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 an 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.

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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 (e.g., gas sensors, catalysis, batteries, gas molecules separators) (Liu et al. 2011; Otsubo et al., 2012; Sun et al., 2005; Xiong et al., 2012), as well as in optical, electronic and magnetic devices (Huan et al., 2011; 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 evaporation-induced self-assembly, dealloying, or electrodeposition (Brezesinski et al., 2006; Malgras et al., 2015; Scaglione et al., 2012) among others. Electrodeposition (either using hard templates - e.g. anodic aluminum 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., 2015).

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 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 at., 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

$Cu_{20}Zn_{80}$ 2mm-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. Figure 1 corresponds to a cross-section SEM image of the dealloyed copper where an homogeneous microstructure across its depth can be observed.

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/galvanostat (Ecochemie). Electrolyte was prepared by mixing the pluronic P123 amphiphilic block copolymer surfactant and aqueous solution of 0.4 M $NiSO_4$, 0.5 M $NaSO_4$, 0.2 M boric acid and 0.5 g/L saccharine. To prepare the mixture, 4 g of P123 was heated to 60°C in a beaker prior to the addition of the aqueous phase and mixed manually for 5-10 min at constant heat. Then certain amount of ethanol was added to the mixture to assure a ratio of 0.2 g P123 per mL of ethanol. The resulting solution was subjected to vigorous magnetic stirring until it showed a turbid milky appearance. The nanoporous Ni was obtained at room temperature by applying a constant potential of -1.8 V for 1200 s.

The concentration of surfactant was set at 8 wt% which is above the critical micelle concentration of P123. The hydrophilic Au substrate serves as aggregation site for P123, as the surfactant gathers spontaneously at the solid-liquid interface. The surfactant micelle directs the Ni^{2+} ions towards the substrate and acts as structure-directing agent. As depicted in Figure 2 (a), the growth of Ni follows a quasi-perfect layer-by-layer process, in which the pore size decreases gradually along the vertical direction. This layer-by-layer growth fashion is evident from the corresponding SEM picture, see Figure 2 (b). Layer III, which corresponds to the first stages of electrodeposition, exhibits the largest pore size. As deposition proceeds, a second Ni layer is formed on top of the first porous Ni. This second layer (II) features smaller pore size. Consequently, the uttermost layer (layer I) has the smallest pore size (around 10-20 nm). Contrary to the average pore size, the width of the pore walls (i.e., lateral size of the ligament) progressively increases with film thickness, from $10-15$ nm (layer III) to $50-60$ mn (layer I).

2.3 Nanoindentation experiments, extraction of mechanical properties and finite element simulations

Nanoindentation experiments were performed in load-control mode, using a UMIS instrument from Fischer-Cripps Laboratories equipped with a Berkovich pyramidal-shaped diamond tip. The maximum applied load ranged from 2 to 25 mN. The thermal drift was always kept below 0.05 nm/s. At least 10 indents were performed at each maximum applied load to verify the accuracy of the indentation data. The same protocol was followed for both porous Cu and Ni.

For the extraction of mechanical properties, the hardness and the reduced Young's modulus values were evaluated at the beginning of the unloading segment by means of the method of Oliver and Pharr, 1992. In order to estimate the yield stress, σ_{ys}, we used the methodology described in Alcalá et al., 2009; Casals and Alcalá, 2005. It is well known that during sharp indentation of a homogeneous material, the relation between the applied load and the displacement of the indenter can be expressed through (Cheng and Cheng, 1999; Giannakopoulos et al., 1994; Lawn and Howes, 1981):

$$P = K h_{s}^{2} \,, \tag{1}$$

being P the applied load, h_{s} the indenter's displacement and K a constant that depends on the indented material. The unloading stage can be fitted using (Oliver and Pharr, 1992):

$$P_{u} = B(h_{s} - h_{r})^{m} \,, \tag{2}$$

where B and m are fitting parameters and h_{r} is the remaining h_{s} at $P = 0$. Additionally, the Sneddon's relation states that:

$$E_{\mathrm{eff}} = \frac{\eta}{\sqrt{A_{\max}}} \left. \frac{\mathrm{d}P}{\mathrm{d}h} \right|_{h_{\max}} \,, \tag{3}$$

being E_{eff} the effective Young's modulus, η is assumed to vary with the indenter's shape (Cao et al., 2007; Meza et al., 2008; Xu and Li, 2008) and it is equal to 0.793 for a Berkovich indenter (Alcalá et al., 2009), and $A_{\max}$ is the projected contact area between the material and the indenter at $(h_{\max}, P_{\max})$. E_{eff} can be written as:

$$E_{\text{eff}} = \left(\frac{1}{E_{\text{r}}} + \frac{1 - \nu_{\text{i}}^2}{E_{\text{i}}} \right)^{-1} , \tag{4}$$

where ν_{i} and E_{i} are the Poisson's coefficient and Young's modulus of the indenter, respectively, and E_{r} the reduced Young's modulus of the material under indentation. The slope at $(h_{\text{max}}, P_{\text{max}})$ during unloading can be calculated through:

$$\left. \frac{\mathrm{d}P}{\mathrm{d}h} \right|_{h_{\text{max}}} = \frac{P_{\text{max}}}{h_{\text{max}} - h_{\text{e}}} = \frac{P_{\text{max}}}{h_{\text{max}}(1 - h_{\text{e}}/h_{\text{max}})} , \tag{5}$$

where h_{e} is the penetration depth at which the tangent curve at $(h_{\text{max}}, P_{\text{max}})$ crosses the h_{s} axis. Figure 3 shows an schematic of a loading – unloading indentation curve including the expressions for the loading and unloading stages and the expression for the slope of the unloading stage.

Once parameters B, m and h_{r} in Eq. 2 are fitted, dP/dh evaluated at h_{max} can be obtained by differentiating Eq. 2 and h_{e} can be calculated through Eq. (5). Combining Eqs. (1), (3) and (5) for $(h_{\text{max}}, P_{\text{max}})$ one can write:

$$E_{\text{eff}} = \eta \sqrt{K \bar{p}} \left(1 - \frac{h_{\text{e}}}{h_{\text{max}}} \right)^{-1} , \tag{6}$$

being $\bar{p} = P/A$ the obtained hardness from nanoindentation experiments and A the projected contact area between the material and the indenter.

Finally, once having the values for E_{eff} and $\bar{p}$, one can use the expression (Casals and Alcalá, 2005):

$$\frac{\bar{p}}{\sigma_{0.1}} = A_1 + A_2 \cdot exp \left(\frac{-E_{\text{eff}}/\sigma_{0.1}}{A_3} \right) + A_4 \cdot exp \left(\frac{-E_{\text{eff}}/\sigma_{0.1}}{A_5} \right) \tag{7}$$

to obtain $\sigma_{0.1}$, a characteristic stress corresponding to an uniaxial deformation of 0.1. Expressions for A_1, A_2, A_3, A_4 and A_5 can be found in Table 7 for Eq. (A.1) in Casals and Alcalá, 2005. Relation between $\sigma_{0.1}$ and σ_{ys} can be written as:

$$\sigma_{\text{ys}}^{n-1} = \frac{(0.1E)^n}{\sigma_{0.1}} \tag{8}$$

where E is the Young's modulus and n is the strain hardening coefficient during an uniaxial test.

With the extracted mechanical properties, we performed finite element (FE) simulations with the commercial ABAQUS finite element code under a full integration scheme. As the porous structure was not considered during simulations, the finite element mesh, constructed following

a refining strategy, comprised two-dimensional 43,359 four-node axisymmetric quadrilateral elements and the Berkovich indenter was modelled using an equivalent conical indenter with an azimuthal angle equal to 65.3°. Simulations were performed under frictionless contact conditions and large-strain formulations. A linear elastic-perfectly plastic relation was assumed in the simulations with the Von Mises flow theory of plasticity, allowing to correlate directly $\sigma_{0.1}$ to σ_{ys}, as the strain hardening coefficient n was taken to be equal to zero.

3   Results and discussion

Figure 4 shows the nanoindentation curves at different maximum applied loads (Fig. 4 (a)) and the extracted mechanical properties (Figs. 4 (b) – (d)) for the dealloyed porous Cu. From Fig. 4 (a) it can be seen that the applied load (P) – penetration depth (h_{s}) curves at different maximum applied loads P_{max} are coherent with each other, i.e., the loading stages match rather well, except for $P_{\text{max}} = 15$ mN. Figs. 4 (b) and (c) show, respectively, the extracted values for the reduced Young's modulus (E_{r}) and hardness $\bar{p}$, according to Oliver and Pharr, 1992, as a function of the maximum penetration depth h_{max} for the different P_{max}. Given the scattering, one can observe that the values for E_{r} and $\bar{p}$ do not show a significant tendency to increase, as one could expect on the event of a densification process. Analogously, Fig. 4 (d) shows the evolution of the scaled hardness ($\bar{p}/\sigma_{0.1}$) with h_{max} for different applied P_{max}, being the value of $\bar{p}/\sigma_{0.1}$ practically constant. For a homogeneous bulk metal one can expect that the constraint factor $C = \bar{p}/\sigma_{0.1} = 2.6$ (Casals and Alcalá, 2005; Mata et al., 2002). However, by introducing porosity, this value will be necessarily reduced due to reduction of hydrostatic pressure (Domingo-Roca et al., 2015; Zeeshan et al., 2015). Fig. 4 (a) also includes FE simulations capturing the experimental $P - h_{\text{s}}$ curves. Interestingly, a single set of mechanical properties was used for the simulations, namely $E_{\text{r}} = 13.0$ GPa and $\sigma_{0.1} = \sigma_{\text{ys}} = 478.9$ MPa, supporting the idea that the present dealloyed porous Cu is homogeneous across the entire thickness. These values were obtained by averaging the extracted mechanical properties in Table 1 for P_{max} from 2.5 to 15 mN. The resulting simulated $P - h_{\text{s}}$ curve was able to capture the experiments for the entire range of applied loads fairly well (here, just simulations for $P_{\text{max}} = 10$ mN and 15 mN are included for representation purposes). Most likely, simulations were not able to perfectly capture the loading stages due to slight structural changes in the dealloyed porous Cu during indentation. Table 1

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summarizes the extracted mechanical properties according to what has been explained in Section 2.3 and also the relative density of the porous Cu, ρ^*/ρ_s, being ρ^* and ρ_s the densities of the porous and bulk materials respectively, calculated using Eq. 9 (Gibson and Ashby, 1997):

$$E_r = C_2 E_s \left(\frac{\rho^*}{\rho_s} \right)^n \quad , \tag{9}$$

where E_r is the reduced Young's modulus of the porous material. As the morphology of the dealloyed porous Cu approaches to an open-cell foam, the values $C_2 = 1$ and $n = 2$ can be assumed (Gibson and Ashby, 1997; Williford et al., 2005) giving as a result $\rho^*/\rho_s = 0.33$ (taking $E_s = 120$ GPa as the reduced Young's modulus of bulk Cu). This relative density is not far from the value of 0.20 that one could expect from the starting material ($Cu_{20}Zn_{80}$), if Zn was fully removed during the dealloying. The slight discrepancy could be due to: (i) small amounts of Zn still present in the dealloyed Cu (although not easily detected by EDX) or (ii) C_2 and n not being exactly equal to 1 and 2, respectively. It is worth mentioning that to extract $\sigma_{0.1}$, as explained in Section 2.3, the used methodology was first thought for bulk-homogeneous materials. However, we have proven that the dealloyed porous Cu can be understood as a homogeneous material, therefore this methodology can apply. A proof of that is the excellent agreement between experiments and simulations (using a single set of parameters) and also between the values of Young's moduli obtained through the method of Oliver and Pharr and the presented methodology, as it can be seen in Table 1.

In the same fashion as for Cu, Figure 5 shows the $P - h_s$ curves (Fig. 5 (a)) and extracted mechanical properties (Figs. 5 (b) – (d)) for different P_{max} for electrodeposited Ni. Contrary to what was observed in Fig. 4 (a) for Cu, here the loading stages for different P_{max} do not overlap so much with each other, anticipating heterogeneity across the electrodeposited porous Ni sample. Furthermore, Fig. 5 (b) shows that E_r decreases with h_{max} for different applied P_{max}, being this coherent with what was shown in Fig. 2 (a) and (b), i.e., a material whose porosity increases with depth. Hence, if porosity increases it is natural to obtain a reduction in E_r, not considering, though, densification effects that, on the contrary, would increase E_r. However, this explanation seems to fail in Figs. 5 (c) and (d) that show, respectively, the variation of $\bar{p}$ and $\bar{p}/\sigma_{0.1}$ with h_{max}. From Fig. 5 (c) one can see that hardness remains approximately constant for the whole range of h_{max}. Instead, the constraint factor, $\bar{p}/\sigma_{0.1}$, decreases with h_{max} similar, to E_r. Then, since $\bar{p}/\sigma_{0.1}$ decreases while $\bar{p}$ remains constant with h_{max}, it is clear that the

yield stress σ_{ys} increases with P_{max}. Here, as for the dealloyed Cu, one can consider that $\sigma_{0.1}$ $\sim \sigma_{ys}$, as it corresponds to a linear elastic – perfectly plastic material with no strain hardening, being this idea supported by Schwaiger et al., 2003. The decrease of E_r and $\bar{p}/\sigma_{0.1}$ with h_{max} is rather straightforward to understand taking into account that the present porous electrodeposited Ni shows an increased porosity with depth. As h_{max} increases, the material experiences less hydrostatic pressure, resulting in a progressively lower constraint factor. However, this does not explain the increase of σ_{ys} with P_{max}. Actually, compaction of the material would certainly induce an increase of σ_{ys} but it would also increase E_r. Nonetheless, the works by Biener et al., 2005 and Hodge et al., 2007 provided an answer for this apparent contradiction. These authors studied the yield strength of nanoporous open-cell Au foams for different relative densities (ρ^*/ρ_s). Although ρ^* was decreasing, indicating an increment of porosity, the yield strength increased, as in our study. The explanation for this phenomenon was that the ligaments' size was reduced as ρ^* became lower, leading to an effect analogous to the Hall-Petch relationship, where the characteristic length scale was, instead of the grain diameter, the ligament size:

$$\sigma^* = C_s[\sigma_o + k \cdot L^{-1/2}] \cdot \left(\frac{\rho^*}{\rho_s}\right)^{3/2} \quad , \tag{10}$$

where σ^* is the yield strength of the porous metal, C_s is a fitting parameter, σ_o is the yield strength of the bulk material, k is the Hall-Petch type coefficient for the theoretical yield strength of the metal, L is the ligament size and ρ^* and ρ_s the densities of the porous and bulk materials respectively. Eq. 10 is the result of combining a Hall-Petch type of relation:

$$\sigma_{yc} = \sigma_o + k \cdot L^{-1/2} \quad , \tag{11}$$

(being σ_{yc} the yield strength of a ligament with size L) with the Gibson and Ashby, 1997 scaling prediction for foams:

$$\sigma^* = C_2 \sigma_s \left(\frac{\rho^*}{\rho_s}\right)^{3/2} \quad , \tag{12}$$

with coefficient $C_2 = 0.3$ according to Gibson and Ashby, 1997 and $\sigma_s \equiv \sigma_o$ is the yield strength of the bulk material.

For the present nanoporous Ni, given its morphology, it was possible to estimate the ligament size at the top surface of the electrodeposited film (i.e., $L \sim 50 - 60$ nm) and the first layer (III)

, i.e., $L \sim 10 - 15$ nm. Table 2 summarizes the extracted mechanical properties according to Section 2.3 along with the different relative densities using Eq. 9 for open-cell porosity and $E_s = 200$ GPa. Taking $\sigma_{ys} = \sigma^* = 4.0$ GPa, the bulk value for Ni $\sigma_s = 21.8$ MPa (Carlton and Ferrari, 2007; Thompson, 1975), and $k_{Ni} = 7$ GPa$\sqrt{nm}$ (El-Sherik et al., 1992; Hughes et al., 1986) then, from Eq. 10 one can obtain $C_s = 3.2$ - 4.0. Having the values of $\sigma_{ys} = \sigma^*$ in Table 2 for different P_{max} and the corresponding values of ρ^*/ρ_s along with the fitting value C_s, now one can calculate the corresponding ligament sizes that would produce the different values of σ_{ys}. These values are listed in Table 2 and they are in rather good agreement with the SEM observations (Fig. 2). As for the case of the porous dealloyed Cu, the extracted values for the Young's moduli with the method of Oliver and Pharr, 1992 and the present methodology are in excellent agreement. Also, this methodology was previously used in the framework of Cu single crystalline thin films on top of silica (Si) substrates (where the thin film/substrate interface acts as an inhomogeneity), with excellent results (Esqué-de los Ojos et al., 2014).

As in Fig. 4 (a) for the dealloyed porous Cu, here we also performed FE simulations of the indentation experiments on electrodeposited porous Ni, Fig. 5(a). Given the evolution on the mechanical properties shown in Fig. 5(b) for the reduced Young's modulus and for the extracted yield stress in Table 2, in this case it was not possible to use a single set of parameters for the simulations, but different values of E_r and σ_{ys} were used for each P_{max}, in accordance with Table 2.

4   Conclusions

Here we have studied the mechanical behaviour of porous Cu obtained by dealloying and porous Ni prepared by electrodeposition, combining nanoindentation experiments with finite element simulations. The following are the most remarkable conclusions reached during the present study.

- For dealloyed porous Cu it has been shown that, as a result of its homogeneous structure, mechanical properties such as the reduced Young's modulus, hardness and yield stress do not vary significantly with different maximum applied loads. This enables to capture the applied load – penetration depth experimental indentation curves with a single set of mechanical properties through finite element simulations. As no evolution of the mechanical properties was observed, densification effects could be essentially disregarded up to 15 mN

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maximum applied load.

- For electrodeposited porous Ni, the reduced Young's modulus and constraint factor decrease with the maximum applied load, while hardness stays constant. This variation of the mechanical properties precludes the use of a unique set of mechanical properties to fit the entire applied load – displacement indentation curves through finite element simulations. Actually, with each set of mechanical properties it is, at most, only possible to capture through finite element simulations the corresponding maximum load and the unloading stage, but not the loading stage. This is due to the inherent structure heterogeneity of the sample.

- Concerning the evolution in the mechanical properties of electrodeposited porous Ni, the reduction of the Young's modulus and constraint factor with $P_{\max}$ can be understood from the increase of the porosity with depth, but this is in principle contradictory with the constancy of hardness and the increase of yield stress. To overcome this paradox, the critical role played by the ligament size was taken into account. The very small ligament sizes act similar to the small crystallite sizes in the Hall-Petch relation, in the sense that as the ligament size is reduced the yield stress increases. SEM images indeed reveal that while the porosity is increased, the ligament size is reduced across the electrodeposited porous Ni sample.

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