Structural Differences of TiB_2 Coatings Electrodeposited from Molten Salts by Direct Current and Pulsed Current Methods

M.F. Souto[1,2], R. Krendelsberger[1], G.E. Nauer[1,2]

[1]ECHEM Center for Applied Electrochemistry

Viktor Kaplan Straße 2, A-2700, Wiener Neustadt, Austria

[2]Institute of Physical Chemistry, University of Vienna

Währinger Straße 42, A-1090, Vienna, Austria

The goal of this work is to study the influence of direct current (DC) vs. pulsed plating (PP) methods in the structure of TiB_2 electrodeposited layers. The characteristics of the coatings for different substrate materials is also analyzed.
For the characterization of the structure, the crystallite size, the morphology, the roughness and the texture of the electrodeposits are discussed.
Titanium diboride is an important refractory compound used in many industrial applications, for its exceptional properties. It has a high melting point, exhibits metallic conductivity, high resistance to scale formation up to 1273 K, low heat resistance, high corrosion resistance, and high microhardness [1].
TiB_2 can be synthesized by several methods, of which direct current electrodeposition from molten electrolytes has been widely studied from diverse molten salt systems [2-7]. There is only one precedent on the application of PP techniques to the electrosynthesis of TiB_2 [8-9], besides this present work. However, results are not comparable, since they worked with other salt system (FLINAK), different substrates, and at different temperatures.
The electrodeposition was performed from the NaCl-KCl-NaF-KBF_4-K_2TiF_6 molten salt system at 700°C, by DC and PP electrolysis, both on molybdenum and stainless steel substrates. The electrodeposited layers were analyzed by scanning electron microscopy, with a Philips XL-30 ESEM-FEG, with the elemental analysis performed with an energy dispersive X-ray-fluorescence detector. The presence of TiB_2 was confirmed by X-ray diffraction, with a Philips MPD diffractometer, and with this device, using an Eulerian cradle, the texture of the layers was studied. The surface roughness of the samples was measured by atomic force microscopy, using an ATOS Explorer AFM.
The idea behind the use of pulsed plating is to study the dependence of microstructure on different deposition parameters. The PP technique is much more versatile than DC, since the variables involved are many: j_{cat}, j_{an}, $t_{on,cat}$, $t_{off,cat}$, $t_{on,an}$, $t_{off,an}$, frequency, number of cathodic/anodic cycles, etc.
As an example, Fig. 1 shows a TiB_2 layer on a steel substrate, plated by DC. The crystallite size decreases significantly when the same layer is deposited using PP, as shown in Fig. 2.
All studied samples clearly show a fiber texture without any relation to the texture of the substrate. This can be expected for deposited layers with a thickness of about 30µm, since it has been shown e.g. for Cu electrodeposits that the influence of the substrate disappears after a few microns distance from the substrate [10].
DC-plated TiB_2 samples exhibit a strong [001] texture, as shown in Fig. 3, whereas in pulse plated samples the (101) planes are oriented preferentially parallel to the sample surface.
An explanation for the formation of these different textures will be given, based on the competition between oriented nucleation and oriented growth behavior.

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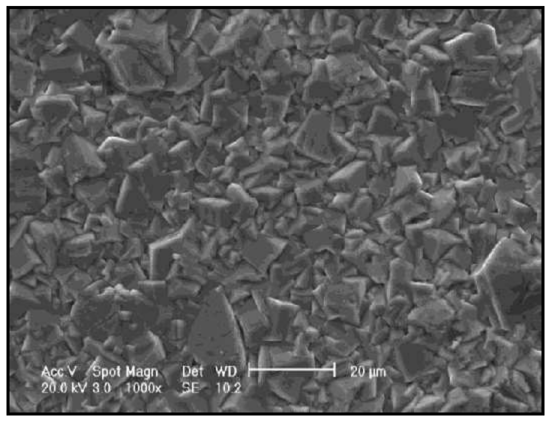

Fig.1: Direct current plated TiB_2 on steel SEM picture, magnification 1000x

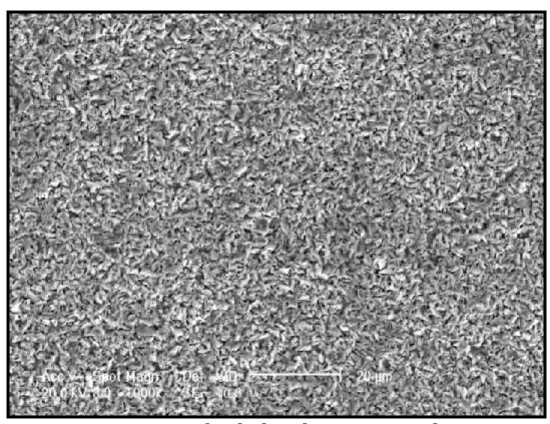

Fig. 2: Pulsed plated TiB_2 on steel SEM picture, magnification 1000x

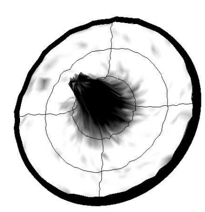

Fig. 3: Pole figure of the plane (001) on a DC plated sample

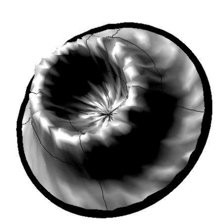

Fig. 4: Pole figure of the plane (101) on a DC plated sample

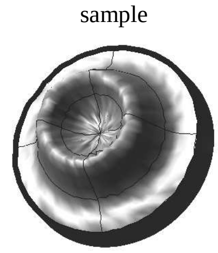

Fig. 5: Pole figure of the plane (001) on a PP plated sample

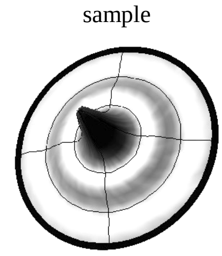

Fig. 6: Pole figure of the plane (101) on a PP plated sample