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Identifying rhenium substitute candidate multi-principal-element alloys from electronic structure and thermodynamic criteria

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Abstract

While rhenium has proven to be an ideal material in fast-cycling high-temperature applications such as rocket nozzles, its prohibitive cost limits its continued use and motivates a search for viable cost-effective substitutes. We show that a simple design principle that trades off average valence electron count and cost considerations proves helpful in identifying a promising pool of candidate substitute alloys: The Mo-Ru-Ta-W quaternary system. We demonstrate how this picture can be combined with a computational thermodynamics model of phase stability, based on high-throughput ab initio calculations, to further narrow down the search and deliver alloys that maintain rhenium's desirable hcp crystal structure. This thermodynamic model is validated with comparisons to known binary phase diagrams sections and corroborated by experimental synthesis and structural characterization demonstrating multi-principle-element hcp solid-solution samples selected from a promising composition range.

Representative figure: Figure 5

Keywords: electronic structure, phase equilibria, alloy

Introduction

Among the refractory metals, rhenium exhibits a unique combination of a high melting point, good ablation resistance, good high temperature strength and creep resistance. Rhenium is known to be the only refractory element that does not display a measured ductile-brittle transition, such that it features relatively high ductility at low temperature [1,2]. The combination of low-temperature ductility and high melting point makes Re-based materials attractive as structural materials for applications such as rocket nozzles, which involve high temperatures and fast thermal cycling. However, the high cost (which have reached just over 10,000 \$/kg in the past 15 years) and limited worldwide reserves of Re place a limit on its use [3,4]. This situation has motivated the search for a viable and cost-effective replacement strategies for rhenium as a material for solid propellant rocket nozzles.

In this paper, we use an approach based on both electronic structure and computational thermodynamics that is aimed at focusing the search for such a substitute material. We first develop and motivate a simple design principle based on the candidate material's average valence electron count per atom. We then intersect this criterion with the thermodynamic constraint that the candidate material should retain the most important determinant of rhenium's desirable property, namely, its single-phase hcp crystal structure. As the determination of phase equilibria in an alloy system with a potentially large number of components and phases via purely experimental means is expensive and time-consuming, we leverage a recently developed framework [5] for high-throughput computational thermodynamics based on the integration of first-principles electronic structure calculations with the well-established CALculation of PHase Diagram (CALPHAD) framework. These predictions are then validated by comparison to earlier thermodynamic assessments and by synthesizing and characterizing alloy samples at selected compositions. The space of candidate alloys identified in this fashion happens to include multiple principal component (or "high entropy") alloys.

Design principles

Within a "rigid band" picture, the properties of transition metals (and their alloys) is determined by their number of d valence electrons per atom [6]. This picture is best illustrated by observing that the same systematic sequence of crystal structure is seen across the $5d$ and $4d$ sequences: hcp, bcc, hcp, fcc (see Table 1). From a physical point of view, this phenomenon can be understood by the fact that, if the electronic density of states for a given crystal structure is independent of the number of valence electrons (i.e. "rigid"), then materials properties can only be a function of how many electrons are available to fill the possible electronic states up to the Fermi level. This picture provides us with one simple guiding principle to identify possible alternative hcp alloys: focus on alloys having roughly between 5 and 6 valence electrons per atom on average.

This band filling picture turns out to also govern other more complex properties of relevance in to our design goal. It has been shown [7] that rhenium's exceptional twinning behavior contributing to its desirable mechanical properties can also be traced back to its specific number of valence electrons. In essence, rhenium's mechanical behavior is driven by twinning, and the local structure of the dominant twin grain boundary mimics the Frank-Kasper coordination polyhedra of so-called tetrahedrally close packed (TCP) transition metal intermetallic compounds that also tend to be stabilized near half d -band filling [8-12].

Another constraint is to maintain rhenium's high melting point. Once again, the number of d valence electrons per atom is a good predictor of melting point (See Table 1): Along both the $4d$ and $5d$ series, the maximum melting point is reached for about 4 valence electrons per atom (just one less than for Re). The high melting point constraint also suggests avoiding $3d$ elements additions.

Intersecting these various constraints leads us to consider a simple alloy design approach: Form a substitutional alloy of $4d$ and $5d$ elements yielding a target of roughly 5 valence electrons per atom that

minimizes cost. This constrained optimization problem can be visually represented by plotting each element's price per mol as a function of the number of valence electrons (see Figure 1). The cost of a suitable Re-equivalent binary alloy can be simply read off from the intersection between a segment joining the two elements and a vertical line at centered at the desired number of electrons. A similar construction holds for multicomponent alloys and gives a range of theoretically attainable cost.

From this construction, we can immediately rule out some elements: It is clear that alloying Rh, Pt or Au with even the best-case scenario of W would not yields a lower cost than rhenium's. One can also readily identify a priori cost-effective candidates: For instance, a Mo-Ru-W alloy would appear to provide an especially inexpensive option. Although the addition of Ag may appear desirable from a cost perspective, Ag has a very low melting point and is known to exhibit a low solid solubility in either Ru [13] or bcc elements such as Mo [14], thus making its addition unlikely to be beneficial. The addition of Ta or Nb leads to an only slightly more expensive alloy and we thus consider this possibility as well. However, since the melting point of Nb is significantly lower than the one of Ta, we do not currently consider Nb in our search. This leaves us with the task of exploring the Mo-Ru-Ta-W quaternary system, with a special focus on the plane where the effective number of valence electron per atom matches that of Re, as defined by the linear equality:

$$4x_{Mo} + 6x_{Ru} + 3x_{Ta} + 4x_W = 5$$

where x_A denotes the atomic fraction of element A, subject to the obvious constraint $x_{Mo} + x_{Ru} + x_{Ta} + x_W = 1$. We call this region the Re-equivalent plane. Although this simple design principle can quickly rule out clearly unfavorable choices and target desirable candidates, it remains essential to further assess the thermodynamic stability of the hcp phase near the Re-equivalent plane, as the rigid band picture is not a perfect predictor of phase stability.

Results and Discussion

To assess the accuracy of our thermodynamic model, we first compare predicted binary sections with prior assessments available in the literature. Our primary focus is on single-phase hcp microstructures, and on phases that might limit the size of the hcp phase stability region. We do not report a detailed comparison with the Mo-Ta, Mo-W and Ta-W binary sections since these phase diagrams simply exhibit perfect mutual solubility within a bcc solid solution [15-17] that is not of interest for our primary goal.

As shown in Figure 2, in the Mo-Ru system, our thermodynamic model predicts the presence of the same phase relations as those reported in previous assessments [18,19]. In particular, the presence of the σ phase limits the solubility of Mo in Ru. In contrast, it should be noted that traditional *ab initio* high-throughput approaches are unable to predict the stability of the σ phase [20], as this phase is largely stabilized by configurational entropy. Nevertheless, the temperature range where the σ phase is stable is not perfectly reproduced in the present model and the solubility of Mo in Ru is overpredicted at high temperature.

The Ru-Ta system exhibits a number of competing phases (labeled ht1 and ht2 in Figure 3) near 50% composition that are difficult to accurately model due to their very similar free energies and the presence of mechanically unstable phases that are dynamically stabilized at high temperature due to anharmonic effects [21], a phenomenon that is characteristic of shape memory alloys [22]. Since these phases do not directly affect the boundary of the hcp region and all have very similar free energies, we chose to collectively model these phases as a single B2-ordered phase. The phase that does primarily limit the hcp region is a Ga_3Pt_5 -ordered phase. While this phase's specific crystal structure was not clearly identified in earlier experimental assessments [23], a prior first-principles high-throughput analysis of possible ordered phases in rhenium alloy systems [20] suggests that this phase indeed exhibits the Ga_3Pt_5 structure. Our calculations corroborate this and further indicate that configurational

and vibrational entropic effects are not detrimental to this phase's stability at high temperature.

Compared to the experimental assessment, our calculations appear to underpredict the solubility of Ta in hcp Ru and slightly overstabilize the Ga_3Pt_5 phase.

As seen in Figure 4, compared to an earlier assessment [24], our model's prediction of the Ru-W phase diagram understabilizes the σ phase: It is masked by two-phase equilibrium between the hcp and bcc phases at all temperatures. The hcp phase appears slightly over stabilized at high temperature, relative to the earlier assessment. This can be investigated further with a metastable phase equilibrium computed without the bcc phase. This shows that the σ phase appears in the correct composition range and that its free energy at lower temperatures should be reliable since it there leads to nearly the same hcp solubility limit.

The Mo-Ru-Ta and Mo-Ru-W ternary sections of this system have been studied [25,26] at temperatures lower than of interest in the present work ($<1500^\circ\text{C}$). These studies do not suggest the presence of additional phases that are not seen in the binary subsystems.

We now turn the prediction of the full quaternary phase diagram (Figure 5) and its comparison with actual samples synthesized (Table 2) with the goal of exploring the limit of the hcp region. The structure of all the phases present in each sample were identified via X-Ray Diffraction (XRD) (see Figure 8). We generate an isothermal section of the phase diagram at $T = 2000\text{K}$, as this is expected to approximate the sample synthesis and annealing temperature. All samples that were single-phase as synthesized (shown as blue points), are indeed in the predicted hcp stability region (whose boundary is shown by a red surface). Two experimental samples (labeled 1-1 and 1-2 in Table 2 and shown as white points on Figure 5 and Figure 6) clearly exhibit two phases, namely hcp and tetragonal. Our thermodynamic model also predicts a two-phase region at these compositions, but between an hcp phase and the orthorhombic Ga_3Pt_5 phase. These data points are, however, close to a tie-triangle joining the hcp,

Ga_3Pt_5 and σ phases (see Figure 6). The refined lattice parameters for the tetragonal phase ($a = 9.6 \text{ \AA}$ and $c = 5.0 \text{ \AA}$) closely match those of the thermodynamic model for the σ phase appearing in that tie-triangle ($a = 9.7 \text{ \AA}$ and $c = 5.0 \text{ \AA}$) and also match its $P4_2/mnm$ spacegroup. The other experimental samples (labeled 3-4 and 3-5 in Table 2 and shown as red points on Figure 5 and Figure 7) showed two phases (hcp and tetragonal) as-synthesized but the tetragonal phase disappeared upon annealing at a slightly higher temperature (2125K) than the isothermal the cross section shown (2000K). These compositions fall into multiphase equilibria involving the σ phase and either 1 or 2 hcp phases but lie very close to a 2-phase equilibrium involving two hcp phases at different compositions, i.e., a miscibility gap in the hcp phase (see Figure 7). Hence the thermodynamic model's predictions are nearly consistent with the observed phases equilibria. These compositions are of particular interest, as they straddle the Re-equivalent plane, as seen in Figure 5.

From an alloy design perspective, the phase diagram (Figure 5) reveals that the hcp stability field extends the closest to the Re-equivalent plane for Mo-rich compositions, although one should keep in mind that our model may over overpredict Mo solubility. The region near samples 3-4 and 3-5 is also very promising and the thermodynamic model predicts that there should be actually a fairly wide range of compositions that stabilize an hcp structure (or a perhaps mixture of two hcp phases at different compositions) near the Re-equivalent plane.

Conclusion

We have presented a theoretical basis for a simple design criterion for the identification of Re candidate substitutes: Based on a rigid-band picture, one should focus on alloys whose composition lies on a *Re-equivalent plane*, defined such that average number of valence electron per atom matches that of Re. Optimizing cost under this constraint over all alloys made of 4d and 5d elements lead us to consider the Mo-Ru-Ta-W quaternary system. A thermodynamic model based on the integration of electronic

structure calculations with the Calphad framework then enabled us to identify alloy compositions near the Re-equivalent plane that maintain rhenium's desirable hcp structure. The accuracy of this thermodynamic model was assessed with comparisons to known binary phase diagrams sections and further corroborated by experimental synthesis and structural characterization of samples selected from a promising composition region. This region includes multiple principal component alloys having an hcp structure at compositions near $\text{Mo}_{0.3}\text{Ru}_{0.512}\text{Ta}_{0.064}\text{W}_{0.125}$ and $\text{Mo}_{0.292}\text{Ru}_{0.555}\text{Ta}_{0.031}\text{W}_{0.122}$, which straddle the Re-equivalent plane. More broadly, we hope that the approach described here in will suggest novel avenues for materials design and optimization.

Methods

Computational. The phase equilibria were computed using high-throughput Calphad tools based on electronic structure calculations [5] that calculates the free energy of solid solutions (including ordered phases with sublattice disorder) using the Special Quasirandom Structure (SQS) formalism [27], implemented via an efficient stochastic algorithm [28] in conjunction with a truncated cluster variation method-based approximation to model short-range order [5]. This data is then fitted with a Calphad-type model based on the Compound Energy Formalism (CEF) [29-31]. The free energies of the stable end members of the solid solution phases are taken from the SGTE elemental database [32] while those of the unstable end members are obtained with the inflection detection method [33]. The formation free energies of the ordered compounds and solid solutions are based solely on electronic structure calculations.

The electronic structure calculations were performed with VASP [34,35] using the projector-augmented wave (PAW) method [36]. For all calculations, the PBE functional [37] was used, the planewave cutoff was set to 300 eV, the number of k -points per reciprocal atom [38] was set to 8000 and fermi level smearing was performed with the Methfessel-Paxton [39] method with $\sigma = 0.1$ (for relaxation runs and

phonon calculations). Energies were calculated with a static run on the relaxed geometries using the tetrahedron method with Blöch corrections [40].

The computation of the quaternary thermodynamic model required 135 electronic structure total energy calculations. Of these, 32 involved mechanically and thermodynamically unstable structures. To assign them a plausible free energy (as required by the Calphad framework), we used the recently developed inflection detection approach, combined with the epicycle method [41,42], using the `robustrelax_vasp` command of Alloy Theoretic Automated Toolkit (ATAT) [43,44] with its defaults settings. In addition, to ensure that free energy differences between different crystal structures are accurately reproduced, 36 lattice dynamics calculations were performed using the supercell method [45] with the `fitfc` code [43] within the harmonic approximation. These calculations encompass all end members (in which all sublattices are fully occupied by one element) and some solid solution datapoints within the Ru-rich hcp phase.

The accuracy of the calculated free energy is in part a function of the density of the sampling of composition space with SQSs. This density for each phase is indicated below by the “level” of accuracy used (level 0 means only end members, level 1 also includes midpoints between endmember, level 2 also includes sublattice compositions in steps of $\frac{1}{4}$, etc. See [5] for further details). For each phase, the level was selected in proportion to the accuracy needed: hcp (level 2, with level 6 sampling of the Ru-rich region, including ternary compositions; level 2 for phonon, with a few level 6 datapoints), σ phase (level 1 for energies, level 0 for phonons), bcc (level 2, with some level 5 datapoints for energies, level 0 with some level 1 datapoints for phonons), Ga_3Pt_5 (level 1 for energies, level 0 for phonons), B2 (level 1 for energies, level 0 for phonons). Following earlier descriptions [29], the σ phase is modeled with 3 sublattices and with Wyckoff position a_j hosting the hcp element (Ru), site g hosting bcc elements (Mo,Ta,W) and the two i sites hosting any element. The two sublattices of the Ga_3Pt_5 phase are also

selectively occupied based on the coordination of each site, with *a,e,j* sites hosting Ru and *b,h* sites hosting Mo,Ta,W.

The binary and ternary sections were plotted with the Pandat software [46] while the quaternary sections were generated with the `ocplodpd` [47] command of the Alloy Theoretic Automated Toolkit (ATAT) [43,44], which relies on OpenCalphad [48,49] as its thermodynamic equilibria calculation engine.

Experimental. The experimental alloy samples were cast using powder metallurgy from >99.9% pure 250-mesh powders. The constituent powders were mechanically mixed to the correct wt% of alloy composition and then ball milled for 30 minutes. The resulting milled powder was then pressed into pellets using 30,000 psi of force to be sintered at 1850 °C for 8 hours. The pellets were then arc melted in vacuum, flipped, and re-melted. Slag from on the ingot surface was removed and the ingot was finally annealed at 1850 °C. The resulting ingots were roughly 0.5-1 cm³ in volume. As such, little solute gradients should be present due to the rapid heating and cooling rates inherent to the arc-melting process, unlike typical larger scale casting methods. The surfaces were oxide- and contaminant-free and exhibited a generally small grain size (~100µm for the single-phase alloys). This combination allowed for the ingots to be directly investigated in the XRD without further processing or polishing. Samples 1-1, 1-2, 3-4 and 3-5 were annealed at 1850 °C for 8 hours (the other samples were already single phase as synthesized).

Determination of alloy structure was accomplished with the aid of a D8-Discover X-Ray diffractometer with a Co source operated at 40mA 35kV giving a K α wavelength of 1.79Å. The x-ray spectra were taken using a 300 second exposure time for each frame. The samples were translated over a large area during the spectra collection, to sample as many grains as possible during investigation. This XRD system uses an area detector that is able to collect 30° sections of the diffraction pattern per image, allowing for powder diffraction type measurements that would be much more difficult with more conventional

detector systems. The frames from the area detector are stitched together and integrated with the accompanying Bruker™ software to provide a single 2θ vs intensity profile that is more typically used in XRD analysis. We used MDI-Jade software version 4.2.0 to index the XRD profiles, which uses constituent elements and their chemically close neighboring elements to match known crystal structure's intensity vs 2θ plot found in commercial powder diffraction file (PDF) databases.

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Tables

Table 1: Selected properties of selected transition metals [50]. (Prices are approximate and were collected from <http://www.metalprices.com> and <http://www.metal-pages.com> in June 2011)

Element	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Structure	hcp	Bcc	bcc	hcp	hcp	fcc	fcc	fcc
valence electrons	2	3	4	5	6	7	8	9
T melting (°C)	1852	2468	2617	2200	2250	1966	1552	962
\$/mol	2.3	4.1	6.8	>10 ⁵	590	6600	2500	130

Element	Hf	Ta	W	Re	Os	Ir	Pt	Au
Structure	hcp	Bcc	bcc	hcp	hcp	fcc	fcc	fcc
valence electrons	2	3	4	5	6	7	8	9
T melting (°C)	2150	2996	3410	3180	3045	2410	1772	1064
\$/mol	130	29	6.9	1900	2300	3000	12000	11000

Table 2: Characteristics of synthesized alloy samples

Sample	Mo (at. %)	Ru (at. %)	Ta (at. %)	W (at. %)	Phases Indexed
1-1	0	0.689	0.049	0.262	HCP + Tetragonal
1-2	0	0.645	0.072	0.283	HCP + Tetragonal
2-1	0	0.942	0.035	0.023	HCP
2-2	0	0.878	0.074	0.048	HCP
2-3	0	0.879	0.025	0.097	HCP
2-4	0	0.911	0.018	0.071	HCP
2-5	0	0.879	0.007	0.114	HCP
3-1	0.229	0.652	0	0.119	HCP
3-2	0.285	0.596	0	0.119	HCP
3-3	0.234	0.612	0.031	0.122	HCP
3-4	0.292	0.555	0.031	0.122	HCP + Tetragonal†
3-5	0.300	0.512	0.064	0.125	HCP + Tetragonal†

†phase present in small amount; disappeared upon annealing at 2125K.

Figures

Figure 1: Cost per mol as a function of number of valence electrons per atom for selected 4d (black squares) and 5d (grey squares) transition metals. The cost of alloys having the desired number of electrons (grey rectangle) can be identified by the intersection of a line joining the elements of the alloy and the grey rectangle.

Figure 2: Mo-Ru phase diagram found in earlier assessments [19] (a), compared with our prediction (b).

Figure 3: Ru-Ta phase diagram from an earlier assessment [23] (a), compared with our prediction (b).

Figure 4: Ru-W phase diagram from an earlier assessment [24] (a), compared with our prediction (b).

Figure 5: Calculated isothermal ($T = 2000\text{K}$) section of the quaternary Mo-Ru-Ta-W phase diagram, shown in stereoscopic view. Experimental sample compositions are shown by small spheres while the Re-equivalent plane is shown in yellow.

Figure 6: Calculated Ru-Ta-W isothermal section at 2000K. The experimental sample compositions are indicated by circles.

Figure 7: Calculated Mo-Ru-W isothermal section at 2000K. The experimental sample compositions (projected onto the $x_{Ta} = 0$ plane from their positions in a Gibbs tetrahedron) are indicated by circles. The $x_{Ta} = 0$ plane is shown here (instead of the actual, small, Ta composition) to better visualize the tie lines.

Figure 8: XRD spectra for (a) all samples containing single phase and (b) those exhibiting two phases as synthesized. The primary phase is always hcp while the secondary phase was identified as a tetragonal structure with space group $P4_2/mnm$. In (b), only the peaks for the tetragonal phase are indexed. It can be seen that the Series 1 alloys have much more secondary phase than the Series 3 alloys. Series 1 alloys have been annealed at 1850 °C while the Series 3 alloys in the top panel of (b) have not. After annealing at 1850° for 8 hours, all secondary phase in alloys 3-4 and 3-5 have disappeared, leaving only the hcp phase (bottom panel of (b)).