

# Influence of the Time Factor on the Formation of Equilibrium Double Electrical Layer on Renewable Electrodes of Ag-Sn Alloys

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Alloy composition usually differs on the surface and in the bulk. This phenomenon largely determines the electrochemical, corrosion, electrocatalytic, etc. behavior of alloys in contact with electrolytes. The examples of the accumulation of individual (surface-active) components of liquid metal alloys on the surface are well known. The results of measuring the electrical double layer capacitance on electrodes of binary alloys of Ga with Tl, In, and Cd are described in detail in the literature (e.g., see [1] and the references there). These data suggest that second components of these alloys are surface active. Moreover, it follows that the surface enrichment with the second component is a very fast process, which is due to the high values of diffusion coefficients of metal atoms in such systems.

A more complicated situation arises when we pass to solid alloys. Because the diffusion coefficients of atoms in a solid phase are rather low, we can assume that an excessive (as compared with the bulk) concentration of surface-active components of alloys is fixed as the alloys harden (during their preparation). This assumption agrees with the results of comparing the double-layer structures on liquid and solid Sn-Pb alloys, correspondingly, in fused salts and electrolyte solutions [2]. On the other hand, it is evident that a mechanical renewal of a solid alloy (cutting off of a thin metal layer) should level its bulk and surface compositions. By studying the electrical double layer structure on renewable electrodes of eutectic alloys (Sn-Pb and Sn-Cd), we have shown [3-5] that, in the ideal polarizability region, such electrodes demonstrate sufficiently fast (characteristic times of about tens minutes) processes of surface enrichment with Pb and Cd atoms. This means that enrichment also proceeds on these alloys in their solid state, and Pb and Cd are the surface-active components. The analysis of the kinetic data and the X-ray spectral analysis results allowed us to propose and substantiate a model, in accordance with which the accumulation of Pb and Cd in the near-surface layer proceeds via a mechanism of surface diffusion from enriched by these components areas (grain boundaries of Sn crystals).

The purpose of this work was to study the kinetic effects that take place on mechanically renewable electrodes of solid alloys whose phase diagram fundamentally differs from that of eutectic alloys studied earlier. We have chosen Ag-Sn alloys with Sn content ranging from 3 to 9 at. % (solid-solution domain).

Electrolyte was 0.01 mol/l NaF. The salt was twice crystallized and calcinated. Water was purified by means of a Millipore (Simplicity™) unit. The alloys were prepared by melting the calculated amounts of Ag and Sn in an induction furnace. The ingots were drawn into a wire of 0.8-mm diameter. The wire was pressed into Teflon tubes and fixed in a special hermetically sealed cell, equipped with a sapphire tool for periodically renewing

the surface. The wire end served as the electrode; the cut-off layer was ca. 10- $\mu$ m thick. The procedure used was described in detail in [3]. The impedance components were measured on a PAR device (Electrochemical Impedance Analyzer, Model 6310) in the potential ( $E$ ) range from  $-1.5$  to  $-0.5$  V with respect to a saturated calomel electrode. Similar experiments were preliminarily carried out on Ag and Sn electrodes. In the mentioned potential range, these electrodes can be considered as ideally polarizable (the steady-state current did not exceed  $1 \mu\text{A}/\text{cm}^2$ , the capacitance dispersion was less than 10% in the frequency range from 10 to 2500 Hz).

The measurement procedure was as follows. At each potential value, the alloy surface was renewed, and the dependence of the electrical double layer capacitance ( $C$ ) on time ( $t$ ) of electrode exposure to solution was recorded for the succeeding 120 min. Similar long-term measurements on electrodes of Ag and Sn showed the differential capacitance to change only slightly during 60 min (by 3-4%), which is much lower than the effects observed on the alloys. On the basis of the processed  $C$  vs.  $t$  dependences measured at different  $E$  on alloy electrodes,  $C$  vs.  $E$  curves that pertain to different  $t$  were plotted.

A qualitative analysis of the results obtained allows us to state that the observed time effects substantially differ from those taking place on the renewable eutectic alloys. With time after the renewal,  $C$  vs.  $E$  curves shifted from the capacitance curve close for Ag electrode to that for Sn electrode. This means that tin is surface-active component of this alloy. However, in contrast to eutectic alloys, a  $C$  vs.  $E$  curve measured 60 min after the exposure of a renewed surface to solution stopped to change further, even though this limiting curve appears to be located rather far from  $C$  vs.  $E$  dependence of a Sn electrode. On the basis of these results, an assumption is put forward that the diffusion of Sn atoms from the bulk to the surface layer is complicated by a process of formation of a certain surface intermetallic compound in this layer. In a sense, this assumption correlates with the recently published results on the behavior of 2D tin clusters on (111) face of copper single crystal [6].

To gain a deeper insight into the processes occurring on the surfaces of renewable Ag—Sn alloys, we measured  $C$  vs.  $E$  curves on an electrode of intermetallic compound that, according to the phase diagram, is formed at silver to tin atomic ratio of ca. 3:1. Then, the possibilities were considered of describing the observed time effects within the framework of phenomenological models of interface.

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## References

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