Regional Symposium on Electrochemistry

RSE-SEE

South-East Europe

1st REGIONAL SYMPOSIUM ON ELECTROCHEMISTRY OF SOUTH-EAST EUROPE

BOOK OF ABSTRACTS

Rovinj, Croatia, 2008.

RAMAN SPECTRA OF ANODIZED VALVE METAL ELECTRODES

I. Mickova, Lj. Arsov

Faculty of Technology and metallurgy, University "Ss Cyril and Methodius", Skopje, Macedonia e-mail: mickova@tmf.ukim.edu.mk

The electrochemical anodization of valve metal electrodes from: Ti, Nb and Zr in various concentrations of H_2SO_4 and KOH electrolytes has been studies by in-situ Raman spectroscopy. For each electrolyte anodization was carried out at various fixed voltages and for each voltage the evaluation of Raman spectra was followed as a function of time. The critical voltage of film transformation from the amorphous to the crystalline state has been detected accurately. The spectra were measured in a cylindrical cell made of quartz and the 514.5 nm line of an argon ion laser operated at 300-400 mW was used as excitation. Spectra were recorded at room temperature using a Spex 1877 spectrograph in connection with a 512 diode multi-channel analyzer. The working electrodes were made from a massive cylindrical Ti, Nb, and Zr rods with diameter of 6 mm. Before each measurement the electrode surfaces were abraded using silicon carbide paper (1000 grade) and then gradually polished with diamond sprays of decreasing particle (1 μm) to yield a mirror finish. A spiral platinum wire was used as a counter electrode.

On fig. 1, 2 and 3 the Raman spectra are shown recorded for various voltages and time of anodization

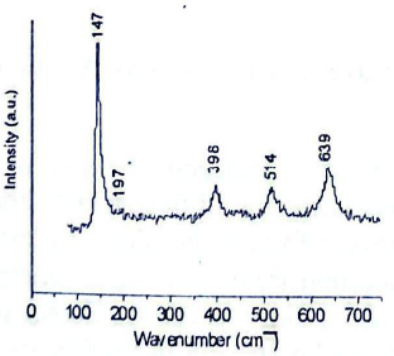

Fig.1. Raman spectrum of Ti anodized at 120 V in 1 M H_2SO_4 for 30 s

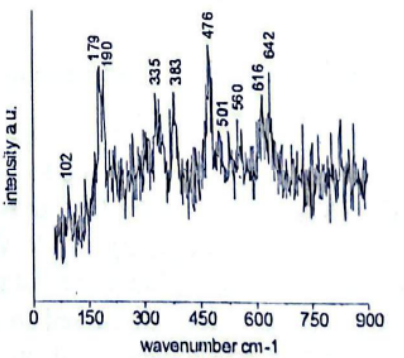

Fig. 2. Raman spectrum of Zr anodized at 80 V in 2 M KOH for 2 s

The appearance of active Raman bands due to the anodic oxide layers on the electrode is found to be a function of the voltage and time of anodization. For Ti in 1 M H_2SO_4 the first Raman bands appear at the voltage of 15 V and anodization time of 3 h. For higher anodic voltage, as in fig.1, the Raman spectrum develops within 30 s. Four strong bands are seen at: 147, 398, 514 and 639 cm^{-1} and a weak band at 197 cm^{-1}, which corresponds to TiO_2 anatase mineral form.

The appearance of Raman bands of anodized Zr at 80 V in 2 M KOH for very short time, is shown on fig.2. At the same voltage for anodization time of 15 s, 13 strong peaks located on: 180, 190, 224, 308, 335, 348, 384, 476, 501, 538, 562, 614 and 641 cm^{-1} and one weak band on 761 cm^{-1} appear. All that bands are characteristic for ZrO_2 crystalline form.

The evaluation of Raman bands on Nb electrode in 1 M KOH at various voltages for anodization time of 30 s is shown on fig.3. For anodic voltage of 30 V two broad bands located at 234 and 702 cm^{-1} appear, Fig.3. Increasing the voltage the bands rise in intensity and additional bands located on: 261, 308, 470, 485, 550, 606, 630, 660, 672, 892 and 992 cm^{-1} appear. But on 92 V the Raman spectrum is changing. The band on 702 cm^{-1} characteristics for NbO_2 is split into two new bands located on 630 and 660 cm^{-1} tentatively assigned to the beginning of transformation of NbO_2 to the Nb_2O_5.

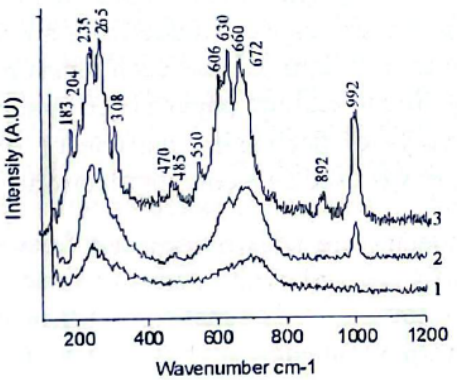

Fig.3. Raman spectra of Nb anodized in 1 M KOH for 30 s at: 1 – 30 V; 2 – 80 V; 3 – 92 V

From Raman spectra measurements of 3 valve anodized metals the following conclusions can be drawn:

- For natural oxide films and up to 10 V, no Raman bands could be observed. For anodic voltage of 15 V the first active Raman bands for all three metals begin to appear. At low voltage, up to 10 V, the oxides formed are either hydrated or amorphous oxides. In literature data the transition from hydrated or amorphous oxides to crystalline is discussed in terms of the film breakdown. Some authors suggested that crystallization of anodic oxide films occurs in parallel with the breakdown [1]. Others observed crystallization of anodic films after breakdown [2]. Wood and Parsons have established a relation between the breakdown voltage and the electrolyte conductivity [3]. They concluded that the breakdown processes depends on the specific ion transport properties of formed layers. The present results have shown that the crystallinity develops in close relation with breakdown. During the anodic polarization, the current was oscilloscopically monitored showing small fluctuation at 15 V.

- The thickness of anodized Ti, Zr and Nb is nearly independent of the electrolyte concentration. Generally higher electrolyte concentrations lead to lower threshold

voltages for transformation of amorphous to crystalline forms.

- In KOH electrolytes the transformation from amorphous to crystalline structure occurs abruptly. The breakdown process is more pronounced with increasing the concentration of KOH. In higher concentration of KOH solutions, during the anodic polarization at higher voltages, the visible spark were observed. Under these conditions a strong warming-up of the electrolyte is noticed. The breakdown process and evolution of crystallinity is a thermal effect resulting from local heating of the oxide film.

[1] J.Yakalom, J.Zahavi – *Electrochim. Acta*, **15**, 1429 (1970)
[2] J.Marchenoir, J.Loup, J.Masson – *Thin Solid Films* **66**, 357 (1980)
[3] G.Wood , C.Parsons – *Corr. Sci.*, 7, 284 (1967)