Amorphous Electrolytic Deposits (Re–Ni, Co–Mo, Ni–Mo etc.) as Efficient Catalysts for Hydrogen Evolution Reaction in Alkaline Solutions: Structure and Electrocatalytic Properties

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Search for new non-platinum catalysts for hydrogen evolution reaction (HER) and elucidation of the mechanism of their catalytic activity are important for enhancement of the process of electrolytic hydrogen production. From this point of view, of interest are systems containing an iron-group metal (typically, Co or Ni) and a refractory metal (Re, Mo, or W). Electrodeposition is a simple and convenient method for preparation of these alloys.

It was previously found that X-ray amorphous deposits immediately after their electrodeposition possess the highest catalytic activity towards HER. Heat treatment of such materials in vacuum accompanied by their recrystallization results in a decrease in the catalytic activity of alloys. Therefore, data on the structure of electrolytic deposits and their chemical and phase composition are necessary for understanding the causes of catalytic activity.

Both XPS and EXAFS methods are applied for determining the composition and structure of Re–Ni, Co–Mo, and Ni–Mo electrolytic deposits. It is found that these materials are amorphous. The metals in Co–Mo and Ni–Mo systems are in a metallic state; however, Re–Ni deposits contain both metallic and oxidized rhenium.

The catalytic activity of electrolytic deposits generally decreases in the following row: Re–Ni ≥ Co–Mo > Ni–Mo, although their catalytic activity strongly depends on the refractory metal and iron-group metal percentages. The Tafel slope in voltammetric dependences of HER also depends on both the chemical composition and structure of the cathode material. It increases from *ca*. 80 mV dec^{-1} for Re–Ni cathodes to *ca*.120 mV dec^{-1} for Ni–Mo cathodes. The results of the investigations are discussed.

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