

ELECTROCHEMICAL REDUCTION OF IONS IN METALS/ALLOYS AT A LIQUID CATHODE VERSUS A SOLID CHEMICALLY IDENTICAL ONE

Oleg B. Girin^{*}, Dmytro G. Korolyanchuk

Ukrainian State University of Chemical Technology, Department of the Materials Science, Gagarin Ave., 8, Dnipro, 49005, Ukraine

*Corresponding author: girin@ua.fm

Received: February, 04, 2019

Accepted: October, 28, 2019

Abstract: The purpose of this work was further experimental verification of the existence of the phenomenon of electrochemical phase formation in metals and alloys via a supercooled liquid state stage. It was assumed that replacing a solid cathode with a chemically identical liquid one would lead to higher electrochemical reduction rates of ions of the electrodepositing metal/alloy. The experimentation involved a cathode of Wood's alloy having melting point at 68.5 °C. The electrocrystallization of some metals (Ni, Co, Fe) and alloys (Fe-Cr, Fe-Cr-Ni) was carried out at 65 °C with a solid cathode and at 75 °C with a liquid one. The experimentation revealed the anticipated electrochemical features of the interface between a cathode in its predetermined state of aggregation and the electrodepositing metal or alloy in full measure. It was concluded that the phenomenon of electrochemical phase formation in metals and alloys via supercooled liquid state stage is proved by the deionization acceleration in electrodepositing metals and alloys on replacing a solid cathode with a chemically identical liquid one.

Keywords: *electrochemical phase formation, electrodepositing metal, ion electrochemical reduction, liquid cathode, liquid state*

INTRODUCTION

During the last time many experimental results proving the existence of the phenomenon of electrochemical phase formation in metals and alloys via a supercooled liquid state stage were obtained [1 – 3]. Essentially, this phenomenon is to be understood as follows: during metal electrodeposition onto a solid cathode in an aqueous environment, a deeply supercooled metal liquid evolves in the form of multiple liquid atomic clusters avalanching at various sites near the cathode or the growing deposit and solidifies ultra-rapidly at the deposition temperature. This phenomenon is due to an extremely rapid, burst-like liberation of metal resulting from a chain reaction of electrochemical formation of atoms and transition of the atomic clusters from a liquid to a more stable solid state.

The proposed concept is fundamentally different from the existing ones, according to which, the phase formation in electrodeposited metal or alloy occurs by embedding ions from an aqueous solution, or atoms formed on their surfaces, into their crystal lattice [4 – 7].

The purpose of this work was further experimental verification of the existence of the discovered phenomenon.

Assuming the original phase of electrodepositing metal/alloy to be metallic liquid, one should expect its formation rate at a maximum with a cathode having the same state of aggregation. In such a case, if a solid cathode is replaced with a chemically identical liquid one, the electrochemical reduction rate of metal ions is expected to increase due to the state of aggregation of the cathode material and the initial-stage electrodepositing metal being the same. Should the electrochemical reduction be accelerated following replacement of a solid cathode to a chemically identical liquid one, this will be an argument for the phenomenon in point.

MATERIALS AND METHODS

The experimentation involved a cathode of Wood's alloy having melting point at 68.5 °C and containing 50 % bismuth, 25 % lead, 12.5 % tin and 12.5 % cadmium. The electrocrystallization of some metals (Ni, Co, Fe) and alloys (Fe-Cr, Fe-Cr-Ni) was carried out at 65 °C with a solid cathode and at 75 °C with a liquid one. Table 1 shows electrolyte compositions used for the electrodeposition.

Table 1. Solution compositions for electrodeposition of metals or alloys

| Metal / alloy | Electrolyte composition [g·L ⁻¹] |
|---------------|---|
| Ni | NiSO ₄ ·7H ₂ O – 250; NaCl – 10; H ₃ BO ₃ – 30 |
| Co | CoSO ₄ ·7H ₂ O – 250; H ₃ BO ₃ – 40; H ₂ SO ₄ – 40 |
| Fe | FeSO ₄ ·7H ₂ O – 400; Al ₂ (SO ₄) ₃ ·18H ₂ O – 100 |
| Fe-Cr | FeSO ₄ ·7H ₂ O – 40; Cr ₂ (SO ₄) ₃ ·6H ₂ O – 160; NH ₄ CH ₂ COOH – 150; CrO ₃ – 0,5 |
| Fe-Cr-Ni | FeCl ₃ ·6H ₂ O – 30; NiCl ₂ ·6H ₂ O – 50; CrCl ₃ ·6H ₂ O – 170; NH ₄ Cl – 200 |

Galvanostatic rating was used for electrodeposition with a cell having a horizontal cathode (Figure 1). An electronic potentiostat was employed in the potentiostatic process to record polarization curves.

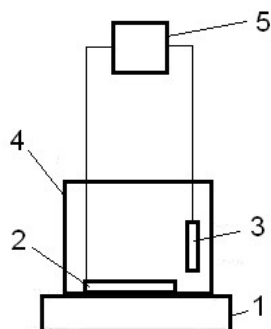


Figure 1. Experimental rig for electrodeposition of metals/alloys at a solid or liquid cathode: 1 – heating element; 2 – cathode; 3 – anode; 4 – electrochemical cell; 5 – current source

RESULTS AND DISCUSSION

One feature of the polarization curves for the electrodeposition of metals and alloys was a cathode potential shift towards a greater electropositivity as the solid cathode was replaced with a liquid one. It is clearly illustrated by Figure 2. Such cathodic depolarization appears to be due to interactions of the depositing metal with metallic constituents in the liquid cathode. The depolarization is particularly strong when the electrodepositing nickel or cobalt forms intermetallic with metal atoms in the liquid cathode, compare curve 1 in Figure 2a and Figure 2b, respectively.

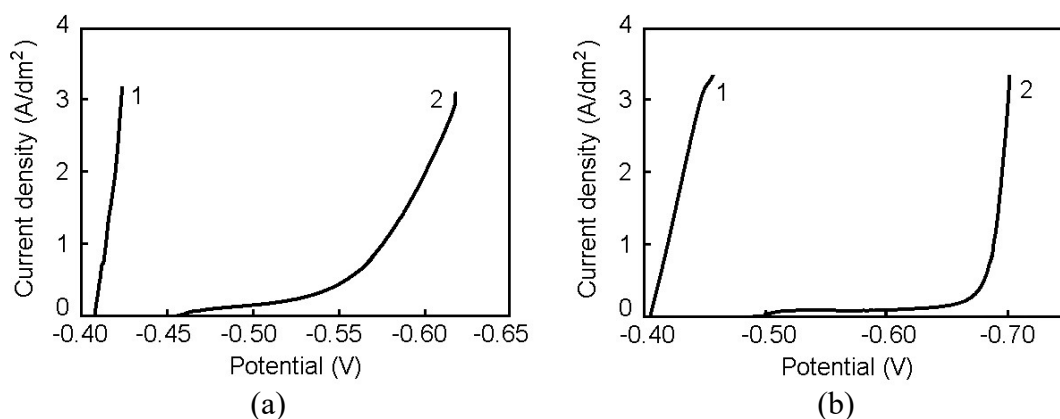


Figure 2. Polarization curves for electrodeposition of nickel (a) and cobalt (b) at a liquid (1) and a solid (2) cathode

The electropositive shift as seen from polarization curves for metal electrocrystallization at a liquid cathode (as compared to a solid cathode case) is an indication of accelerated metal formation. Indeed, the greater the metal deposition over potential, the slower the cathodic reaction, which implies slower electrochemical deionization of metal ions. Therefore, lower metal deposition over potentials lead to higher deposition rates. Since metal/alloy precipitation overvoltage at a liquid cathode is lower than at a solid one, metal/alloy formation at a liquid cathode will be more rapid than at a solid cathode.

This finding suggests that replacing a solid cathode with a chemically identical liquid one would result in acceleration of metal/alloy ion electrochemical reduction.

This suggestion is clearly confirmed by comparing ion cathodic reduction rate constants for chemically identical cathodes having different states of aggregation, see Table 2.

Table 2. Cathodic reduction rate constants for metal/alloy ions at a solid (k_S) or a liquid (k_L) cathode having the same chemical composition

| Rate constants | Metal or alloy | | | | |
|----------------|---------------------|---------------------|---------------------|----------------------|----------------------|
| | Ni | Co | Fe | Fe-Cr | Fe-Cr-Ni |
| k_S | $2.5 \cdot 10^{-7}$ | $6.4 \cdot 10^{-8}$ | $9.6 \cdot 10^{-7}$ | $2.06 \cdot 10^{-7}$ | $9.21 \cdot 10^{-7}$ |
| k_L | $2.1 \cdot 10^{-6}$ | $4.9 \cdot 10^{-6}$ | $1.6 \cdot 10^{-6}$ | $4.1 \cdot 10^{-6}$ | $2.3 \cdot 10^{-6}$ |

It is seen from Table 2 that the rate constants k_L for reactions at a liquid cathode are much in excess of corresponding k_S values pertaining to a solid cathode of the same chemical composition. Among the metals and alloys investigated, the highest k_L/k_S ratios are observed with Co (76.6) and Fe-Cr (19.9).

Replacing a solid cathode with a chemically identical liquid one thus increases the ion cathodic reduction rates for depositing metals/alloys. This experimental finding is a proof that the phenomenon of electrochemical phase formation in metals and alloys via a supercooled liquid state stage does exist.

CONCLUSION

It was concluded that the phenomenon of electrochemical phase formation in metals and alloys via supercooled liquid state stage is proved by the deionization acceleration in electrodepositing metals and alloys on replacing a solid cathode with a chemically identical liquid one.

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