

TitaniumDiboride (TiB_2) Formation ByElectroplating inMoltenSalt With Continuous & Pulsed Current

G. Ett & E.J. Pessine

The improvement of TiB_2 coatings over graphite was investigated by comparing the electrochemical techniques of continuous current plating (CCP) and pulse current plating (PCP). The electrolyte used was the molten eutecticum of sodium, lithium and potassium fluorides, often called Flinak, and $\text{K}_2\text{TiF}_6 + \text{KBF}_4$ in a proportion of one to four (mass). The coatings produced by pulsed current (PCP) show improvements in morphology and microstructure if experimental conditions, such as current density, frequency and $t_{\text{cathodic}}/t_{\text{off}}$ pulse duration ratio, are appropriate.

TiB_2 as a surface coating has most interesting properties, such as high hardness and corrosion resistance, high melting point and electrical conductivity, low solubility in liquid metals, high thermal shock resistance and good adhesion to substrates.

Andrieux (1929)¹ is considered the precursor of the electrochemical preparation of TiB_2 . The substantial work of Makyta² and Wendt,³ besides the important fundamental aspects presented, consolidate the electrochemical use of molten chlorides and fluorides.

In this study, we report the investigation of the morphological and microstructural improvements of TiB_2 coatings over graphite substrates by pulse current plating (PCP). Preliminary experimental parameters were determined both by cyclic voltammetry (CV) and continuous current plating (CCP). The electrolyte is a fluoride mixture maintained at 600 °C. The surface was characterized by scanning electron microscopy (SEM).

Experimental Procedure

The electrolyte used was prepared with analytical grade chemicals. The eutectic fluoride mixture⁴ (46.5 LiF-11.5

Variation of Weight Percentage of Ti & B in TiB_2
As a Function of Frequency

F (Hz)	B (%)	Ti (%)
0.5	30.32	69.68
1	30.41	69.59
10	31.62	68.38
100	30.54	69.46
1000	30.32	69.68
Average	30.64	69.35
Theoretical	30.6 (±0.5)	69.4 (±0.5)

NaF -42 KF) mol pct, Flinak, was used as solvent; a mixture of K_2TiF_6 and KBF_4 in a mass proportion of 1:4, as solute. The temperature used in this study was 600 °C, because earlier thermogravimetric tests showed that at higher temperatures an accentuated loss of solute occurs, mainly as a result of evaporation of KBF_4 in the form of BF_3 .

The working electrode was graphite because it has a thermal expansion coefficient (4.3 $\mu\text{m}/\text{m}/^\circ\text{C}$) close to the TiB_2 (4.6 $\mu\text{m}/\text{m}/^\circ\text{C}$). A platinum wire was used as a pseudo reference electrode and, when necessary, a Ni/Ni^{+2} //BN reference electrode was used during the electrochemical experiments. The coatings obtained were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescence.

Results & Discussion

Deposition by continuous current at high current densities normally produces nodular, dendritic coatings instead of the uniform coatings obtained at lower values. While reproducible, compact coatings still can be obtained, the measurement of coating thickness is difficult because of the irregular surface of the nodular deposits.

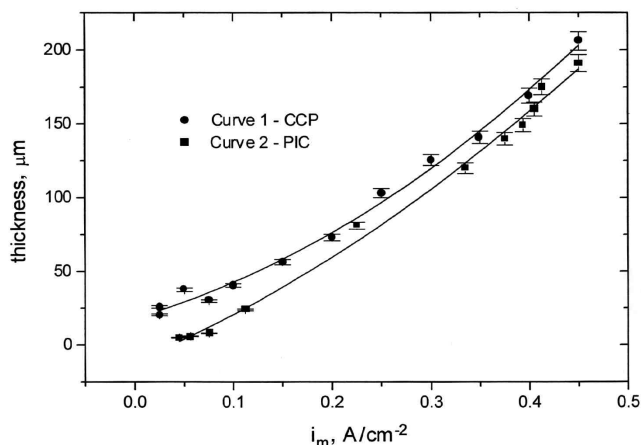


Fig. 1— TiB_2 coating thickness as a function of mean current density ($T = 600$ °C, $t = 30$ min).

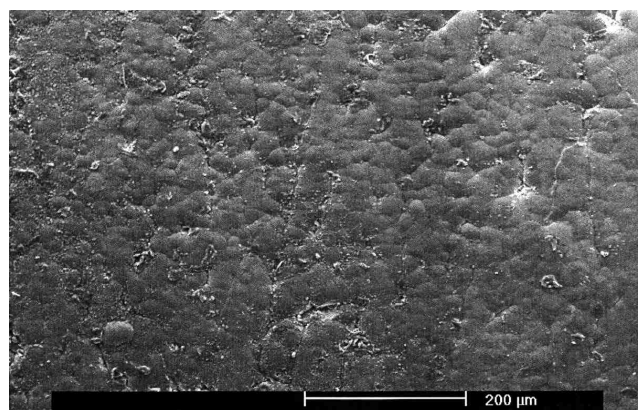


Fig. 2— TiB_2 CCP SEM micrograph; $i_m = 0.30$ A/cm², $t = 30$ min, 600 °C.

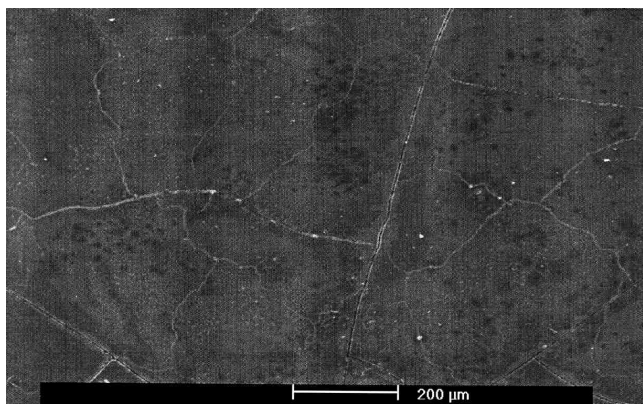


Fig. 3—TiB₂ PIC SEM micrograph; $i_m = 0.33 \text{ A/cm}^2$, 30 min, 600 °C, 100 Hz.

The PCP technique^{5,6} is usually subdivided into PIC (periodically interrupted current) and PRC (periodically reversed current). This paper deals with PIC in comparison to CC (continuous current). By increasing the nucleation rate on substrates, PCP increases coating uniformity, while the coating growth rate is not significantly affected. Previous studies by cyclic voltammetry⁷ allowed determination of the TiB₂ deposition potential for the application of both CCP and PIC techniques.

The thickness increase shows the same pattern for both CCP and PIC at different mean current densities, i_m , at an arbitrarily chosen electrolysis duration of 30 min and a frequency of 100 Hz, as shown in Fig. 1. All experiments performed with CCP (curve 1) do not show the expected linear thickness increase resulting from the formation of nodular deposits. The typical surface structure shown in Fig. 2, by SEM surface examination, was obtained at $i_m = 0.30 \text{ A/cm}^2$. At higher current densities, nodular deposits predominate.

The influence of pulsing and pulse duration on the growth of the TiB₂ coatings is shown for PIC by curve 2. The time t_c/t_{off} (cathodic current on / current off) was varied from 0.5:1 to 11:1, at a frequency of 100 Hz. It also follows the pattern, but the coatings show a distinct structure, typical for the use of PIC. When the diffusion coefficient of ions to be reduced or oxidized becomes too low, however, for the time interval in which current pulses are applied, the morphology of the coatings is comparable to those applied by CCP.

At mean current densities lower than 0.05 A/cm^2 , deposits are smooth, still showing the graphite substratum. Above 0.05 A/cm^2 , the deposits continue smooth, without nodules or dendrites and in the range $0.2\text{--}0.4 \text{ A/cm}^2$ have a bright

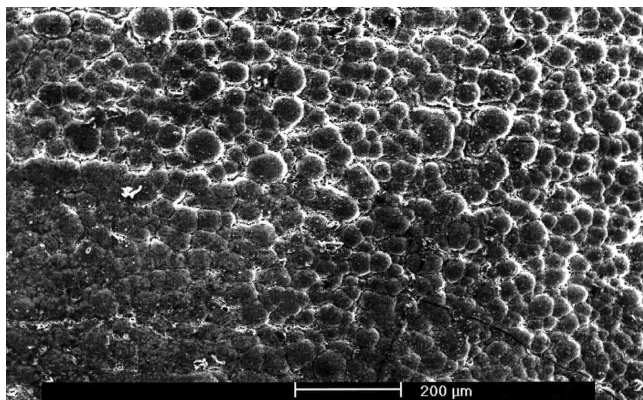


Fig. 5—SEM photo of mixture of nodular and lamellar crystallization; $f = 0.5 \text{ Hz}$ for $i_c = 0.45 \text{ A/cm}^2$, $i_{off} = 0$, $t_c/t_{off} = 10:1$, 30 min.

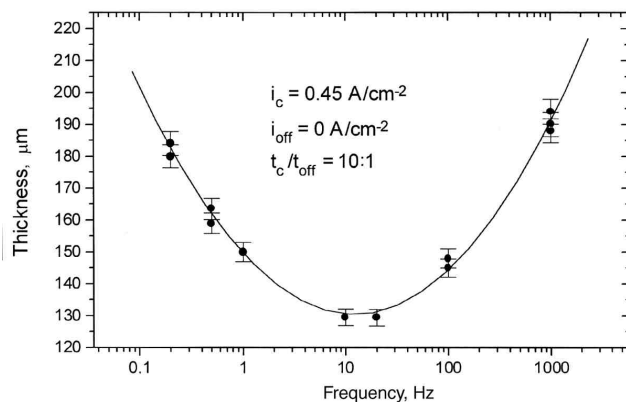


Fig. 4—Thickness variation as a function of pulse frequency.

metallic luster, as demonstrated by Fig. 3 for $t_c/t_{off} = 3:1$. The observed cracks can be attributed to the differences in thermal expansion coefficients. At mean current densities greater than 0.4 A/cm^2 the deposits are nodular, showing the same aspects and properties as those obtained by the CCP plating process.

The thickness variation of the TiB₂ coating as a function of frequency is shown in Fig. 4 for frequencies between 0.5 and 1,000 Hz, a current density $i_c = 0.45 \text{ A/cm}^2$, (established in CCP experiments), and a ratio $t_c/t_{off} = 10$. In the region of decreasing thickness growth, the deposit exhibits a mixture of nodular and lamellar crystallization, as can be seen in Fig. 5 (despite some attack caused by dissolution), suggesting a behavior similar to that observed with CCP (Fig. 2).

At frequencies above a minimum of 0.5 Hz, the improvements in deposit quality are substantial, as can be observed by comparing Figs. 3, 5 and 6, even considering the inferior thickness values obtained at 100 Hz.

Figure 7 demonstrates that, as frequency increases, the open-circuit potential (i_{off}) and the reduction potential get closer to each other. At low frequencies (0.5 Hz), the deposition potential during a longer period of time is sufficient to form nodules. The time intervals in which oxidation can occur is insufficient to eliminate them to allow uniform coating growth.

At higher frequencies (1,000 Hz), the periods between the open-circuit and reduction potentials are shorter and the deposition potential is reached, although this does not happen with the oxidation potential. The deposits obtained are thicker and have more nodules, similar to those shown in Fig. 6. At frequencies greater than 2,000 Hz, the reduction and oxidation potentials are practically identical to those obtained by CCP.

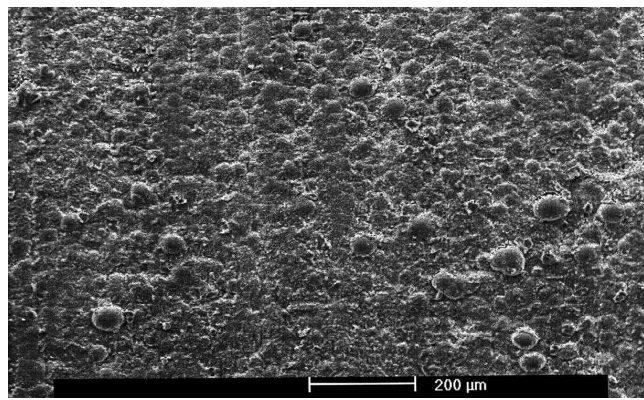


Fig. 6—SEM photo of deposit at 1,000 Hz; $i_c = 0.45 \text{ A/cm}^2$, $i_{off} = 0$, $t_c/t_{off} = 10:1$, 30 min.

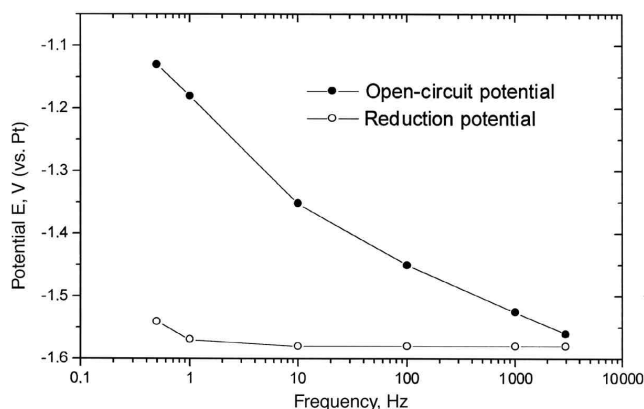


Fig. 7—Open-circuit potential and cathodic potentials resulting from frequency variation; $i_c = 0.45 \text{ A/cm}^2$, $i_{\text{off}} = 0$, $t_{\text{off}} = 10:1$.

The hexagonal structure of the TiB_2 deposits was identified by X-ray diffraction; the results obtained for the weight percentages of B and Ti in the TiB_2 by X-ray fluorescence are listed in the table. No indication of other intermetallic compounds was observed.

The small deviation between the theoretical value, calculated or obtained from the phase diagram (30.1-31.1% B)⁸ and the average of the weight percentages obtained by the X-ray fluorescence can be attributed to the cylindrical surface of the electrode and, mainly, to the fact that boron, as a light

element, is almost at the limit of detection of available equipment. Even at high current densities, no anodic effect was observed when using pulsed current.

Conclusions

The PCP technique produces coatings with better quality, showing fewer cracks and better adhesion to the substrate when compared with those obtained by CCP, for comparable thickness values. The suitable interval of frequencies for the current pulses application is between 5 and 100 Hz.

Editor's note: Manuscript received, October 1999.

Acknowledgments

This research was supported by FAPESP through grant No. 96/7923-0 and CNPQ (No. 142297/97-6).

References

1. M.L. Andrieux, *Annales de Chimie*, **12**, 423 (1929).
2. M. Makyta, K. Gjorheim & M. Matiasovsky, *Metall.*, **42**(12), 1196 (1988).
3. H. Wendt, K. Reuhl & V. Schwarz, *Electrochim. Acta*, **37**(2), 263 (1991).
4. G. Ett, E.J. Pessine, D.M. Soares & V.L. Salvador, *1st Latin-American Interfinish*, São Paulo, Brazil, October (1997).
5. B.A. Wilson, D.M. Turley, *C. Trans. IMF*, **67**, 104, (1989).
6. P. Bercot, A. Jaquet, J. Pagetti, *Int'l Union Surface Fin.-Interfinish*, São Paulo, Brazil **2**, 205 (1992).
7. G. Ett, E.J. Pessine, *193rd Mtg. Electrochem. Soc.*, San Diego, CA, (May 1998).
8. *Binary Alloy Phase Diagram*, B. Massalski, Ed., ASM Int'l, **2-85** (1990).

About the Authors

Dr. Gerhard Ett is a chemical engineer at the Instituto de Pesquisas Energéticas e Nucleares, CEP: 05422-970, Travessa R, 400, Universidade de São Paulo, Caixa Postal 11.049, São Paulo, Brazil. He holds a DSc in materials engineering from the Nuclear and Energy Research Institute of the University of São Paulo. His research interests include electrodeposition of intermetallic compounds and composite coatings, as well as special coatings for light metals, surface finishing and fuel cells.*

Dr. Elisabete J. Pessine is head of research of the Molten Salts Electrochemistry Group of the Materials Engineering Department of the Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo. She holds a DSc from the University of São Paulo and her research interests include molten salt and aqueous electrochemistry, hard anodizing, surface finishing and fuel cells.

* To whom correspondence should be addressed.



Reference Library

The Properties of Electrodeposited Metals and Alloys

(Second Edition)

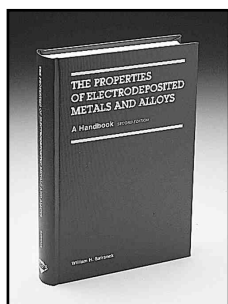
W.H. Safranek, CEF

(550 pages/1986, hardcover)

Order Number 20-105

Members/\$72.00;

Non-members/\$82.00



This edition completely updates and expands an earlier, exceptional finishing reference book—a “must” for shop owners, managers, design engineers and researchers. The introductory chapter summarizes material presented in the book, and serves to emphasize the importance of appreciating and relating properties and structures to coating selection and application. Properties and structure of individual electrodeposited metals and alloys are covered—from aluminum electrodeposition to zinc plating.

Two chapters address copper and its alloys and composites; three cover nickel, its alloys and composites. Chapters on both electrodeposited and electroless cobalt give information on magnetic properties. Cadmium, chromium, gold, iron, platinum-group metals, rhodium, silver, tin, zinc and their alloys, as well as nickel and cobalt alloy processes, are covered.



Call the AESF Bookstore
1-800/334-2052

or

Go On-line
www.aesf.org
(secure site)

