

Non-electrolytic Deposition of Silver on Tungsten Powders for Functionally Gradient Composite Powder

Jae-Ho Lee^{1,a}, Gun-Ho Change^{2,b}

¹Dept. of Materials Science and Engineering, Hongik University
72-1 Sangsu-dong, Mapo-gu, Seoul 121-791 Korea
^ajhlee@hongik.ac.kr, ^ba119129@naver.com

Abstract

Particles of high strength material when coated with silver offer a means of obtaining desirable electrical properties and high strength. The coating process employed aqueous ammoniacal silver-nitrate electrolytes with a formaldehyde solution as the reductant. Modifying additives were also applied. The reduction and subsequent deposition of silver occurred selectively on the surface of the tungsten particles. The morphologies of the coated particles were assessed by SEM imaging. The silver was uniformly coated on tungsten powder and its thickness was estimated to be approximately 100nm on the basis of a mass account.

Keywords : electroless plating, silver, tungsten powder, composite

1. Introduction

For electrical and other application where silver particles are employed to create a low-resistivity conductor, the electroless coating of a lower cost particulate-materials with silver is economically attractive. The reason is that the conduction mechanism in these dispersed-particulate systems is primarily associated with the surface of the particles. Electroless silver coating onto glass is a well established silver-coating technology [1]. However, silver is deposited onto any contacting surface and there is no inherent selectivity. Diem et al selectively coated ceramic beads with silver for use as a catalyst [2]. Several reducing agents and inhibitors for coating porcelain beads with silver from a silver electrolyte were investigated. Hydrazine, and its derivative, formaldehyde, and hydroxylamine were assessed as candidate reductants. Carboxylic acid amino-compounds were explored as inhibitors. The aqueous silver electrolyte was formulated from silver-nitrate salt, with ammonia serving as a complexing ligand. Several of the organic reagents cited in this reference are either very toxic, or carcinogenic. The reductant and inhibitor employed in the research were selected so as to obviate any hazard-potential. Formaldehyde was selected since it is a well known metal-cation reducing agent, and less toxic than hydrazine [3-5]. Glycine, also non-toxic, was selected as the inhibitor. The objective of the research was to silver-coated tungsten particles for the functionally gradient materials application.

2. Experimental and Results

Two types of modifying reagents were used - an inhibitor and an activator. The coating solutions with inhibitor consisted of a reductant and the silver electrolyte. The

reductant was formaldehyde. The silver precursor-electrolyte consisted of AgNO₃, glycine and NH₄OH. The mixed solutions with activator contained: reductant, activator and silver electrolyte. The silver electrolyte consisted of AgNO₃ and NH₄OH. The activator solution was consisted of NaOH and NH₄OH. The reductant solution consisted of sorbitol and formaldehyde. Tungsten powder with particle size of 12 μm was obtained from AESAR. Pyrex glass vessel with a variable speed impeller drive was employed for the batch run. Tungsten powder was contacted with reducing solution prior to silver reduction. Silver solution was continuously added to the system with peristaltic pump at a constant flow rate.

A volume of 1ml of the reducing solution was added to 2ml of the silver electrolyte. There was no evidence of silver precipitation over 1 hour period. This established that for the proposed reductant, deposition of silver onto particles would be promoted by the surface characteristics of the galvanic action of the tungsten particles.

The reducing behavior was determined by adding 1g of tungsten, powder to 5ml of reducing solution. A volume of 10ml of the silver electrolyte was instantaneously added and stirring was for 2 minutes. The settled powder washed with methanol and vacuum dried prior to SEM imaging being conducted. Tungsten was completely covered with silver.

Glycine was excluded from the silver electrolyte and runs were repeated. Thus, the role of glycine was examined. The tungsten powder was completely covered with silver, however, the deposited silver was porous, and some cracks were present.

It is postulated that the silver deposition mechanism, associated with the formaldehyde reductant, can be correlated to the following electrochemical electrode-reactions.

Anodic reaction (oxidation of formaldehyde) [3,4]
 $2\text{HCHO} + 4\text{OH}^- = 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$
 $E^\circ = -1.32\text{V}$

or

$\text{HCHO} + 3\text{OH}^- = \text{HCOO}^- + 2\text{H}_2\text{O} + 2\text{e}^-$
 $E^\circ = -1.08\text{V}$

Cathodic reaction (reduction of silver)
 $[\text{Ag}(\text{NH}_3)_2]^+ + \text{e}^- = \text{Ag}^\circ + 2\text{NH}_3$
 $E^\circ = 0.373\text{V}$

It is noted that the silver is complexed with ammonia, and silver diamine is the predominant species. Also, the reduction occurs on the surface of the tungsten particle or in the interfacial region, close to the particle surface. In the absence of formaldehyde, or simultaneous with the previous anodic electrode reaction, galvanic reduction of silver by tungsten occurs according to the following scheme;

Anodic: oxidation of tungsten [6]
 $\text{W} + 8\text{OH}^- = \text{WO}_4^{2-} + 4\text{H}_2\text{O} + 6\text{e}^-$
 $E^\circ = -1.10\text{V}$

And the cathodic reaction is identical to electrode reaction.

On the basis of the observations, it appears that the primary coating of a particle occurs via contact reduction of silver by tungsten according to the galvanic mechanism described above as well as by reduction by formaldehyde adsorbed onto the particle surface. However, once a primary silver coating is established on the particle surface the reduction of silver by formaldehyde becomes autocatalytic electrochemical reaction, and a continuous coating is promoted rather than nodules discontinuously distributed over the particle surface.

3. Summary

In summary, the research conducted has demonstrated that coating of tungsten particles with silver can be affected by electroless deposition with the reductant. Satisfactory silver coating of tungsten particle can be achieved with a formaldehyde reductant and a silver glycine-inhibitor-containing electrolyte formulated.

4. References

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