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New Functional Materials Based on Nano- and Micro-Objects with Developed Surface

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The paper describes the materials with a developed surface fabricated on the basis of electrodeposited copper icosahedral small particles and coatings made of such particles. Increasing the specific surface area of the electrolytic metal is achieved by special heat and/or chemical treatments. Changes in the structure and morphology of icosahedral small particles are analyzed with scanning electron microscopy and X-ray diffraction. The specific surface area of the material is determined with low-temperature gas adsorption technique. Annealing of icosahedral small particles and coatings leads to the formation of the porous structure and a "forest" of whiskers on their surface. Chemical etching of icosahedral small particles corrodes the inside material and provides the formation of hollow particles. Possible applications for obtained materials with a developed surface are offered.

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1. Introduction

Ability of materials to possess a developed surface, i.e. large surface areas, is important in various practical applications, e.g. in catalysis. Numerous catalysts are now widely used not only in chemical industry in the production of chemical compounds, but also for waste and environmental management [1, 2]. In spite of the fact that modern chemical industry has a need in a big amount of catalysts, the majority of catalysts are currently fabricated of expensive materials such as platinum group metals. Except high price the shortcomings of existing catalysts, e.g. those on oxidic or ceramic carriers [3], include low mechanical stability, high hydrostatic resistance and a relatively low specific surface area (usually no more than 50 m^2/g) and, as a consequence, low catalytic activity [4]. There is an important task to reduce the cost of the catalysts used by switching to a cheaper base metals and to reduce the amount of materials in a chemical reactor by increasing the catalytic activity. Promising for these purposes can be all-metal catalysts with a large surface area. The same type of materials with a large surface area are needed in water treatment and purification [5].

This paper describes the methods for fabricating the materials with a large surface area that are based on copper icosahedral small particles (ISP) of electrolytic origin. The increase in the specific surface area is achieved by a choice of special conditions for metal electrodeposition, subsequent heat treatment, and chemical etching.

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2. Experimental procedure

Our technique for obtaining materials with a large surface area can be divided into two stages.

At the first stage we applied the electrodeposition of metals to coat the substrate with copper microparticles or solid copper layer. As the substrate we used stainless steel (type "12X18H10" in accordance with Russian steel nomenclature) mesh with cell size of 40 μm and wire diameter of 30 μm. For copper deposition, sulphuric electrolyte was used with the following composition: 250 g/l $CuSO_4 \cdot 5H_2O$, 90 g/l H_2SO_4. Deposition was carried out in a standard three-electrode cell in potentiostatic mode at 50–200 mV overvoltage and the processing time of 5–30 min. The anode was a copper plate, and the reference electrode — a copper wire.

At the second stage, to consolidate the copper particles on the mesh carrier and to facilitate the appearance of developed surface heat treatment was carried out in different atmosphere (air, oxygen, vacuum, etc.). In this paper we consider annealing of copper particles in air, the results of annealing in other media are described in Refs. [6–8]. The annealing temperature was chosen within the range 400–900 °C. In order to increase the specific surface area chemical etching was conducted, too. The composition of the etchant consisted of the following reagents: hydrochloric acid, ferric chloride ($FeCl_3$) and distilled water. Etching of the samples was performed at room temperature, and etching time varied from 10 to 250 s.

Surface morphology studies were conducted by scanning electron microscopy (NovaNanoSEM 450 and JEOL JCM 6000). Phase analysis was carried out by X-ray diffraction methods (X-ray diffractometer Shimadzu XRD 7000). The specific surface area was determined by low-temperature gas adsorption technique (Porosimeter Thermo Scientific Surfer).

3. Results and discussion

As a result of electrodeposition, copper icosahedral small particles (ISPs) were formed on the stainless mesh in a large amount. A typical example of an ISP is shown in Fig. 1a. There exists substantial literature devoted to the structure and properties of ISPs, for a review see Ref. [9]. Such particles demonstrate axes of fivefold symmetry; their internal structure is characterized by twin boundaries and high-energy defects of disclination type. Already in their initial state, ISPs possess high level of internal mechanical stresses and store a large amount of elastic energy. Described features of the internal structure and stresses affect the behaviour of ISPs in the temperature fields [6] and in the chemical environment [7]. By using special processing routes, i.e. etching and annealing, it is possible to spend the stored internal elastic energy on the formation of a new surface and to get, as a result, a developed surface. In particular, in such a way we have fabricated the materials with a large surface area: either in a form of array of CuO whiskers or nanoporous metal/metal oxide coating.

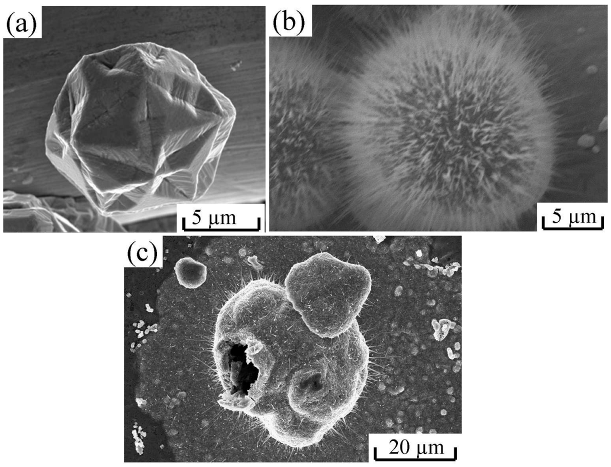

Fig. 1. Copper ISP before (a) and after (b), (c) heat treatment in air; annealing at 400 °C for 15 min (b) and for 1 h (c).

It was established experimentally that annealing in vacuum to temperatures 600 °C causes no visible changes of the surface morphology of ISPs; starting at 700 °C the particles lost their crystallographic facets and acquired spheroidal shape.

In case of heat treatment in air with annealing temperature above 250 °C, the sintering of icosahedral copper fine particles was observed and the formation of CuO whiskers on the particle surface was detected (Fig. 1b). Annealing ISPs at higher temperatures (above 400 °C) and for longer duration (1 to 3 h) resulted in the formation of voids in the particle interior with a thinning of the outer ISP shell up to nanometer diapason (Fig. 1c). The optimal annealing temperature in air atmosphere, whereby the surface of the particles was covered by whiskers with maximum surface density ($10^{10}-10^{11}$ cm^{-2}), laid in the interval 350–450 °C (see Fig. 1b). X-ray diffraction demonstrated that the annealed ISPs had a layered subsurface structure with the layers of Cu_2O and CuO with the whiskers being copper oxide CuO. The methods for the preparation of CuO whisker arrays and the description of whisker structure were discussed in Ref. [8].

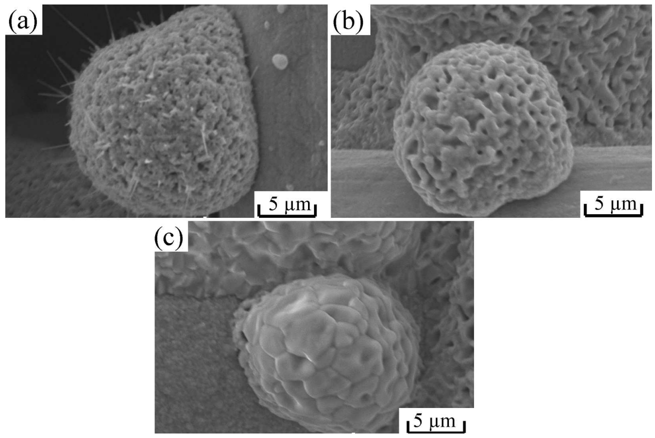

Fig. 2. Change in ISP surface morphology after annealing in air at 500 °C (a), 600 °C (b), 800 °C (c) for 30 min.

Annealing in air at higher temperatures (above 500 °C) led to a gradual reduction in the density of whiskers on the surface of ISP. Thus, for 500 °C annealed samples, individual whiskers on the surface of ISPs were still observed (see Fig. 2a), but their density is much lower than for samples annealed at 400 °C (as shown in Fig. 1b). At the same time for 500 °C annealed objects, nano- and microporous loose structure on ISP surface already formed, which was also observed after 600 °C annealing (see Fig. 2b). Annealing at 700 °C gave a decrease in porosity, and increasing the annealing temperature to 800 °C led to formation of a "scaly" particle surface (see Fig. 2c). At further increase in temperature to 900 °C individual particles coalesce to form a continuous coating with a pronounced "scaly" morphology.

Thus, annealing copper ISPs in oxygen containing atmosphere allows one to get materials with a large surface area in the form of nanowhisker and nanoporous structures of copper oxide. Such materials can be used as sorbents or catalysts in various chemical reactions. High catalytic activity of copper oxide in a nano state was mentioned in Ref. [10]. However, many chemical processes require the use of pure metal catalysts. For example, copper is the most widely used catalyst for the polymerization of acetylene. To obtain the pure metal (e.g. copper) with a developed surface, we have proposed a technique of ISP chemical etching. In the process of chemical treatment, the most intensive material etching took place at the disclinations emerging ISP surface and along twin boundaries (see Fig. 3a). By increasing the etching time, the growth of etch pits was observed (see Fig. 3b), and more time of treatment it was possible to detect the formation of internal cavities (see Fig. 3). Because of ISP

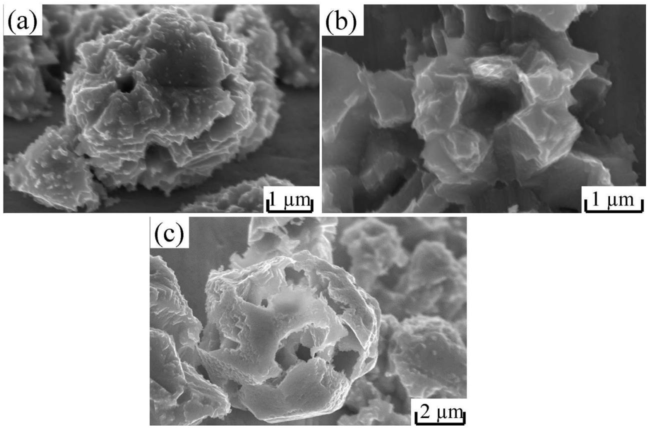

Fig. 3. Copper ISP after etching with the duration 10 s (a), 90 s (b), and 250 s (c).

defective nature, the etching proceeded more intensively inside particles than on their surface.

Experiments show that ISP chemical etching reduced the size of the particles, led to the loss of faceting and caused the formation of the internal cavities. The surface area of the particles increased in orders of magnitude, and, as a consequence, the reaction activity of the material enhanced many times. Applying this method, μm size particles can be transformed into nano-objects in the form of hollow particles having a nanoscale shell. We expect that the chemical etching method can be extended to other metals by varying the composition of reactants and etching mode with the aim to obtain new materials with a developed surface.

Finally, a special heat treatment and/or chemical etching of continuous copper ISP electrodeposited coating gave a variety of large-scale structures with a developed surface: an array of CuO whiskers (Fig. 4a), nanoporous CuO coating (Fig. 4b) or pure copper material with "exploded" hollow particles (Fig. 4c).

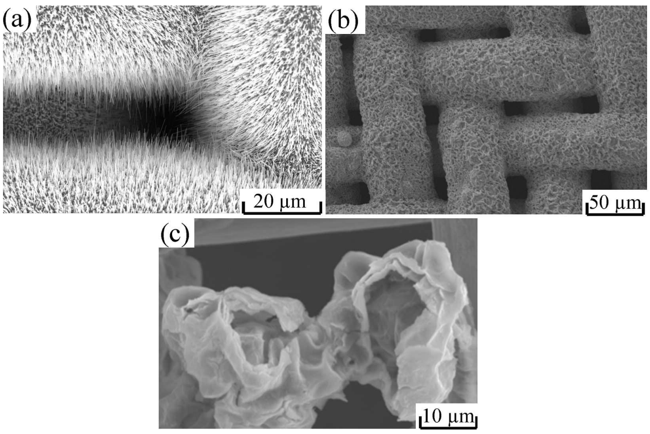

Fig. 4. Copper based materials with a developed surface in the form of nanowhisker array (a), nanoporous coating (b), and hollow microparticles (c).

4. Summary and conclusions

We have developed the methods to create materials with a large surface area on the basis of icosahedral small particles (ISPs) of electrolytic origin.

It was experimentally established that:

- copper oxide whiskers are formed during ISP annealing in an atmosphere containing oxygen starting from a temperature of 250 °C, while the maximum concentration of whiskers is observed after annealing at 400 °C. Annealing at higher temperature leads to a decrease in the concentration of whiskers and forming a porous structure;
- the most developed porous surface for oxidized particles is formed during annealing in an oxygen atmosphere at 600 °C;
- chemical etching of the initial ISPs produces copper hollow particles with nanoscale shell; such objects have a large specific surface area and enhanced catalytic activity.

The studied materials possess high catalytic activity and sorption capacity. One can expect that copper-based materials with a developed surface will be widely used in medicine, biology, ecology, engineering and chemical industries as catalysts and filter materials, nano-porous coatings and films.

Acknowledgments

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