Study of the Morphology of TiB_2 Coatings on Molybdenum Substrates Electrodeposited from a NaCl-KCl- NaF-K_2TiF_6-$NaBF_4$ Melt at 700°C

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Due to its outstanding characteristics, titanium diboride is an important refractory compound used for many technological applications, mainly as layers on different substrates. 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]. It can be synthesized by several methods [1], of which electrodeposition from molten electrolytes offer some advantages, like lower energy consumption, better stoichiometry of the product, and lower concentration of impurities in the coating.

The objective of the present work is to study the variation in the morphology of TiB_2 deposits obtained on molybdenum substrates according to the current density used in a direct current galvanostatic mode. Although the electrochemical synthesis of TiB_2 layers has been widely studied from diverse molten salt systems [2-7], the morphology of the coatings thus obtained has not been studied systematically so far.

The electrodeposition was performed by direct current electrolysis from NaCl-KCl-NaF-KBF_4-K_2TiF_6 molten salt system at 700°C. The electrodeposited layers were analysed by scanning electron microscopy, with the elemental analysis performed with an energy dispersive X-ray-fluorescence detector. The presence of TiB_2 was confirmed by X-ray diffraction (fig.1), the surface roughness of the samples was measured by atomic force microscopy, and the depth concentration profiling, with a glow discharge optical emission spectrometer.

As the current density increases, the morphology goes from not clearly defined in shape crystallites, to spherolitic growth, to the obtention of dendrites (figs. 2-4), with the boundary limits being (fig. 5):

-not clearly defined crystals:	up to 50 mA/cm^2
-spheres:	50-70 mA/cm^2
-dendrites:	70 mA/cm^2 upwards

The coatings thickness ranges from 10 to 50 μm, with the exception of the dendrites, which can be as high as 300 μm. The composition of the deposit varies across it, with some partial diffusion of boron into the substrate, resulting in the formation of a thin layer of molybdenum borides at the interphase.

The impurities level remain low in the middle of the coating, and raise near the exposed surface of TiB_2, consisting mainly of C and O. This effect is possibly due to the variation in the deposition potential in the last stages in the electrolysis, given the modification in the melt composition. The highest level of impurities is observed during dendritic growth, as expected.

References:

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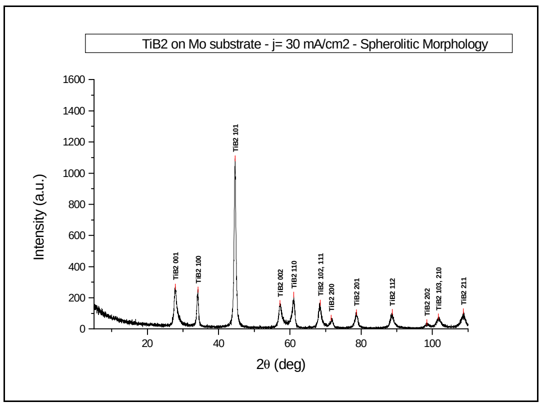

Fig. 1: X-ray diffraction pattern of a TiB_2 coating.

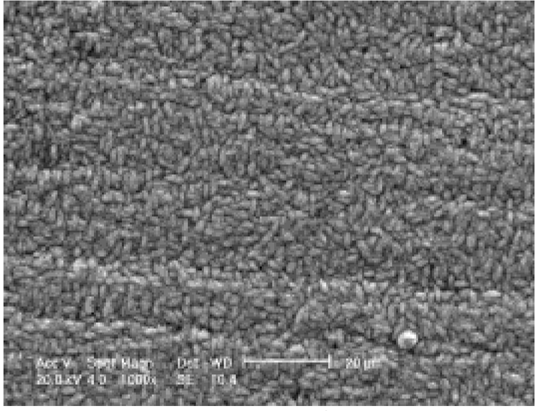

Fig. 2: Not clearly defined morphology, j=40 mA/cm^2.

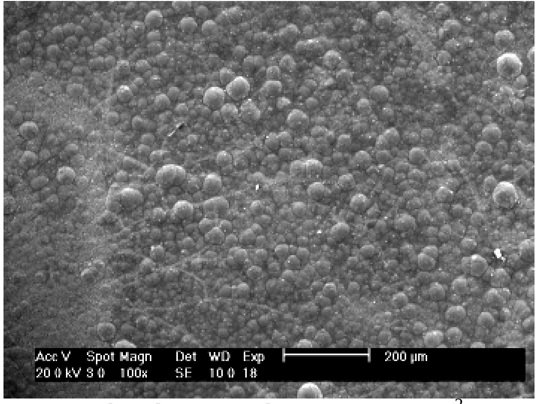

Fig. 3: Spherolitic growth, j=59.3 mA/cm^2.

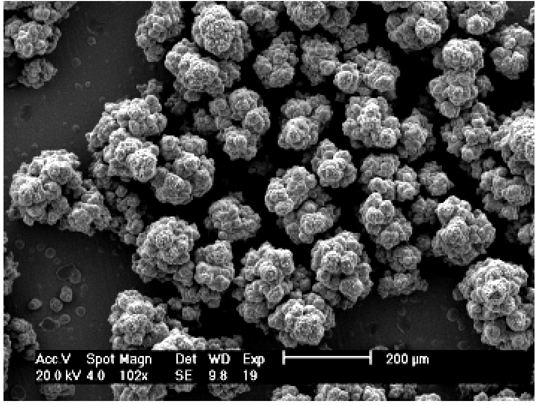

Fig. 4: Dendritic growth on a Mo substrate, j =85,5 mA/cm^2.

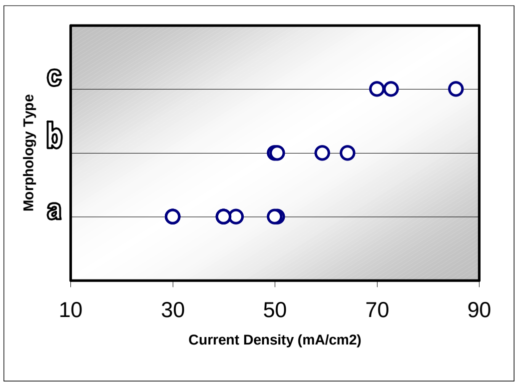

Fig. 5. Correlation between morphology type encountered and current density used (mA/cm^2) - a. not clearly defined morphology, b. spherolitic growth, c. dendritic growth. (There are 16 data points, some of which overlap).