



## Forum Inżynierii Materiałowej Materials Engineering Forum

- The Materials Engineering and Metallurgy Committee of the Polish Academy of Sciences
- Polish Materials Science Society

### Dealloying as an advanced and facile synthesis technique for the production of nanoporous metals

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Nanoporous metals represent a new class of materials with promising properties as actuators, storage and conversion of energy, electrodes for electrocatalysis and surface-enhanced Raman scattering (SERS). They are constituted by a scaffold of interconnected ligaments with pores in between. They can be fabricated by electrochemical or chemical dealloying: the less noble elements are selectively dissolved while the noble components reorganize in ligaments by surface diffusion.

In this work, different examples of applications are reported to show the versatility of these materials in terms of properties and possible applications: nanoporous Au (NPG) and nanoporous Pd as substrates for Surface Enhanced Raman Spectroscopy (SERS) with ultra-low detection limit; nanoporous Ti as biocompatible material with enhanced antibacterial properties.

The production of Nanoporous gold (NPG) was addressed starting from different precursors, both crystalline and amorphous. The synthesis was performed by both free corrosion and electrochemical dealloying, in different acidic media. XRD and SEM analyses were performed to check the final morphology of the produced samples (in Fig 1 an example of SEM image of NPG morphology).

SERS activity of NPG was investigated using 4,4'-bipyridine as a probe molecule. Such a microstructure showed homogenous SERS response in terms of average enhancement all across the surface, as demonstrated by SERS mapping measurements. NPG samples produced by dealloying Au<sub>20</sub>Cu<sub>48</sub>Ag<sub>7</sub>Pd<sub>5</sub>Si<sub>20</sub> amorphous ribbons in a mixture of nitric and hydrofluoric acid show a SERS detection limit of 10<sup>-16</sup> M. The signal was strongly enhanced and, by exploiting SERS maps, it was found to have a signal highly homogeneous on the surface. The extremely high enhancement obtained is attributed both to the small size of ligaments and crystals of which they are made.

A novel Ti-based amorphous alloy was developed containing biocompatible elements (TiCuZrFeSnAg) and metallic glass ribbons were synthesised by melt spinning. To produce antimicrobial implant materials, the surface was modified using chemical dealloying in an acidic media for producing a nanostructured topography. The effect of dealloying in different electrolyte was investigated. The surface morphology and composition of dealloyed samples was characterized using XRD, SEM, XPS, TEM and AFM analysis. The formation of nano porosities and ligaments mainly related to the formation of TiO<sub>2</sub> on the sample surface was observed. Different morphology were produced by changing the parameters used for the synthesis, i.e. electrolyte, concentration, temperature and time. The produced morphologies enable a change in wettability and hemocompatibility of the samples, with an increased hemocompatibility with the formation of a nanoporous structure on the surface.

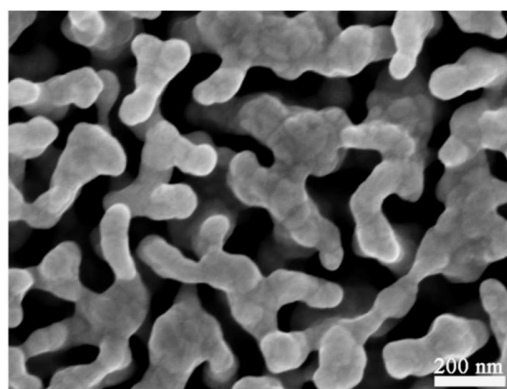


Fig 1: SEM image of NPG surface morphology



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### Towards Biomedical Metallic Glasses: Exploring CuAgZr Alloys through High-Throughput Methods and Machine Learning

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This study focuses on CuAgZr metallic glasses (MGs), which are notable for their potential in biomedical applications thanks to their exceptional strength, resistance to corrosion, and antibacterial properties. By employing a synergistic approach that combines combinatorial synthesis, high-throughput characterization, and machine learning, we have conducted a thorough examination of the mechanical attributes of CuAgZr MGs. Our findings indicate that the presence of high oxygen levels in Cu-rich areas, resulting from post-deposition oxidation in regions of less dense packing, markedly influences the mechanical performance of these alloys. Additionally, our research uncovers that nanoscale structural nuances play a significant role in determining the plastic yield and flow behavior of the alloys. Among various machine learning models evaluated, the multi-layer perceptron algorithm stood out, delivering accurate predictions of hardness for alloys not previously tested, thereby offering insightful directions for ongoing material research. This investigation underscores the efficacy of leveraging combinatorial synthesis, high-throughput analysis, and machine learning to accelerate the development of new metallic glasses with enhanced mechanical properties and cost-effectiveness.