Journal of Mining and Metallurgy, 39 (1–2) B (2003) 269 - 274.

TEXTURE EFFECTS IN TiB_2 COATINGS ELECTRODEPOSITED FROM A $NaCl$-KCl-K_2TiF_6-NaF-$NaBF_4$ MELT AT 700 °C

R. Krendelsberger*, M.F. Souto*, J. Sytchev, J.O. Besenhard*, G. Fafilek*, H. Kronberger* and G.E. Nauer***

*K-plus ECHEM, Center of Competence in Applied Electrochemistry,
Viktor-Kaplan-Straße-2, 2700 Wiener Neustadt, Austria
**University of Miskolc, Department of Physical Chemistry,
3515 Miskolc-Egyemtevaros, Hungary

(Received 12 March 2003; accepted 7 April 2003)

Abstract

TiB_2 layers have been electrodeposited on steel and molybdenum substrates from a molten salt electrolyte at 700 °C by either direct current (DC) or pulsed plating techniques. The crystallographic textures of the coatings obtained are described and discussed.

Keywords: titanium diboride, texture, preferred orientation, electrodeposition, refractory compounds

1. Introduction

Titanium diboride (*TiB_2*) is one of the most promising refractory compounds of transition metals for a wide variety of technological applications. It has a high melting point, exhibits metallic conductivity, low heat and high corrosion resistance, and high microhardness [1].

Usually, *TiB_2* coatings were synthesized using different methods: hot pressing of *TiB_2* powder onto a substrate, plasma spraying, CVD by reducing titanium and boron chlorides, etc [1], but the electrodeposition of titanium and boron from high-temperature molten salt electrolytes seems a much more interesting approach, with lower energy consumption, lower level of impurities, and a more precise stoichiometry of the product [2].

The electrochemical synthesis of TiB_2 layers has been widely studied from diverse molten salt systems [3-8], but the characteristics of the coatings thus obtained have not been systematically studied.

The effect of different current densities used for the electrodeposition on the morphology of TiB_2 coatings on molybdenum substrates has been described recently by M. F. Souto et al. [9]. Direct current (DC) conditions were used for the galvanostatic electrodeposition of layers up to a thickness of 45 µm. In order to improve the deposition of TiB_2 from the chloride-fluoride molten salt system, the layers were deposited using pulsed current techniques. In literature a pulsed plating procedure has only once been described for the synthesis of TiB_2 from FLINAK melts by Ett and Pessine [10].

This work is focused on the description of various textures of the TiB_2 layers deposited and on the correlation of these textures with the experimental parameters used during the electrodeposition.

2. Experimental

Electrodeposition experiments were performed in a steel cell under argon atmosphere (Ar 99.995 %) at 700 °C. A $NaCl\text{-}NaF\text{-}KCl\text{-}K_2TiF_6\text{-}KBF_4$ melt was used as the electrolyte. The cathodes were either stainless steel or molybdenum, mechanically polished up to a shiny finish. As the anode a glassy carbon crucible was used. For the pulsed plating experiments a power pulse pe.86-20-10-50-G plater (Plating Electronics GmbH, D) was employed.

Out of the prepared samples, four were selected for closer analysis, as summarized in Table 1.

Table 1. Deposition conditions of samples investigated

Sample Name	Current Mode	Current Density (mA/cm^2)	Time (minutes)
Mo-DC	Direct Current	26.8	60
St-DC	Direct Current	30	120
Mo-PP	Pulsed Reversed Current	270	5
St-PP	Pulsed Reversed Current	320	20

X-ray diffraction data were collected with a Philips MPD diffractometer (Philips Analytical, Almelo, NL) in asymmetric geometry (fixed angle of incidence was five degrees), and *Cu* K_α-radiation (λ_{mean}=0.15418 nm). X-ray diffraction data were evaluated using the WinXPow™ software package [11].

Direct pole figures were measured with the same diffractometer using a Philips ATC-3 Eulerian cradle. The obtained data were evaluated with the Philips X´Pert Texture program [12].

3. Results and Discussion

The measured X-ray diffraction patterns were indexed on the basis of hexagonal TiB_2, lattice parameters *a*=0.303 nm, *c*=0.322 nm, space group P6/mmm No. 191, Pearson code hP3. *Ti* atoms occupy the 1a positions at fractional coordinates 0,0,0; B atoms occupy the 2d positions at fractional coordinates 1/3, 2/3, 1/2 as given in [13]. Using these data, all reflections detected could be indexed, thus indicating the presence of single phased TiB_2 (Fig.1).

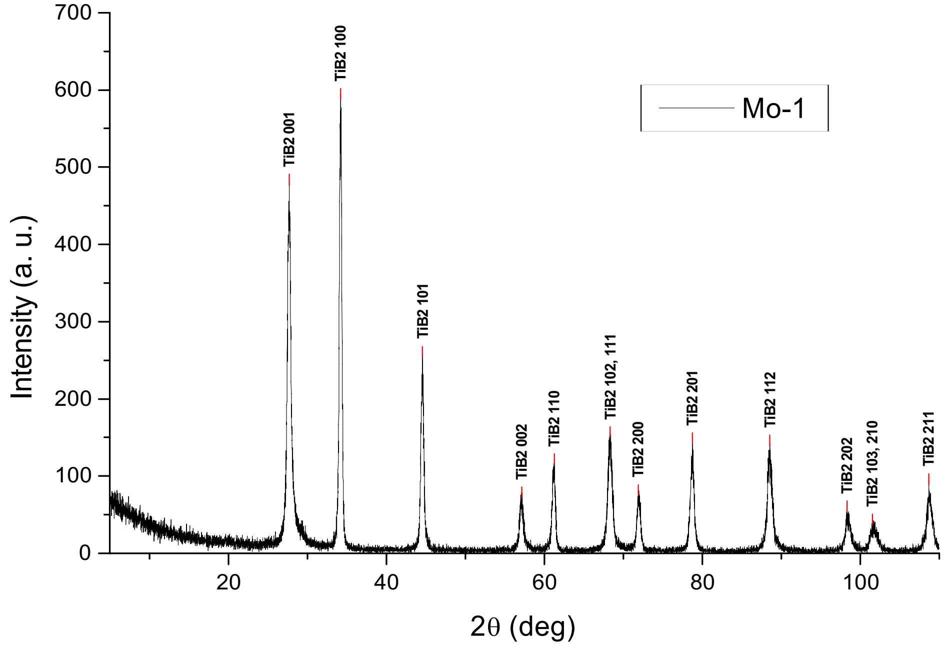


Figure 1. X-ray diffraction pattern of a TiB_2 coating on sample Mo-DC

However, the intensities of the reflections in the experimental diffraction patterns (Fig.1) show a deviation from those calculated from crystal structure data [13] indicated above (Fig.2). This effect is due to the cyclic fibre texture found for all of the examined samples.

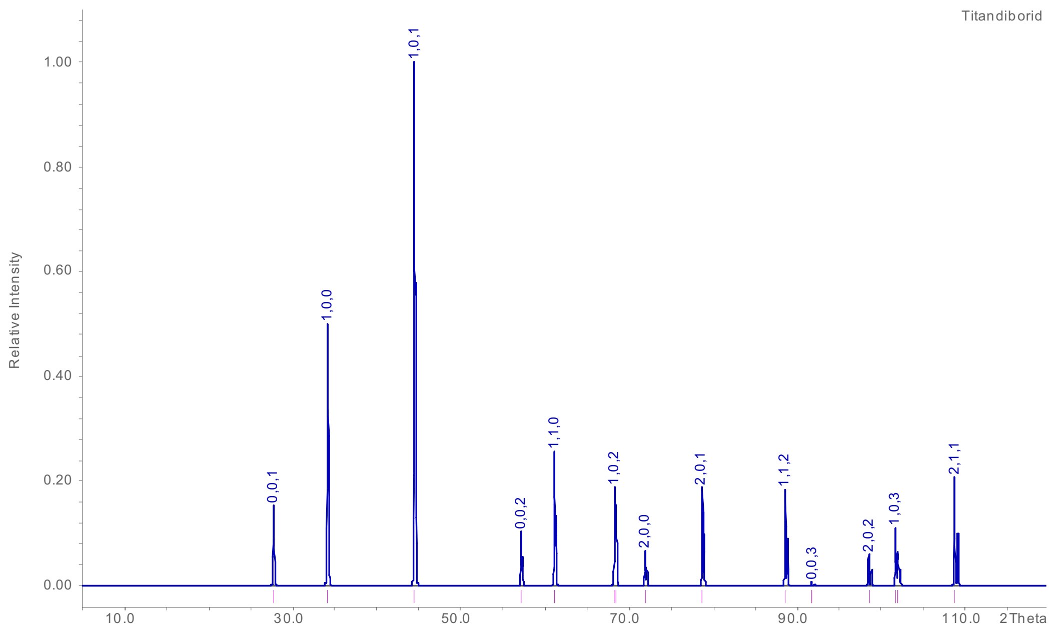


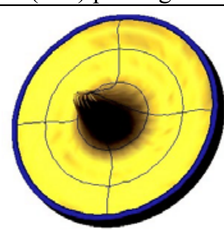
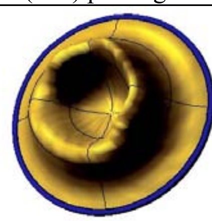
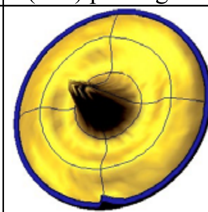
Figure 2. Calculated TiB2 diffraction pattern

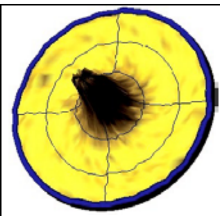
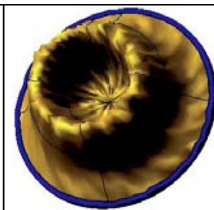
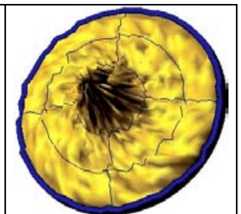
In the case of DC plating, the examined samples show a texture with <001> and <110> orientations being the main components (Figs. 3a to 4c). Layers deposited on *Mo* as well as on steel substrates exhibit nearly the same pole figures. The layers consist mainly of crystallites with a mean size between 100 and 150 nm, with a preferred orientation of the (001) plane or the (110) plane parallel to the substrate surface.

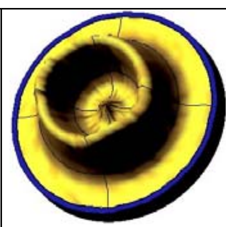
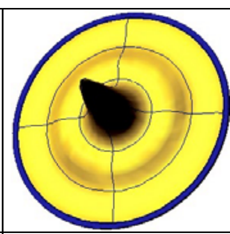
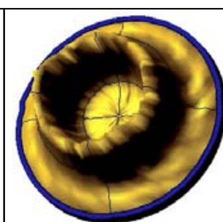
The layers deposited by pulsed reversed plating show the <101> orientation as main texture component. Again, nearly the same results were obtained for molybdenum and steel substrates, respectively (Figs. 5a to 6c). In contrast to DC-plating, crystallites oriented with the (101) plane parallel to the substrate surface were produced.

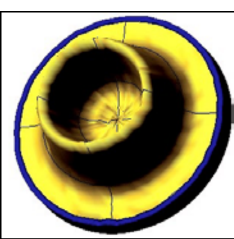
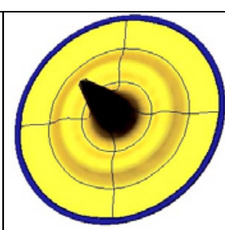
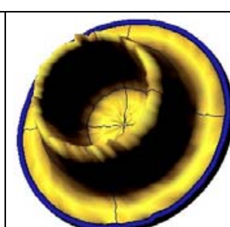
It has been shown, e. g. for electrodeposited *Cu* and *Zn* layers [14,15], that the influence of substrate textures on the textures of the coatings (inheritance effects) diminishes with increasing thickness of the coating. Since the thickness of the layer ranges from 20 to 50 µm, substrate effects of the texture should be expected to be negligible. This is in agreement with the experimental data.

Thus, the observed textures can be seen as a function of melt composition, temperature and electrochemical parameters of the deposition procedure.

Sample	(001) pole figure	(101) pole figure	(110) pole figure
Mo-DC			
Fig. 3. Pole figures of sample Mo-DC	a) (001)	b) (101)	c) (110)

St-DC			
Fig. 4. Pole figures of sample St-DC	a) (001)	b) (101)	c) (110)

Mo-PP			
Fig. 5. Pole figures of sample Mo-PP	a) (001)	b) (101)	c) (110)

St-PP			
Fig. 6. Pole figures of sample St-PP	a) (001)	b) (101)	c) (110)

4. Conclusions

The textures of the TiB_2 layers deposited using similar experimental conditions do not show any significant dependence on the substrate material. However, a change in the galvanostatic deposition procedure from direct current mode to pulsed reversed plating mode causes a substantial change in texture. DC plated samples show <001> and <110> orientations as the main texture components, whereas coatings obtained by pulsed plating procedure exhibit mainly <101> orientations.

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