



# Facile synthesis of dendritic Cu by electroless reaction of Cu–Al alloys in multiphase solution



Ying Wang, Shuhua Liang\*, Qing Yang, Xianhui Wang

Shaanxi Province Key Laboratory of Electrical Materials and Infiltration Technology, School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048 PR China

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## ABSTRACT

Two-dimensional nano- or micro-scale fractal dendritic coppers (FDCs) were synthesized by electroless immersing of Cu–Al alloys in hydrochloric acid solution containing copper chloride without any assistance of template or surfactant. The FDC size increases with the increase of Al content in Cu–Al alloys immersed in  $\text{CuCl}_2 + \text{HCl}$  solution. Compared to  $\text{Cu}_{40}\text{Al}_{60}$  and  $\text{Cu}_{45}\text{Al}_{55}$  alloys, the FDC shows hierarchical distribution and homogeneous structures using  $\text{Cu}_{17}\text{Al}_{83}$  alloy as the starting alloy. The growth direction of the FDC is  $\langle 110 \rangle$ , and all angles between the trunks and branches are  $60^\circ$ . Nanoscale  $\text{Cu}_2\text{O}$  was found at the edge of FDC. Interestingly, nanoporous copper (NPC) can also be obtained through  $\text{Cu}_{17}\text{Al}_{83}$  alloy. Studies showed that the formation of FDC depended on two key factors: the potential difference between  $\text{CuAl}_2$  intermetallic and  $\alpha$ -Al phase of dual-phase Cu–Al alloys; a replacement reaction that usually occurs in multiphase solution. The electrochemical experiment further proved that the multi-branch dendritic structure is very beneficial to the proton transfer in the process of catalyzing methanol.

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## 1. Introduction

In recent years, scientists have been working on the preparation of morphology-controlled nano- to micro-scale metals [1]. Special size, shape and inter-particle distance of nanomaterials are very important to their performances and applications [2]. Various shapes (fiber, rod, wire, cube, pine needle and dendrite) were obtained by chemical or physical methods, such as polyol process [3], electrospinning [4], hydrothermal approach [5,7], self-assembly [8], colloidal synthesis [9], vapor deposition [10], electrochemical and electroless deposition [11,12]. Among them, metal nanocrystals with highly branched nanostructures have drawn considerable attention due to their unique physicochemical properties as well as great potential as catalysts [13,14], surface-enhanced Raman spectroscopy (SERS) [15,16], solar cells [17], sensors [17,18], energy conversion and storage [19], nanoscale devices [20].

Dendritic structure, as a kind of fractal structure, is generally observed in nonequilibrium growth processes [21]. At present, the diffusion-limited aggregation (DLA) model and cluster-cluster aggregation (CCA) model are widely used to explain fractal

phenomenon [22,23]. Despite that the formation mechanism of dendritic structures remains unclear, it is quite certain that most synthesis strategies used organic additives or templates [7]. Copper has been used in a wide variety of commercial applications at lower cost due to its high electrical and thermal conductivity. To date, the widely used approaches for synthesizing Cu dendritic structure include electroless deposition, electrodeposition and electrochemical [5,11,12,24]. However, the dendrites obtained generally depends on the cell geometries, electrolyte concentration, applied voltage and others parameters. However, either method involves a complicated process and high cost.

In addition, the nanoporous Cu is regarded as one of the important metal, which can be fabricated by dealloying Mg–Cu, Ti–Cu and Al–Cu [25–27]. So far, studies on the dealloying solution are primarily focusing on a single medium, such as acidic, neutral or alkaline solution [28]. The physiochemical mechanism of single medium is quite different from multiphase medium, and the mechanism exactly plays a key role in the formation of final morphology. Unfortunately, the related studies have not been conducted, so these investigations are needed on the dissolution processes of dual-phase Cu–Al alloys in multiphase solution that is composed of copper salt and hydrochloric acid. The corrosion process is quite different between single medium and multiphase medium, which determines the evolution of nano-morphological of Cu. It could

\* Corresponding author.

E-mail address: [liangxaut@gmail.com](mailto:liangxaut@gmail.com) (S. Liang).

be helpful to further investigate the dealloying processes of Cu–Al alloys in  $\text{CuCl}_2$  and hydrochloric acid solution.

In this paper, we report a facile and novel one-step synthesis to fabricate FDCs just by immersing Cu–Al alloys in an electroless  $\text{CuCl}_2 + \text{HCl}$  solution. The micro-morphologies of the two-dimensional FDC are investigated. In addition, the formation mechanism of different fractal structures using different  $\text{CuCl}_2$  concentration and Al content of Cu–Al alloy systems are discussed.

## 2. Experimental

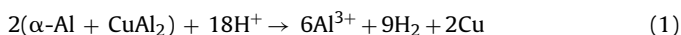
The  $\text{Cu}_{45}\text{Al}_{55}$ ,  $\text{Cu}_{40}\text{Al}_{60}$ ,  $\text{Cu}_{17}\text{Al}_{83}$  (nominal composition, at.%) alloys were prepared by vacuum melting pure Al (99.9 wt%) and pure Cu (99.9 wt%) in a vacuum sintering furnace. The Cu–Al alloy ingots and Al bulk with dimensions of  $10 \times 2 \times 1$  mm were prepared by wire cutting. And then, the samples were immersed into a hydrochloric acid solution containing copper chloride to perform free corrosion for a period of between 3 and 24 h until the solution changed from green to colorless and no obvious bubbles emerged, the concentration of  $\text{CuCl}_2$  was 0.5, 1–3 wt.%, respectively. And the concentration of HCl was 5 wt.%. Finally, the attachments were peeled off the surface of samples by ultrasonic shock and sealed in dehydrated alcohol.

The phase constituents of  $\text{Cu}_{17}\text{Al}_{83}$  alloys and as-eroded samples were determined by a X-ray diffraction (Shimadzu Limited, XRD-7000, Cu K $\alpha$  radiation,  $k = 0.15406$  nm). The morphologies of FDCs and porous structures were observed using a field emission scanning electron microscopy (JEOL, JSM-6700F) with an energy dispersive X-ray analyzer (EDX). The morphologies of single FDC were investigated by a transmission electron microscopy (JEOL, JEM-3010) (TEM) and an high resolution transmission electron microscopy (HRTEM). Cyclic voltammetry studies of FDC electrode were performed in a conventional three electrode cell systems. The system was run on an electrochemical workstation (CHI 660D).

## 3. Results and discussion

Fig. 1 shows the schematic diagram of the immersing of  $\text{Cu}_{17}\text{Al}_{83}$  alloy in  $\text{CuCl}_2 + \text{HCl}$  solution. The silvery white rectangle represents Cu–Al alloy, the hydrogen bubbles (blue circles) was released after the reaction. The step represents constantly proceed of Cu–Al alloy containing  $\alpha$ -Al and  $\text{CuAl}_2$  phase. Ultimately, the FDCs loosely accumulate on the surface of samples in the solution and its volume becomes larger than the sample itself due to the air bubbles between the FDC and substrate. After losing electrons, the Cu ions (II) become zero-valent copper, and aluminum atoms become Al ions (III). Regardless of the internal or surface of the alloy, overall reaction products present dark red color due to size effect, including needle-like dendrites (FDCs) on the alloy surface and porous structures inside the alloy. In this process, leaf-like structural Cu and nanoporous Cu appear simultaneously. The result is displayed on the right hand side in Fig. 1.

As well known, the standard electrode potential (SHE) of aluminum is far lower than that of copper, ( $E^{\ominus}_{\text{Al/Al}^{3+}} = -1.662$  V,  $E^{\ominus}_{\text{Cu/Cu}^{2+}} = 0.337$  V). In Cu–Al alloy, copper is an inert element, but aluminum is an active element, so Al atoms were quickly corroded and copper atoms did not participate in the reaction in the same acid solution. On the other hand, due to the joined  $\text{CuCl}_2$  in hydrochloric acid, the Cu ions can be used as a reactant to participate in the reaction and were reduced to metallic copper. Therefore, the copper atoms of alloy were preserved when the aluminum atoms were dissolved and the hydrogen bubbles overflowed. Simultaneously, the copper ions were reduced in the solution. The specific reaction process is shown as follows:



All processes can be described as follows. Since  $\alpha$ -Al phase is more active than  $\text{CuAl}_2$  phase in the alloy, a large number of corrosion micro-batteries can be formed in the alloy/solution interface. The  $\alpha$ -Al merely participates in the oxidation reaction as an anode. However,  $\text{CuAl}_2$  not only acts as a cathode of micro-battery to attend the reduction reaction, but also plays a key role in the deposition of Cu ions. As the reaction begins,  $\text{Cu}^{2+}$  ions can be displaced by Al atoms in the Cu–Al alloy because of the larger voltage difference between Cu and Al, as shown in Eq. (1). On one hand, the undissolved copper atoms of the alloy quickly form porous copper skeleton. On the other hand,  $\text{Cu}^{2+}$  of  $\text{CuCl}_2 + \text{HCl}$  (aq.) can continuously supply reducing agent for the reduction of copper, which results in the assembly of active Cu atoms and continuous reaction of Al atoms until they are eventually depleted (Eq. (2)). The copper atoms in the supersaturate solution precipitate as FDCs on the alloy surface, as shown in Eq. (3). The copper-rich environment plays a significant role in the complete dissolving Al atoms. Therefore, when pure aluminum is used as a starting metal, the FDCs can still be produced. By Galvanic replacement [29], Cu in solution can be separated, this process is similar to that of electroless plating.

On the basis of the above discussion, the dendritic structures can be formed in non-equilibrium growth environment. According to the theory of electrodeposition, high current density profited from huge potential drop will cause metal ion concentration polarization, which is an indispensable premise condition for dendritic sediment. It shows that, if Cu–Al alloy is used as precursor for preparing FDC, two conditions may be essential: firstly, the replacement reaction can occur between the matrix metal and metal ions of the solution. Secondly, the higher potential difference than a few hundred millivolts should be existed between the two metallic elements inside of the original alloy.

Fig. 2a–c shows the microstructures of as-immersed  $\text{Cu}_{17}\text{Al}_{83}$  alloy in 0.5 wt.%  $\text{CuCl}_2 + \text{HCl}$  (aq). These products on the alloy surface are obviously dendritic. According to SEM analysis, all FDCs exhibit two-dimensional, feathered fractal structure, every angle of the trunks and branches is  $60^\circ$ , and it is a typical characteristic of hexagonal crystal, as shown in Fig. 2a–b. The primary-, secondary-, and tertiary-branches can be observed on the FDCs, and these FDCs are about 3–8  $\mu\text{m}$  in length, as shown in Fig. 2b. Moreover Fig. 2c shows nanoporous structure, which formed during the period of FDC generation, and the pore size is about 70–100 nm. The EDX shows that the FDCs consist of a large quantity of Cu, and trace amount of Cl and O. Besides Cu, however, the porous structures also include few O and scarce Al as seen from Fig. 2e. It exactly proves that  $\text{Cu}^{2+}$  ions have been completely transformed and became elementary substance, namely FDC. In addition, Cl element appears in the spectrum, the reason may be that the sample has not been rinsed clean leading to adsorption of unreacted Cl ion, or trace amounts of insoluble  $\text{CuCl}$  owing to the reaction of Cl and active copper atoms. In contrast, Al and O element confirms that the formation mechanism of porous structure is different from that of FDC. In fact, Al atoms can be entirely removed by acid solution etching for a long time (above 24 h). And then, FDCs were stewed in deionized water for 2 h at room temperature. Subsequently, in the EDX spectrum, the peak of element Al is very weak, almost can't be seen. Free Cu ions gathered on the surface of the porous copper when the Al atoms were removed, which resulted in the formation of uniform size of pore wall and narrow channel in hydrochloric acid solution containing copper chloride. The EDX spectrum shows that the FDCs contain a small amount of oxygen, but it is too few to be detected by a XRD analyzer. The above results show that the formation mechanism of copper with different morphologies is different formation

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