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Microstructure and Crystallographic Determination of Nanoporous Catalysts.

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Nanostructured materials, such as nanoporous catalysts with specific architectures, are currently being developed for energy applications. To improve the understanding of catalytic processes and optimize the catalytic reactions, information about the surface structure, composition and morphology of the active materials needs to be determined. Within the past few years, the dealloying method has been established as an efficient synthesis route towards high-quality monolithic nanoporous metals, which provides both compositional flexibility and a high level of morphological control. The mechanism of morphology evolution has been investigated in details for single-phase solid solution precursor alloys such as the AuAg system [1,2]. But the dealloying mechanism is less understood for more complex intermetallic starting alloys where both crystal structure and lattice constant change dramatically during dealloying.

Nanoporous copper (npCu) prepared by dealloying of CuZn alloys has recently been used as catalyst for ethanol hydrogenation [3]. In the present work, we studied the grain morphology of different CuZn alloys via Electron BackScatter Diffraction (EBSD) at different steps of the dealloying process. Polished $Cu_{50}Zn_{50}$ and $Cu_{20}Zn_{80}$ alloy disks were studied before and after dealloying in HCl solution. Samples were then rinsed in deionized water and dried under vacuum. EBSD experiments were performed on a FEI Helios Nanolab 660 with an EDAX EBSD system and TEAM software. The electron beam was set to 30 kV and 13-26 nA, with a working distance of approximately 11.5 mm. Fiducials were produced to analyze the same ROI before and after dealloying.

The selective etching of Zn during the dealloying process induces the presence of different macro- and microstructure which depend on alloy composition and on the presence of defects in the initial alloy. The dealloying kinetics was measured by weight loss during dealloying, SEM cross-sections and EDX maps before and after dealloying. During the dealloying, the formation of porosity induces roughness on the surface, as well as the presence of possible oxidation, two effects that hinder the acquisition of a decent EBSD pattern, as it is the case for Cu_5Zn_8 or $Cu_{20}Zn_{80}$. In other cases, it is however possible to analyze the crystallography by EBSD. Especially, our results show that crystal grain structure and orientation of intermetallic with a majority component of *bcc* $Cu_{50}Zn_{50}$ starting alloy is surprisingly preserved during dealloying in 5M HCl, despite the *bcc* $Cu_{50}Zn_{50}$ to *fcc* npCu phase transformation (**Figure 1**). This is the first EBSD study for nanoporous metals from an intermetallic phase to clearly show this behavior.

In addition to this, we studied nanoporous gold (npAu) catalysts for selective methanol oxidation. The ligament size of those samples is in the 50-70 m range, and the porosity of the materials corresponds to 70 %. The catalytic performance has been attributed to the presence of traces of silver (approximately

3 %), originating from the sample preparation by dealloying. In order to improve both the efficiency and selectivity, it is crucial to understand the behavior of Ag during the reaction and to control the micro- and nanostructure of the catalyst. Transmission-EBSD was used to study the nano-crystallography of npAu. Samples were prepared as “mono-ligaments thin” lamellae using the lift-out method. The electron beam was set to 30 kV and 6.4-13 nA, with a working distance of approximately 4 mm. The high resolution of the t-EBSD allows probing the crystallography of npAu down to 2 nm, which proves the monolithic nature of the sample down to the nanoscale.

As a conclusion, our EBSD study revealed the retention of grain structure and orientation for the $Cu_{50}Zn_{50}$ intermetallic phase, which may be of importance for catalytic systems since the reaction selectivity strongly depends on the local structure of the catalyst. By marking the region of interest with fiducials, we ensured reliability and reproducibility of the backscatter experiments. We provide new insights for improved models of dealloying from complex alloy systems [4].

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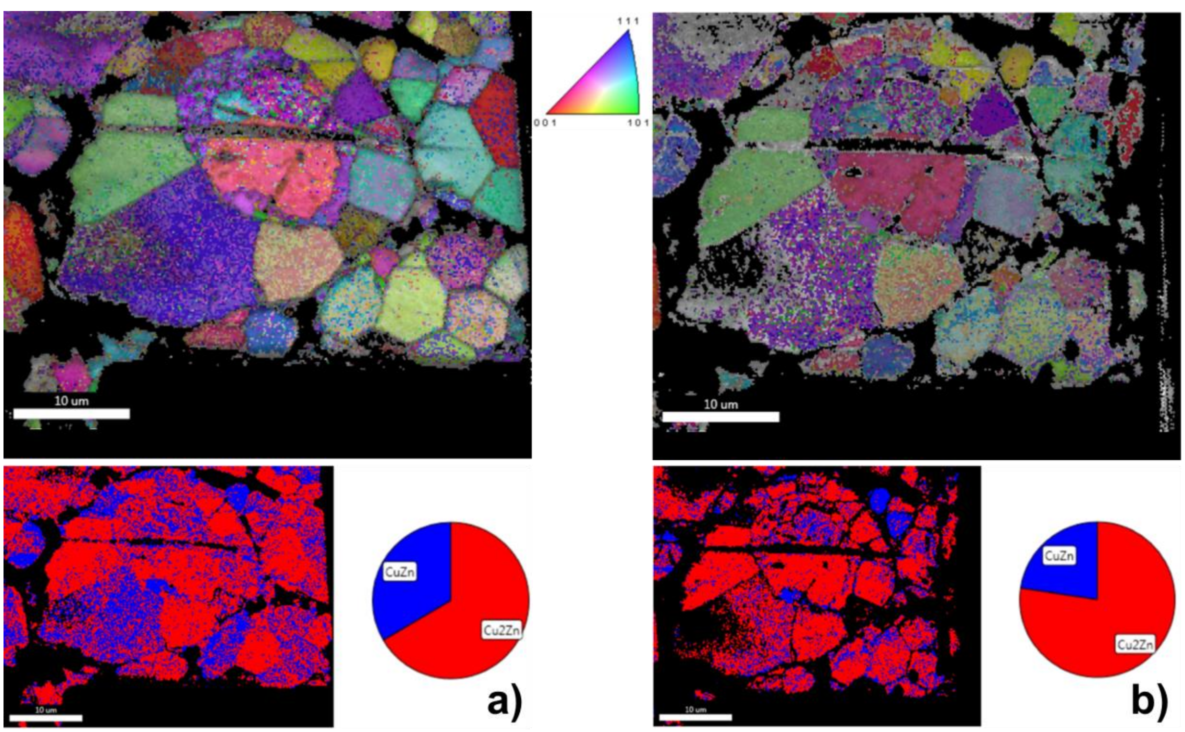

Figure 1. EBSD and phase maps of a $Cu_{50}Zn_{50}$ sample **a)** before and **b)** after 2h of dealloying showing the decreasing Zn content, the decreasing quality of the map and the retention of the crystallography. The step size is 0.2 μm.

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