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Research paper

Nanomechanical behaviour of open-cell nanoporous metals: Homogeneous versus thickness-dependent porosity

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ABSTRACT

Two different nanoporous materials, porous copper prepared by dealloying and porous nickel prepared by electrodeposition, have been studied by means of nanoindentation experiments at different maximum applied loads. While nanoporous Cu is homogeneous along its cross-section, the electrodeposited Ni films show a graded porosity, with smaller pores and thicker pore walls close to the film's surface. The mechanical properties of the two materials have been extracted using a methodology based on scaling laws and subsequent interpretation has been performed using finite element simulations. Two different deformation mechanisms are observed for nanoporous Cu and nanoporous Ni, respectively. Dealloyed porous copper behaves as a homogeneous material without evident effect of densification and with mechanical properties that are independent of the applied load. Given this homogeneity, it is possible to fit the entire loading - unloading curve for different maximum applied loads with a single set of mechanical properties. Conversely, electrodeposited porous nickel shows a decrease in the reduced Young's modulus, an increase in yield stress and a constant hardness when the maximum applied load during nanoindentation is increased. While the decrease in the reduced Young's modulus can be explained in the context of thickness inhomogeneity of the electrodeposited porous nickel (i.e., increase of porosity with depth), this cannot explain, and actually would go against, the observed increase in the yield stress, which is instead associated to the decrease in the ligament size.

1. Introduction

Owing to their extraordinarily high surface area, nanoporous materials have become ideal candidates for a widespread range of technological applications, both in chemistry (Otsubo et al., 2012; Xiong et al., 2012), as well as in magnetic devices (Pellicer et al., 2013). From a structural point of view, porous materials are being used for impact-energy absorption and in lightweight construction, as well as in various types of thermal insulation and acoustic damping (Linul et al., 2013).

Several strategies are currently being pursued for the preparation of nanoporous films. These include dealloying or electrodeposition (Malgras et al., 2016; Scaglione et al., 2012) among others. Electrodeposition (either using hard templates - e.g. anodic aluminium oxide - or soft templates - e.g. block copolymers - in the electrolytic bath) and de-alloying are particularly suited for the preparation of metallic porous alloys (sometimes referred to as metallic foams). Selective de-alloying techniques typically produce materials with an open sponge-like structure of interconnecting ligaments and pore sizes of a few nm. During de-alloying, the least noble component in a solid solution is leached from the alloy, while the noblest elements undergo surface diffusion and agglomeration, forming the sponge-like metallic structure (Malgras et al., 2016).

Irrespectively of the application, the mechanical properties of porous materials are of uppermost importance to ensure robustness and endurance of any device in which they are integrated. In fact, despite their extended utilization in industry, porous materials suffer from the drawback of being usually rather brittle. Therefore, the study of their mechanical properties by uniaxial tension, macroscopic compression or torsion experiments is often not possible. For this reason, nanoindentation has become one of the most appropriate methods to measure the mechanical properties of these materials since this technique keeps the induced deformation constrained into very local length scales. However, proper

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interpretation of the mechanical properties of porous materials using nanoindentation remains still rather challenging. First, a densified zone can form underneath the indenter during indentation, thus precluding a clear-cut assessment of the properties of the initially non-deformed material. Secondly, most of the models existing in the literature to correlate mechanical properties (i.e., hardness and Young's modulus) with the porosity degree are only applicable to some particular arrangements of porous networks (e.g., honeycomb-like geometries or close-cell pore structures) (Pellicer et al., 2012; Ramakrishnan and Arunachalam, 1993). Remarkably, while the porosity degree is often taken into account in these models, the important role played by the pore size itself on the resulting mechanical performance is often overlooked. Furthermore, most mechanical studies so far have only focussed on fully homogeneous porous films or foams. The mechanical response of heterogeneous (i.e., thickness-dependent porosity) nanoporous alloys has essentially not been investigated.

In this work, the mechanical response during nanoindentation of homogenous nanoporous Cu films, prepared by dealloying, and that of heterogeneous nanoporous Ni (i.e., with graded porosity across thickness) directly grown by electrodeposition from a block polymer-containing solution, are compared. Interpretation of the experimental results is supported with finite element simulations. While the properties of homogeneous nanoporous Cu are found to be rather independent of the applied indentation load, the Young's modulus of porosity-graded nanoporous Ni decreases for higher loads, while the opposite trend is observed in the corresponding values of yield stress. Such results are ascribed to the structural evolution of nanoporous Ni with depth, i.e., to the interplay between the increase of the average pore size (and porosity degree) and the decrease of the ligament size as the distance from the film's surface increases.

2. Materials and methods

2.1. Copper-Zinc dealloying

$Cu_{20}Zn_{80}$ 2 mm-thick sheets were purchased from Goodfellow. Nanoporous copper (Cu) samples were obtained by dealloying these sheets in 85 wt% H_3PO_4 for 4 days following the methodology described by Chung Cheng and Hodge (2012). Scanning Electron Microscopy (SEM) equipped with Energy-dispersive X-ray (EDX) was used to prove the Zn depletion. The morphology of the obtained nanoporous layer was observed by SEM. Further verification of Zn depletion was carried out by X-ray diffraction (XRD).

Prior to indentation and SEM imaging, the sample was hot embedded in a conductive resin and polished with diamond suspension to mirror like appearance. Fig. 1(a) corresponds to a cross-section SEM image of the dealloyed copper where a homogeneous microstructure across its depth can be observed. Fig. 1(b) and (c) show the XRD patterns and EDX spectra of this sample before and after dealloying, respectively. While no Zn is detected by EDX (Fig. 1(c)), low-intensity diffraction peaks from the intermetallic Cu_5Zn_8 phase are observed by XRD (Fig. 1(b)). This apparent contradiction is due to the different penetration depths of X-rays and electrons in the two techniques. Namely, a small quantity of Zn seems to be still present in the sample but it is located well inside the central part of the ribbons. The mechanical properties are determined at the surface of the ribbons, which consists only of nanoporous Cu. In a first approximation, we thus neglected the minor amount of Zn in the analyses. Total thickness of the dealloyed porous Cu film was 50 ± 0.5 μm. AFM scans on the surface of the samples provided a roughness value of Ra = 10.5 nm.

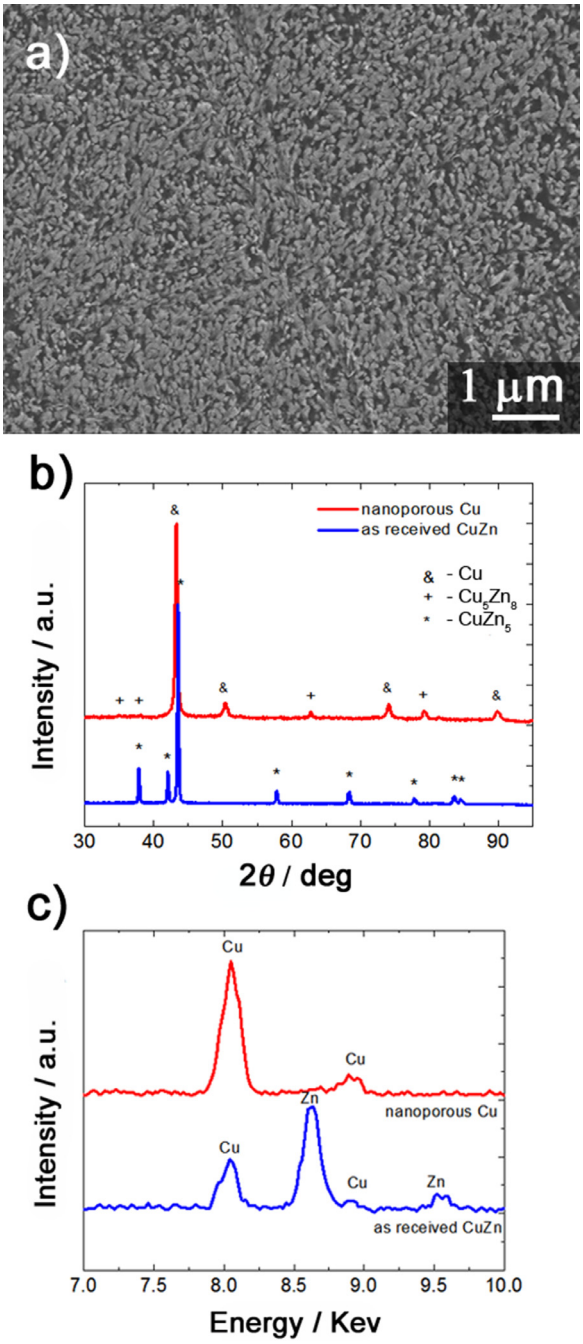

Fig. 1. (a) SEM image of the nanoporous Cu film (prepared by dealloying), observed along its cross section (notice the pore homogeneity across film thickness); (b) XRD patterns corresponding to the as-cast $Cu_{20}Z_{80}$ ribbon and the nanoporous Cu obtained by dealloying of the ribbon; (c) EDX analyses of the as-received and dealloyed $Cu_{20}Z_{80}$ ribbon.

2.2. Nickel electrodeposition

Nanoporous nickel (Ni) film was obtained by potentiostatic electrodeposition in a single compartment double-jacketed three-electrode cell. Si|Ti (25 nm)|Au (125 nm) substrate was used as cathode with working area of 0.25 cm^2 exposed to the electrolyte. A platinum spiral served as counter electrode, which was positioned vertically facing the working electrode. A double junction Ag|AgCl 3M KCl electrode (E = + 0.210 V versus standard hydrogen electrode) was utilized as reference electrode. Electrodeposition was conducted using a PGSTAT302N Autolab potentiostat/