Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information:

Binary Phase Diagrams:

Configurational energies of the pseudo-binary systems $Zr_{1-x}Ti_xNiSn$ and $Hf_{1-x}Ti_xNiSn$ were used in separate cluster expansion fits in order to obtain more accurate phase boundaries. The $Zr_{1-x}Ti_xNiSn$ was fit to the DFT formation energy of 55 configurations and had a CV score of 0.90 meV. The $Hf_{1-x}Ti_xNiSn$ was fit to 55 configurations and had a CV score of 0.87 meV. The cluster expansion fits were then used in Monte Carlo simulations. The simulations enable the calculation of thermodynamic averages which are then used to find the free energies required for constructing a temperature-composition phase diagram. The results of the phase diagram calculations are shown in figure S1. Calculated points of the phase boundary are shown as black dots. Calculations are in close agreement with those of Mena *et. al.* [*1*].

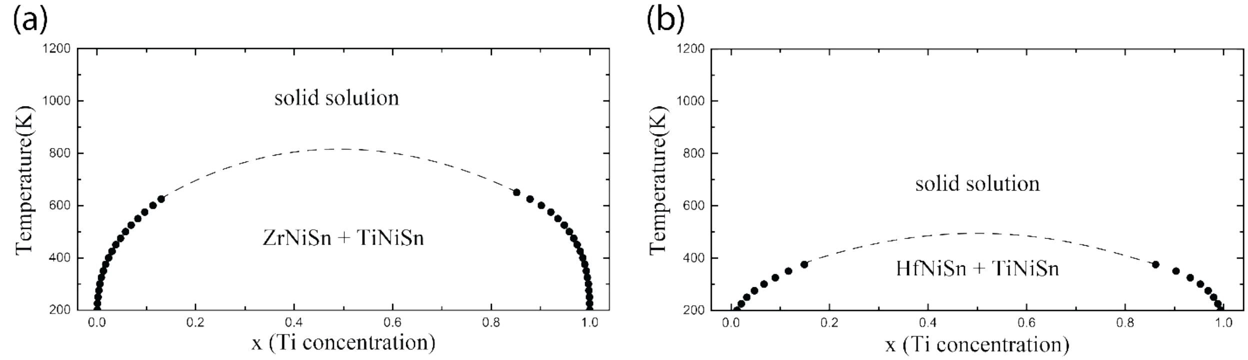

Figure S1. The temperature-composition phase diagrams for (a) $Zr_{1-x}Ti_xNiSn$ and (b) $Hf_{1-x}Ti_xNiSn$. Black dots represent calculated points along the phase boundary. Outside of the boundary, a solid solution minimizes the free energy. Inside the boundary, a two phase coexistence minimizes the free energy.

Migration Barrier Calculations:

We calculated the migration barriers associated with the self-diffusion of *M* site atoms: Ti, Zr and Hf. The diffusion of *M* atoms within the stoichiometric HH matrix is likely to occur via a vacancy mechanism, where a vacancy located on the *M* site, Va_M, swaps with an M atom. The mechanism can be thought of as two separate processes: the formation of vacancies in the matrix and vacancy-atom exchange. The diffusion coefficient in solids, can be expressed as [2],

$$D = D_0 \exp\left[\frac{-E_a}{k_B T}\right]$$

where E_a is an activation energy, k_B is the Boltzmann constant, T is the absolute temperature, and D_o is the diffusion prefactor, which depends on the jump distance, an effective jump frequency, and the vibrational entropy of vacancy formation [3]. The prefector D_o, in this form has a weak temperature dependence arising from anharmonic vibrational excitations. The prefactor is commonly calculated from first principles within the harmonic approximation [*4, 5*]. The activation energy of vacancy-mediated diffusion is made up of two contributions, $E_a = \Delta E_V + \Delta E_m$, where ΔE_V is the formation energy of a single vacancy in the matrix, and ΔE_m is the migration energy. The migration energy was calculated using the VASP software in this work, and values of vacancy formation were taken from literature [*6, 7*].

The energy of migration, ΔE_m, is defined as the difference in energy between the initial state and the energy of the transition state. The transition state is the saddle point between the initial state and the final state defined as the highest energy point of the lowest energy migration path from the initial to the final state. The migration barrier energy is found by fully relaxing 3x3x3 supercells of the initial and final states. The Nudged Elastic Band (NEB) calculations are performed in VASP to find the location and energy of the saddle point. Initial NEB calculations showed that the saddle point is located half way along the reaction path and the barrier energy is symmetric about the saddle point, thus following NEB calculations were carried out with a single image at the saddle point. Geometrically, the saddle point was found to be shifted off of the direct line connecting nearest neighboring *M* sites (shown as dashed line in Figure S2(a)) towards the vacant (3/4, 3/4, 3/4) site (shown as an empty black circle Figure S2(a)). Calculated migration barriers of Ti, Zr, and Hf self-diffusion are 1.9, 3.0, and 2.7 eV respectively, as shown in Figure S2(b).

The activation energy of the self-diffusion of Ti is estimated by adding the calculated migration barrier to the defect energy reported in literature [*6*, *7*], giving Ti an activation energy between 5 and 6 eV, and are expected to be higher for Zr and Hf on account of their larger migration barriers, assuming similar values of vacancy formation energy.

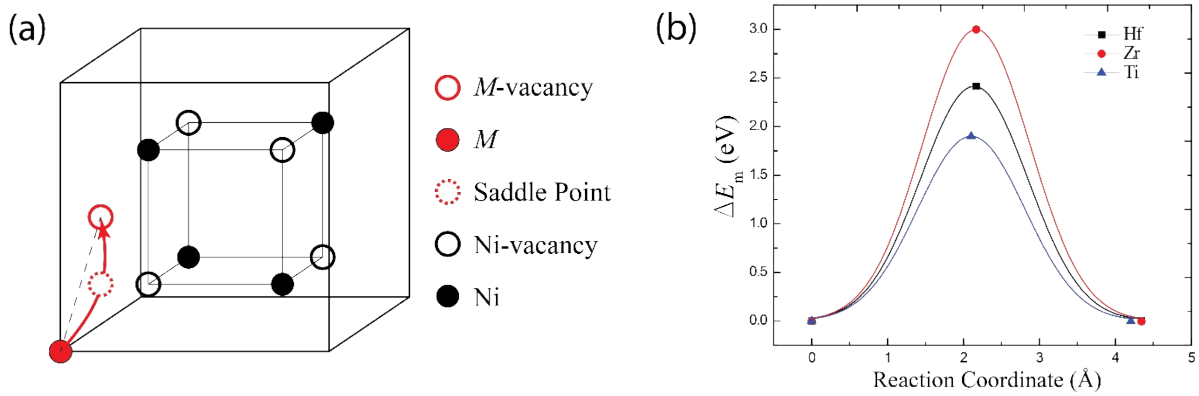

Figure S2. (a) Schematic of the migration paths in the *M*NiSn (*M* = Ti, Zr, Hf) matrix of M-vacancy diffusion. (b) plot of migration barrier energy along the reaction path for Ti, Zr and Hf atoms in TiNiSn, ZrNiSn, and HfNiSn respectively. Symbols represent calculated points along the reaction path and schematic lines are drawn to guide the eye.

References

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