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Microscopic failure behavior of nanoporous Gold

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Nanoporous Au –a brittle yet ductile material

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Nanoporous metals have recently attracted considerable interest fueled by potential sensor[1] and actuator applications.[2,3] One of the key issues in this context is the synthesis of high yield strength materials. Nanoporous Au (np-Au) has been suggested as a candidate due to its monolithic character.[2] The material can be synthesized by dealloying Ag-Au alloys,[4] and exhibits an open sponge-like morphology of interconnecting Au ligaments with a typical pore size distribution on the nanometer length scale.[5] Unfortunately, very little is known about the mechanical properties of np-Au besides a length-scale dependent ductile-brittle transition.[6] A key question in this context is: what causes the macroscopic brittleness of np-Au? Is the normal dislocation-mediated plastic deformation suppressed in nanoscale Au ligaments, or is the brittleness a consequence of the macroscopic morphology? Here, we report on the fracture behaviour of nanoporous Au studied by scanning electron microscopy. Specifically, we demonstrate the microscopic ductility of nanometer-sized Au ligaments. The observed fracture behaviour seems to be general for nanoporous metals, and can be understood in terms of simple fuse networks.[7]

Recently, we studied the mechanical properties of np-Au under compressive stress by depth-sensing nanoindentation, and determined a yield strength of 145 (±11) MPa and a Young's modulus of 11.1 (± 0.9) GPa.[8] A striking result of this study is that the experimentally determined value of the yield strength is almost one order of magnitude higher than the value predicted by scaling laws developed for open-cell foams,[9] thus potentially opening the door to the development of a new class of high yield strength / low density materials. This example illustrates that the mechanical properties of nanoporous metals are not well understood yet.

Tensile tests have been performed on nanometer-sized Au contacts.[10-12] On a microscopic length scale, failure of a single Au ligament in np-Au under tensile stress is closely related to the yielding of nanometer-sized Au contacts which proceeds via quasicontinuous neck elongation involving a series of order-disorder transitions.[10-12] The resulting Au nanowires exhibit a yield strength in the order of 4-8 GPa,[10,12] which is comparable to the ideal shear strength of Au (~2 GPa[13]) in absence of dislocations. However, larger contacts seem to yield in a fracture-like mode where the neck abruptly contracts in a catastrophic event.[10,14] The present study addresses the failure mechanism of np-Au by examining fracture surfaces, with particular emphasis on the relationship between microstructure and macroscopic fracture behavior under tensile stress.

In the present study, samples of nanoporous Au with a relative density of 0.42 were subjected to a bending force until fracture occurred. The samples were prepared by selective electrolytic dissolution of Ag from a $Ag_{0.58}Au_{0.42}$ starting alloy. Bending caused transverse fracture triggered by failure on the tension side, indicating that np-Au is stronger in compression than in tension. As the crack propagates, the region of tensile stress spreads through the whole sample. The specimens showed no macroscopically visible plastic deformation prior to failure, consistent with brittle fracture. SEM was used for further micro-structural characterization of the fracture surfaces. On a micrometer length scale (Fig. 1a), the fracture surfaces exhibit both apparently featureless regions (I) and regions with a “rock candy” appearance (II). “Rock candy” features are a characteristic sign of intergranular brittle fracture, where the crack path follows the grain boundaries.[15] However, transmission electron micrographs reveal that the np-Au samples investigated in the present study exhibit a nano-crystalline grain structure.[8,16] Thus the intergranular facets in Figure 1a cannot reflect the grain structure of np-Au, but seem to be a remnant of the coarse-grain microstructure of the Ag-Au starting alloy (see discussion below).

On a microscopic level, however, characteristic necking features reveal ductile fracture due to overloading of individual ligaments (Fig. 1b, c). The macroscopically apparently featureless regions (I) of the fracture surface are microscopically very rough and exhibit a high density of disrupted ligaments, whereas the “rock candy” regions (II) have a very smooth appearance with only a few disrupted ligaments. Extended two-dimensional void-like defects are observed at the boundary between “rock candy” (I) and featureless (II) fracture surface regions (Fig. 1d). These defects seem to have their origin in a Ag enrichment along the grain boundaries of the original Ag-Au alloy: dealloying when leads to the development of a reduced density material (voids) along the original grain structure. Indeed, Ag surface segregation during annealing has been reported for the Ag-Au system.[17] Thus “rock candy” regions of the fracture surface are produced by intergranular fracture (intergranular with respect to the grain structure of the Ag-Au starting alloy), and featureless regions indicate transgranular fracture (through the grains of the Ag-Au starting alloy).

The two-dimensional void-like defects discussed above presumably act as crack nucleation sites due to local stress enhancement. Ligaments connecting the regions on opposite sides of a defect experience the highest stress fields and are the first to fail. In case of a penny-shaped defect in a three-dimensional cubic network, the local stress enhancement would be proportional to $n^{1/4}$ where n is the number of missing ligaments.[18] Once an unstable crack is formed, the crack propagates along the 2D-defects until intersecting with another 2D-defect at an oblique angle, where the fracture may or may not switch from “intergranular” to “transgranular”.

The deformation of np-Au in the vicinity of crack tips was further studied by controlled introduction of microcracks via high-load Vickers indents (300 g). SEM micrographs (Fig. 2a) reveal that microcracks nucleate and propagate along the indenter edges where the stress is concentrated. Individual ligaments, still bridging the crack, can be observed in the vicinity of the crack tip (Fig. 2b). Some of these ligaments are strained by as much as 200%. High magnification micrographs of larger cracks formed in the same area reveal pronounced necking prior to failure (Fig. 2c). The observation of ligaments bridging microcracks suggests that, on a nanometer length scale, the elongation to failure is in the order of hundred percent, which is a remarkable result in the context of the macroscopic brittleness of np-Au. However, the observed high strain values are consistent with the fact that Au is the most malleable metal. Indeed, even higher strain values might have been expected; thus the ductility seems to be limited by the nanocrystalline nature of the ligaments. Nevertheless, microscopically, np-Au is a very ductile material, despite of its apparent macroscopic brittleness.

Annealing of np-Au leads to an increase of the length-scale of the structure, and thus allows one to study cell size effects. For example, annealing at 570 C for a period of 2h increases the pore size/ligament diameter from ~ 100 nm to ~ 1µm. Changes of the fracture mechanism were studied by SEM (fig. 3). Overall, the fracture morphologies of annealed and unannealed samples are very similar, i.e. both featureless (I) and “rock candy” (II) regions can be observed. However, in case of the annealed sample, extensive plastic deformation of the nanoporous structure occurs in a larger region around cracks: cell collapse in a layer-by-layer mode indicates regions of compressive stress, and elongation of the cell structure reveals regions of tensile stress (fig. 3a). In addition, plastic deformation of individual ligaments by slip can be detected (fig. 3b). The slip bands (s) indicate slip on the {111} planes in <110> direction. Slip plays an important role in the rupture process of thin Au wires: Successive slip events on two or more slip systems can lead to necking and failure.[19] The larger degree of plastic deformation on fracture surfaces of annealed samples indicates strengthening of the network structure, probably by eliminating the two-dimensional defects which serve as crack nucleation sites. Indeed, Ostwald ripening of the nanoporous network leads to the collapse of the two-dimensional void-like defects, and originally only weakly connected regions of the network fuse together (fig. 3c).

What causes the macroscopic brittleness of np-Au, although it is microscopically a very ductile material? In analogy to the case of a random fuse network analyzed by Kahng et al.,[7] “brittle” failure can be expected for a sufficiently narrow ligament-strength distribution, regardless if the ligaments fail microscopically in a ductile or in a brittle manner: in the limit of a narrow ligament-strength distribution, rupture of the weakest ligament initiates the catastrophic failure of the network structure by overloading adjacent ligaments. The unstable crack then propagates quickly through the bulk of the material following the path of weakest resistance. This interpretation is consistent with the narrow pore size /ligament width distribution of np-Au which implies an uniform failure strength.

The overall strength of a random fuse network is determined by the largest “critical” defect, i.e. the defect which causes the highest stress enhancement at its edge.[18] In the present study, two-dimensional void-like defects serve as crack nucleation sites by concentrating the stress on adjacent ligaments. Thus, instead of plastic deformation of the whole sample, the failure of a few ligaments triggers the brittle fracture of the network. Interestingly, the failure mechanism of the ligaments seems to change with the length-scale: Microscopic characterization of fracture surfaces of as-prepared np-Au with a ligament diameter of ~ 100 nm suggest that the ligaments fail by plastic flow and necking. On the other hand, failure by slip was observed for ligaments with a diameter of ~ 1000 nm. The latter observation indicates dislocation activity as the stress required to cause slip is reduced by several orders of magnitude by the presence of dislocations.[20] The absence of slip marks on fracture surfaces of as-prepared np-Au suggests that the dislocation activity is suppressed by the nanoscale ligament /grain structure. A suppressed dislocation activity is also consistent with the high yield strength of Au nanocontacts.[12]

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Methods:

Nanoporous Au samples with a relative density of 0.42 were prepared by selective electrolytic dissolution of Ag from a $Ag_{0.58}Au_{0.42}$ alloy. The grain size of the Ag-Au alloy was in the mm range. The details of alloy preparation and the dealloying procedure can be found in Ref. 8. In short, dealloying was performed by applying an electrochemical potential of ~ 1V versus a saturated calomel electrode, using 75% nitric acid as an electrolyte. The complete removal of Ag was verified by energy dispersive X-ray (EDX) spectroscopy, and the morphology of the material was studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD).

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Figure Caption:

Figure 1: Microstructure and fracture appearance of nanoporous Au shown at different magnifications. **(A)** Low magnification SEM micrograph revealing a combination of transgranular (featurless region I) and intergranular brittle fracture ("rock candy" region II). **(B**) Boundary region between transgranular (region I) and intergranular fracture (region II) at higher magnification. **(C)** A close-up of the outlined area in Fig. 1b reveals the ductile nature of the fracture: the ligaments fail by necking due to overloading. **(D)** Region I (transgranular) and region II (intergranular) are separated by two-dimensional, void-like defects (marked by arrows) which serve as crack nucleation sites.

Figure 2: SEM micrographs showing crack formation during high-load Vickers indents (300 g): **(A)** Microcracks nucleate and propagate along the indenter edges between the pyramid faces of the indenter (the residual impression of one indenter edge is marked by arrows). **(B)** High magnification micrograph from the crack tip region showing highly strained ligaments bridging a microcrack. Elongations in the order of one hundred percent have been observed. **(C)** Detail of a larger crack revealing pronounced necking prior to failure.

Figure 3: Fracture surface of a np-Au sample that had been heat treated for 2h at 570 ºC prior to fracture at room temperature. The heat treatment increases the pore size/ligament diameter from ~100 nm to ~1µm. **(A)** Extensive plastic deformation is observed in a larger region around cracks: cell collapse in regions of compressive stress (c), and elongation of the cell structure in regions of tensile stress (t). **(B)** A higher magnification view of the area within the rectangle reveals plastic deformation of individual ligaments by slip (s). **(C)** The heat treatment strengthens the network structure by eliminating the two-dimensional void-like defects which serve as crack nucleation sites.

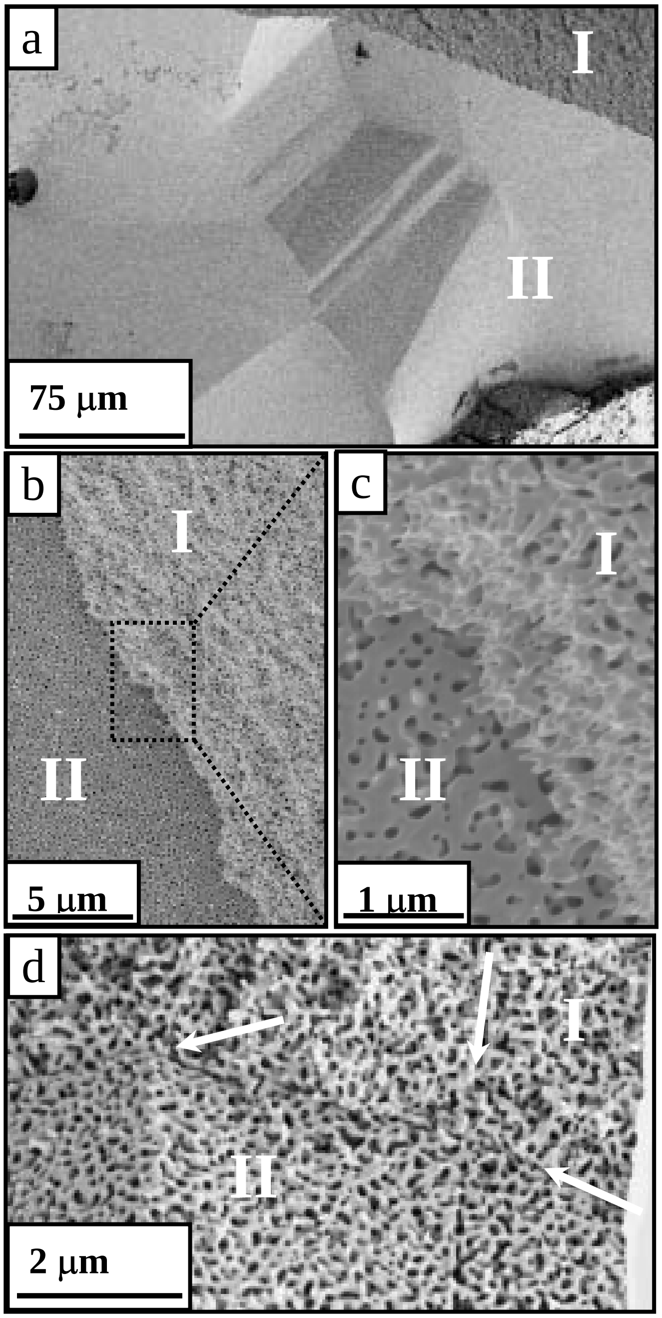

Figure 1

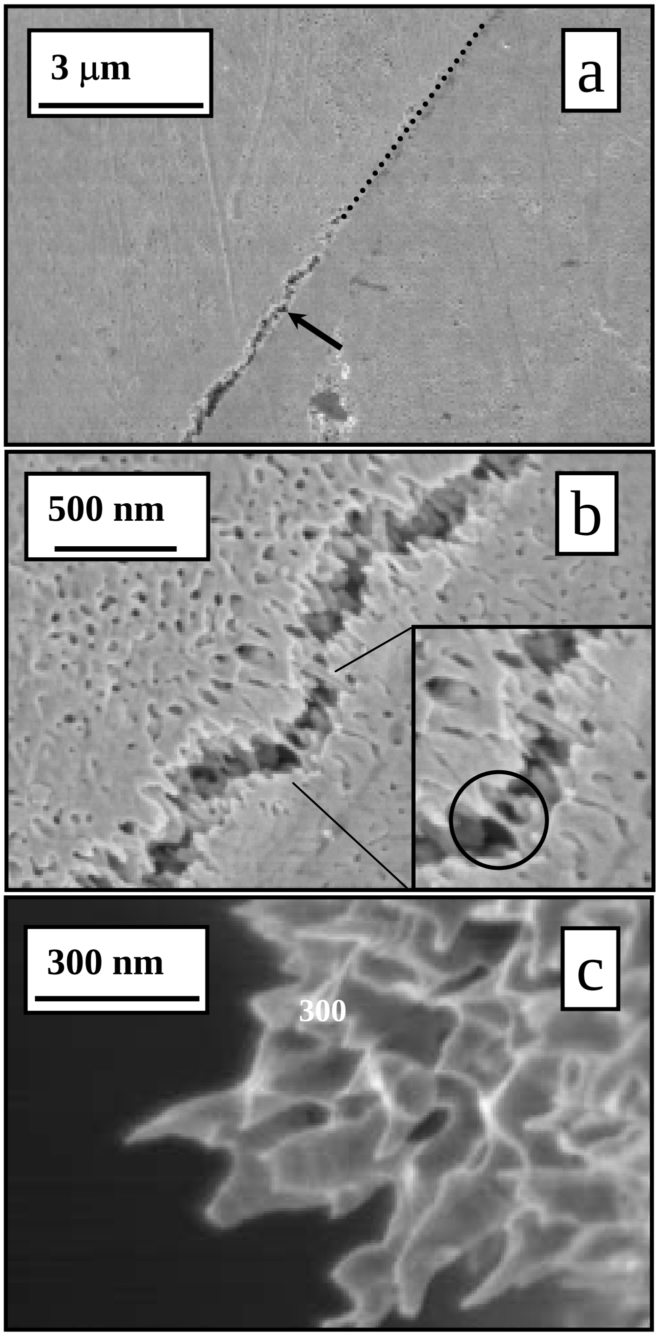

Figure 2

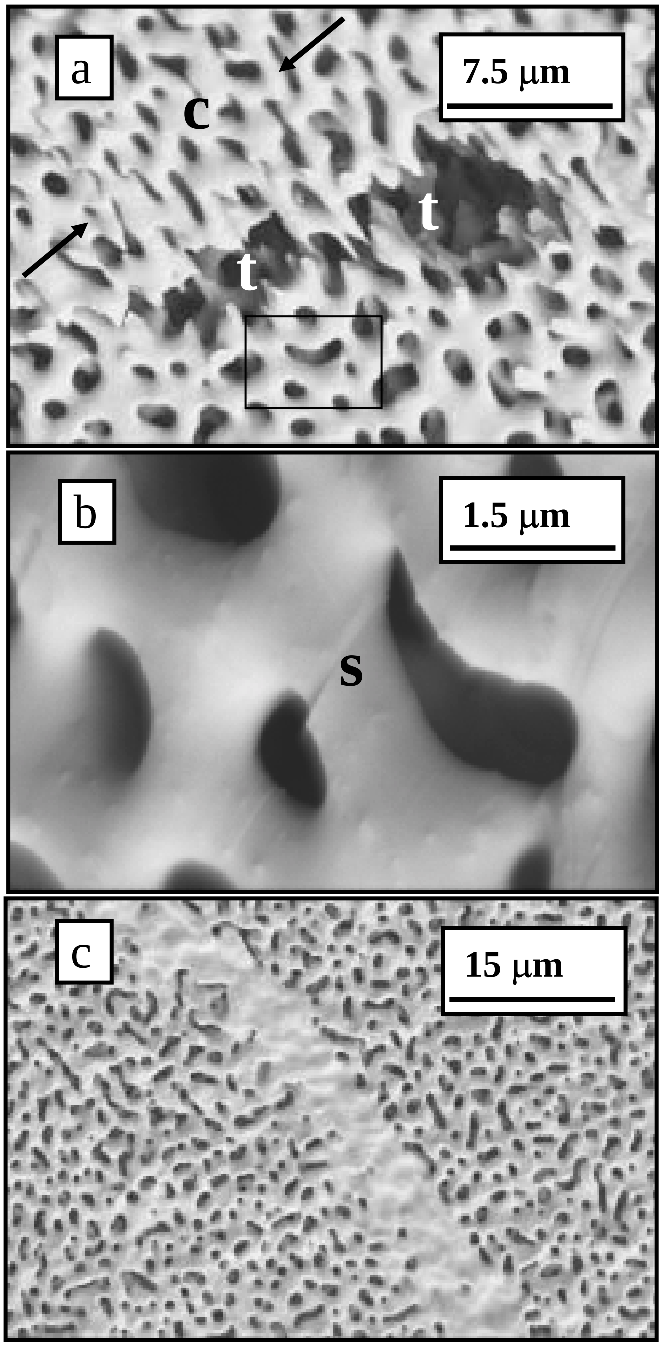

Figure 3