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Multiscale modeling of charge-induced deformation of nanoporous gold structures

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ABSTRACT

Recent experimental studies have shown that nanoporous metals undergo dimensional changes when a potential difference is applied in an electrochemical environment. The primary actuation mechanism is the electric-double layer charging of the internal surface in combination with a large surface-to-volume-ratio. To account for the excess charge we have developed an atomistic model that is calibrated to density functional theory. To make a scale transition from the atomistic to the continuum scale, we propose a surface layer model that is informed by atomistic simulations. We use this multiscale approach to study the charge-induced actuation response of ordered (cubic lattices and gyroids) and disordered nanoporous gold (npg) architectures. Results are presented in terms of the charge-induced actuation strain and work density as a function of relative density, ligament size and architectural morphology. The differences between ordered and disordered structures are critically addressed.

1. Introduction

Nanoporous metals have attracted much attention recently, because of their potential for a wide range of applications, such as catalysts, sensors, supercapacitors and actuators (Wittstock et al., 2010; Detsi et al., 2012a; Lang et al., 2011; Jin et al., 2009; Biener et al., 2008). The use of nanoporous metals as electrochemical actuator is especially interesting since strain amplitudes comparable to those of piezoelectric ceramics can be generated at much lower voltages (1 V compared to 100 V). This, combined with their relatively high ductility (compared to ceramics), high specific yield strength (Hodge et al., 2007; Hakamada and Mabuchi, 2007; Volkert et al., 2006) and potential for enhanced strain amplitudes (Detsi et al., 2012b; Jin et al., 2009), makes nanoporous metallic actuators a promising new class of materials.

The actuation response of nanoporous metals is triggered by the electrochemical injection of charge, basically employing their super-capacitance related to the high internal surface area. When charge is injected, a narrow space-charge layer of approximately one to two atomic layers thick is formed at the surface. In these layers the atomic bonding is altered due to the presence of the excess charge, resulting in a lateral atomic equilibrium spacing that differs from that in the bulk. Despite the limited width of this surface layer, macroscopic strains can be generated when the ligament size is on the order of tens of nanometers (Ibach, 1997; Weissmuller et al., 2003). Having a very large internal surface area per unit volume (i.e., small ligament width) is the key in generating large actuation strokes. The current generation of nanoporous metals are mostly

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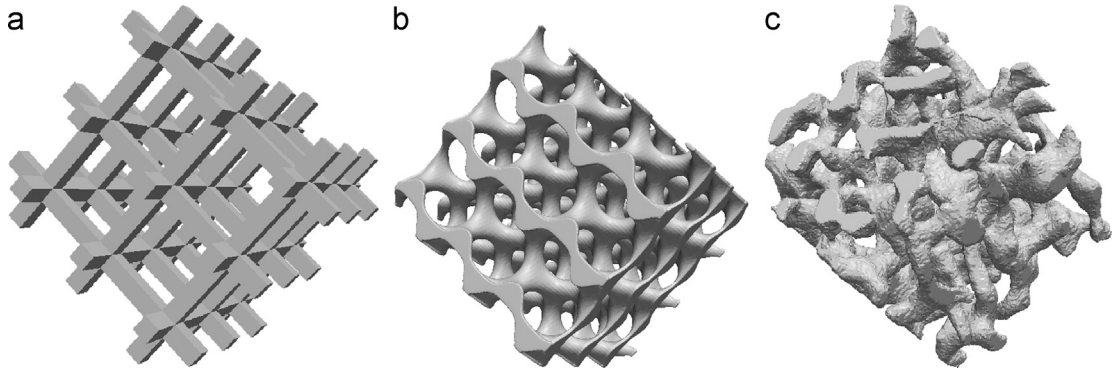

Fig. 1. Different architectures of nanoporous structures studied in this paper. (a) Cubic lattice, (b) gyroid and (c) nanoporous gold (npg).

produced using electrochemically driven dealloying of binary alloys, resulting in a disordered foam-like structure of interconnected ligaments (Erlebacher et al., 2001; Detsi et al., 2013a, 2013b; Biener et al., 2005; Weissmüller et al., 2009), see Fig. 1(c). Although these materials feature high internal surface areas, their topological disorder and imperfections will knock-down the mechanical properties (Ashby et al., 2000), leading to a sub-optimal work output against an applied load. However, generating order in metals at the nanoscale is not trivial. Considerable progress has been made recently by utilizing the unique self-assembly properties of block copolymers to synthesize ordered nanoporous metals featuring a gyroidal architecture (Vukovic et al., 2011; Hsueh et al., 2011), see Fig. 1(b). Clearly, the overall charge-induced deformation of nanoporous metals will be strongly size-dependent due to the surface-charge-driven actuation mechanism. This introduces the ligament size as a characteristic length scale in the problem. In addition to the ligament size, there are two more important parameters: the relative density, and the morphology of the nanoporous architecture, which can both affect the actuation strain and overall mechanical properties. No experimental or theoretical studies exist that contain a detailed analysis of the charge-induced actuation response as a function of relative density, ligament size and morphology. The goal of this paper is to find these dependencies by studying a range of nanoporous materials with profoundly different morphologies: cubic lattices, ordered gyroids and disordered nanoporous gold structures, see Fig. 1. We will use a multiscale modeling approach to bridge the gap between the excess-charge-modified atomic bonding at the metal surface and the overall macroscopic actuation strain and study how this is mediated by the specific morphology of the nanoporous architecture.

When a bias voltage is applied on electrolyte-immersed nanoporous metals, an electrical double layer forms at the metal–electrolyte interface leading to charge deposition at the metal surface (Bockris and Reddy, 1970). This excess charge alters the electron distribution of the surface atoms resulting in a change in atomic bond strength. When a negative charge is injected the excess electrons increase the bond strength of the surface atoms, leading to a decrease in their equilibrium atomic spacing, thus prompting the inner layers to move along with them, eventually contracting the metal. The opposite happens when positive charge is injected, i.e., the bond length increases resulting in expansion (Umeno et al., 2007). This reversal of strain with charge rules out electrostatic (Coulombic) effects to contribute, because electrostatic effects would lead to deformation that is independent of the sign of charge. It is now well-accepted from experimental (Jin et al., 2008; Jin and Weissmüller, 2010; Weissmuller et al., 2003) and density functional theory (DFT) (Umeno et al., 2008) studies that quantum-chemical effects are responsible for the charge-induced deformation. To investigate the effect of the altered electron density distribution on the surface stress, Umeno et al. (2007) carried out DFT calculations on charged gold surfaces. The surfaces were characterized by the surface-stress-charge coefficients, which indicate the change in surface stress per unit surface charge density injected. Although *ab initio* calculations are accurate and can give fundamental insights into the actuation mechanism, they are computationally too expensive to perform on larger atomic systems such as individual ligaments or nanowires. To overcome this, we developed an atomistic model in order to bridge the gap between the local electron density redistributions and the overall charge-induced straining of nanowires (Saane et al., 2013). We modified the surface embedded atom (SEAM) potential (Haftel, 1993; Haftel and Rosen, 2001; Möller et al., 1996; Rousset et al., 1993) to take into account the bond strengthening and weakening due to the addition of excess negative and positive charge. The model parameters were calibrated to the surface-stress-charge coefficient of Au(100) surface obtained from DFT simulations (Umeno et al., 2007). Using the modified potential, the charge-induced deformation of gold nanowires with different crystal orientations and cross-sectional sizes was studied (Saane et al., 2013). In the current paper we will apply this atomistic model to ordered nanoporous gold structures, i.e., cubic lattices (Fig. 1(a)) and gyroids (Fig. 1(b)). However, in order to probe the actuation of disordered structures such as nanoporous gold (Fig. 1(c)), atomistic simulations become computationally too expensive. To overcome this, we will develop a continuum, surface-layer, model that is informed by atomistic simulations. We will use the ordered gyroidal structures to calibrate the model parameters and then apply the model to simulate the charge-induced deformation of disordered nanoporous gold.

The paper is organized as follows. In Section 2 we briefly discuss the modified atomistic (SEAM) potential that accounts for the excess charge on the metal surface and we discuss the proposed continuum model. In Section 3, we will investigate