Hierarchical nanoporous material by liquid metal dealloying of additively manufactured precursor

Nanoporous materials possessing large surface area and high electrical conductivity demonstrated advantages for various energy applications. The efficiency of these materials would be greatly improved through creating regular microscale channels for improved mass transport. Here, we propose an approach for the synthesis of nanoporous materials with regular microscale channels via a combination of additive manufacturing and liquid metal dealloying.

Liquid metal dealloying is a metallurgical method for the synthesis of open porous materials established by Kato and co-workers [1-2]. Liquid metal dealloying implies selective removal of one or more elements from a multielement precursor material by a reactive liquid metal during its contact with this liquid metal. The remaining elements of the precursor material rearrange themselves into an open porous structure.

The selection of materials for liquid metal dealloying is based on the free energy change during mixing of elements $\Delta Gmix = \Delta Hmix - T\,\Delta Smix$, where $\Delta Hmix$ is the heat of mixing, $\Delta Smix$ is the entropy of mixing, and T is the absolute temperature. Usually, the entropy $\Delta Smix$ increases after mixing. So, from a thermodynamic point of view, if $\Delta Hmix < 0$, the $\Delta Gmix < 0$, and the mixing reaction can occur spontaneously. Thus, the precursor material should consist of elements having high positive and high negative heat of mixing $\Delta Hmix$ with liquid metal.

In this work, Inconel 718 alloy was selected for dealloying in liquid magnesium. The Inconel 718 mainly consists of Ni, Fe, Cr, Nb, and Ti elements. The heat of mixing $\Delta Hmix$ between Mg and Ni is negative. The heat of mixing $\Delta Hmix$ between Mg and each of the remaining elements is positive. Therefore, Ni will be dissolved into Mg during liquid metal dealloying. The remaining elements will be rejected by liquid magnesium and rearranged into an open porous structure.

The Inconel 718 samples consisting of strut structures and having regular porous channels were additively manufactured using a commercial selective laser melting set-up (Figure 1). Thereafter, the samples were subjected to liquid metal dealloying, namely immersed in liquid magnesium, to create nanoscale porosity in the strut structures. After dealloying, the evolved nanoscale pores were filled with magnesium. Magnesium was removed by chemical etching of the samples in 3M aqueous solution of nitric acid. Finally, the hierarchical porous samples were obtained.

Figure 2 shows the microstructure of the Inconel 718 samples struts after liquid metal dealloying. According to the microstructural analysis, the struts mainly consist of two nanoscale phases. These are FeCrNbTi-based and Mg-based phases. It has to be emphasized that the typical for the selective laser melting melt pool profiles remained after dealloying and are clearly distinguished as a bright contrast in the form of thin lines (Figure 2).

Fig. 1 shows additively manufactured Inconel 718 samples

The chemical etching of the dealloyed samples resulted in the formation of an open porous ligament structure typical for liquid metal dealloying. The size of ligaments is a few tens of nanometers (Figure 2). This is comparable with that of the recently reported nanoporous high-entropy alloys [2] and two orders of magnitude smaller as compared with the ligament size of dealloying-based porous Fe [3].

The hierarchical porous material synthesized in this study implies advantages for both functional and structural applications. In the case of functional applications, large pores enable efficient mass transport and small pores provide a high surface area. In the case of structural applications, the yield strength of the nanoscale ligaments typically reaches the theoretical strength of the material [2]. Thus, together with the low sample density due to a high fraction of pores, the hierarchical porous samples might possess significantly improved specific strength characteristics.

References

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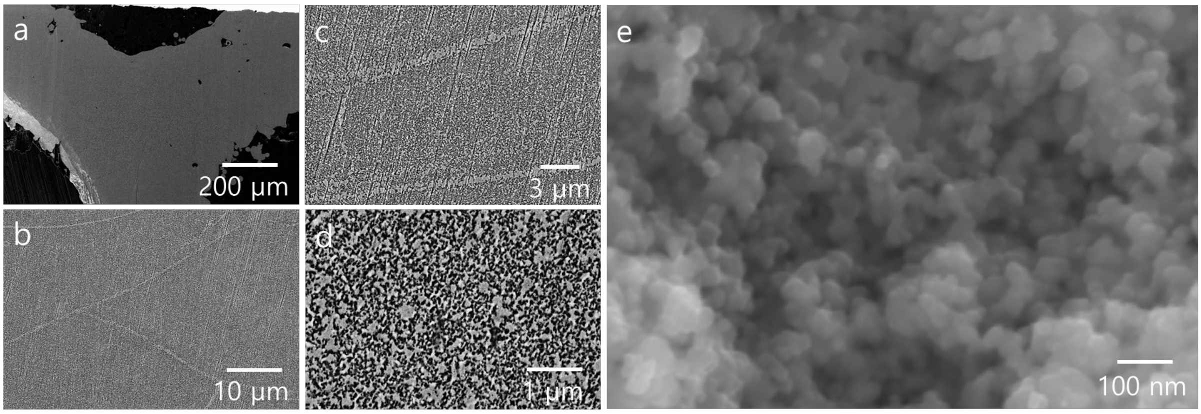

Fig. 2 Microstructure of additively manufactured Inconel 718 sample after liquid metal dealloying: (a) Joining of sample struts, (b-c) Melting pool profiles (bright lines), (d) Multiphase microstructure, and (e) Nanoporous structure after chemical etching of dealloyed samples

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