Thermodynamic Modeling of Hf-Re

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Introduction

Nickel-based superalloys are extensively used in the aerospace industry due to excellent oxidation and creep resistance at elevated service temperatures. This is largely attributed to the formation of an ordered fcc phase, γ′ ($L1_2$). At a given composition however, the fraction of γ′ decreases with increasing temperature, hafnium and rhenium are two of the most common alloying elements to stabilize the γ′ phase. Hafnium is a carbide former and precipitates at grain boundaries to reduce grain boundary sliding. Rhenium improves the creep strength by promoting rafting and increasing lattice misfit.

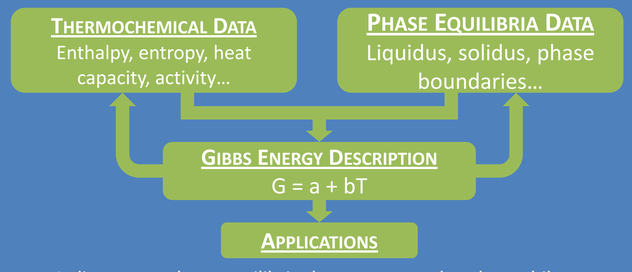
Traditional alloy design can costly and time-consuming to discover the optimal alloy composition. The presence of undesirable phases could negatively impact the phase stability of the alloy. A more efficient approach is to investigate phase equilibria through the CALPHAD (CALculation of PHase Diagrams) method, which computationally predicts thermodynamic descriptions of multi-component systems from lower order systems. Experimental data are supplemented with first-principles calculations for Gibbs energy evaluations.

Literature Review

The Hf-Re system has been experimentally investigated by Savitskii [1,2] and Taylor [3]. Hf is a polymorph, transforming from the low temperature hcp phase to the high temperature hcp phase. Re has the hcp structure up to the melting temperature.

There are three intermetallic compounds in the system: $Hf_{21}Re_{25}$ (rhomohedral, prototype $Zr_{21}Re_{25}$, space group R-3c, 167) [4], $HfRe_2$ (C14 hexagonal Laves, prototype $MgZn_2$, space group $P6_3/mmc$, 194), and Hf_5Re_{24} (cubic, prototype Ti_5Re_{24}, space group I-43m, 217). The enthalpies of formation for the compounds have been calculated by Levy [5]. No previous modeling of the system has been found.

Methodology



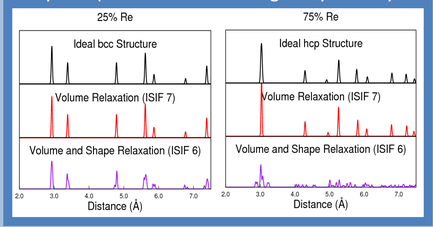
In literature, phase equilibria data are more abundant while thermochemical data are much less available. In the absence of experimental data, first-principles calculations based on Density Functional Theory have been shown to adequately predict thermodynamic properties of phases. Enthalpies of formation can be calculated to provide a more unique model of the system.

Calculation Details

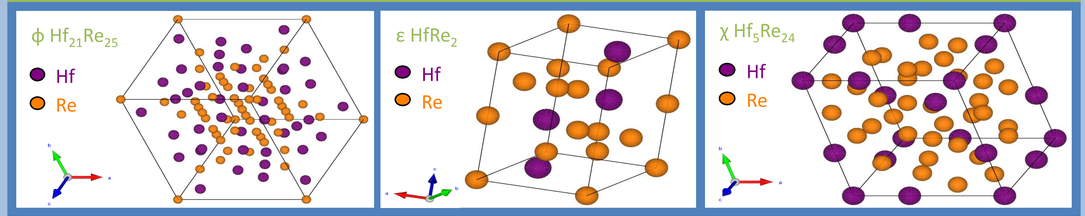
All first-principles calculations are carried out using VASP with PAW-PBE pseudopotentials. A plane wave energy cutoff of 300 eV and a k-point mesh of at least 5,000 per reciprocal space atom are used. For pure elements and compounds, the structures are fully relaxed.

SQS and RDF

SQS (Special Quasirandom Structure) mimics interactions of disordered phases with only a few atoms. Two relaxation schemes are used: volume relaxation and volume and shape relaxation. RDF (Radial Distribution Function) analysis is performed to investigate symmetry.



Intermetallic Compound Crystal Structures

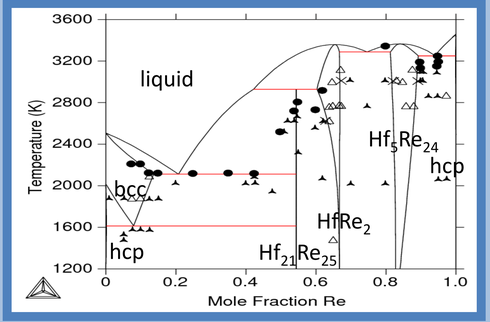


First-Principles Predictions

Phase	Enthalpy of Mixing (kJ/mole)		
	25% Re	50% Re	75% Re
bcc	-9.82	-24.55	-25.40
hcp	20.35	27.22	20.80

Phase	Enthalpy of Formation (kJ/mole)	a (Å)	c/a
$Hf_{21}Re_{25}$	-1848	15.12	
$HfRe_2$	-118	5.26	1.64
Hf_5Re_{24}	-1478	9.74	

Calculated Phase Diagram



Summary

A preliminary Hf-Re phase diagram based on experimental phase equilibria data and calculated thermochemical data has been modeled using the CALPHAD approach. Enthalpies of formation of the compounds and enthalpies of mixing of the bcc and hcp solid solutions are predicted with first-principles calculations. $HfRe_2$ is modeled with a two-sublattice model, Hf_5Re_{24} a three-sublattice model, and $Hf_{21}Re_{25}$ is treated as a stoichiometric compound.

Future Works

Future works include improve the Hf-Re phase diagram, combine Hf-Re, Hf-Ni, and Ni-Re into the Hf-Ni-Re ternary system, and perform ternary SQS on bcc and hcp structure to calculate interactions.

References

[1] E. M. Savitskii, *et al.*, *Russian Metallugy,* pp. 130-135, 1969.

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[3] A. Taylor, *et al.*, *Journal of the Less-Common Metals,* vol. 5, pp. 26-40, 1963.

[4] K. Cenzual, *et al.*, *Acta Crystallographica Section C-Crystal Structure Communications,* vol. 42, pp. 261-266, Mar 1986.

[5] O. Levy, *et al.*, *Acta Materialia,* vol. 58, pp. 2887-2897, May 2010.

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