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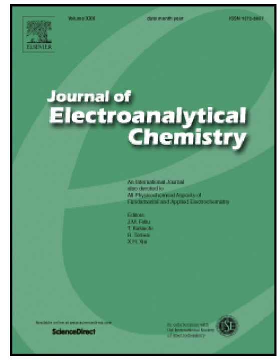

Surface segregation of bismuth atoms in Ag-Bi alloys (based on results obtained by traditional electrochemical methods and the laser heating-induced temperature potential shift)

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PII: S1572-6657(16)30719-6
DOI: doi: 10.1016/j.jelechem.2016.12.025
Reference: JEAC 3021

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 16 September 2016
Revised date: 8 December 2016
Accepted date: 13 December 2016

Please cite this article as: V.A. Safonov, M.A. Choba, A.G. Krivenko, A.R. Manzhos , Surface segregation of bismuth atoms in Ag-Bi alloys (based on results obtained by traditional electrochemical methods and the laser heating-induced temperature potential shift). The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Jeac(2016), doi: 10.1016/j.jelechem.2016.12.025

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ACCEPTED MANUSCRIPT

SURFACE SEGREGATION OF BISMUTH ATOMS IN Ag-Bi ALLOYS (BASED ON RESULTS OBTAINED BY TRADITIONAL ELECTROCHEMICAL METHODS AND THE LASER HEATING-INDUCED TEMPERATURE POTENTIAL SHIFT)

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ABSTRACT

The time effects observed on mechanically renewed electrodes of eutectic-type Ag–Bi alloys in NaF solutions in the potential range of ideal polarizability are studied by traditional electrochemical methods: cyclic voltammetry and electrochemical impedance spectroscopy. The observed effects are shown to be a result of surface segregation of Bi atoms (enrichment of the metal surface layer by these atoms) realized at a rate very high as compared with usual solid-state processes. The analysis of these data carried out in the framework of phenomenological models made it possible the assumption that the mechanism of surface (not bulk) diffusion is responsible for the “anomalously” high rate of electrode surface enrichment with Bi atoms to be substantiated. The additional information on the segregation processes at the interface of Ag–Bi electrode with NaF solution acquired by the method of laser heating-induced temperature potential shift correlates with the results of electrochemical investigations.

Key words: eutectic Ag-Bi alloy, surface segregation, cyclic voltammetry, impedance, laser heating-induced temperature potential shift, double layer capacitance, model description.

INTRODUCTION

In studying the structure of charged interfaces formed by metals with different types of electrolytes, the solid binary alloys represent a promising but so far insufficiently explored model object. A peculiarity of such systems is that their surface composition and structure can differ substantially from the corresponding bulk characteristics. One of the reasons for this difference is surface segregation, i.e., the phenomenon of preferential accumulation of certain alloy components in the surface layer. Its "driving force" is the difference in specific works of surface formation for individual alloy components that leads to extrusion of surface active components of these alloys to their interface.

Studying the peculiarities of the surface segregation process occurring on different interfaces is obviously of interest both for fundamental science and practical applications. The attention to this phenomenon is associated with the fact that having a substantial effect on the structure and

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