Porous metal-intermetallic composites by liquid metal dealloying

Nanoporous metals with a bicontinuous structure, produced by liquid metal dealloying (LMD), are regarded as promising materials for energy-related applications because of their good electrical conductivity, mass transportability, and bulk specimen formability by the top-down process, that are distinct from other nanomaterials. Here, we explore synthesis of porous metal-intermetallic composites as promising hybrid battery electrode materials combining open porous metallic collector and TiSi-based active material.

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 multi-element 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, four precursor $(TiCu)_{100-x}Si_x$ at% alloys, where x=1, 5, 10, 20 at%, have been synthesized using an arc-melter.

The heat of mixing $\Delta Hmix$ between both couples Mg and Cu (-3 kJ/mol) as well as Mg and Si (-26 kJ/mol) is negative. The heat of mixing $\Delta Hmix$ between Mg and Ti (16 kJ/mol) is positive. Therefore, it is expected that Cu and Si will be dissolved into Mg during liquid metal dealloying. The remaining Ti is expected to be rejected by liquid magnesium and rearranged into an open porous structure. However, our experimental results demonstrate that Si in the presence of Ti is rejected by Mg. This is likely due to a very high negative enthalpy of mixing between Ti and Si (-66 kJ/mol).

The as-arc-melted $(TiCu)_{50-x}Si_x$ precursor samples were cut into 1 mm thick samples which were subjected to liquid metal dealloying, namely, immersed in liquid Mg (Fig. 1). The dealloying conditions are 1073 K and 20 min. After liquid metal dealloying, the evolved pores were naturally filled with magnesium. Mg was chemically removed by immersing as-dealloyed samples into 3M aqueous solution of nitric acid for 5 h (Fig. 1).

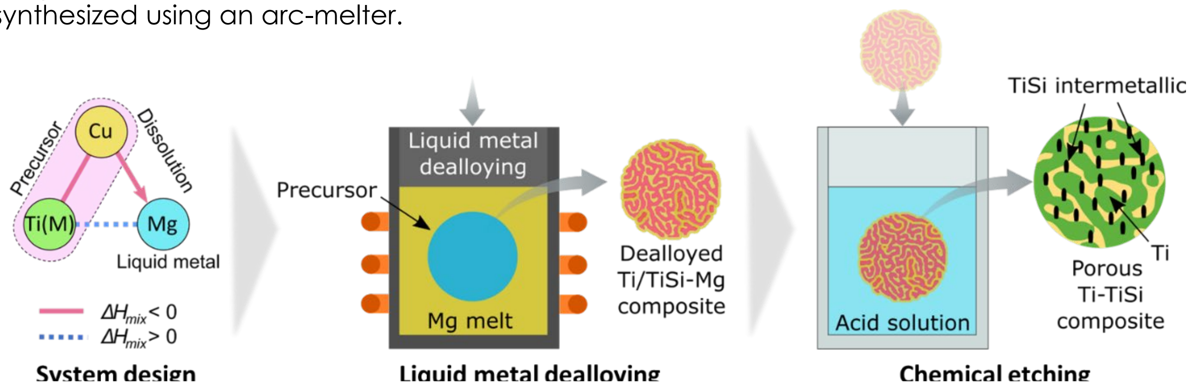

Fig. 1 Schematic illustration of the synthesis of porous metal-intermetallic composites by means of liquid metal dealloying and chemical etching.

Fig. 2 shows the microstructure of the $(TiCu)_{50-x}Si_x$ at% samples after liquid metal dealloying and chemical etching. According to the microstructural analysis, the porous samples mainly consist of two phases. These are Ti and TiSi-based intermetallic phases. The TiSi-based phase contains about 30 at% of Si as detected by EDX-SEM. The volume fraction of the TiSi-based phase significantly increases with the increasing Si concentration in the precursor alloys. At x=1 at%, the microstructure of the open porous metal-intermetallic composite consists of µm-scale Ti ligaments covered by TiSi-based ligaments of a few hundred nanometers.

At x=5 at%, large crystals of the TiSi-based intermetallic phase, approximately 10 µm in cross-section, are observed instead of nm-scale TiSi-based ligaments. At x=10, 20 at%, the volume fraction as well as size of those TiSi-based crystals increases. Specifically, at x=20 at%, the crystals reach a few tens of µm in cross section. Furthermore, the faceting of the TiSi-based crystals becomes more pronounced.

References

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[2] S.-H. Joo et al. Adv. Mater. 6 (2020).

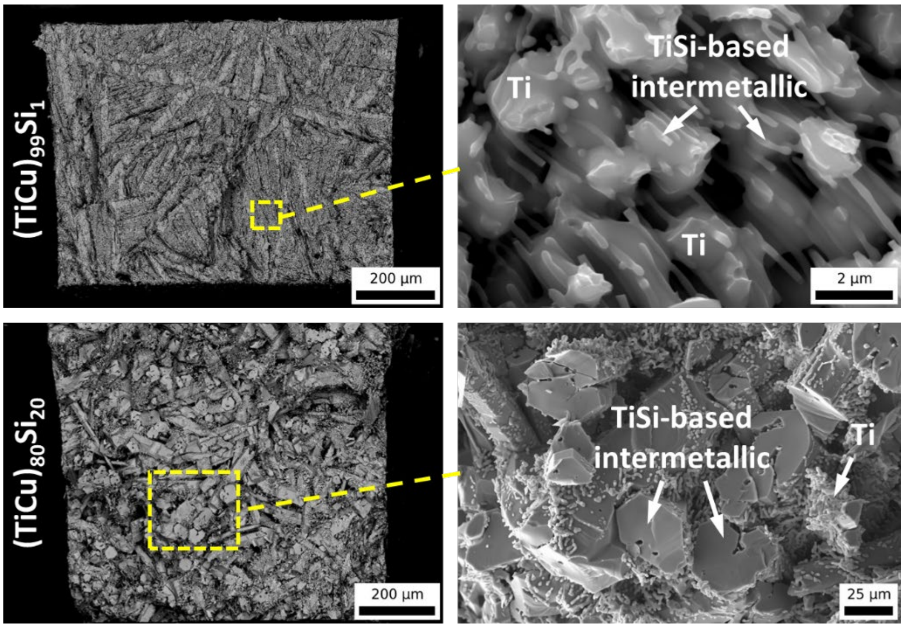

Fig. 2 Secondary electron micrographs of porous Ti-TiSi composites obtained from $(TiCu)_{99}Si_1$ (top panel) and $(TiCu)_{80}Si_{20}$ (bottom panel) at%.

Keywords: Porosity
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