High-temperature thermal evolution of nanostructured thermoelectrics observed by in-situ electron microscopy

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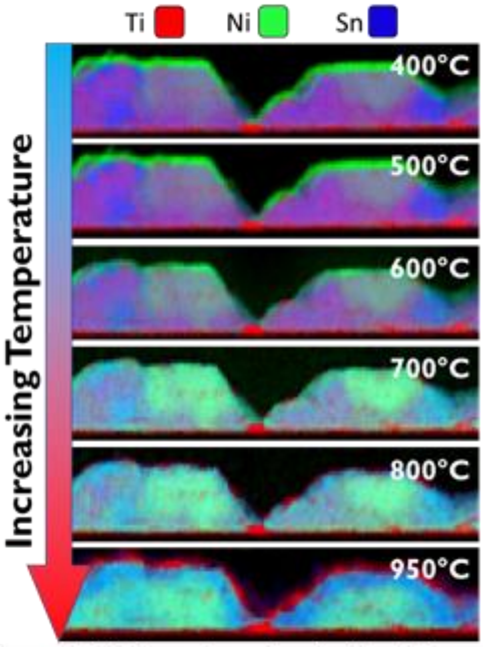
Thermoelectric generators, which directly convert heat into electrical power, can be used to 'scavenge' heat that would otherwise be wasted, improving global energy efficiency in the process. To produce thermoelectric generators with more widespread applications, Heusler alloys have attracted much attention owing to the potential to use cheap, non-toxic materials. The Heusler class has also been of broader interest in the condensed matter community for their broad range of properties, though the phase information is often poorly understood despite its pertinence to their functionality. The most efficient thermoelectric Heusler alloys overcome a performance-limiting thermal conductivity through the incorporation of nanostructures that scatter phonons and thereby interrupt thermal transport. However, nanostructures such as the formation of full-Heusler inclusions need to be thermally stable if they are to operate under high-temperature environments for prolonged periods of time. In many cases, the thermodynamics of these kinetically-limited structures have not been studied in detail.

Here we demonstrate how the use of in-situ electron microscopy can address these factors for thin films of the half-Heusler TiNiSn, a particularly promising and economic material for thermoelectric power generation. TEM cross-sections of epitaxial thin films were mounted on a DENSsolutions heating chip to permit rapid in-situ annealing cycles at high temperatures. Used in conjunction with aberration-corrected STEM-EELS spectrum imaging, we showcase near real-time analysis of bulk diffusion and thermal evolution of TiNiSn material phases with nanometre chemical resolution. Probing the stability of off-stoichiometric Heusler compositions, we pay particular attention to the occupation of the interstitial atoms, which are found above 750°C to migrate from a phase segregated regime to a uniform nickel distribution, indicating the instability of phase segregated nanostructures at high temperatures. This and broader information regarding the activation temperatures for elemental diffusion which underpin the phase stability help assess the viability of nanostructured materials for thermoelectric generators. We anticipate that these results will be of broader interest to anyone working with Heusler alloys.



Elemental false-colour visualisation taken from STEM-EELS annealing series of a phase segregated TiNiSn thin film.

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