers followed by the formation of cavities at the boundary of the TiB_2 layers and the substrate.

References

1 A. J. Caputo, W. J. Lackey and I. G. Wright, *Proc. 9th Int. Conf. on Chemical Vapour Deposition*, Electrochemical Society, Pennington, NJ, 1984, p. 782.
2 A. J. Caputo, W. J. Lackey, I. G. Wright and P. Amgelini, *J. Electrochem. Soc.*, *132* (1985) 227.
3 S. Motojima, M. Yamada and K. Sugiyama, *J. Nucl. Mater.*, *105* (1982) 335.
4 S. Motojima and H. Kosaki, *J. Mater. Sci. Lett.*, *4* (1985) 1350.
5 H. J. L. Van der Valk and J. H. F. Grondl, *Solid State Ion.*, *16* (1985) 99.
6 H. O. Pierson and A. W. Mullendore, *Thin Solid Films*, *95* (1982) 99.
7 H. O. Pierson and A. W. Mullendore, *Thin Solid Films*, *72* (1980) 511.
8 E. Landich and T. M. Gerlach, *Thin Solid Films*, *75* (1981) 271.
9 J. Bouix, H. Vincent, M. Boubehira and J. C. Viala, *J. Less-Common Met.*, *117* (1986) 83.
10 H. Vincent, M. Boubehira, J. Bouix, C. Bernard and A. Roche, *J. Cryst. Growth*, *75* (1986) 504.
11 T. Sato, M. Kudo and T. Tachikawa, *Denki Kagaku*, *55* (1987) 542.
12 E. Randich, *Thin Solid Films*, *63* (1979) 309.
13 T. M. Besmann and K. E. Spear, *J. Electrochem. Soc.*, *124* (1977) 790.
14 B. S. Covino, Jr., S. D. Cramer, J. P. Carter and D. Schlain, *J. Less-Common Met.*, *41* (1975) 211.