Science Bulletin 63 (2018) 1173–1174

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Research Highlight

Nanosized Cu-Li glass

Peng Gao [a,b,c]

[a] International Center for Quantum Materials, Peking University, Beijing 100871, China
[b] Electron Microscope Laboratory, School of Physics, Peking University, Beijing 100871, China
[c] Collaborative Innovation Centre of Quantum Matter, Beijing 100871, China

Amorphous metallic alloy (also known as metallic glass) was firstly discovered in the 1960s as a "young" member of the amorphous material family [1]. Their unique metastable disordered structure imparts metallic glasses many fascinating properties and features such as high elasticity and high strength, excellent wave-absorption ability and ultralow elastic moduli [2,3]. In general, the formation of an amorphous alloying phase requires a relatively large negative heat of mixing between the constituent elements, such that they have got the tendency to spontaneously alloy on atomic scale due to the reduction of Gibbs free energy upon intermixing [4]. The systems with heat of mixing being near zero or even positive, however, is an "immiscible" systems, for which the formation of the amorphous alloying phase is difficult to achieve [5]. Cu-Li is a well-known immiscible system, which means that Cu and Li have little tendency to spontaneously alloy on atomic scale in thermodynamic equilibrium [6]. It is for this reason that Cu foils are widely used as the anodic current collectors in worldwide lithium ion batteries, to ensure that the current collector does not undergo electrochemical lithiation during battery cycling [7,8]. However, in a very recent in-situ transmission electron microscopy (TEM) study [9], Dr. Muhua Sun, Prof. Wenlong Wang and Prof. Xuedong Bai from the Institute of Physics, Chinese Academy of Sciences, show that ultrafine Cu nanocrytallines can, unexpectedly, be electrochemically lithiated to form amorphous alloying phases (Fig. 1).

The researchers constructed a nanoscale Li/Li_2O/CuO solid-state electrochemical cell inside TEM with a single CuO nanowire as the working electrode. The electrochemical lithiation of CuO first results in the formation of ultrafine Cu nanocrystals ($CuO + Li^+ + e^- \rightarrow Cu + Li_2O$) with sizes centered on 2–5 nm regions, which are uniformly dispersed in the insulating Li_2O matrix to form percolation conductive channels. With further lithiation, the newly generated ultrasmall Cu nanoparticles undergo solid-state amorphization reaction to form amorphous $CuLi_x$ nanoalloys ($Cu + Li^+ + e^- \rightarrow CuLi_x$). Based on in-situ TEM observations, the detailed nanocale dynamics and kinetic behaviors of Cu-Li solid-state amorphization are revealed.

The occurrence of the electrochemical alloying and amorphization in immiscible Cu-Li binary system can be understood by the size effect. For ultrasmall Cu nanocrsytals, a substantial increase in surface energy will significantly enhance the reactivity, which triggers the formation of a $CuLi_x$ alloying phase. It is the nanoscale size effect that constitutes the thermodynamic basis for driving the electrochemical lithiation and amorphization processes in such an immiscible system, while the heat of mixing is no longer the decisive factor. The critical size of Cu nanoparticles is measured to be ~6 nm, above which Cu cannot alloy with Li. In addition, the "dealloying" by electron beam irradiation was also observed, suggesting that the amorphization process of Cu-Li alloy is intrinsically reversible.

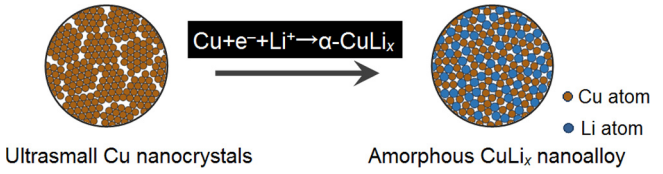

Fig. 1. (Color online) Schematic diagram showing the electrochemical lithiation of ultrasmall Cu nanocrsytals to form amorphous $CuLi_x$ alloys.

Amorphous alloying in the immiscible Cu-Li system gives us an important clue to understand the thermodynamic behavior of the solid-state reaction via non-equilibrium process, especially in those nanoscale systems with pronounced size effect. In addition, this study fully exploits the advantages of in-situ TEM observations, i.e., real-time with millisecond temporal resolution, atomic-scale spatial resolution, and capability to correlate the structure and properties at nanometer scale. Such state-of-the-art methodology provides a truly unique and powerful tool to analyze, with unprecedented details, the characteristics of solid-state phase transformations not only in the battery field but also in fields of solid-state physics and chemistry with respect to material processing, catalysis, ionic conductors, phase-change, and dielectric-based resistive memories.

Conflict of interest

The author declares that he has no conflict of interest.

E-mail address: p-gao@pku.edu.cn

https://doi.org/10.1016/j.scib.2018.08.005

References

[1] Klement W, Willens RH, Duwez POL. Non-crystalline structure in solidified gold-silicon alloys. Nature 1960;187:869–70.
[2] Wang W. Bulk metallic glasses with functional physical properties. Adv Mater 2009;21:4524–44.
[3] Chen M. Mechanical behavior of metallic glasses: microscopic understanding of strength and ductility. Annu Rev Mater Res 2008;38:445–69.
[4] Schwarz RB, Johnson WL. Formation of an amorphous alloy by solid-state reaction of the pure polycrystalline metals. Phys Rev Lett 1983;51:415–8.
[5] Ma E. Alloys created between immiscible elements. Prog Mater Sci 2005;50:413–509.
[6] Li D, Fürtauer S, Flandorfer H, et al. Thermodynamic assessment of the Cu-Li system and prediction of enthalpy of mixing of Cu-Li-Sn liquid alloys. Calphad 2016;53:105–15.
[7] Fan XY, Ke FS, Wei GZ, et al. Sn-Co alloy anode using porous Cu as current collector for lithium ion battery. J Alloys Compd 2009;476:70–3.
[8] Lu LL, Ge J, Yang JN, et al. Free-standing copper nanowire network current collector for improving lithium anode performance. Nano Lett 2016;16:4431.
[9] Sun MH, Wei JK, Xu Z, et al. Electrochemical solid-state amorphization in the immiscible Cu-Li system. Sci Bull 2018;63:1208–14.

Peng Gao is an assistant professor in the International Center for Quantum Materials and a deputy director of Electron Microscopy Laboratory, Peking University. He received his Bachelor of Physics from University of Science and Technology of China in 2005 and Ph.D. of Physics in the Institute of Physics, Chinese Academy of Sciences in 2010. Before he joined in Peking University at 2015, he worked in University of Michigan, Brookhaven National Laboratory, and The University of Tokyo. His primary research interest is characterization of low dimensional materials and devices through electron microscopy and spectroscopy, including in situ techniques, quantitative image analysis, and electron energy loss spectroscopy.