Dealloying of Cu-Zr-Ti Bulk Metallic Glass in Hydrofluoric Acid Solution

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The dealloying behavior of $Cu_{60}Zr_{30}Ti_{10}$ metallic glass was investigated under free corrosion conditions using hydrofluoric acid (HF) solutions at room temperature. After immersing in HF solutions with various concentrations (0.05, 0.1, 0.5 and 1 M) for 300 s, color of all samples changed to be pinkish or peachy, which was ascribed to Cu based on the XRD patterns. According to the SEM-EDS study, HF immersion selectively leached the Zr and Ti elements, leaving Cu behind. Increasing the HF concentration increased the dealloying rate. Moreover, the HF concentration strongly influenced the surface morphology of the resulting Cu.   [doi:10.2320/matertrans.ME200823]

1. Introduction

Selective leaching or dealloying, which is a type of corrosion for some solid solution alloys, occurs under conditions suitable to preferentially leach a component from a material. The less noble metal can be removed from the alloy by a microscopic-scale galvanic corrosion mechanism.[1,2] Although dealloying has received attention in the context of corrosion, it has recently been receiving renewed attention because particular systems exhibit nanostructure or nanoporosity evolution upon dealloying.[1,2] Interesting dealloying behaviors have been observed for binary systems, including Ag-Au,[1–5] Cu-Zr,[6–8] Cu-Pt,[9] and Pt-Si.[10]

Compared to the crystalline alloys, multicomponent metallic glasses are monolithic in phase with a homogeneous composition and structure down to the subnanoscale. Thousands of metallic glasses have been found in different alloy systems.[11,12] The changeable component elements and relatively wide composition ranges may make metallic glasses interesting systems for dealloying induced structural controls at room temperature. Recently, nanoporous Pd has been fabricated by selective leaching from $Pd_{30}Ni_{50}P_{20}$ of glassy alloy ribbon.[13]

The authors have also demonstrated a room-temperature amorphous/crystal transition of a copper agglomerate by selective complete leaching out of Zr and Ti elements from metallic glass of a Cu-Zr-Ti ternary system.[14] Cu is more noble than Zr and Ti, *i.e.*, the standard equilibrium electrode potentials for the Cu/Cu^{2+}, Zr/Zr^{4+} and Ti/Ti^{2+} pairs are $+0.337\,V_{SHE}$, $-1.53\,V_{SHE}$ and $-1.63\,V_{SHE}$, respectively.[15] The most susceptible alloys are the ones containing metals with a large distance between each other in the galvanic series, and thus the large difference in electrochemical potential between Cu and Zr/Ti can facilitate selective dissolution of Zr and Ti in the Cu-based glassy alloy.

Herein, we report the dealloying behavior of $Cu_{60}Zr_{30}Ti_{10}$ metallic glass under free corrosion conditions using hydrofluoric acid (HF) solutions with an emphasis on the influence of HF concentration on the resulting microstructures of the remaining Cu metals.

2. Experimental

The rotating wheel method under an argon atmosphere was used to prepare $Cu_{60}Zr_{30}Ti_{10}$ metallic glassy ribbon from argon arc-melted ingots. The glassy ribbon was cut into $\sim 10\,mm \times \sim 10\,mm \times \sim 25\,\mu m$ samples. Electrolyte solutions of 1, 0.5, 0.1, and 0.05 M HF were prepared from reagent-grade chemicals and deionized water with a specific resistivity of $18.2\,M\Omega cm$. The samples were immersed in HF solutions at different concentrations, i.e., free corrosion conditions or open circuit conditions.[5] After immersion, the samples were removed from the solution, washed in H_2O, and allowed to dry in air. All experiments were performed at room temperature. Electron microscopy was performed using FE-SEM (ERA-8800FE, Elionix, Japan) with energy dispersive X-ray spectroscopy (EDS: EDAX, Japan). Compositional mapping of the samples was performed by the SEM-EDS. The samples were also characterized by X-ray diffraction (XRD. JDX-3530M, JEOL, Japan) using Ni filtered Cu-Kα radiation.

3. Results and Discussion

Figure 1 shows photographic images of the as-quenched and HF treated glassy ribbons. In this HF treatment, the sample was immersed in 1 M HF solution for 300 s at room
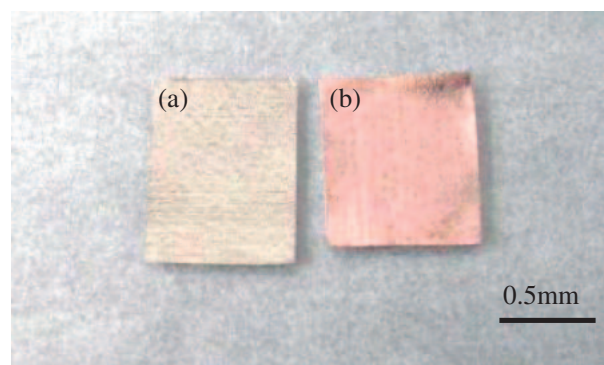

Fig. 1   Photograph of (a) a glassy alloy ribbon of $Cu_{60}Zr_{30}Ti_{10}$ and (b) the ribbon after immersion in 1 M HF solution for 300 s.

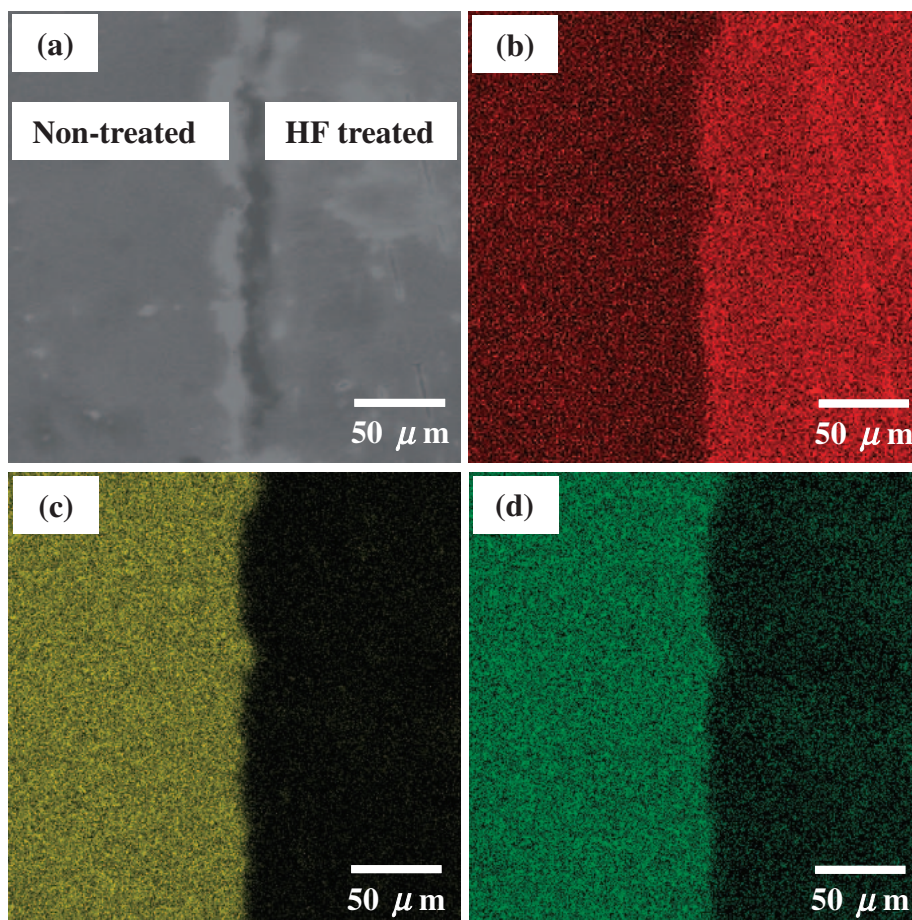*Corresponding author, E-mail: h-abe@jwri.osaka-u.ac.jp

Fig. 2   (a) SEM micrograph of partly HF treated sample and corresponding elemental distribution mapping of (b) Cu, (c) Zr and (d) Ti.

temperature. The color of the sample surface changed almost uniformly to pinkish or peachy, indicating that the present dealloying leaves behind pure Cu on the entire surface. Similar color changes were also observed after immersion in 0.5 M, 0.1 M, and 0.05 M HF solutions.

Figure 2 shows the SEM image and corresponding elemental distribution mappings of the sample. Half of the surface area of the sample was immersed in 1 M HF solution for 300 s for the SEM-EDS study. The boundary or crack between the as-quenched area and the HF treated area originated from the large volume reduction of the HF treated area. Compared to the as-quenched area, the Cu concentration increased, and elemental Zr and Ti were negligible in the HF treated area. To further investigate the selective leaching of Zr and Ti, ICP mass analysis was performed by immersing the sample in 0.1 M HF solution for 1200 s. The remaining Zr and Ti elements were 0.25 and 0.036% in mass, respectively.[8] These results indicate that Zr and Ti were almost completely leached under the corrosion conditions using a HF solution. The other HF solutions displayed similar SEM-EDS maps.

Figure 3 shows the XRD patterns for the as-quenched ribbon and the samples after immersion for 300 s in 1 M, 0.5 M, 0.1 M, and 0.05 M HF solutions. For the as-quenched ribbon, diffraction pattern peaks from a crystalline phase were not detected (a typical amorphous pattern). After immersion in 0.05 M HF solution, the Cu phase was identified with the amorphous pattern. After immersion in

0.1 M HF solution, the intensity of the Cu peak increased, and a CuO_2 phase appeared. For 0.5 M and 1 M HF solutions, the amorphous pattern disappeared. Only Cu and CuO_2 were identified. Oxidation of Cu may be promoted by exposure to air at room temperature after washing and drying the samples. Additionally, a cross-sectional inspection revealed that dealloying induced a Cu phase evolution, which began from the sample surface and penetrated into the interior, leaving a well-defined interface between the Cu layer and metallic glass. The thickness of the Cu layer increased as the HF concentration increased, i.e., the rate of dealloying increased with HF concentration. Employing 0.1 M HF solution, the entire thickness of the ribbon was etched within 1200 s. Hence, the estimated etching rate was ~20 nm/s at room temperature.

Figure 4 shows magnified SEM images of the sample surfaces after immersion in 0.05 M, 0.1 M, and 0.5 M HF solutions for 300 s, respectively. The surface morphology differed significantly according to the HF concentration. Similar to bicontinuous nanoporous structures dealloyed from crystalline alloy systems,[1–6] treating the sample with 0.05 M HF solution gave a nanoporous structure. A denser surface was obtained by treating with 0.1 M HF solution. In 0.5 M HF solution, a vigorous dealloying reaction immediately commenced with strong H_2 bubbling from the sample surface, and a relatively rough surface, including large grains (~50–100 nm), were observed after immersion. The grains of the resulting Cu film cannot be fully characterized by the
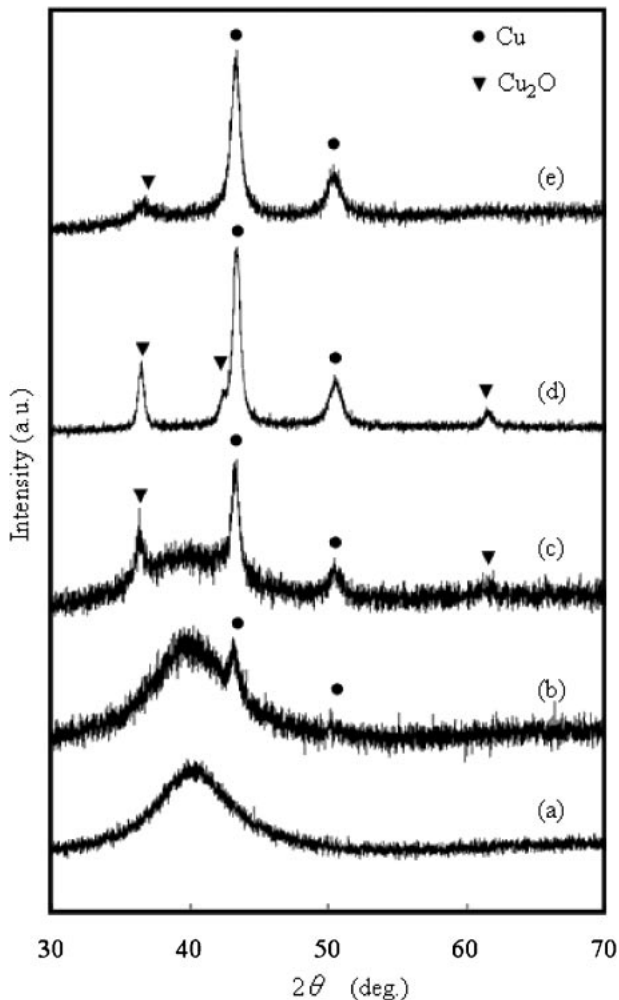
Fig. 3 XRD patterns for (a) the as-quenched sample, (b) the samples after immersion for 300 s in 0.05 M, (c) 0.1 M, (d) 0.5 M, (e) 1.0 M. HF.

Fig. 4 SEM micrographs of surfaces of the HF treated ribbons. (a) after immersion for 300 s in 0.5 M, (b) 0.1 M, (c) 0.05 M.

present SEM resolution, but it is suggested that the average crystalline size of the resulting Cu increased slightly with HF concentration because the half-width of the XRD peaks slightly sharpened as the HF concentration increased, as shown in Figs. 3(a), 3(b), and 3(c). The estimated crystalline size of the dealloyed Cu after 0.5 M HF immersion was about 12 nm, indicating that the volume fraction of the large grains (Fig. 4(a)) is very low.

Although the present dealloying process has yet to be fully comprehended, it may be analogous to the model for Ag-Au alloy system proposed by Erlebacher et al.[1,2] The model involves a type of "interfacial phase separation" in which the more noble atoms (Au for Ag-Au alloy) not dissolved from the alloy/electrolyte interfaces tend to cluster and form islands, rather than be uniformly distributed over the surface. This process continuously opens up regions of virgin alloys, and allows the dissolution front to penetrate through the bulk of the alloy. At the alloy/electrolyte interface, diffusion of the more noble atoms (Au) is extremely fast compared to surface diffusion in other environments, although this is a relatively unappreciated phenomenon.[5] Thus, structural evolution during dealloying depends only on interfacial kinetics. In the present case, the surface structure of the resulting Cu film was drastically changed by increasing HF
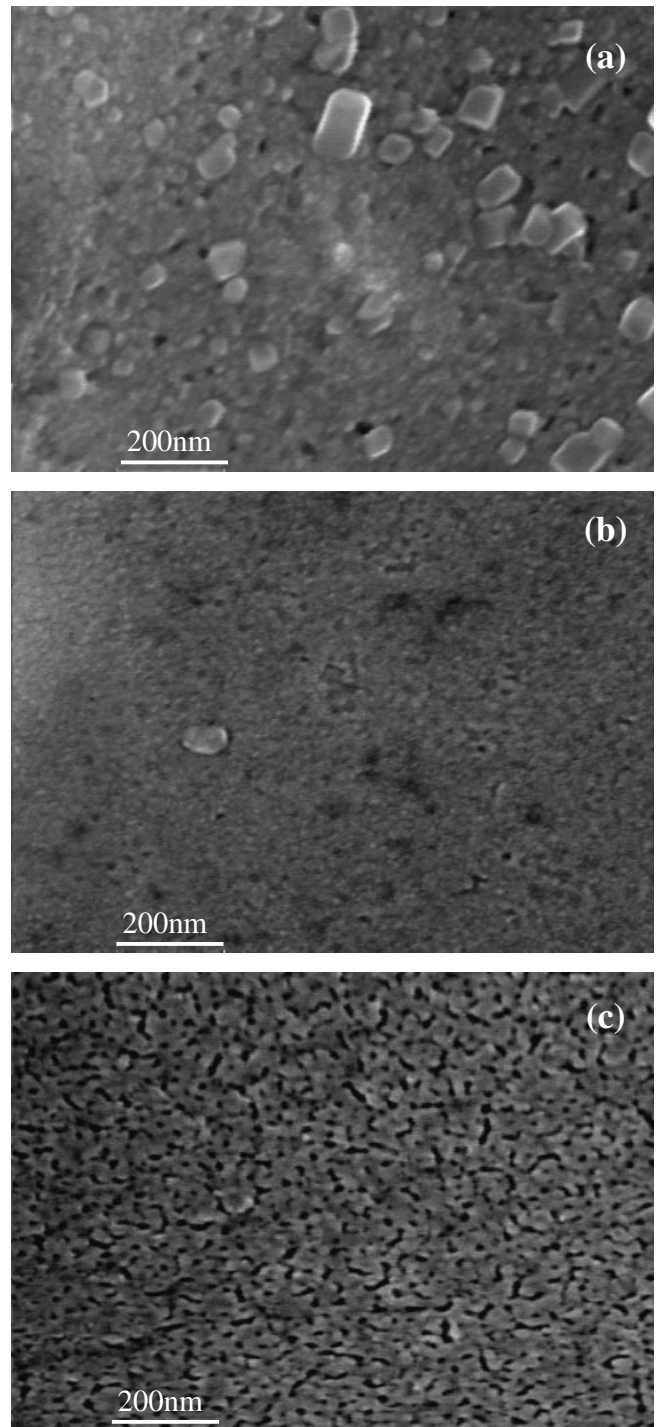
concentration, indicating that the rate of dealloying of the metallic glass significantly influences the interfacial kinetics. Details of the interfacial kinetics associated with various HF concentrations will be reported in the near future.

HCl is another important halide solution. However, employing HCl solutions do not result in the relatively rapid dealloying behavior observed with HF solutions. We have performed an immersion test using 1 N HCl solution for 24 h, but the results are not shown here. In optical microscopy, many pits, which measured up to about 50 μm, were observed, and the Cu phase was detected only in the pit

regions. These results are similar to those observed in Cu-Zr metallic glasses.[16] Cl^- ions in solution have been associated with the dissolution behavior in Cu due to the formation of the slightly soluble CuCl and soluble $CuCl^{2-}$.[17] In our HCl treatment, dissolution of Cu was also observed. Under free corrosion conditions, effective selective leaching of Zr and Ti was not observed with HCl solution.

4. Conclusion

Dealloying a ternary $Cu_{60}Zr_{30}Ti_{10}$ metallic glass was investigated under free corrosion conditions using HF solutions. Selective leaching of Zr and Ti occurred upon immersing the glassy alloy into HF solution, which resulted in the formation of nanostructured crystalline Cu at room temperature. Increasing the HF concentration increased the thickness of the Cu layer formed, i.e., the rate of dealloying increased with HF concentration. With 0.1 M HF solution, the entire thickness of the ribbon was etched within 1200 s, indicating an etching rate of $\sim$20 nm/s at room temperature. Additionally, the HF concentration strongly influenced the resulting microstructures of Cu. Thus, dealloying metallic glasses may be a possible candidate for developing nanostructured metals.

Acknowledgements

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