In situ insights into the thermal stability and oxygen reactivity of high-entropy nanoalloys

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Abstract

The structural stability of high entropy nanoalloys (HENA) brings hope to developing more stable nanomaterials for high-temperature catalysis applications. Nevertheless, the enhanced thermal stability of nearly equiatomic nanoalloys containing at least 5 metals is nothing more than theoretical speculations about the impact of thermodynamic contributions and sluggish diffusion kinetics on their structural properties and remains to be proven. In this context, studying the thermal behavior of HENA both under vacuum and under oxygen is a necessary first step to understanding their structural properties and evaluate their structural stability.

In the present work, FCC AuCoCuNiPt NPs were directly synthesized on the silicon nitride membrane of a TEM gas cell, using pulsed laser deposition, allowing control of NP composition and size. Then, we used in situ scanning transmission electron microscopy (STEM), corroborated with atomistic simulations, to study in real-time and at the atomic scale the structural and compositional evolution of HENA from 298 K to 973 K, both under vacuum and under 1 atm of oxygen.

In situ STEM and molecular dynamic simulations reveal strong structural and chemical evolutions in the NPs with the formation and melting of an AuCu layer at the surface of NPs at high temperature. Besides ruling out the existence of sluggish diffusion in AuCoCuNiPt nanoalloys, our study allows distinguishing kinetic and thermodynamic effects on their structural properties. The presence of oxygen drastically boosts the growth dynamic of NPs and affects their structural stability at high temperatures due to the preferential oxidation of Co and Ni. From a practical point of view, this work calls into question the use of AuCoCuNiPt HENA for high-temperature applications and more generally reveals the necessity to investigate the structural stability of HENA under realistic conditions to determine if and how surface effects govern their structural properties and adapt their potential applications.