

APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Electrochemical Method for Obtaining a Finely Dispersed Silver Powder

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Abstract—Specific features of the influence exerted by the electrolyte composition on the formation of finely dispersed silver powders were studied. It was demonstrated that the use of the redox reaction occurring in the presence of a system of M^{n+} and M^{m+} ions raises the current efficiency of silver powder formation. The optimal electrolysis parameters for obtaining finely dispersed silver powders were determined.

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One of highly promising fields of modern nonferrous metallurgy is the powder metallurgy producing metallic articles via compression and thermal treatment of metal powders below their melting point. Compared with the classical methods for fabrication of metallic articles, the method of powder metallurgy has a number of indubitable advantages. These are, first, the nearly waste-free nature of the technology and, second, the possibility of fabricating articles of most intricate configuration. Powder metallurgy makes it possible to create novel materials with prescribed composition, structure, and properties.

The key issue in powder metallurgy is method of obtaining raw material and, in the case in question, a powdered metal. This method not only determines the economical efficiency of the whole technology, but also noticeably affects the structure and properties of the resulting article [1].

However, not only qualitative characteristics of a powder govern the choice of a method used to obtain powders. Not less important in assessing the method used to produce powders are economical issues, production cost of a powder, capital investment, and cost of further processing of the powder into articles.

The goal of our study was to examine the process in which silver powders are formed in aqueous sulfuric acid solutions in the presence of metal cations in various oxidation states.

EXPERIMENTAL

Experiments on electrolytic production of powdered silver were performed in a glass cell. Lead served as anode, and titanium, as cathode. The electrode spaces were not separated. As the electrolyte serve a solution of composition (g L^{-1}): silver sulfate 6 and sulfuric acid 1, at $i_{\text{pb}} = 500 \text{ kA m}^{-2}$ and $i_{\text{Ti}} = 1500 \text{ A m}^{-2}$.

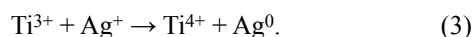
In the course of a cathodic reduction of silver ions at high current densities, the reaction of hydrogen evolution becomes inevitable and the following reactions occur at the electrode:



Naturally, the occurrence of the side process results in that the current efficiency (CE) of the main process is always lower than 100%. Thus, it is necessary to find a

fundamentally new solution that could raise the current efficiency of the process without impairing the quality of the product.

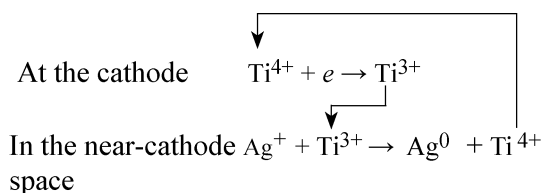
The current efficiency of silver powder formation can be raised by using the redox reaction occurring in the presence of Ti^{3+} and Ti^{4+} ions. The process occurs as follows: at high cathodic current densities, the cation in the highest oxidation state is reduced at the cathode to give a cation in a lower oxidation state by the scheme $Ti^{4+} + e \rightarrow Ti^{3+}$; further, Ti^{3+} reduce silver(I) ions in the near-cathode space to a powdered state by reaction (3), being themselves oxidized to Ti^{4+} :



The occurrence of reaction (3) is due to the rather pronounced difference between the standard potentials of the systems Ag/Ag^+ and Ti^{3+}/Ti^{4+} (the standard potential of the former is +0.799 V, and that of the latter, -0.05 V).

The CE by silver powder can be raised by combining two processes: direct discharge of silver(I) ions and redox reaction (3). As shown above, metal ions in the lowest oxidation state, formed on the cathode surface,

immediately react in the near-electrode space with silver ions by reaction (3), which yields an additional amount of powdered silver, with the current efficiency accordingly increasing. Simultaneously, metal ions in the highest oxidation state are regenerated, again reduced at the cathode, and involved in the next powder formation event, i.e., in the given process, too, Ti^{4+} ions serve as a catalyst. This process will be repeated in cycles by the scheme:



Thus, the scheme described above provides a continuous cycle of silver reduction and makes it possible to raise the current efficiency. The maximum CE of powder formation is 95.3%.

Below are presented data on how the initial concentrations of silver(I) and titanium(IV) ions affects the CE of silver powder formation at an electrolysis duration of 30 min:

Effect of the concentration of silver ions on the CE of silver powder formation $c(Ti^{4+}) = 4 \text{ g L}^{-1}$; $i_{pb} = 500 \text{ A m}^{-2}$; $i_{Ti} = 1500 \text{ A m}^{-2}$; $\tau = 30 \text{ min}$

Ag^+ concentration, g L^{-1}	1.0	2.0	3.0	4.0	5.0	6.0
BT CE, % (without Ti^{4+})	58.6	64.0	69.6	79.6	82.0	84.0
CE, % (with Ti^{4+})	71.2	78.5	81.4	89.7	91.3	95.3

Effect of the concentration of titanium ions on the CE of silver powder formation $c(Ag) = 6 \text{ g L}^{-1}$; $i_{pb} = 500 \text{ A m}^{-2}$; $i_{Ti} = 1500 \text{ A m}^{-2}$; $\tau = 30 \text{ min}$

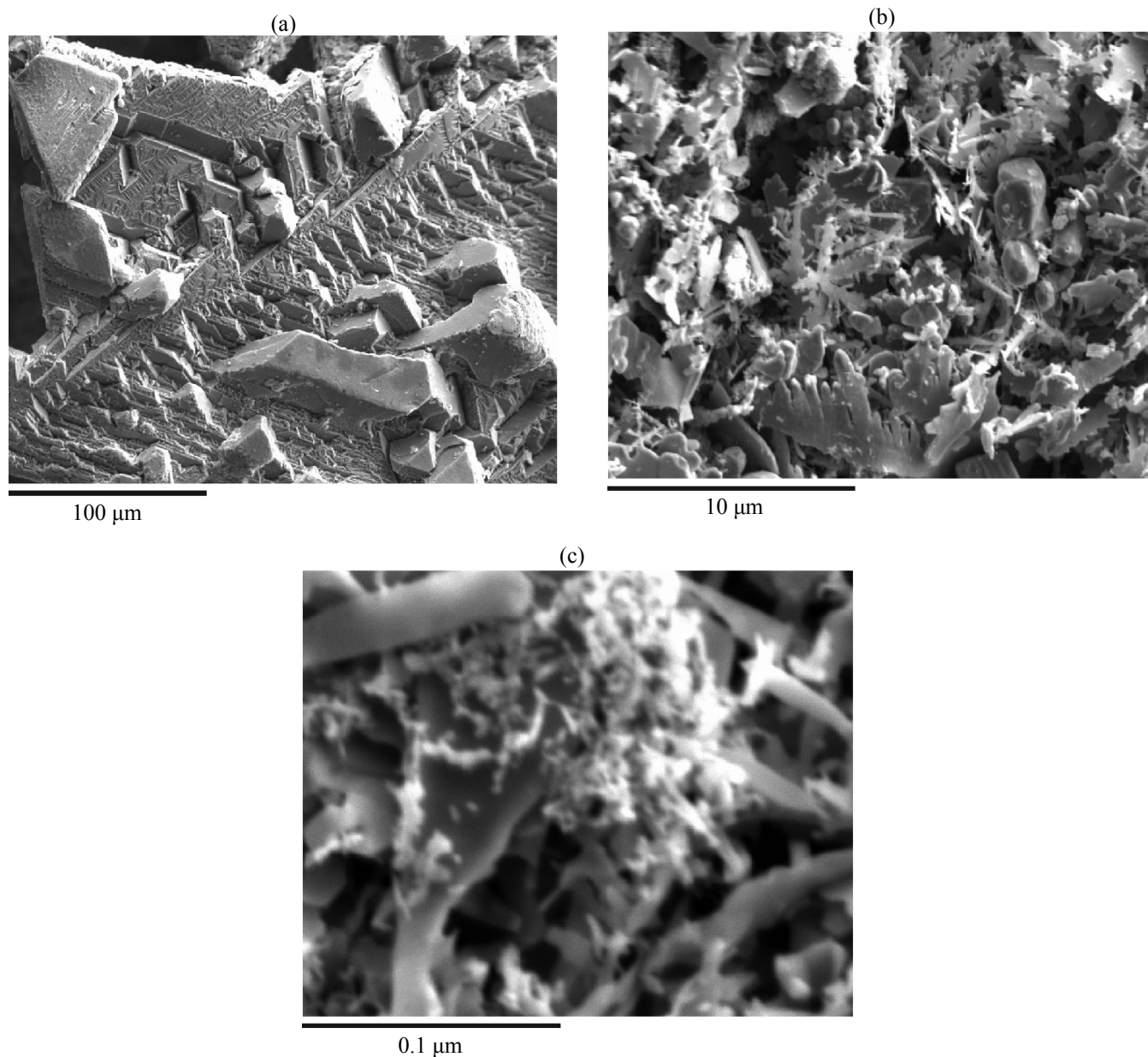
Ti^{4+} concentration, g L^{-1}	1.0	2.0	4.0	6.0	8.0
CE, %	79.8	86.7	95.3	95.3	95.3

The data we obtained demonstrate that the optimal concentration of the electrocatalyst is 4 g L^{-1} . As the concentration of the electrocatalyst grows, so does the rate of its reduction and, accordingly, the concentration of the reducing agent in the near-electrode layer will also be higher, which quantitatively affects the CE of silver powder formation. After the concentration of 4 g L^{-1} is reached, a saturation plateau is observed, and no further increase in the current efficiency occurs.

These data also demonstrate that the part of electricity fully consumed for reduction of hydrogen in the existing

methods for obtaining a silver powder is expended for formation of additional amounts of the powdered metal when ions in various oxidation states are introduced into solution. Therefore, the CE of silver powder formation increases by 12–15%.

An important characteristic of powders is the shape of their particles, which mostly depends on the fabrication method. It is known that the average particle size of the silver powder electrochemically produced from a nitric acid solution are 200–500 μm . Micrographs of a silver powder produced from a sulfuric acid electrolyte in the



Micrographs of a silver powder produced from sulfuric acid solutions of silver (magnification $\times 80\,000$). (a) In the absence of titanium cations; content of Ti^{4+} (g L^{-1}): (b) 1 and (c) 4.

absence and presence of Ti^{4+} ions were obtained using the method of electron-microscopic analysis. It can be seen in the figure that the powder produced from the electrolyte containing the $\text{Ti}^{4+}/\text{Ti}^{3+}$ system is highly dispersed. A possible reason is that, in the presence of cations in various oxidation states, the silver powder is mostly formed as a result of the chemical reaction (3), and, therefore, its particles will be substantially smaller than those of the cathodically formed powders. Presumably, the share of

reaction will mostly depend on the initial concentration of silver ions and on the cathodic current density.

The silver powder produced from a sulfuric acid solution has an average size of acicular particles of 200–500 μm . The presence of ions in various oxidation states strongly affects the particle size of the powders formed. At a content of Ti^{4+} ions of 1 g L^{-1} , dendritic powders with average particle size of 10–20 μm start to be formed, whereas at a Ti^{4+} content of 4 g L^{-1} , powders with particle

sizes of 0.1–10 μm are formed. Our experimental results show that the presence of Ti^{4+} cations makes it possible to raise the dispersity of the silver powder by more than a factor of 200–400.

CONCLUSIONS

The process of cathodic formation of a silver powder from sulfuric acid solutions in the presence of $\text{Ti}^{4+}/\text{Ti}^{3+}$ cations was studied for the first time. It was shown that

cations in various oxidation states have a catalytic effect on the process in which the silver powder is formed, with both the current efficiency of its formation and its dispersity increasing.

REFERENCES

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