QUEST FOR NOBURNIUM: 1300C CYBERALLOY

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Abstract

A multi-institutional, multidisciplinary project addresses optimal integration of computational design and efficient experimentation for the accelerated design and development of high performance materials using the example of Nb-based superalloys combining oxidation resistance, creep strength and ductility for aeroturbine applications operating at 1300˚C and above. Integrated within a systems engineering framework, the effort tests the limits of ab-initio quantum mechanical methods to accelerate assessment of thermodynamic and kinetic databases enabling comprehensive predictive design of multicomponent multiphase microstructures as dynamic systems. Based on established principles underlying Ni base superalloys, the central microstructural concept is a dispersion strengthened system in which coherent cubic aluminide phases provide both creep strengthening and a source of Al for Al_2O_3 passivation enabled by a Nb-based BCC alloy matrix with required transport and oxygen solubility behaviors. A combination of FLAPW all-electron and VASP pseudopotential calculations assess thermodynamic and molar volume behaviors of $L2_1$ Pd_2HfAl and B2 PdAl based intermetallics as well as BCC Nb-based solutions. Toward an optimal balance of phase stability and interphase misfit, the $L2_1$ phase assessment has been extended to the $(Pd,Pt)_2(Hf,Zr,Nb)Al$ system with validation by diffusion couple experiments. To identify slow diffusing species to enhance dispersion coarsening resistance, quantum methods predict an activation energy for Re diffusion in Nb 50% higher than that for Mo in Nb. Employing the DICTRA system, a multicomponent diffusivity database is developed for substitutional alloying elements and interstitial oxygen to enhance the diffusivity ratio of Al to O for promotion of Al_2O_3 passivation. To minimize O solubility, quantum bond topology calculations show trends in interstitial site charge density supporting a dependence of O chemical potential on solution e/a ratio. Integrating the databases and models thusfar developed, a team of students in an undergraduate Materials Design class has performed theoretical designs of 7 component

dispersion strengthened alloys with matrix transport and solubility properties supporting feasibility of Al_2O_3 passivation at 1300˚C.

Research Objectives

In support of the US Air Force MEANS (Materials Engineering for Affordable New Systems) program, the objective of this multidisciplinary collaboration is to develop optimal strategies for the integration of theory and efficient experimentation for the accelerated design and development of advanced structural materials, using the example of Nb-based superalloys combining oxidation resistance, creep strength and ductility for future aeroturbine blade applications operating at 1300˚C and above.

Approach

Building on demonstrated successes in computational materials design [1], a central theme of the AF-MEANS initiative is the acceleration of the full materials design, development and qualification cycle. This requires not only the extension of materials design tools to process optimization, scaleup, and control of variation, but also the development of new strategies for more efficient integration of theory and experiment. Our systems engineering approach to materials design is represented by Figure 1, summarizing the process-structure-property-performance connections governing the behavior of a multilevel-structured coated Nb-based superalloy system. While the total system integrates compatible thermal barrier and bondcoat subsystems, our initial research has focused on predictive design of the underlying precipitation-strengthened alloy. The specific tools employed in this effort explore the limits of modern quantum engineering methods based on total energy calculations.
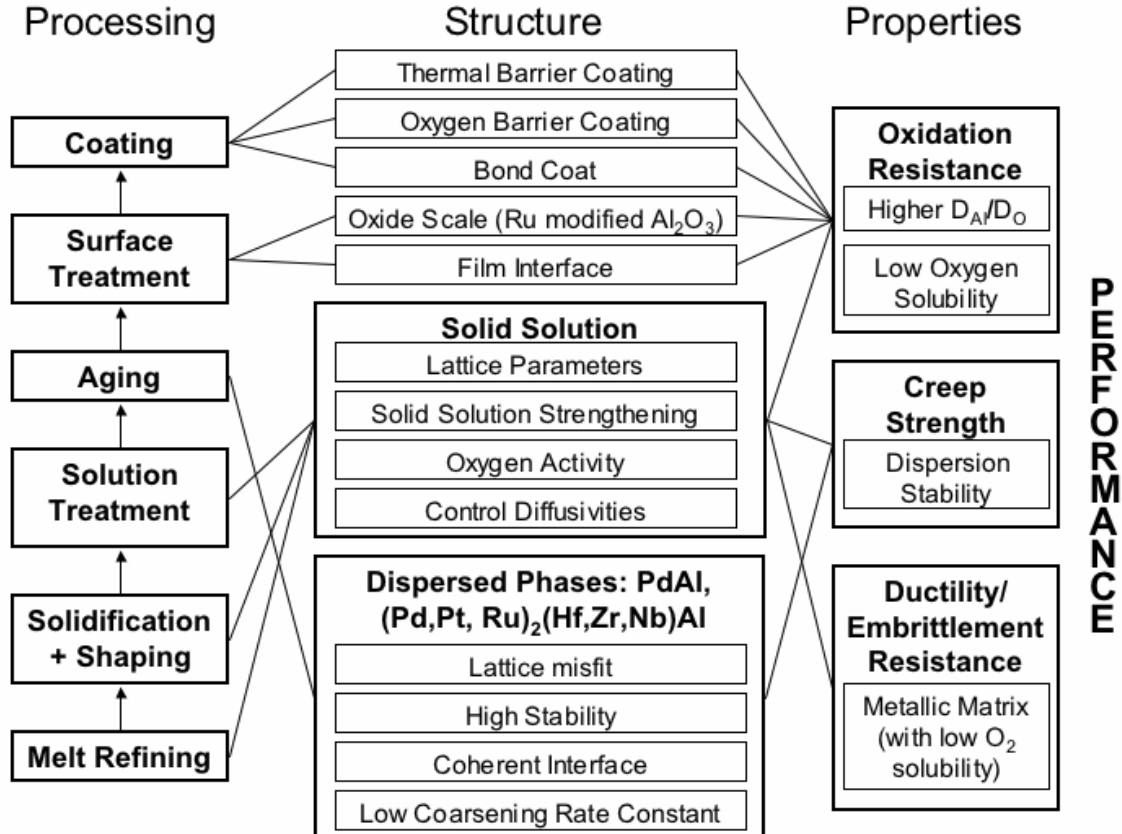

Figure 1. System chart representing coated Nb-based superalloy for aeroturbine blade applications.

Based on experience in Ni-based superalloys, the primary microstructural concept is a metallic matrix alloy solution, strengthened by a fine dispersion of low-misfit coherent aluminide precipitates incorporating low diffusivity components for coarsening resistance. The precipitates contribute both creep strength and a source of Al for oxidation resistance via Al_2O_3 passivation. As predicted by Wagner's analysis [2] the critical alloy Al content, N_{Al}^{Crit}, for formation of a stable passivating Al_2O_3 film is expressed by:

$$N_{Al}^{Crit} = A \left(\frac{N_O^{(s)} D_O}{D_{Al}} \right)^{1/2}$$

(1)

where A is a constant, $N_O^{(s)}$ is the oxygen solubility in the alloy matrix, and D_O and D_{Al} are the diffusivities of oxygen and aluminum, respectively. Matrix solution requirements thus include low O solubility and a high diffusivity ratio of Al to O to maintain passivation.

Results and Discussion

As summarized in Table 1 [3,4], a survey of potential aluminide phases employing available solution thermodynamics and FLMTO quantum-mechanical calculations of compound stabilities identified the Pd_2HfAl L2$_1$ Heusler phase as the most promising first candidate in terms of stability and lattice parameter, supported by preliminary calculations using the FLAPW method. Quaternary alloys were studied to validate and refine phase relations. Measured tie-tetrahedra in the Nb-Pd-Hf- Al system directly established the composition limits of the desired BCC-Pd_2HfAl two phase field, and a potentially useful BCC-Pd_2HfAl-PdAl three-phase field, as reported in a recent publication [5]. The tie-tetrahedra in the Nb-Pd-Hf-Al system existing at 1200°C and the projection of the tetrahedra on the Pd-Hf-Al basal plane are shown in Figures 2 and 3 respectively.[1]

Table I. Calculated properties for selected Heusler phases [3,4]

Compound	a (calc), nm (at 0 K)	a (expt), nm (at 298 K)	Lattice mismatch (w.r.t pure Nb at 298 K)	$-\Delta E$ (formation) (kJ/mol-atom)
Ni_2TiAl	0.587	0.5872, 0.5865	-11.1% to -11.05%	82.71
Ni_2VAl	0.578	0.633	-12.4% to -4.11%	62.36
Ni_2ZrAl	0.610	0.6123	-7.58% to -7.24%	80.35
Ni_2NbAl	0.600	0.5974	-9.5% to -9.09%	66.83
Ni_2HfAl	0.610	0.6081	-7.88% to -7.58%	91.51
Ni_2TaAl	0.595	0.5949	-9.88% to -9.87%	75.89
Pd_2HfAl	0.633	0.6367	-4.11% to -3.55%	77.69

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[1]Numbers in parentheses in Figure 3 represent the phase Nb content in at. pct. measured by standard EDS (Energy Dispersive Spectroscopy) SEM analysis using Nb L-alpha Xrays, typically showing less than 1 at. pct. Nb. Recent analysis using Nb K-alpha Xrays however indicates the Nb contents may be as high as 10 at. pct., suggesting high L-alpha absorption, and further microanalysis conducted at a higher accelerating voltage is underway to resolve this apparent discrepancy.
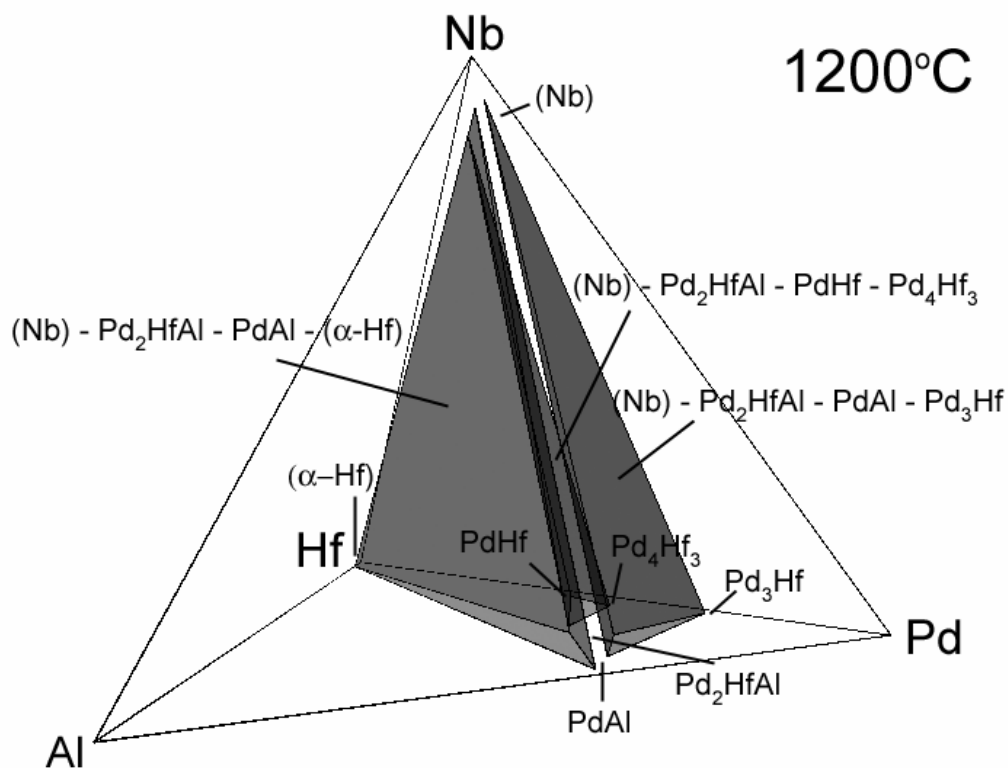
Figure 2. Tie-tetrahedra in the Nb-Pd-Hf-Al quaternary system at 1200˚C.
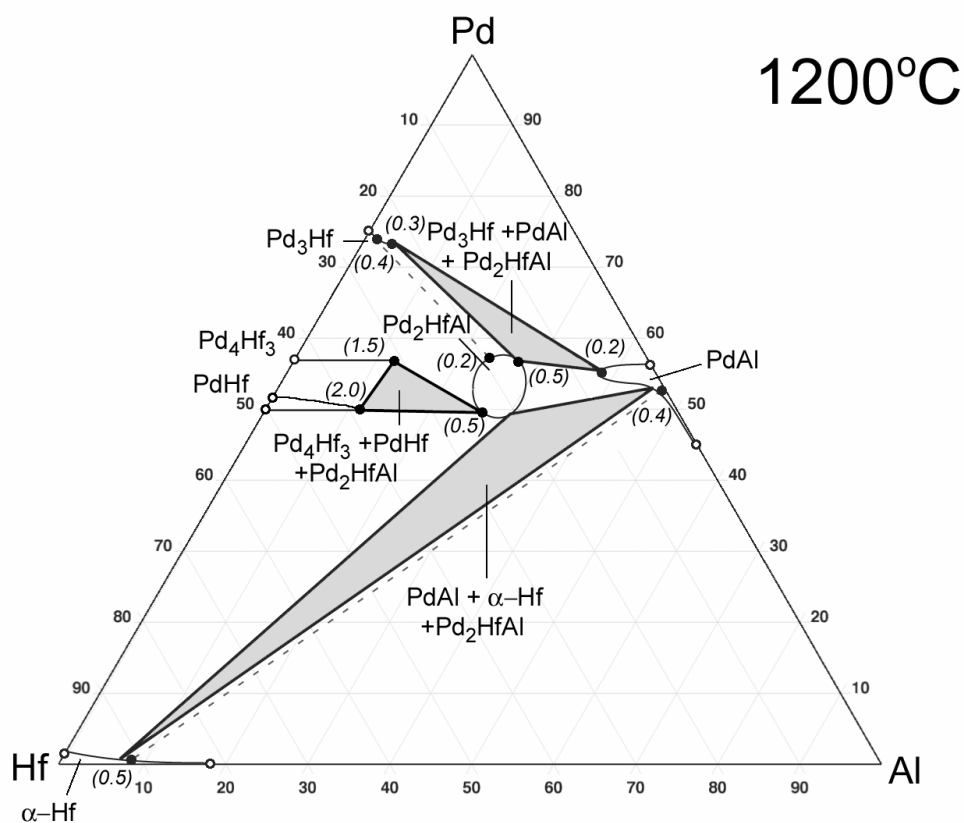

Figure 3. Projection of the Nb-Pd-Hf-Al tie-tetrahedra bases on the Pd-Hf-Al plane (1200˚C).

A thorough reassessment of the solution thermodynamics of this system is underway integrating well chosen electronic calculations of compound formation energies employing both FLAPW all-electron and VASP pseudopotential methods. New procedures for efficiently integrating CALPHAD thermodynamic assessments with selective electronic-level total-energy calculations have been developed in collaboration with Prof. Mark Asta of Northwestern using a cluster expansion description of solid solutions. Our recently published assessment of the Nb-Hf system [6] has now been expanded to the Nb-Al and Hf-Al systems to describe the Nb-Hf-Al ternary system (Figure 4). Lattice parameter calculations are integrated into a molar volume database for control of interphase misfit. Efficient thermodynamic assessments combine calculated 0˚K formation energies with measured compound melting points and phase boundaries to define entropic contributions.
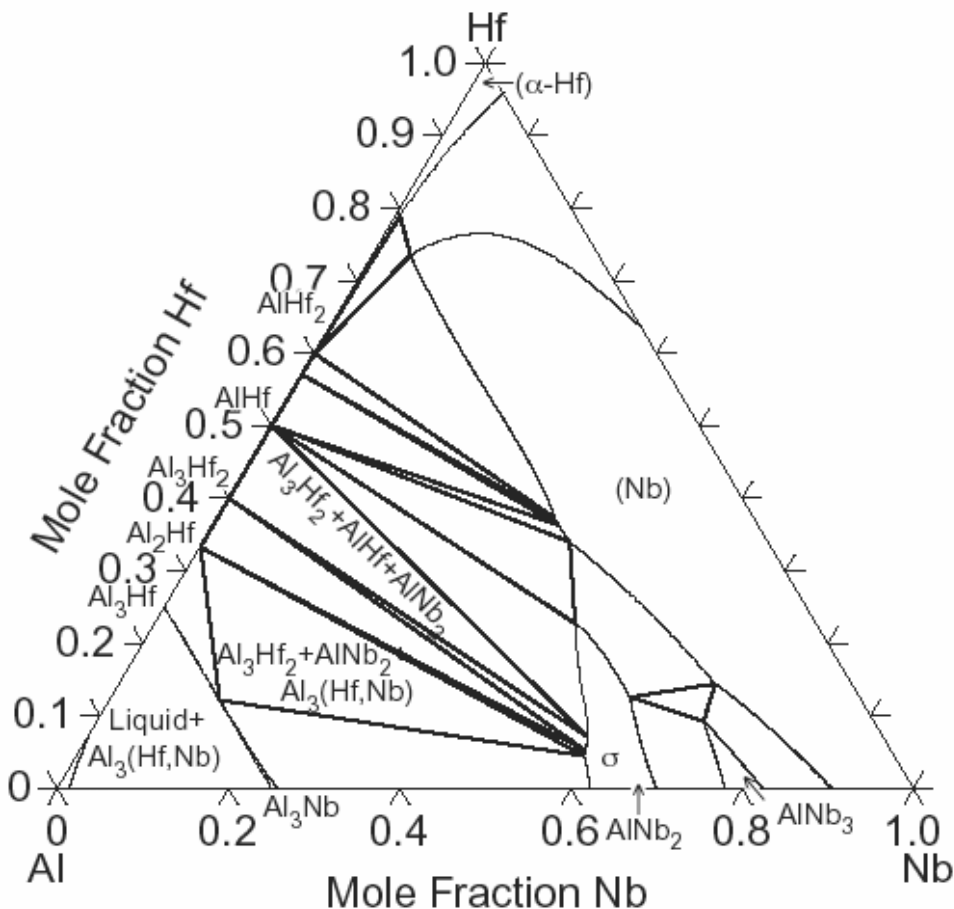

Figure 4. Calculated isothermal section of the Nb-Hf-Al system at 1300˚C.

Based on the thermodynamics so far established, model alloys demonstrate desired fine dispersions of $L2_1$ Pd_2HfAl and $B2$ $PdAl$ in a Nb matrix as shown by the dark field TEM micrographs of Figure 5 taken using aluminide superlattice reflections [7]. The model alloys show a high microstructural stability at 1000˚C compared to Ni-base alloys. Further TEM studies are underway to test for a novel octahedral morphology of coherent precipitates predicted for the unusual "inverse" elastic anisotropy of Nb alloys.

FLAPW calculations for the Heusler phase with partial substitution of Zr in the Hf sublattice predict slight improvement of both thermodynamic stability and lattice parameter for low misfit with Zr addition. Based on relative stabilities of B2 binary compounds, partial substitution of Pt for Pd was next explored for further improvement. Figure 6 summarizes the predicted enthalpy

of formation, enthalpy of mixing, and molar volume for both the Hf-Zr and Pd-Pt intermixing in the $L2_1$-structured $(Pd,Pt)_2(Hf,Zr)Al$ Heusler phase. The curves represent best fits of the Redlich-Kister polynomials employed in our solution thermodynamic databases. Although Pt substitution strongly enhances thermodynamic stability and lattice expansion for reduced misfit, the $L2_1$ Heusler phase treated here is no longer the ground state structure in the limit of the $Pt_2(Hf,Zr)$ Al compositions. The predicted Hf-Zr intersolubility in $Pd_2(Hf,Zr)Al$ has been confirmed by Pd_2HfAl-Pd_2ZrAl diffusion couple experiments at 1100˚C (Figure 7). A manuscript reporting these results is in preparation [8].

(a) Prototype Nb-Al-Hf-Pd Alloy
81.51Nb-9.34Pd-2.80Hf-6.34Al, at%;
As cast followed by 1000°C for 200 hrs

(b) Prototype Nb-Al-Pd Alloy
84Nb-8Pd-8Al (in at%)
As cast followed by 1000°C for 500 hrs

Heusler (Pd_2HfAl) Precipitates
in a (Nb) Matrix

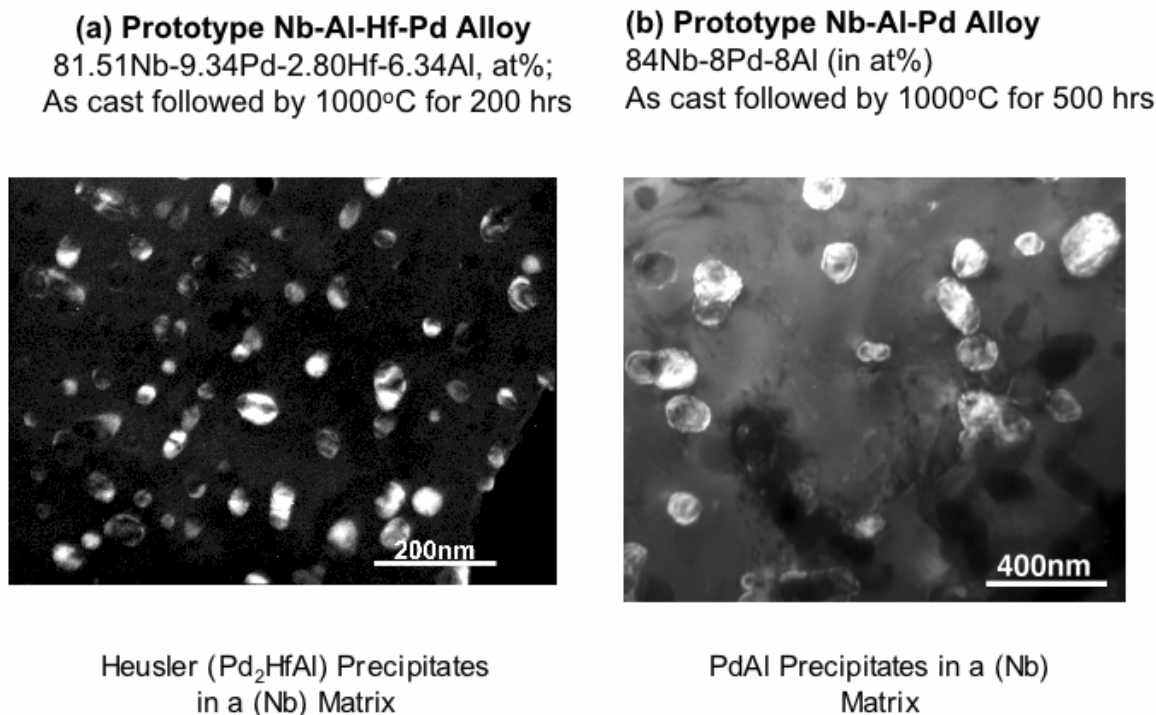PdAl Precipitates in a (Nb)
Matrix

Figure 5. Dark-field TEM micrographs of Pd_2HfAl and PdAl dispersions in Nb alloys [7].

Toward optimization of matrix solution composition, electronic calculations also explore valency effects on interstitial O activity employing bond topological concepts [9]. Computed charge densities in the octahedral sites of BCC Nb and Mo account for an observed [10] dependence of O solubility on alloy electron/atom (e/a) ratio. The predictions for alloying elements in BCC Nb are summarized in Figure 8 showing the trend holds until the e/a of Ru. Short-range order of B2 type is being investigated for the BCC Nb-based solid solution in order to promote 2nd neighbor bonding across the octahedral site as a more efficient means of increasing the site charge density. Incorporating O in both thermodynamic and atomic mobility databases, composition directions are predicted for reduced O solubility and enhanced Al/O diffusivity ratio. The mobility database is also augmented by electronic-level calculations of diffusion energetics with emphasis on prediction of slow-diffusing components for control of multicomponent coarsening resistance [11]. The predicted activation energy for self-diffusion in BCC Ta is in very good agreement with experiment, but is 15% low for the case of Nb. For dilute solution interdiffusivities in Nb alloys, we have employed a five-frequency model for correlation effects incorporating vacancy-solute interactions up to second nearest neighbors. Figure 9 summarizes measured and predicted diffusivities at 1300°C relative to the self-diffusivity of Nb. The predicted relative diffusivity of Mo is in good agreement with experiment. In our search for slow diffusers to enhance microstructural stability, we are very encouraged by the prediction that the activation energy for Re diffusion is 50% higher than that of Mo, giving a Re diffusivity as low as W, the slowest diffuser yet measured. In support of the

prediction, a Nb/Re diffusion couple has shown no measurable intermixing at 1100°C, and higher temperatures are next being investigated.
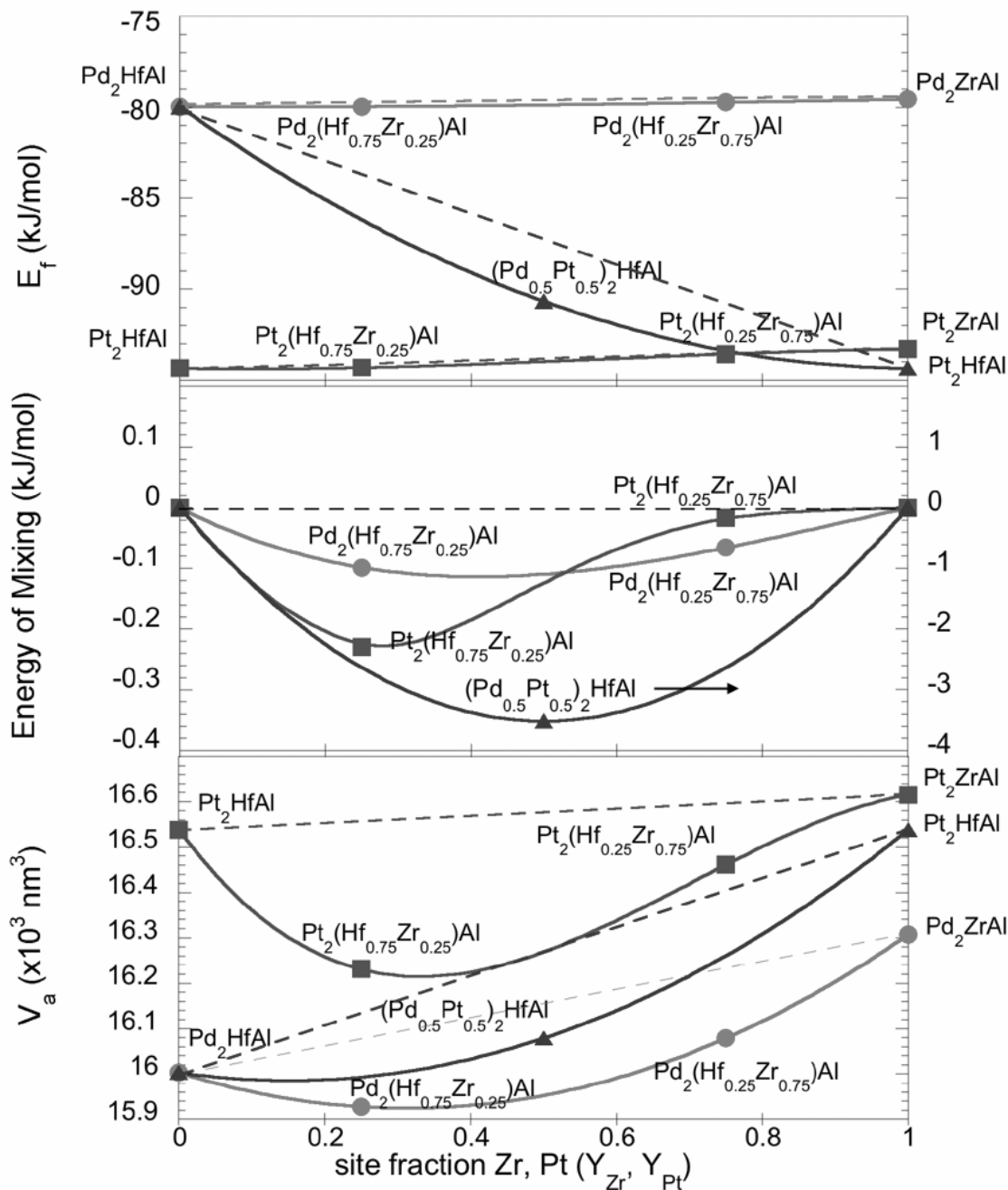

Figure 6. FLAPW calculations of heat of formation, heat of mixing, and molar volume in the (Pd,Pt)$_2$(Hf,Zr)Al $L2_1$ phase.

Preliminary oxidation studies on both model alloys and Heusler intermetallics demonstrate continuous scale formation involving varying combinations of Al_2O_3 and HfO_2, but do not yet demonstrate desired recession rates. Employing the models and databases thus far developed integrated via the THERMOCALC thermodynamic and DICTRA diffusion kinetic codes, a team of students in an undergraduate Materials Design class at Northwestern has performed the theoretical design of oxidation resistant Nb alloys with a combination of Pd$_2$HfAl and PdAl phases dispersed in a multicomponent BCC Nb-based matrix. With thermodynamically compatible additions of Mo, W and Ru in the matrix, the theoretical designs satisfy the Wagner criterion for Al_2O_3 passivation at 1300°C reducing O solubility by 10^{-2}, reducing O diffusivity

by 10^{-1} and enhancing Al diffusivity by 10^3. Their project report [12] was submitted to the TMS-AIME Undergraduate Design Competition, winning 1st Prize for 2004. Prototype alloy validation is underway. Further designs to be evaluated in the next year employ multicomponent oxide scales for more efficient passivation.
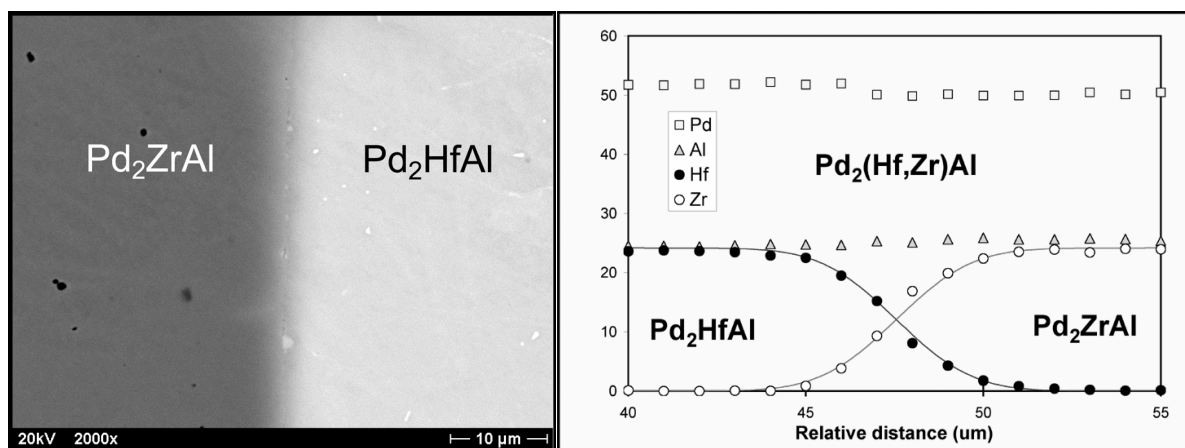

Figure 7. (a) BSE image of cross section of the Pd$_2$ZrAl/Pd$_2$HfAl diffusion couple; (b) Concentration profile obtained from (a) by EPMA [8].
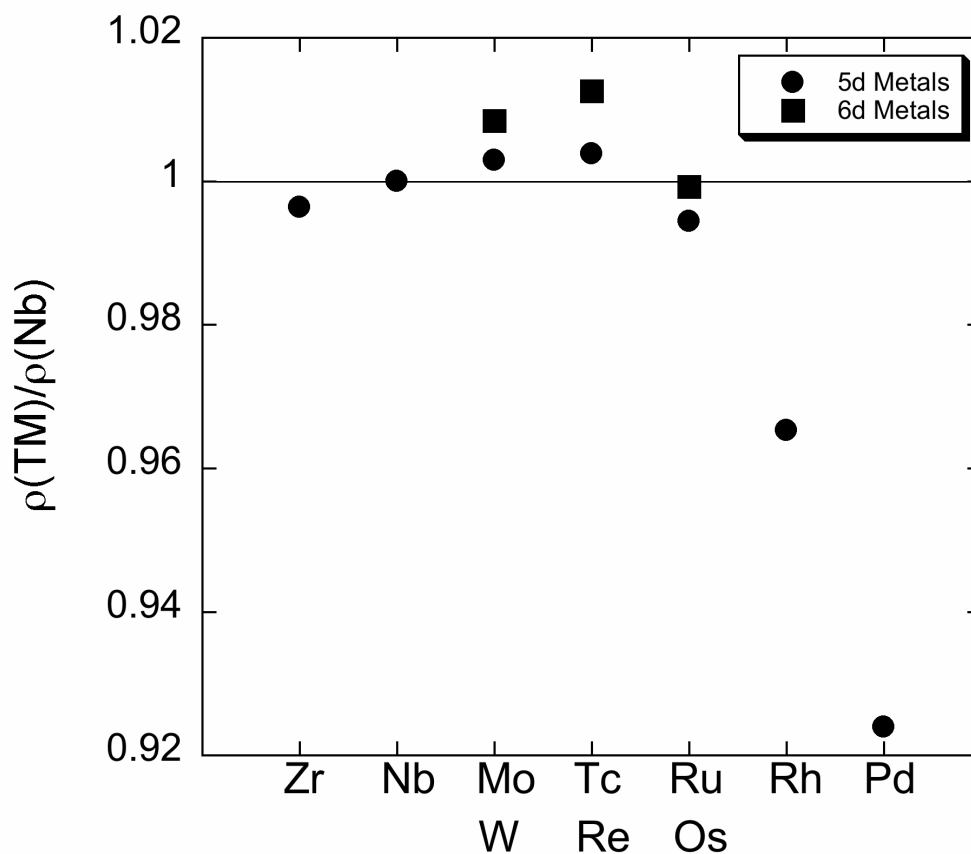

Figure 8. Computed charge density in BCC octahedral sites adjacent to solute atoms in Nb solid solution, scaled to pure Nb case [9].
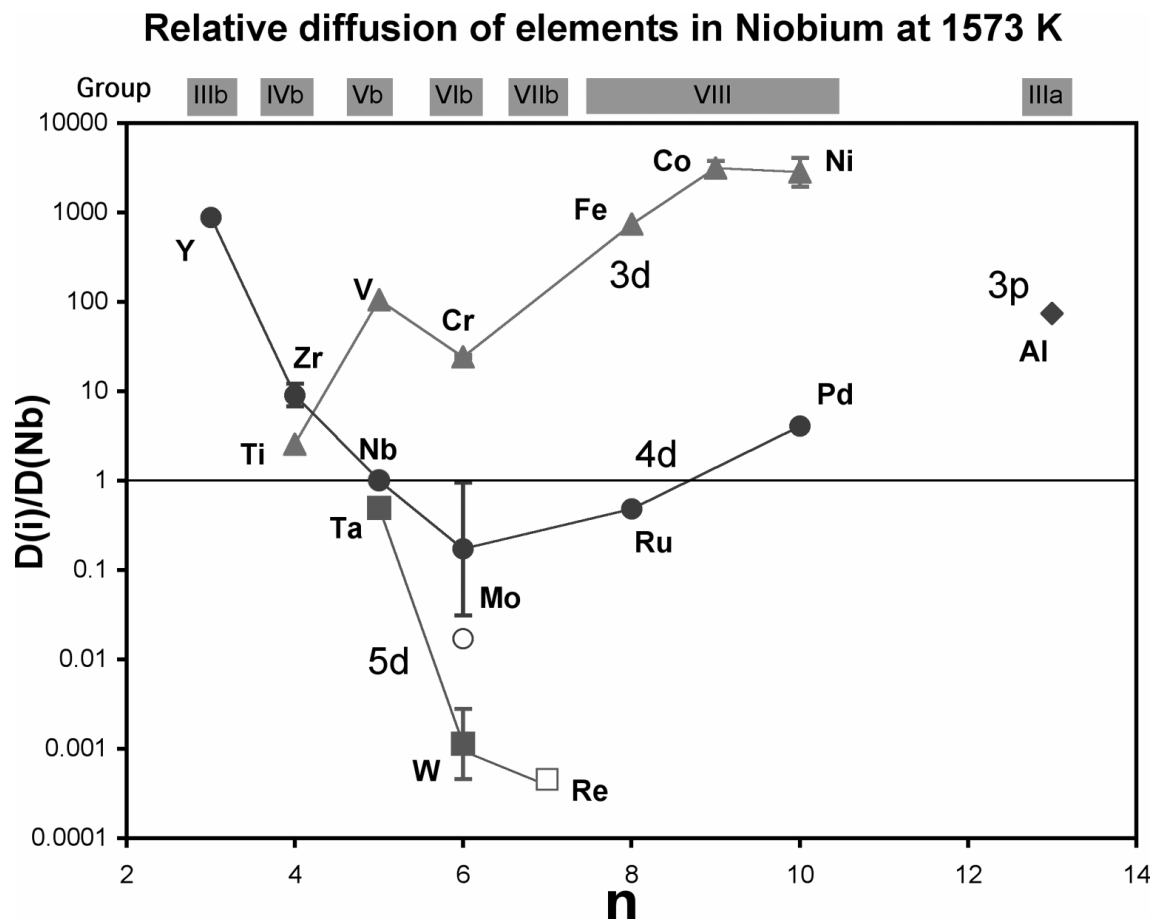
Figure 9. Measured and predicted dilute interdiffusivities in Nb at 1300˚C, normalized to Nb self-diffusivity [11].

Conclusions

Efficient integration of quantum mechanical 0˚K formation energy calculations with selective measurement of high temperature phase relations allows accelerated development of thermodynamic databases for computational materials design, of particular importance for novel systems such as Nb base alloys where experimental phase diagram data is limited. An important byproduct of the quantum mechanical calculations is the rapid development of molar volume databases supporting control of interphase misfit. Quantitative charge density calculations can also provide guidelines for rapid assessment of interstitial solution thermodynamics governing oxygen solubility behavior. Computational quantum mechanics can also provide useful estimates of substitutional component diffusivities, identifying candidate slow diffusers to enhance microstructural stability at high temperatures.

The integration of these capabilities in the computational design of Nb base alloys exploiting precipitation strengthening by coarsening resistant controlled-misfit coherent multicomponent aluminide phases offers a high potential for combining oxidation resistance and creep strength for application at 1300˚C and above.

Acknowledgments/Disclaimer

References

1. G.B. Olson, "Computational Design of Hierarchically Structured Materials," *Science*, 277 (5300) (1997), 1237-1242.

2. C. Wagner, "Reaction Types with the Oxidation of Alloys", *Z. Elektrochemie*, 63 (1959), 772-782.

3. W. Lin and A.J. Freeman, *Physical Review B*, 45 (1992), 61-68.

4. M. Kim and A.J. Freeman, Northwestern University, Evanston, IL, unpublished research, 2002.

5. A. Misra, R. Bishop, G. Ghosh and G.B. Olson, "Phase Relations in Prototype Nb-Pd-Hf-Al Alloys," *Metallurgical and Materials Transactions A*, 34A (2003), 1771-1781.

6. G. Ghosh, A. van de Walle, M. Asta and G. B. Olson, "Phase Stability of the Hf-Nb System: From First-Principles to CALPHAD," *CALPHAD,* 26 (4) (2002), 491-511.

7. G. Ghosh and G.B. Olson, Northwestern University, Evanston, IL, unpublished research, 2003.

8. M. Kim, A.J. Freeman, S. Kim, J. Perepezko and G.B. Olson, "Phase Stability of the Multicomponent Intermetallic $L2_1$ Heusler Phase $(Pd,Pt)_2(Hf,Zr)Al$," manuscript in preparation.

9. M. Eberhart, Colorado School of Mines, Golden, CO, unpublished research, 2003.

10. R.T. Bryant, "The Solubility of Oxygen in Transition Metal Alloys", *Journal of Less-Common Metals*, 4 (1962) 62-68.

11. C. Woodward, Northwestern University, Evanston, IL, unpublished research, 2003.

12. E. Altinoglu, J. Bolos and N. Colligan, "Noburnium: Oxidation Resistant Nb Superalloy," Northwestern University, MSc 390 Materials Design project report (May 2003), submitted to TMS-AIME Undergraduate Design Competition.