

# Hierarchical porous copper materials: fabrication and characterisation

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Hierarchical porous copper bulk can be fabricated through chemical dealloying of porous CuAl intermetallics under free corrosion conditions. The obtained precursor porous CuAl intermetallics and as-dealloyed hierarchical porous copper were characterised using X-ray diffraction, a field-emission scanning electron microscope and energy dispersive X-ray spectroscopy. It was found that the hierarchical porous copper can be easily prepared by this method. The dealloying solution will dramatically influence the morphology of the resultant hierarchical porous materials. As a result, trimodal porous copper composite material and bimodal porous copper can be achieved after being dealloyed in NaOH and HCl solutions, respectively. Therefore, the mechanisms of the evolution of hierarchical pores structure are also discussed.

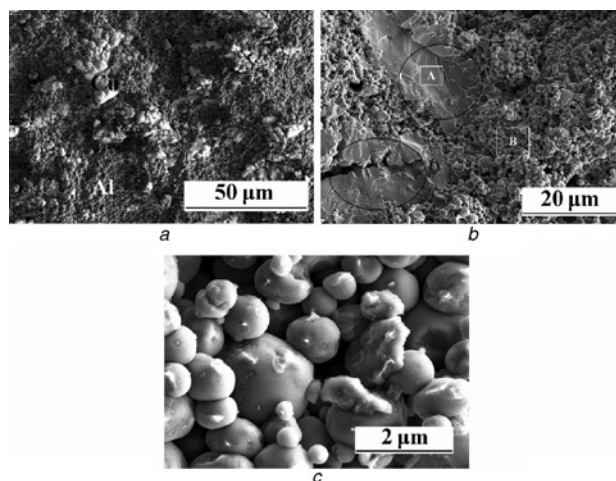
**1. Introduction:** Nanoporous metals (NPMs) are promising materials for various applications owing to their attractive properties including very low density, large surface area, high sensitivity and so forth [1–3]. Recently, most of the reported NPMs were fabricated by the dealloying method, which refers to the selective dissolution of one or more components out of an alloy [4]. Investigations of NPMs were mainly focused on synthesis porous metals with homogeneous pore size distributions, whereas studies on hierarchical porous materials are scant. Porous metal with multimodal pore size have many advantages in some specific applications, such as microfluidic-based sensors [5] and the applications with gas flow [6]. In the former situation, the larger sized pores provide an effective path by which gas or liquid can easily pass through, whereas the highly porous channel walls can achieve fast response time and high sensitivity because of their high surface area. Thus, the construction of a hierarchical nanoporous architecture may be a key technology for the functional development of materials and/or devices, exhibiting features of large porosity channels and as well as high surface areas.

A two-step dealloying strategy was reported to make free-standing noble metal membranes with a typical bimodal pore size distribution by performing an annealing/redealloying cycle on Ag-plated nanoporous gold [5]. Obviously, this method would prolong the production time and also increase the cost. Liu *et al.* [7] developed a one-pot route to synthesise nanoporous copper (NPC) with controlled hierarchical pore size distributions by chemical dealloying of melt-spun Al–35Cu alloy in an NaOH solution at an elevated temperature. However, the pore size of the NPC is limited to several hundred nanometres and is difficult to process. The Kirkendall effect and reactive synthesis have been used to, produce porous intermetallics or a hollow structure when large diffusion rate discrepancies exist between components in the alloy system, such as FeAl and TiAl [8, 9]. Therefore, it can be expected theoretically that hierarchical pore size distribution in NPMs could be achieved through dealloying the resultant porous intermetallics prepared by the above-mentioned method. In this Letter, we report a facile technique through a two-step strategy to fabricate free-standing porous metal bulk materials with a hierarchical porous architecture through firstly preparing porous CuAl intermetallics by powder metallurgy and then dealloying. Moreover, so far little research has dealt with the fabrication of porous CuAl intermetallics through powder metallurgy because of their minor diffusion rate discrepancies, and this is worth investigating.

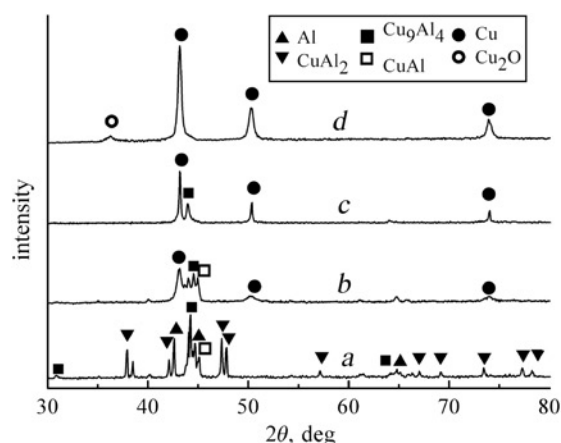
**2. Materials and methods:** The raw materials used in this study were commercially available Cu (>99.9%, –30 µm) and Al (>99.9%, –2 µm). To achieve ultimate compositions of CuAl, Cu and Al powders with the atom ratio of Cu:Al = 4:6 were blended in acetone and dried at room temperature. No lubricant was added in the mixture in order to maintain a sound metal–metal contact to enhance the atomic interdiffusion. The compact discs were cold pressed (200 MPa) and sintered in a silica tubular furnace under Ar atmosphere. The sintering was carried out at temperatures of 400°C for 120 min. To maintain the original shape of the compact discs, the heating rate of 2°C/min was used [10]. The resultant porous CuAl intermetallics were then dealloyed in an HCl aqueous solution and an NaOH aqueous solution under free corrosion at room temperature, respectively. The corrosion process was terminated when no bubbles existed in the solution. After dealloying, the samples were rinsed with distilled water and dehydrated alcohol. The as-dealloyed samples were kept in a vacuum chamber to avoid oxidation. The samples were observed with a field-emission scanning electron microscope (FESEM, XL30SFEG) equipped for energy dispersive X-ray spectroscopy (EDS) for elemental analyses. X-ray diffraction (XRD) patterns were recorded by an XRD(DX-2000).

**3. Results and discussion:** Typical microstructures of CuAl compacts before and after sintering are shown in Fig. 1. From Fig. 1a, image analysis showed that the Cu particles were distributed evenly in the Al matrix after mixing. Both a porous structure (Fig. 1c) and a monolithic structure (highlighted by the circle in Fig. 1b) can be observed in Fig. 1b. different from porous TiAl and FeAl [8, 9], only a porous structure can be observed after sintering. The EDS spectrum shows that the Cu/Al ratio of the porous structure (B) is about 0.5, which is comparable with the CuAl<sub>2</sub> phase. However, the Cu/Al ratio of the monolithic structure (A) is about 1. As seen in Fig. 1c, many pores are connected, which form a bicontinuous interpenetrating particle-channel structure. The fundamental reason for the formation of the open pores is that the atomic diffusion would preferentially take place in grain boundaries [11].

Fig. 2 shows XRD patterns of porous CuAl intermetallic and as-dealloyed samples. From Fig. 2a, CuAl, Cu<sub>9</sub>Al<sub>4</sub>, CuAl<sub>2</sub> and Al phases are identified. CuAl, Cu<sub>9</sub>Al<sub>4</sub> and Cu can be identified in the as-dealloyed samples from the 0.1 M NaOH solution (Fig. 2b). However, in contrast, Cu<sub>9</sub>Al<sub>4</sub> and Cu remained in the sample after being dealloyed in a 1 M NaOH solution. CuAl can



**Figure 1** Cross-sectional view of CuAl compacts  
*a* Green compact  
*b* Sintered at 400°C and 120 min  
*c* Porous structure in *b*



**Figure 2** XRD patterns of porous CuAl intermetallic and as-dealloyed samples  
*a* Porous CuAl intermetallic  
*b* Dealloyed in 0.1 M NaOH solution  
*c* Dealloyed in 1 M NaOH solution  
*d* Dealloyed in 0.1 M HCl solution

be dealloyed in NaOH solution with high concentration. From Fig. 2*d*, a face-centred cubic (fcc) Cu phase can be identified in the as-dealloyed samples from HCl solution. It should be noted that a Cu<sub>2</sub>O peak is detectable in Fig. 2*d*, indicating that the oxidation took place during and/or after the formation of the porous structure through chemical dealloying of Al–Cu alloys, especially in HCl solution.

It is well known that ideal bicontinuous nanoporous structures are obtained from binary alloys with a single-phase solid solubility across all compositions by chemical/electrochemical dealloying [12]. If multiple phases exist in an  $A_xB_{1-x}$  alloy (here, *A* is a less noble element and *B* is a more noble element), typically only the *A*-rich phase would be dealloyed [13]. The present results demonstrate that both CuAl<sub>2</sub>, Cu<sub>9</sub>Al<sub>4</sub> and CuAl can be fully dealloyed in HCl solution. Only the CuAl<sub>2</sub> phase can be dealloyed in 0.1 M NaOH solution. However, the CuAl phase can be dealloyed in NaOH solution with a high concentration. Accordingly, different microstructures of a porous structure can be expected after being dealloyed in different solutions.

Fig. 3 shows FESEM images of hierarchical porous copper after being dealloyed in NaOH solution with different concentrations.

As shown in Fig. 3, the original porous structure of porous CuAl intermetallics can be preserved after dealloying in NaOH solution and an obvious hierarchical porous structure can be observed from Figs. 3*c* and *d*. However, the monolithic structure cannot be eroded. Average ligament diameters of the pore and ligament sizes were increased after being dealloyed in 1 M NaOH solution than in 0.1 M NaOH solution, which were detected by FESEM observation (Figs. 3*e* and *f*). The EDS results (Figs. 3*g* and *h*) revealed that more Al remained after being dealloyed in 0.1 M NaOH solution, which was in accord with the XRD result. Therefore, it is reasonable to confirm that this special morphology originates from the CuAl phase in the precursor porous CuAl intermetallics. Simultaneously, some micropores with pore size of ~20 nm can be observed.

Fig. 4 shows FESEM images of NPC dealloyed in 0.1 M HCl solution. The porous structure of the resultant materials with a length scale of ~20 μm is shown in Fig. 4*a*. Fig. 4*b* is a magnification image of the porous wall. A homogeneous, ligament-pore structure with a length scale of  $75 \pm 5$  nm can be observed. In addition, the EDS (Fig. 4*c*) results demonstrated that all Al atoms were removed after dealloying.

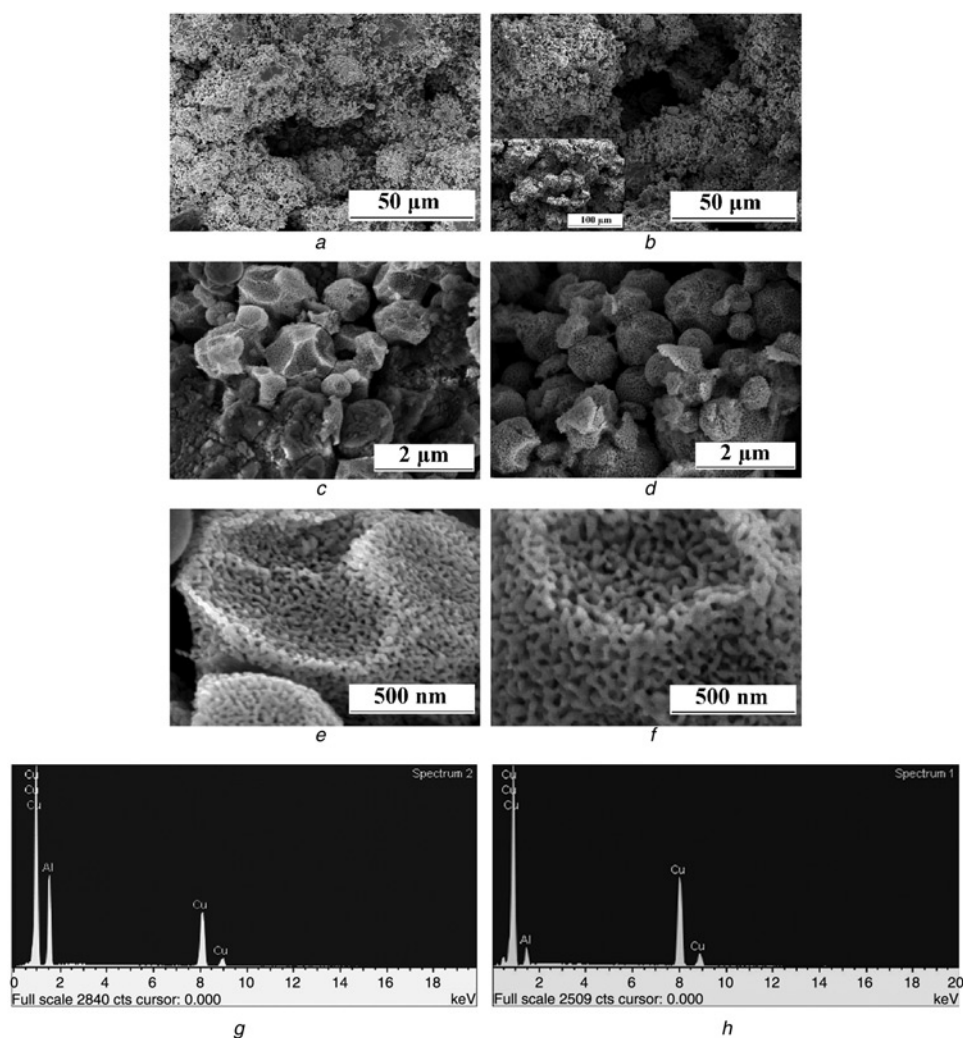
Fig. 5 shows the schematic diagram of a typical morphological evolution of hierarchical porous copper bulk. Interdiffusion took place between Al and Cu powders during the powder sintering process. Cu atoms were easily diffused to Al and it was easier for CuAl<sub>2</sub> to nucleate at the Cu/Al interfaces than Cu<sub>9</sub>Al<sub>4</sub> [14]. However, Cu atoms diffusion to Al was blocked off by CuAl<sub>2</sub> [14]. Thus, the Al phase was still retained in porous CuAl intermetallics according to Fig. 2. As a result, pore sizes of about 20 μm were left in the bulk after being dealloyed in both NaOH and HCl solutions. In addition, because of the low sintering temperature of about 400°C, the morphology of the original Al powder was retained after sintering and interstitial pores in hundreds of nanometres to several micrometres were formed.

Dealloying solutions dramatically influenced the pore structure of resultant materials [15]. According to Ying and Zhang's [14] report, the adsorption of chloride ion (Cl<sup>−</sup>) can greatly enhance the surface diffusion of Cu atoms along the alloy/solution interfaces during the dealloying of the Al–Cu alloys and this leads to the formation of coarse ligaments/channels in the resultant NPC. Based on the surface diffusion controlled coarsening mechanism, the  $D_s$  of Cu atoms along alloy/solution interfaces can be estimated by the equation [16, 17]

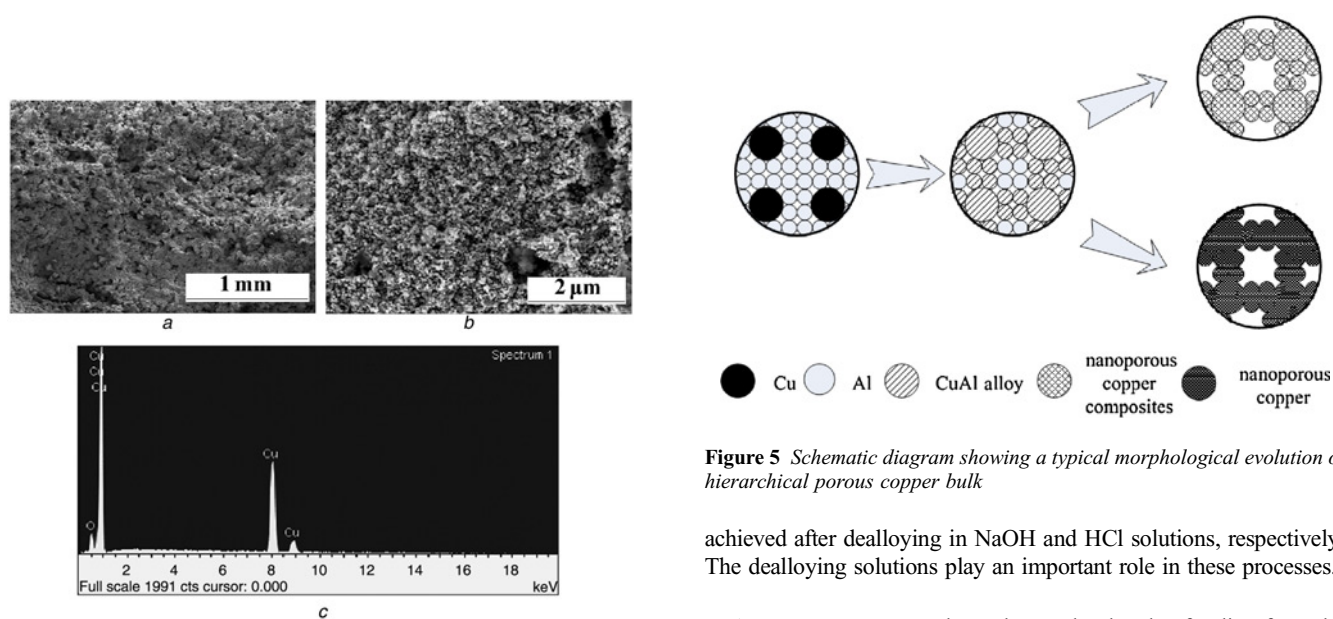
$$D_s = \frac{[d(t)^4]kT}{32\gamma t\alpha^4}$$

where  $k$  is the Boltzmann constant ( $1.3806 \times 10^{-23}$  JK<sup>−1</sup>),  $\gamma$  is the surface energy ( $1.79$  J m<sup>−2</sup>) [19],  $d(t)$  is the ligament size at the dealloying time  $t$ ,  $\alpha$  is the lattice parameter of Cu ( $3.6153 \times 10^{-10}$  m) and  $T$  is the dealloying temperature. According to the parameters of the present study, we can estimate the diffusion coefficient of copper in HCl solution is about 80 times more than that in NaOH solution. On this point, the original structure of porous CuAl intermetallics can be retained after dealloying in NaOH solution (from Fig. 3) and a trimodal porous structure can be prepared. At the same time, the diffusion coefficient of copper in 1 M NaOH solution is about two times more than that in 0.1 M NaOH solution, which is the main reason that the CuAl phase that was eroded after dealloying in 1 M NaOH solution rather than in 0.1 M NaOH solutions.

**4. Conclusions:** Hierarchical porous copper can be fabricated by a two-step strategy through preparing porous CuAl intermetallics firstly by powder metallurgy and then chemical dealloying. The strategy developed here has the advantages of fabricating the hierarchical porous structure with complicated shapes, and it is generally facile and time-saving to implement. Trimodal porous copper composite material and bimodal porous copper can be



**Figure 3** FESEM images and EDS analyses of hierarchical porous copper  
Dealloying was conducted  
*a, c, e* and *g* 0.1 M NaOH solution  
*b, d, f* and *h* 1 M NaOH solution



**Figure 4** FESEM images and EDS analyses of hierarchical porous copper  
Dealloying was conducted in 0.1 M HCl solution

**Figure 5** Schematic diagram showing a typical morphological evolution of hierarchical porous copper bulk

achieved after dealloying in NaOH and HCl solutions, respectively. The dealloying solutions play an important role in these processes.

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## 6 References

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