Investigation of Structure and Properties of Nanoporous Metals Formed by Liquid Metal Dealloying

Liquid metal dealloying (LMD) technique allows us to prepare fine porous materials with base metal elements, which is principally difficult by the conventional chemical dealloying techniques. In this study, mechanism of morphology formation during LMD was studied by SEM, XRD, EBSD and X-ray and electron tomography.

Nanoporous metals have attracted considerable attention for their excellent functional properties[1]. The most promising technique used to prepare such nanoporous metals is dealloying in aqueous solution. Nanoporous noble metals including Au have been prepared from binary alloy precursors[2]. The less noble metals, unstable in aqueous solution, are oxidized immediately when they contact water at a given potential so this process is only possible for noble metals. Porous structures with less noble metals such as Ti or Fe are highly desired for various applications including energy-harvesting devices[1]. To overcome this limitation, a new dealloying method using a metallic melt instead of aqueous solution was developed in Kato lab[3]. Dealloying in the metallic melt is a selective dissolution phenomenon of a mono-phase alloy solid precursor: one component (referred as soluble component) being soluble in the metallic melt while the other (referred as targeted component) is not. When the solid precursor contacts the metallic melt, only atoms of the soluble component dissolve into the melt inducing a spontaneously organized bi-continuous structure (targeted+sacrificial phases), at a microstructure level. This sacrificial phase can finally be removed by chemical etching to obtain the final nanoporous materials. Because this is a water-free process, it has enabled the preparation of nanoporous structures in less noble metals such as Ti, Ni, Si, Fe, Nb, Co and Cr[4].

In this study, researchers from IMR Japan and INSA Lyon France made collaboration to clarify the mechanism of morphology formation during LMD process by taking the advantage of material preparation technique of IMR and material characterization technique of INSA Lyon. In IMR, porous materials were elaborated by the LMD process and microstructure, phase, compositional change was studied. IN INSA Lyon, morphology of the porous materials was three dimensionally studied *in-situ* and *ex-situ* by using X-ray or electron tomography. The analyses were performed on the two typical porous materials, microporous Fe-Cr alloy and nanoporous Si that were promising materials for electrodes, catalysts, supports and filters.

(1) Porous Fe-Cr alloys[5]

The all samples used in this work were prepared in Kato lab., IMR, Japan. The $(Fe_{80}Cr_{20})_{30}Ni_{70}$, $(Fe_{80}Cr_{20})_{50}Ni_{50}$ and $(Fe_{80}Cr_{20})_{70}Ni_{30}$ precursors ingots were prepared and they were dealloyed 1h at 1093K in a Mg melt bath under a high-purity He atmosphere, which resulted in the formation of Fe-Cr/Mg bicontinous structure.

The selective etching step was carried out using highly concentrated nitric acid to dissolve the bath component of Mg, resulting in microporous $Fe_{80}Cr_{20}$. Porous sample obtained from $(Fe_{80}Cr_{20})_{30}Ni_{70}$, $(Fe_{80}Cr_{20})_{50}Ni_{50}$ and $(Fe_{80}Cr_{20})_{70}Ni_{30}$ precursor

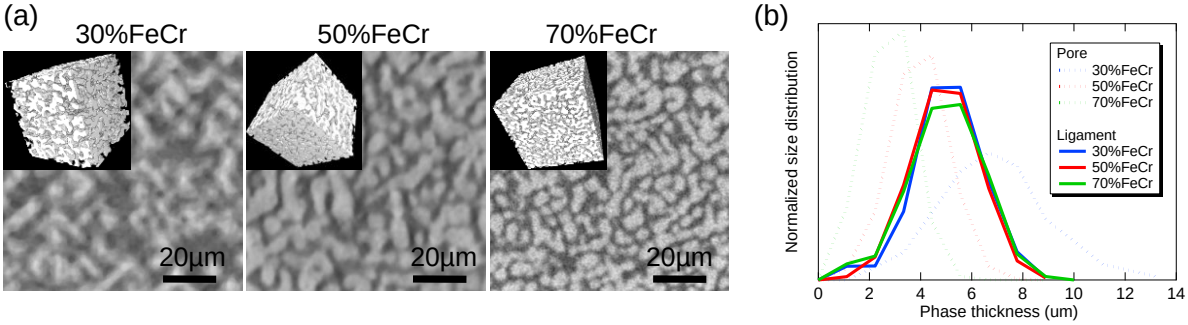

Fig. 1 (a)Images extracted from X-ray tomography scan and 3D view in inset (b) phase thickness distribution[5]

will be referred as respectively 30%FeCr, 50%FeCr and 70%FeCr. The morphology and microstructure of samples were characterized three dimensionally by X-ray tomography apparatus in MATEIS lab., INSA Lyon, France.

Figure 1(a) shows one reconstructed slice for each sample extracted from the reconstruction and a 3D in inset. Two phases are visible. The lighter phase corresponds to the Fe-Cr phase and the darker phase to the air. From these images morphological parameters can be extracted. Figure 1(b) presents the phase thickness distributions of the Fe-Cr and Air phases for all samples. The phases display a unimodal thickness distribution. The Fe-Cr phase thickness distribution are similar for all samples : i.e. ligaments size are independent of precursor composition. Because Fe-Cr phase thickness distribution are similar and materials density are different, pores distributions must be dependent of precursor composition as shown on Figure 1(b). The average ligaments size is 4.8±0.3µm for 1h dealloying at 1093K and this value depends only of dealloying time and temperature.

(2) Nanoporous Si for lithium ion battery[6]

Si is one of the promising material for Lithium ion battery anode. It has theoretical capacity 10 times larger than that of currently used carbon based anode. However, Si anode experiences large volume change upon Li intercalation and self-fractured, resulting in poor cyclic performance. In the previous work, it was found that nanoporous structure greatly improved cyclic performance of Si anode. For understanding the reason for the improvement, the structure of nanoporous Si was analyzed by using electron tomography. The porous Si was prepared by LMD process employing Mg_2Si precursor and Bi metal bath. Precursor was immersed in Bi bath at the designed temperature and time. The representative 3D view of the resulting nanoporous Si is shown in Fig. 2. The 3D images confirm that the aggregates are made of an entanglement of nanorods with a specific surface around 46 m^2/g and a large pore volume fraction representing almost half of the total volume of the particles. The Si nanorods systematically exposing the {111} family crystallographic planes at their facets. These are important features because the large porous volume can provide sufficient space for the silicon expansion preventing the fracture or cracking of the Si particles during the lithiation process.

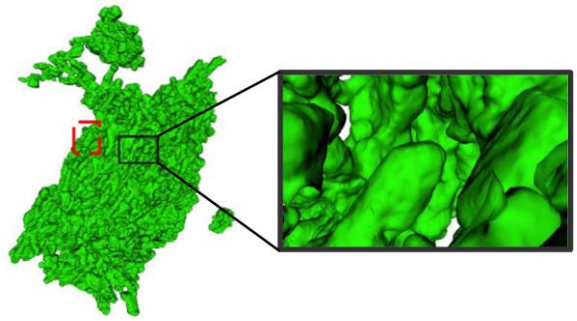

Fig. 2 3D view of nanoporous Si material prepared by LMD treatment using Mg_2Si precursor and Bi metal bath[5].

(3) Metallic glass as a precursor of LMD

For LMD precursor, homogeneous single phase solid solution is required because composition fluctuation in the precursor usually results in inhomogeneous porous structure. However, solid solution phase satisfying LMD reaction condition does not always exist in the equilibrium phase diagrams. Metallic glass, a non-equilibrium metal with disordered atomic configuration, is known to have long range structural and compositional homogeneity which can be a precursor for LMD process. In IMR Kato lab., Ti-Zr-Cu-Ni-Pd bulk metallic glass precursors were prepared and it will be used for measuring X-ray tomography *in-situ* in INSA Lyon MATEIS lab., for further understanding the morphology evolution mechanism of the LMD process.

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Keywords: porosity, foam, morphology
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