Analysis of nanoscale films of alloys of Cu-Sn-Ni-Zn system by stripping voltammetry

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Introduction

Binary alloys of the Cu-Sn-Ni-Zn system have a number of functional properties that determine a wide range of their use. The properties of alloys directly depend on their chemical and phase composition. Therefore, analysis of the composition of alloy coatings is of great importance for both the existing galvanic processes and the development of new ones.

The method of stripping voltammetry is based on the analysis of peaks on anodic voltammograms of dissolution of thin films deposited on an inert substrate. It is a promising analysis method allowing estimation of their chemical and phase composition at the same time. For selective separation of the peaks of dissolution of components and quantitative analysis of their content, it is necessary to select electrolytes and analysis conditions.

The aim of this work is to improve the method of stripping voltammetry in the quantitative analysis of the chemical and phase composition of alloys of Cu-Sn-Ni-Zn system.

Methods

Thin films of alloys were deposited on a platinum electrode from electrolytes for corresponding alloys electrodeposition. After that they were anodically dissolved under conditions of linear potential scan in special electrolytes not containing metal ions. The potential scan rate v was determined experimentally out of the constant value of the product of the specific charge for alloy deposition by v. Anodic linear sweep voltammograms (ALSVs) were obtained using potentiostat Elins P-45X. All the potentials are presented $vs.$ saturated silver-silver chloride reference electrode.

Results

Cu-Zn alloy (Fig. 1). The peak of the most positive alloy phase (α) dissolution is 100 mV more negative than the copper dissolution peak. Dissolution potential of the most negative alloy phase (γ) is 400 mV more positive than zinc dissolution peak. The voltammogram also reveals the β phase, despite its very low content in the alloy.

Cu-Sn alloys (Fig. 2). Dissolution of alloy films in sulfuric acid allows separating dissolution peaks of free tin, α-phase of the solid solution of tin in copper and Cu_3Sn intermetallic compound (ε-phase), after deconvolution of the last peak.

Cu-Ni, Zn-Ni, Cu-Ni-Zn alloys (Fig. 3). Alkaline ammonia-glycinate electrolyte [1, 2] allows selectively dissolving components of alloys containing Cu, Ni and Zn in a wide range of potentials. Nickel dissolves at the most positive potentials in this electrolyte (curve 6). The potential of the copper dissolution peak shifts in the case of the presence of both zinc atoms in its lattice (curve 3, the peak shifts towards negative potential values) and nickel atoms (curve 5, the peak shifts towards positive potential values). The presence of copper in the lattice of nickel shifts the dissolution peak towards negative potential values (curve 5). The electrolyte makes it possible to separate the peaks of zinc dissolution from the γ-phase of Zn-Ni alloy of different structures, γ₁ and γ₂ (curves 2 and 3), as well as to determine the composition of the nickel-enriched phase after dezincification of the alloy.

Conclusions

The method of stripping voltammetry makes it possible to identify components of alloys of Cu-Sn-Ni-Zn system including the case of their low concentration or X-ray amorphism.

References

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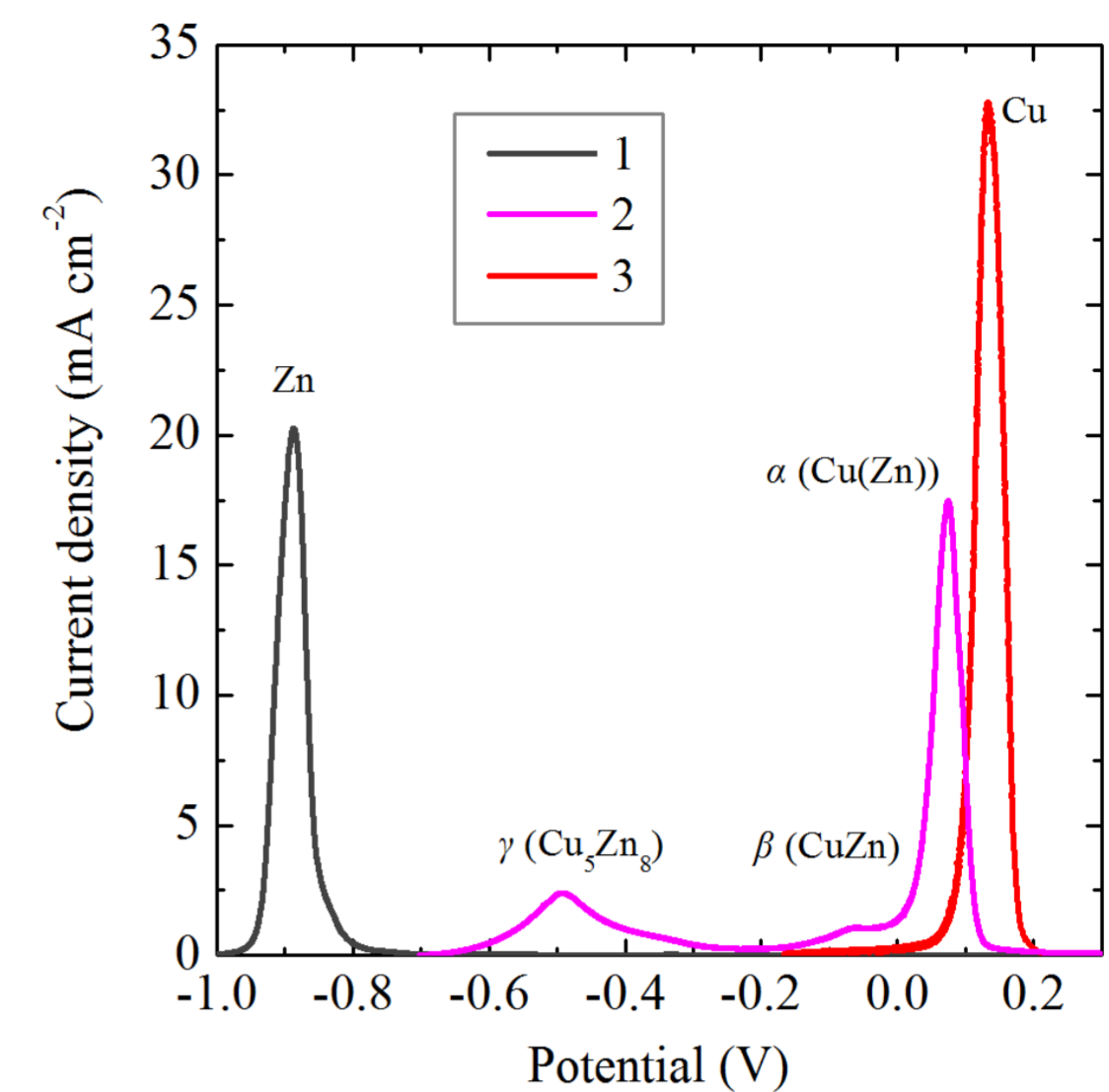
Figure 1
ALSV of films dissolution in 0.3 mol L⁻¹ Na₂SO₄ solution. Electrolyte for films deposition: [Cu²⁺]:[Zn²⁺] = 0:1 (1), 1:2 (2) та 1:0 (3) Current density: 20 mA cm⁻² (1, 3) and 40 mA cm⁻² (2). Specific charge for films deposition: 0.4 C cm⁻². Potential scan rate: 5 mV s⁻¹.
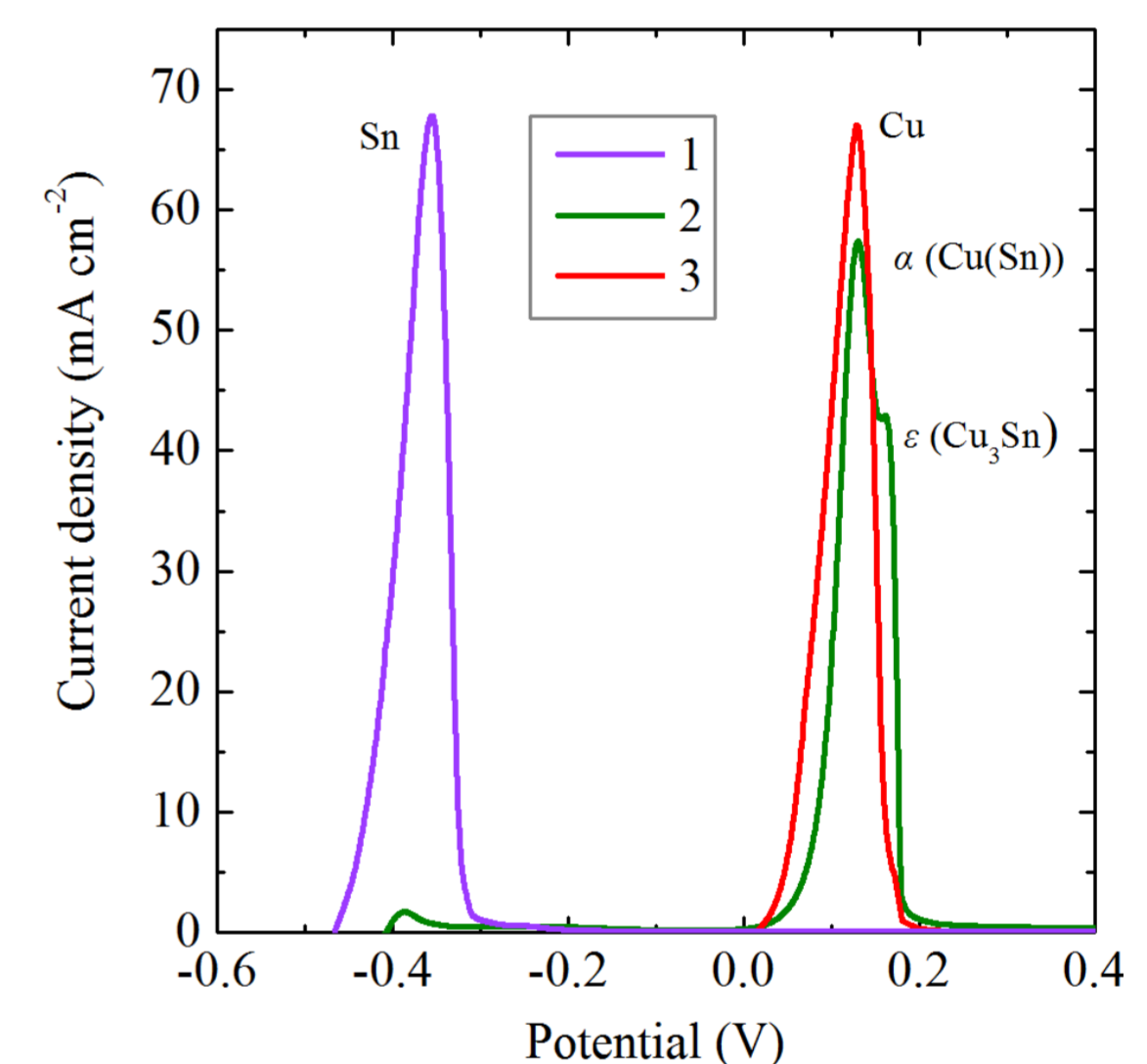

Figure 2
Anode voltammograms of Sn (1), Cu (3), and Cu-Sn (2) films in 0.6 mol L⁻¹ H₂SO₄ solution. Specific charge for films deposition: 0.4 C cm⁻². Potential scan rate: 10 mV s⁻¹.
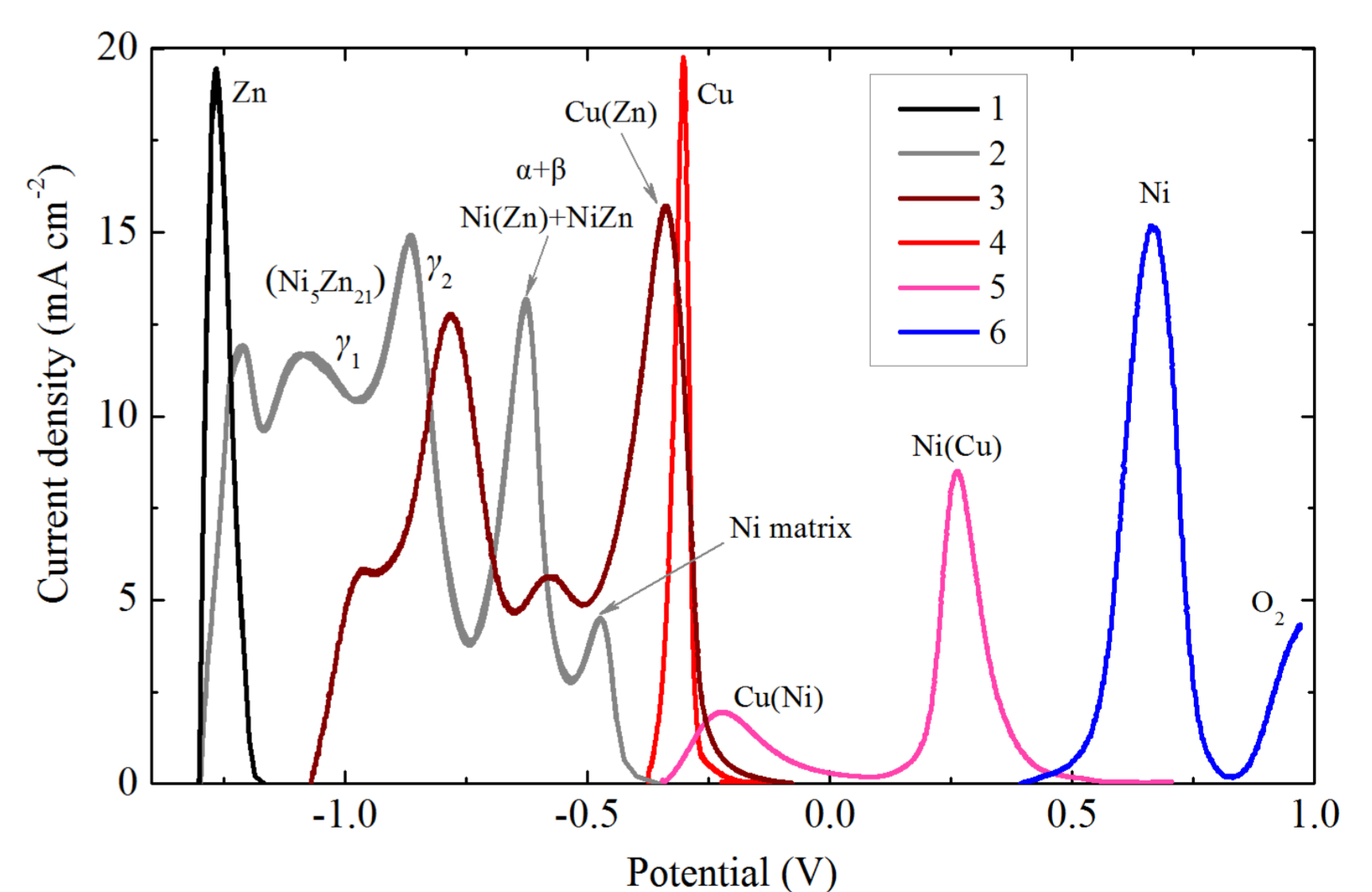

Figure 3
Anode voltammograms of Zn (1), Cu (4), Ni (6) and Zn-Ni (2) Zn-Ni-Cu (3), Cu-Ni (5) alloy films dissolution in solution of 0.5 mol L⁻¹ glycine and 0.5 mol L⁻¹ NH₄Cl (pH 10.5).

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