

NANOPOROUS METALS BY SELECTIVE DISSOLUTION AND CORROSION OF ALLOYS. REVIEW

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Received 04.09.2018 y.

Abstract. Selective dissolution of homogeneous alloys (dealloying) is a promising nanotech method of synthesis of nanostructured materials with increased catalytic activity. The process leads to irreversible decomposition of the solid solution or intermetallide realized under conditions of anodic polarization or corrosion in an oxidizing medium. It allows both to increase the amount of a substance participating in a heterogeneous reaction because of the growth of the reaction surface, and to intensify the electrocatalytic process itself due to the structural-energetic activation of the surface. The material synthesized by selective dissolution at subcritical potentials is characterized by the morphological stability of the surface. The increased defectiveness of the nonequilibrium surface layer and its enrichment by the electropositive component are the main factors in the catalytic effect rise of such modified alloys. At the same time, the role of the structural-vacancy disorder in the surface layer of an alloy in the kinetics of electrode processes as a whole is not unambiguous and depends on the reaction nature. Selective dissolution of homogeneous alloys under overcritical potentials (dealloying) leads to formation of micro- and nanoporous metals with the substantially increased surface area and catalytic activity. The main product of chemical etching of an alloy in an aggressive environment is a dispersed powder with an uncontrolled pore and particle size, whereas electrochemical dealloying is characterized by a number of adjustable parameters including composition, potential, and temperature, variation of which gives a possibility to synthesize nanoporous metals with variable chemical composition, morphological properties, and multimodal structure. The nanopores are not stable and coalesce with changing temperature, potential and the electrolyte composition via surface diffusion mechanism. The most complete characterization of nanoporous metals formed by dealloying include description of their chemical, physical, mechanical, magnetic and optical properties, and is necessary for optimization of their application in catalysis, electrochemical energetics, and micromechanics.

Keywords: selective dissolution, dealloying, homogeneous alloy, intermetallide, nanoporous metals

Physicochemistry of new nanostructured materials based on solid solutions of metals and intermetallides, as well as heterogeneous catalytic processes on their surface is one of the most promising areas of modern physical chemistry. Requirements for the catalytic activity of electrode materials constantly increase, in particular, due to the shortage and high cost of a number of classical catalysts. It should be recognized that unmodified compact metal electrodes have now practically exhausted their electrocatalytic potential.

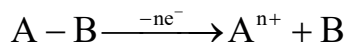
The traditional extensive approach to increasing the amount of a substance participating in a heterogeneous electrochemical reaction uses mainly

the growth of the overall reaction surface as a result of the morphological modification of massive electrodes with the formation of porous, dispersed and metal-polymer composite electrodes. In addition, special attention is paid to the intensification of the electrocatalytic process itself due to the structural-energetic activation of the surface of the metal electrode, for example, of electrodeposited nanostructured materials.

The purpose of this work is to review the current literature data on the selective dissolution (SD) of homogeneous alloys based on solid solutions or intermetallides as a promising nanotech method of increasing the catalytic activity of electrode material, which effectively combines the extensive and intensive approaches.

SELECTIVE DISSOLUTION OF ALLOYS UNDER THE CONDITIONS OF MORPHOLOGICAL STABILITY OF THE SURFACE LAYER

In the course of SD only the electronegative component A of a binary A,B-alloy undergoes oxidation with the transition of its ions to the solution, while the more noble metal B remains electrochemically stable. In the most general form, the process can be described as follows:



The process in fact represents an irreversible decomposition of the solid solution realized under conditions of anodic polarization or corrosion in an aggressive oxidizing medium.

The condition of truly selective dissolution is satisfied by such typical examples of binary homogeneous systems as single-phase brass Zn-Cu contacting with aqueous solutions of electrolytes; nickel and tin bronzes of Ni-Cu, Sn-Cu; solid solutions of gold and palladium with copper and silver Ag-Au, Cu-Au, Ag-Pd, Cu-Pd. A long and intensive SD process is possible only in the case of systems, the volume concentration of the electropositive component in which does not exceed a certain value N_B^{Tamm} corresponding to the Tamman corrosion resistance boundary [1,2].

The electrode material synthesized by selective dissolution at anodic potentials that does not exceed a certain critical value for the given alloy, E_{cr} , is characterized by the morphological stability of the surface. In this case, the main role in the change in the rate of the electrochemical process on the alloy anodically modified at subcritical potentials is played by such factors as increased defectiveness of the nonequilibrium surface layer and its enrichment by the electropositive component, since the area of the morphologically stable alloy surface practically does not change. It has been experimentally confirmed [3,4] that the chemical and microstructural changes in the surface layer of the alloy, which are irreversible and stable to relaxation, can be reflected in the kinetics of chemisorption, electrochemical and heterogeneous chemical transformations taking place on the alloy surface. In this case, the role of the structural-vacancy disorder in the alloy in the kinetics of electrode processes as a whole can not be considered unambiguous. For instance, the change in the fraction of vacancies in the nonequilibrium surface layer of anodic-modified Cu-Au alloys does not affect the rate of electro-oxidation of isopropyl alcohol in comparison with the initial alloys of the

same composition [3]. The preliminary anodic modification of Ag,Au-alloys, which also leads to the formation of a surface layer with an increased concentration of vacancies, does not cause a change in the kinetic scheme and the rate of formaldehyde electrooxidation on Au in an alkaline medium [5]. In the opinion of the authors, the chemisorption and ionization stages are not sensitive to variations in the atomic fraction of monovacancies in the structure of a solid Ag,Au-alloy.

At the same time, the processes of electrooxidation of oxalic acid and cathodic reduction of hydrogen are vacancy-sensitive. Indeed, an increase in the concentration of point defects contributes to the adsorption of the oxalic acid monoanion on Pd-containing alloys, as well as to the simplification of the electrochemical step, generally leading to an acceleration of the electrooxidation process of $H_2C_2O_4$ on the anodic-modified alloy in comparison with palladium [4,6]. A correlation is established between the thermodynamic activity of Pd in the surface layer of Ag,Pd-alloys and their electrocatalytic activity with respect to the oxalic acid electrooxidation reaction. It manifests itself in a simbiatic variation of both characteristics with an increase in the level of the vacancy defectiveness of the surface layer and the volume fraction of Ag in the alloy. A similar correlation was also revealed between the variations in the electrocatalytic activity of Ag,Au-alloys in the electrochemical oxidation of $H_2C_2O_4$ and the thermodynamic activity of gold in the nonequilibrium surface layer of such alloys [3,6].

The formation of such a layer in the case of Ag,Pd- or Ag,Au-alloy in the course of subcritical selective silver dissolution, as well as its reorganization after the termination of anodic polarization, naturally influence the kinetics of the hydrogen evolution reaction [3]. The rate of the cathodic reaction is affected both by the enrichment of the alloy surface by the more electrocatalytically active component (Au or Pd) and by the gradual decrease in its surface fraction during relaxation processes in the nonequilibrium vacancy subsystem of the surface layer of the alloy.

NANOPOROUS MATERIALS BY DEALLOYING

In the case of highly developed, porous alloys, the anodic modification of which was carried out under overcritical polarization conditions, the effect of increasing the amount of matter reacting per unit time on the alloy surface manifests itself to a much greater extent. First of all, this is due to the fact that in this

case the area of the electrode is substantially increased due to the development of its surface. In addition, the transition of the system to a porous, dispersed state can, in principle, lead to an increase in the catalytic activity of the synthesized highly developed material.

It is known that the classical electrochemical technology for the preparation of the skeleton catalyst - microcrystalline porous Raney nickel [7] - is based on the leaching of Al, Co, Fe or Zn from metallurgically formed Ni,Al-; Ni,Co-; Ni,Fe- or Ni,Zn-intermetallides. The chemical etching of the active component of an alloy based on the electronegative component in an aggressive environment - concentrated nitric acid or alkali - is mainly used to produce dispersed powders. Starting with a certain composition (for example, for Ag and Au alloys it is $N_{Au}^v \approx 16\%$ [8]), but under the condition of $N_B^v < N_B^{Tamm}$, mechanical destruction of the alloy does not occur, and in the course of selective corrosion, not powders are formed, but monolithic "spongy" metals: lead [9], gold [10-17], palladium [14], silver [14,18,19], platinum [14], copper [9,14,20-27]. Sequential deposition of the alloy on the substrate and selective etching of the electronegative component produces highly developed films of gold [28-31], palladium [32], copper [29,33], silver [29], tungsten [34].

A significant disadvantage of the method of selective corrosion, along with the use of environmentally hazardous, aggressive electrolytes, is the uncontrolled pore size of the material being synthesized. Anodic selective dissolution of the active component from a homogeneous alloy, on the contrary, is characterized by a number of adjustable parameters. These include alloy composition, anodic potential, anionic composition, pH and temperature of the electrolyte, as well as conditions of anodic polarization [8,35-37]. Variation of these parameters and conditions allows one to regulate the morphological properties, structure and chemical composition of the surface layer of an alloy [38-44]. In addition, the SD method makes it possible to obtain highly developed nanoporous metals [45-55], which do not require additional stabilization in a matrix, which favorably distinguishes them from nanoparticles [35,56-58]. The average pore size of an anodically modified alloy can be noticeably smaller than the radius of nanoparticles synthesized by metal precipitation from the solution [59,60]. Moreover, due to SD, the total area of alloyed nanoparticles can be further increased [61-70].

The pores coalesce with increasing temperature [26], as well as when the electrode potential and the electrolyte composition change. The determining

role in the coarsening of the pores belongs to surface diffusion. Indeed, the process rate is proportional to the coefficient of surface diffusion of the electropositive component, which mainly forms the porous framework. It was shown [71] that the introduction of halide ions into the electrolyte solution increases the surface-diffusive mobility of gold ad-atoms at overcritical selective dissolution of Ag,Au-alloys based on silver, which contributes to the multiple growth of the pore radius. In contrast, the introduction into the alloy-precursor of metal additives with very low diffusion mobility, for example platinum [72], substantially prevents pore enlargement and stabilizes nanoporous morphology.

The SD product can contain a sufficiently high residual amount of active metal [73,74], and if it exceeds the Tamman stability limit $N_A^{Tamm} = 1 - N_B^{Tamm}$, a secondary selective dissolution becomes possible with the formation of a hierarchical, multimodal highly developed structure [73,75,76].

Nanoporous metals obtained by the method of overcritical selective dissolution are an object of intensive research in the field of physical and chemical materials science. Various physical [77], mechanical [78-83], magnetic [84] and optical [42] properties are studied, original methods for determining the true surface area of such materials [85,86] and approaches to the mathematical description of their three-dimensional structure [87] are proposed. The need for the most complete characterization of highly developed and nanoporous anodic-modified alloys is dictated by a wide range of promising fields of application, including catalysis, electrochemical energy sources, micromechanical devices.

The effect of surface development during SD is proposed to be used to produce composite electrodes and collectors for supercapacitors [88,89]. It has been found that nanoporous metals anodically synthesized from homogeneous alloys exhibit appreciable catalytic activity with respect to a number of practically significant reactions. For instance, data have been obtained on the noticeable effectiveness of nanoporous platinum - in electroreduction of oxygen [90,91]; nanoporous palladium - in electrochemical oxidation of glucose [92], formic acid [93] and hydrogen peroxide [94], electroreduction of oxygen [95], as well as hydrogen absorption [32,96] and decomposition of carbon tetrachloride and chlorobenzene [97]. Nanoporous gold works effectively in reactions with participation of methanol [98-100], CO [100,101] and a number of other inorganic and organic compounds, which allows the development of a variety of bio- and

electrochemical sensors [102-111] based on highly developed Au.

It is noted that the observed "catalytic" effect is associated, mainly, with the growth of the area of the reaction surface. It is obvious, however, that this growth does not lead to an increase in the rate of the process, which should be normalized to the area of the growing surface, but to an increase in the amount of a substance entering into a heterogeneous reaction. In this case, such normalization is possible only for processes occurring under kinetic control. If the process is diffusion-controlled, then for the calculation it is necessary to use the cut-off area of the diffusion front, and for mixed-kinetic control the situation is further complicated. In any case, in order to detect a purely catalytic effect, associated, for example, with the change in the electronic state of atoms of the alloy-substrate on the surface of which the electrochemical process proceeds, it is necessary to separately evaluate the effect of the increase in the roughness factor.

The technological realization of the method of anodic synthesis of highly developed alloys enriched with an electropositive component, like nanoporous metals, still faces serious difficulties. The point is that the possibilities of regulating the morphological state and chemical composition of the electrode material, as well as controlling the formation of its catalytic activity during SD, are very limited. First of all, this is due to the fact that the kinetics of the anodic process on homogeneous intermetallic systems obtained by fusing the components has not been fully studied.

CONCLUSION

Electrode material synthesized by the method of selective dissolution of a binary metal alloy may have increased catalytic activity with respect to a number of practically significant chemical and electrochemical reactions. If the synthesis is carried out under subcritical conditions of polarization, the main factor for increasing the catalytic activity is an increase in the vacancy defectiveness of the nonequilibrium surface layer of the alloy and its enrichment with an electropositive metal. If the electrode material is formed at overcritical potentials and charges, the increase in the amount of the substance entering into the reaction can be caused both by the growth of the thermodynamic activity of the electrochemically stable component and by the morphological development of the electrode surface.

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СИНТЕЗ НАНОПОРИСТЫХ МЕТАЛЛОВ МЕТОДОМ СЕЛЕКТИВНОГО РАСТВОРЕНИЯ И ИЗБИРАТЕЛЬНОЙ КОРРОЗИИ СПЛАВОВ. ОБЗОР

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Аннотация. Селективное растворение гомогенных сплавов является перспективным нанотехнологическим методом синтеза наноструктурированных материалов с повышенной каталитической активностью. В условиях анодной поляризации или коррозии в окислительной среде данный процесс приводит к необратимым структурно-морфологическим изменениям в поверхностном слое твердого раствора или интерметаллида. Резкий рост площади поверхности приводит к увеличению количества вещества, участвующего в гетерогенной реакции, а структурно-энергетическая активация поверхностного слоя способствует интенсификации электрокаталитического процесса. Материал, синтезированный путем селективного растворения при докритических потенциалах, характеризуется морфологической устойчивостью поверхности. Повышенная дефектность неравновесного поверхностного слоя и его обогащение электроположительным компонентом являются основными факторами роста каталитической активности таких модифицированных сплавов. В то же время роль структурно-вакансионной разупорядоченности сплава в кинетике электродных процессов в целом неоднозначна и зависит от характера реакции. Селективное растворение гомогенных сплавов при закритических потенциалах приводит к формированию микро- и нанопористых металлов с существенно увеличенными площадью поверхности и каталитической активностью. Основным продуктом химического травления сплава в агрессивной среде является дисперсный порошок с неконтролируемой пористостью и размером частиц, тогда как электрохимическое растворение характеризуется рядом регулируемых параметров, включая состав, потенциал и температуру, изменение которых дает возможность синтезировать нанопористые материалы переменного химического состава, с различными морфологическими свойствами и мультимодальной структурой. Нанопоры нестабильны и коагулируют при изменении температуры, электродного потенциала и состава электролита по механизму поверхностной диффузии. Наиболее полная характеристика нанопористых металлов, образующихся при селективном растворении, включает описание их химических, физических, механических, магнитных и оптических свойств и необходима для оптимизации их применения в катализе, электрохимической энергетике и микромеханике.

Ключевые слова: селективное растворение, гомогенный сплав, интерметаллид, нанопористые металлы

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