

The Size and Composition-dependent Mechanisms of High-Entropy-Alloy Nanoparticle Formation by Laser Ablation in Liquids

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The mechanism of colloidal alloy nanoparticle (NP) formation by laser ablation in liquids (LAL) has been intensively studied e.g. for fully miscible alloy systems like AgAu forming solid solution^[1], partially miscible systems like FeAu with trends for segregation and core-shell structure formation^[2], and immiscible elements (CuAg), where segregation was observable even in the ablation plume during early stage formation^[3]. Recently, this approach has been successfully transferred to multi-component high entropy alloy (HEA) systems, where crystalline solid solution NPs of CrMnFeCoNi were generated by ps-LAL in ethanol^[4] and amorphous structures were found after ns-LAL in acetonitrile^[5]. However, to what extent the composition and crystal structure of laser-synthesized HEA-NP is affected by target composition, pulse duration, and the solvent is underexplored.

In this work, we investigate how crystal structures, particle diameter distribution, and elemental composition of CrMnFeCoNi and CuPdAgPtAu HEA NPs are affected by laser pulse duration (ps vs. ns) and solvent type (ethanol, acetone), and in particular whether and to what extent the excess of one element in the HEA base target leads to elemental segregation in the HEA-NPs. Particle characterization was conducted by TEM/EDX as well as XRD. Preliminary studies showed a high phase stability of the solid solution fcc structure of the HEA-NPs at the excess of specifically chosen elements (Cr, Mn, Ag, Cu, Pt) though individual NPs, particularly in the Mn-rich CrMnFeCoNi samples, displayed segregation due to oxide phase formation. Interestingly, CuPdAgPtAu HEA-NPs displayed two solid solution NP fractions divided into Ag-rich and Pt-rich individual particles of comparable particle diameters. These de-mixing tendencies could be a hint towards particles formed at different cooling rates and could offer interesting insights into the HEA-NP formation mechanism by LAL under thermodynamic and kinetic control.

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