Affection of Cu content on the phase evolution during the dealloying of Ag-Cu alloys using electrochemical noise with Hilbert spectra analysis

Y. Zhao\textsuperscript{a,b}, X. Wang\textsuperscript{a,*}, J.C. Huang\textsuperscript{c,*}, X. Chen\textsuperscript{a}, L. Cao\textsuperscript{a}, M. Mu\textsuperscript{a}

\textsuperscript{a} School of Mechanical Engineering, Liaoning Shihua University, Fushun, 113001 PR China
\textsuperscript{b} Corrosion and Protection Laboratory, Key Laboratory of Superlight Materials and Surface Technology (Harbin Engineering University), Ministry of Education, Nantong ST 145, Harbin, 150001 PR China
\textsuperscript{c} Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung, 804 Taiwan, Republic of China

A R T I C L E   I N F O

Article history:
Received 21 May 2016
Received in revised form 10 July 2016
Accepted 23 July 2016
Available online 25 July 2016

Keywords:
Silver
Copper
Corrosion
Diffusion
Electrochemical noise
Hilbert spectra

A B S T R A C T

The affection of Cu content on the phase evolution of Ag-Cu alloys was investigated by electrochemical noise (EN) with Hilbert spectra analysis. The results showed that the dealloying corrosion rate decreased and contribution of the transient shift from low-frequency parts (diffusion process) to the high-frequency parts (dissolution process) increased with the content of Cu increasing. Due to the increasement of Cu content, amounts of the Ag\textsubscript{2}Cu phases would be promoted. Ag\textsubscript{2}Cu phases had higher potential contrast with Cu phases and promoted the formation of different phase boundary, and different phase boundary would inhibit the diffusion of Ag atom. Thus, the hypoeutectic Ag\textsubscript{15}Cu\textsubscript{85} alloys performed highest dealloying corrosion rate and the contribution of the transient at the highest-frequency parts followed by Ag\textsubscript{20}Cu\textsubscript{80} and Ag\textsubscript{25}Cu\textsubscript{75} alloys.

© 2016 Published by Elsevier B.V.

1. Introduction

Nanoporous metals, as novel functional materials, have attracted considerable interest in recent years, which attribute to their special mechanical, physical, and chemical properties and corresponding broad applications in sensors\cite{1}, fuel cells\cite{2} and micro fluidic flow controllers\cite{3}, etc.

Dealloying, as a simple and effective strategy, is widely used to produce nanoporous metals. Compared to other methods, the dealloying can provide maximum flexibility in controlling the microstructure and property of the mechanism of nanoporous through alloy design of precursors, changing dealloying solutions, time and other factors.

Previous studies on microstructure and phase evolution during dealloying mainly focused on those single phase alloy systems, such as prototypical Ag-Au\cite{4}, Pt-Co\cite{5}, and Mn-Cu\cite{6}, and the diffusion mechanism of alloy elements has been discussed a lot. While the the bi-phase alloys nanopores alloys dealloying from Al-Ag\cite{7} and Al-Cu\cite{8} alloys have been successfully produced and used in variety tougher environment. And both nobler and less noble elements determines the entire dealloying process and the resultant microstructure to some extent\cite{9,10}. Some researchers have explained the dealloying behavior of Ag-contained precursor and the evolution of Ag nanoporous structure during the dealloying process from Ag-Al\cite{11} and Ag-Zn\cite{12} alloys. But it is still not sufficient to explain the mechanism of the dealloying process.

In recent years, Ag and Cu have received attention as a substitution of Au due to their cheap cost, high electrical, high thermal conductivity, and relatively higher strength than Au\cite{13}. However, whether the dealloying process is similar, and how the content of Cu effect on the phase evolution has not been reported.

The electrochemical noise (EN) measurement has been shown to possess unique advantage to monitor the electrochemical processes and corrosion rate in situ. And Hilbert spectra analysis is an innovative way of time-frequency to analyze the EN signals, which separates the specific transient signals from the background electrochemical current noise (ECN) which was first proposed by Huang et al.\cite{11}. The dealloying can be regarded as the corrosion process, the pitting and diffusion information of the alloy atoms can be obtained by the contribution of the transient at different frequency. However, using the EN method based on Hilbert spectra analysis to investigate the dealloying process has not been reported. Thus, in this article, the EN method based on Hilbert spectra transform was used to analysis the phase evolution during the dealloying of Ag-Cu alloys.
2. **Experiment details**

2.1. **Material and solution**

Three Ag-Cu alloys, Ag$_{15}$Cu$_{85}$, Ag$_{20}$Cu$_{80}$, and Ag$_{25}$Cu$_{75}$ in at%, are prepared by melt spinning. The purity levels of Ag and Cu are both higher than 99.99 wt%. The measured results of Ag-Cu ribbons are 6 mm in width, 100 um in thickness, and over 100 mm in length. Prior to electrochemistry noise experiments, the materials were embedded in epoxy resin with exposed working area of 10 mm$^2$, degreased with acetone, rinsed with distilled water and dried in a compressed hot air flow. The testing electrolyte was chosen as 5 wt% HNO$_3$ solution. And the solution remained at 60 °C.

2.2. **Electrochemical measurements**

Electrochemical noise measurements were performed with Zahner electrochemical (IM6, Germany) workstation equipped with electrochemical noise (EN). Two identical specimens were used as the working electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively. Coupling current between two identical working electrodes (WE) kept at the same potential, EN data was simultaneously recorded as a function of time for 2500 s. Each set of EN records were investigated by Hilbert spectra time-frequency analysis, containing 1024 data points and recording with a data-sampling interval of 0.25 s.

2.3. **X-ray diffraction**

The changing of the phases of the starting and dealloyed Ag-Cu alloys were evaluated using an X-ray diffraction (XRD) machine (SHIMADZU XRD-7000 S/L, Japan) with a Cu K$_\alpha$ X-ray source operated at 40 kV and 150 mA. Scans were performed over a range 10–90° using a step size of 0.333 s.

2.4. **Quantify the concentration of Cu$^{2+}$ in the solution**

According to GB -7347-87, the quantities of the Cu$^{2+}$ in solution after Ag-Cu alloys dealloyed using spectrophotometric method.

3. **Results and discussion**

3.1. **Comparison of corrosion resistance of Ag-Cu alloy in 5 wt% HNO$_3$**

The typical electrochemical potential noise (EPN) and current noise (ECN) after direct current trend removal of Ag-Cu alloys in 5 wt% HNO$_3$ are shown in Fig. 1. It shows that when the potential decreased for Ag$_{15}$Cu$_{85}$ alloy, a significant amount of big amplitude with some fast transients current noise appear and decrease greatly as shown in Fig. 1(a). For Ag$_{20}$Cu$_{80}$ alloy, the mount of big fluctuations and fast transients are nearly the same with fast transient amplitudes as shown in Fig. 1(b). While for Ag$_{25}$Cu$_{75}$ alloys as shown in Fig. 1(c), fast transients current noise are dominant. The fast transients currents last 1 s and big amplitude with about 50–70 s exponential decay. According to the references [14], the pattern shape of fast transients was a rapid stepwise rise in current from background, indicated a fast dissolution and repassivation immediately. The rapid rise in big amplitude current and great decrease denoted the fast dissolution of the metal or the diffusion process. Thus, the dealloying process for Ag$_{15}$Cu$_{85}$ alloys is fast dissolution of the Cu phases (Cu$^+$+2 H$^+$→Cu$^{2+}$+H$_2$) and Ag atom diffusion. Fast dissolution and repassivation usually occurs for the Ag$_{25}$Cu$_{75}$ alloys. And for Ag$_{20}$Cu$_{80}$ alloys, the diffusion and fast repassivation occurs simultaneously.

$R_n$ is defined as the ratio of the standard deviations of the potential noise to the current noise between two identical working electrodes and is often obtained by analyzing the electrochemical noise data. Thus, $1/R_n$ was proportional to corrosion rate [15].

![Fig. 1. Electrochemical characteristic of the Ag-Cu samples as a function of dealloying time.](image)

(a) Electrochemical noise of Ag$_{15}$Cu$_{85}$ alloys; (b) Electrochemical noise of Ag$_{20}$Cu$_{80}$ alloys; (c) Electrochemical noise of Ag$_{25}$Cu$_{75}$ alloys; (d) $R_n$ of as a function of dealloying time.
values of the $1/R_n$ for Ag-Cu alloys in 5 wt% HNO$_3$ are shown in Fig. 1(d). It is shown that the corrosion rate can be ranked as a decreasing series: Ag$_{15}$Cu$_{85}$ alloys > Ag$_{20}$Cu$_{80}$ alloys > Ag$_{25}$Cu$_{75}$ alloys. Moreover, the concentration of the Cu$^{2+}$ for Ag$_{15}$Cu$_{85}$ alloys is the highest (1.012 mg/L) followed by Ag$_{20}$Cu$_{80}$ alloys (0.915 mg/L) and Ag$_{25}$Cu$_{75}$ alloys (0.825 mg/L). That may due to the amount of Cu phases decreased with the content of Cu increasing and Cu phase has lower potential contrast with Ag$_2$Cu phases [16]. Thus, the Ag$_{15}$Cu$_{85}$ alloys exhibited the highest corrosion rate and Cu$^{2+}$ concentration in the solution during dealloying process.

3.2. The phase evolution of Ag-Cu alloy in 5 wt% HNO$_3$

In order to investigate the affection of Cu content on the phase evolution, the XRD analysis and Hilbert-Huang spectrum are combined to illustrate the dealloying process.

The The morphologies and composition of Ag–Cu samples are compared in Fig. 2. The precursor Al–Ag alloys consists of two distinct phases: Cu(Ag) and Ag$_2$Cu phases, and the volume fraction of the Ag$_2$Cu phase appears to be higher with increasing Cu content are shown in Fig. 2(a). And after dealloyed, the Cu(Ag) and Ag$_2$Cu phases gradually disappear, resulting in the final single Ag phase are shown in Fig. 2(b). Compared with Ag$_2$Cu phases, less amount of Cu phases have lower potential, and that would dissolve priority and increase the corrosion rate obviously as the Fig. 2(c) shown. Moreover, larger ratio of the Ag$_2$Cu phase would introduce the increased of the amounts of phase boundary. The boundary would inhibit the diffusion of the atom and promote the surface passive with the atoms fill up the dissolve pores as the Fig. 2(d-e) shown.

Ag$_{15}$Cu$_{85}$ alloy consisted with Cu(Ag) phase mainly, and that dissolve faster, leaving the residual Ag atom diffuse without

![Fig. 2](image-url)
different phases boundary inhibiting. Thus, the ECN signals perform big amplitudes and the contribution of the transient is mainly accumulated at the frequency below $10^{-2}$ Hz (diffusion process) as Fig. 3(a-b) shows.

As for Ag$_{20}$Cu$_{80}$ alloy, the amount of Cu and Ag$_2$Cu are nearly the same, the stable diffusion process and fast repassivation occur simultaneously. Thus, the contribution of the transient is accumulated at the whole frequency as Fig. 3(c-d).

Ag$_{25}$Cu$_{75}$ alloy mainly consists of Ag$_2$Cu phases. Ag$_2$Cu phase boundary inhibits the diffusion of the Ag atom. Dealloyed atom filled the vacancy immediately and passived the surface. Thus, ECN signals exhibit big fast transients during dealloying process, performing the EDP accumulated among above $10^{-2}$ Hz (passive process) as Fig. 3(e-f) shows.

4. Conclusion

1. The increased content of Cu would promote the amount of the Ag$_2$Cu phases. Ag$_2$Cu phases had higher potential contrast with Cu phases. Thus, the hypoeutectic Ag$_{15}$Cu$_{85}$ alloys performed highest dealloying rate followed by Ag$_{20}$Cu$_{80}$ and Ag$_{25}$Cu$_{75}$ alloys.

2. Ag$_2$Cu phases promote the amount of the phase boundary, which would inhibit the diffusion of the Ag atom. And diffusion was a slower process, thus the contribution of the transient shift from low-frequency parts to the high-frequency parts with the content of Cu increased.

Acknowledgment

The authors gratefully acknowledge the sponsorship from National Natural Science Foundation of China, under the project No. 51574147, Ministry of Science and Technology of Taiwan, under the project No. MOST 102-2221-E-110-025-MY3, MOST 103-2811-E-110-004 and Scientific research fund of China’s Liaoning Provincial Education Department, under the project No. L2014154.

References


Fig. 3. The Hilbert spectra of the Ag-Cu samples immersion for 2048 s. (a) Ag$_{15}$Cu$_{85}$ alloys immersion for first 1024 s; (b) Ag$_{15}$Cu$_{85}$ alloys immersion for last 1024 s; (c) Ag$_{20}$Cu$_{80}$ alloys immersion for first 1024 s; (d) Ag$_{20}$Cu$_{80}$ alloys immersion for last 1024 s; (e) Ag$_{25}$Cu$_{75}$ alloys immersion for first 1024 s; (f) Ag$_{25}$Cu$_{75}$ alloys immersion for last 1024 s.