

Nanoporous metals from dealloying of ternary noble-metal alloys: composition, morphology, stability and prospects for catalytic activity

Adrián A. Vega, Roger C. Newman

University of Toronto
Department of Chemical Engineering
and Applied Chemistry
200 College Street
Toronto, M5S 3E5, Ontario, Canada

Dealloying is the selective dissolution of one or more elements from a solid-solution metal alloy or intermetallic compound. Usually dealloying is carried out in an aqueous solution under potentiostatic control. The more-noble element(s) are transported by surface diffusion during dissolution of the less-noble element(s). The product is a connected nanoporous structure that retains the crystallography of the original alloy.

Here we report the first systematic study of the effect of small additions of Pt on the dealloying of Ag-Au alloys in aqueous perchloric acid. The Pt, having a lower surface diffusivity than Au, blocks step edges, creating a porous structure with smaller length scale and higher surface area. Snyder et al. [1] showed that the substitution of 6% Pt for Au in a 'white-gold' type of Ag-Au alloy stabilized the ligament size of the dealloyed product and increased its resistance to thermal coarsening by surface self-diffusion. We show, using a range of alloys with 77 at% Ag and 23 at% (Au + Pt), that such stabilization persists down to 1% Pt, but with various subtleties. The dealloyed nanostructures are characterized by high-resolution microscopy including cross-sectional STEM, by BET analysis, and by electrochemical methods including H-UPD to estimate active Pt content on the ligament surfaces [2].

The results reveal many complexities, but these can be rationalized. Promising catalytic activity can be obtained by heating the as-dealloyed material in air, to promote co-segregation of Pt and O to the ligament surfaces, but, there is no simple relationship between the Pt coverage of the ligament surfaces and their catalytic activity (for example, for methanol electro-oxidation). Surface compositions that are apparently intermediate or innocuous can give the best catalysis, and residual Ag plays a role that is still under investigation.

Acknowledgments

This research is funded by the Natural Sciences and Engineering Research Council (NSERC).

References

1. J. Snyder, P. Asanithi, A. B. Dalton and J. Erlebacher, *Adv. Mater.*, **20**, 4883 (2008).
2. A. Vega and R.C. Newman, *Technical Proceedings – 2012 NSTI Nanotech Conference*, **1**, 510 (2012).