Thin Solid Films 518 (2010) 5159–5163

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effect of bromide ions and polyethylene glycol on morphological control of electrodeposited copper foam

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ARTICLE INFO

Article history:
Received 19 April 2009
Received in revised form 22 February 2010
Accepted 11 March 2010
Available online 19 March 2010

Keywords:
Electrodeposition
Copper foam
Hydrogen evolution
3-dimensional
Porous

ABSTRACT

Three-dimensional porous copper foam was fabricated through acid copper electrodeposition under intense hydrogen evolution at an extremely high current density. Bromide ions and polyethylene glycol (PEG) were employed as additives to investigate their effects on the morphology and the microstructure of the foam. As bromide was added, the surface pore size and the thickness of the foam were increased. It also made the wall structure become more compact, and transformed the particles into a more dendritic form. On the other hand, PEG changed the foam in a completely opposed direction. Additionally, the simultaneous effect of the additives was studied. It was indicated that to a large extent the two additives functioned independently on the morphology and the microstructure, but they also developed a synergetic effect on the formation of CuBr.

1. Introduction

Three-dimensional (3D) porous metal foam has intrigued a widespread interest. Its open porous structure is very suited for the electrode of batteries [1], fuel cells [2] and sensors [3,4] which require fast mass transport and large specific surface areas for electrochemical reaction. Recently, many methods have been reported to fabricate the 3D porous structure. Most of these methods were assisted by some kinds of templates, such as liquid crystal [5,6], alumina [7], silica and polymer spheres [8–11]. In particular, a hydrogen bubble dynamic template [12] was proposed, by which it was very easy and effective to form a foam structure with a uniform pore size. This method involved a metal electrodeposition process and the accompanied hydrogen evolution. During this process, hydrogen was reduced and conglomerated into bubbles to act as template, at the same time, the copper particles deposited between the hydrogen bubbles, and formed the foam structure on the substrate. As compared with other methods, this process is much more simplified by eliminating the step of removing the template.

Since the introduction of this method, many efforts have been made to control the pore size and the pore wall structure due to their critical effects on electrochemical and mechanical properties of the foam for some particular applications. To reduce the pore size, the previous reports were focused on bubble stabilizers, such as acetic acid [13] and cetyl trimethylammonium bromide [14]. It was revealed that these additives had a good effect on preventing bubble coalescence, and hence reduced the pore size.

However, in this work, we were interested in the effect of copper deposition rate on the morphology. Previously, Shin and Liu [13] studied the effect of chloride ions. It was shown that by adding a trace amount of chloride, the wall structure of the foam became more compact. Such phenomenon was related to the accelerating effect of chloride ions on copper reduction. In our work, we introduced bromide as the additive because there have been many reports that described the copper deposition process in addition of bromide [15–17], and supposed that the bromide had the same effect as chloride. Another additive selected in this work was polyethylene glycol (PEG). It was widely used as the leveling agent for sulfuric acid copper plating, because of its ability to increase the overpotential of copper reduction and decrease the deposition rate. Finally, according to the industrial experience that the combination of chloride and PEG had a beneficial effect on forming bright coatings [18,19], the simultaneous effects of both additives were investigated.

2. Experimental details

$CuSO_4$ and H_2SO_4 were purchased from Beijing Modern Eastern Finechemical. NaBr was purchased from Shantou Xilong Chemical Factory. Polyethylene glycol (molecular weight = 6000) was purchased from Guangzhou Guanghua Chemical Factory. All the chemicals were of analytic grade. All solutions were prepared with deionized water.

Pure nickel plate was used as cathode, which was polished by #1000 water proof abrasive paper, then electrochemically polished by 70% phosphoric acid at 50 mA cm^{-2} for 3 min, and finally covered with scotch tape to expose only 1 cm^2 geometrical surface to the solutions. Pure copper plate was used as anode. To prevent anode passivation, the geometrical surface area of the anode was larger than 50 cm^2.

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doi:10.1016/j.tsf.2010.03.029

Table 1
Compositions of additives in the deposition baths.

Bath	NaBr (mM)	PEG (mg l^{-1})
A	0	0
B	20	0
C	0	200
D	20	200
E	5	200
F	20	400

The baseline deposition bath contained only $CuSO_4$ (0.16 M) and H_2SO_4 (1.6 M). To investigate the individual effect of bromide ions and PEG, they were introduced to the deposition bath separately. In addition, several combinations of the additives were used to explore their simultaneous effect. The compositions of additives in these deposition baths are given in Table 1. For deposition, a constant current (as high as 3 A cm^{-2}) was applied to the cell for 20 s. All the experiments were performed at room temperature. After deposition the samples were washed with a large amount of deionized water and dried in air, and then preserved in nitrogen. Scanning electron microscopy (SEM) measurements were performed on an LEO 1530 scanning electron microscope

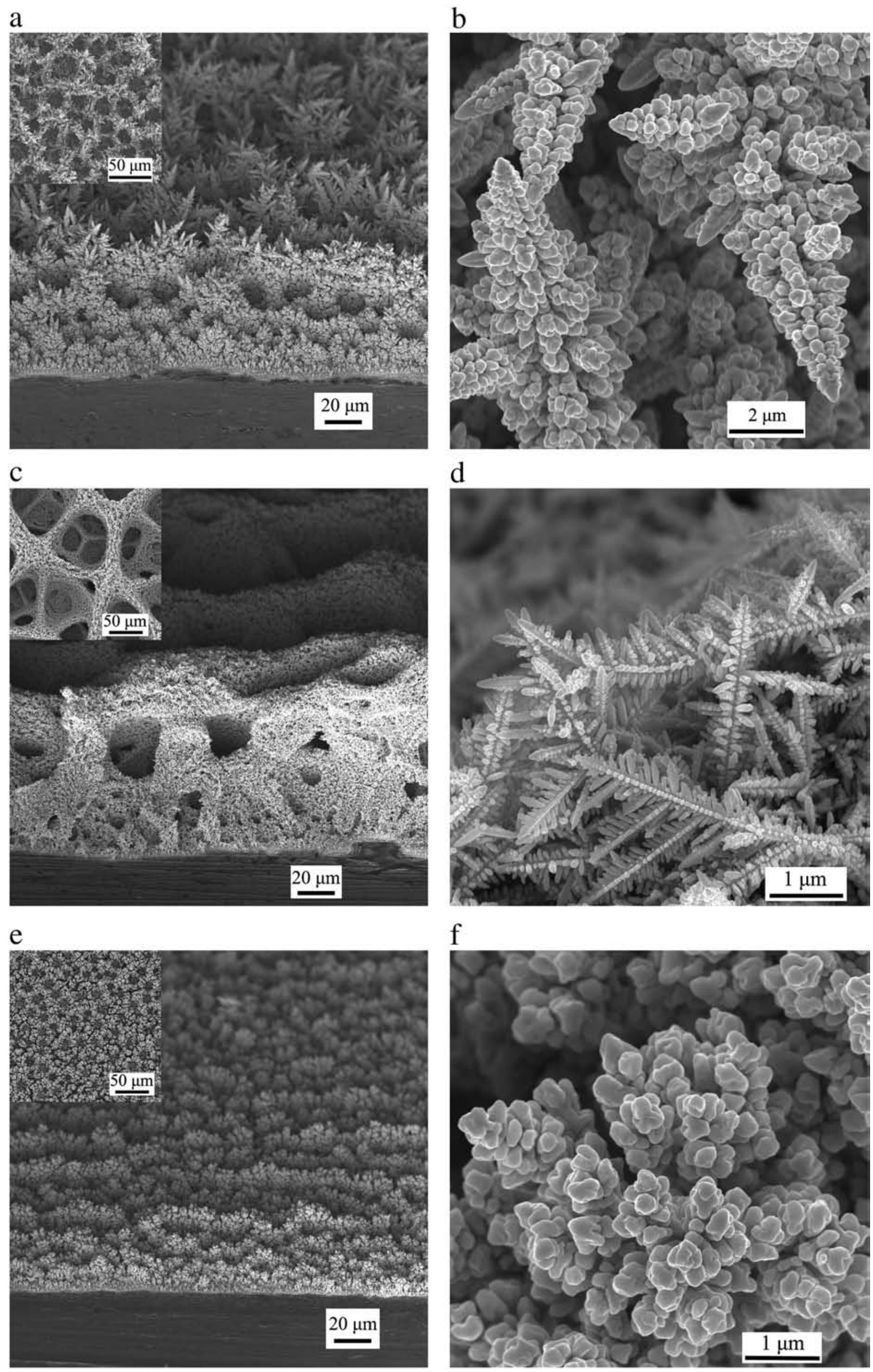

Fig. 1. (a, c, e) Top view and side view images of the copper foams and (b,d, f) micrographs of the particles deposited in baths A (no additives), B (20 mM NaBr), and C (200 mg l^{-1} PEG).