Selective Oxidation in Refractory High Entropy Materials

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Abstract

High entropy materials are a topic of substantial research interest due to the possibility of a large number of new material compositions that could fill gaps in application needs. One such need is high temperature stability, particularly oxidation resistance. A systematic understanding of oxidation behavior in high entropy materials is therefore required. This work uses both analytical and computational thermodynamic approaches to investigate the potential for, and extent of, selective component oxidation. These calculations are compared to experimental results from oxidation experiments conducted on the high entropy ultra-high temperature ceramics (Hf\textsubscript{0.2}Zr\textsubscript{0.2}Ti\textsubscript{0.2}Ta\textsubscript{0.2}Nb\textsubscript{0.2})C and (Hf\textsubscript{0.2}Zr\textsubscript{0.2}Ti\textsubscript{0.2}Ta\textsubscript{0.2}Nb\textsubscript{0.2})B\textsubscript{2} in 1 mol \%O\textsubscript{2} (balance argon) at 1700°C for 5 minutes. The results showed that a large tendency towards selective oxidation is expected, even for elements whose oxides exhibit a small difference in thermodynamic stability. Experimental results are consistent with these thermodynamic predictions.

Key words: high temperature oxidation, high entropy alloys, ultra-high temperature ceramics, high entropy carbides, high entropy borides
1.0 Introduction and Background

High entropy metals and ceramics, which are solid solutions consisting of four or more principal components are a new paradigm in materials design [1–6], and are of interest due to the large number of compositions that can be formulated and explored. Such an expansion of possible compositions can potentially fill challenging application needs, such as materials with improved mechanical and chemical stability at high temperatures. These multiple principal component materials have high configurational entropy, which is hypothesized to stabilize the solid solution phase or provide new combinations of phases. A sizable body of literature currently notes the improvement of mechanical properties [2,7]. Other proposed advantages to multi-principal component, high entropy materials are sluggish diffusion and cocktail effects, a term used to describe the synergistic effects of combining multiple elements in large concentrations [8]. Some researchers have explored the high temperature oxidation resistance of high entropy alloys (HEAs) [9,10] and carbides [11]. However, the effects of oxidation on the stability of the underlying material, its configurational entropy and its attendant properties, still need to be further understood.

High entropy ultra-high temperature ceramics (HE-UHTCs) are multi-principal component single phase ceramics, typically transition metal carbides, borides and nitrides, in which the random distribution of four or more metal species on its respective sublattice leads to the formation of a solid solution phase [3]. The increased configurational entropy further reduces the free energy of the material system, though such a reduction is relatively small—on the order of a few percent, depending on temperature—in comparison with the differences in the formation enthalpies of the oxide products, as discussed below.
Assuming a generic oxidation reaction for species M, \( M + O_2(g) = MO_2 \), the driving force for oxidation is given by the familiar free energy equation,

\[
\Delta G_{rxn}^{ox} = \Delta H_{rxn}^{ox} - T \Delta S_{rxn}^{ox}
\]

where the free energy of reaction is given by the difference in free energies of formation of the products and reactants, as shown in Equation (2).

\[
\Delta G_{rxn}^{ox} = \Delta G_f^{prod} - \Delta G_f^{reac}
\]

Entropy can be further described as in Equation (3).

\[
\Delta S = \Delta S_{vib} + \Delta S_{config}
\]

High entropy materials are characterized by additional configurational entropy, described by Equation (4):

\[
\Delta S_{config} = -k_B \sum_{i=1}^{N} x_i \log x_i
\]

Here, \( k_B \) refers to the Boltzmann constant, \( N \) is the number of species, and \( x_i \) is the mole fraction of each species. The maximum configurational entropy occurs when all species in the alloy occur at equimolar fractions and is given by (5).

\[
\Delta S_{config,max} = k_B \log N
\]

The determination of the products that form during an oxidation reaction is a necessary step in the design of a multi-component oxidation resistant ultra-high temperature system, as discussed in depth in a previous publication [12]. When a multi-component material is exposed to a sufficiently oxidizing environment, it is expected that all species in contact with the
environment will initially oxidize. With this assumption and considering Equations (1), (2) and (5), along with the reasonable assumption that a high entropy alloy does not form a high entropy oxide scale, one could write Equation (6) and simplify to Equation (7).

$$\Delta G_{rxn,HE}^0 = (\Delta H_{f,prod}^0 - \Delta H_{f,reac}^0) - T[\Delta S_{f,prod}^0 - (\Delta S_{f,reac}^0 + \Delta S_{config})]$$  \hspace{1cm} (6)

$$\Delta G_{rxn,HE}^0 = \Delta G_{rxn}^{ox} + T\Delta S_{config}$$  \hspace{1cm} (7)

Any changes in vibrational entropy due to the mixing are neglected here as assumed in prior analyses [7]. In Equations (6) and (7), $\Delta G_{rxn,HE}^0$ is the driving force for oxidation from a high entropy material. Equation (7) suggests that configurational entropy has the potential to reduce the driving force for oxidation, i.e., $\Delta G_{rxn}^0$ becomes more positive. However, for a five-component equimolar solution, $S_{config}=1.61R$. At 2273K, this results in a $T\Delta S$ of 30.4kJ, and the $\Delta G_{rxn,HE}^0$ (Equation (7)) becoming more positive by this amount. The enthalpy for formation of HfO$_2$ (most stable) at that temperature is $-1108.6$kJ/mol and (WO$_3$)$_3$(g) (least stable) is $-437.6$kJ/mol. The reduction in driving force due to the contribution of the configurational entropy is not as significant—by at least an order of magnitude—than the relative differences in the enthalpy of oxidation.

As the reaction progresses and approaches equilibrium, the final product is dependent on the equilibrium partial pressure of oxygen (pO$_2$) at the oxide/alloy interface, the relative thermodynamic stability of the oxides, and the kinetics of their formation. Note the substantial differences in relative thermodynamic stabilities of the oxides of the group IV, V and VI transition metals (see Figure 1). If the relative thermodynamic stability of the oxides is wide ranging, one or more of the elements in the substrate could selectively oxidize, reducing the configurational disorder in the underlying substrate. Both a first-principle surface oxidation study [13] and an
experimental study on bulk material [10] have noted evidence of preferential oxidation according to the thermodynamic favorability indicated in Figure 1, which demonstrates the need for a deeper understanding of the extent to which this phenomenon can be expected to occur in high entropy materials.

**Figure 1:** Ellingham diagram showing the formation reactions of the Group IV, V and VI early transition metal oxides. Filled circles indicate the melting temperatures of the metals; open circles indicate melting temperatures of the oxides. The triangle indicates transition to a liquid oxide (T_L), and squares indicate transition to gaseous oxides (T_V). Adapted from reference [12].
This work uses a thermodynamic approach to provide a quantitative analysis of selective oxidation in refractory multi-principal component materials as a function of composition and compares these predictions to observations in experimental work performed on high entropy carbides and diborides. These calculations are idealized, first to simplify the complex compositional and phase assemblages, and second, because thermodynamic data are not available for many of these multicomponent systems. The overall objective of this work is to characterize the chemistry of multi-principal component materials specifically as it relates to their oxidation properties, and thereby provide insight into the mechanisms that govern their oxidation behavior.

2.0 Methodology

2.1 Thermodynamic Calculations – Equilibrium Constants

An understanding of the equilibrium composition of the oxide scale formed from multi-component base materials is needed. The reduced activities of each of the components in the multi-component material does not necessarily correspond to a like change in the amount of oxide formed from each component. Consider a binary Hf-Zr alloy. One might expect this alloy to oxidize according to the equation

\[
\frac{1}{2} \text{Hf} + \frac{1}{2} \text{Zr} + \text{O}_2 (g) \leftrightarrow \frac{1}{2} \text{HfO}_2 + \frac{1}{2} \text{ZrO}_2
\]

(8)

This equation suggests that a 50-50 (at%) Hf-Zr alloy will yield a 50-50 (at%) solution of HfO₂ and ZrO₂. However, HfO₂ is more thermodynamically stable than ZrO₂ (\(\Delta G^0_{f,\text{HfO}_2} = -829 \text{ kJ/mol}\) and \(\Delta G^0_{f,\text{ZrO}_2} = -768 \text{ kJ/mol at 2000°C}\)). This difference in stabilities will be reflected in the oxide...
composition. When an Hf-Zr alloy oxidizes, it will be in equilibrium with a solid solution of HfO₂ and ZrO₂. The relevant reactions for each alloy constituent are:

\[
Hf + O_2(g) \leftrightarrow HfO_2 \tag{9}
\]

\[
Zr + O_2(g) \leftrightarrow ZrO_2 \tag{10}
\]

Following Gaskell's approach [14], the pertinent reaction describing the equilibrium between the base metal constituents and their oxides can be written as

\[
Hf + ZrO_2 \leftrightarrow HfO_2 + Zr \tag{11}
\]

The equilibrium constant for this equation yields the following relationship for the relative concentrations in mole fraction \((X_i)\) of the components

\[
K = \frac{[X_{HfO_2}][X_{Zr}]}{[X_{ZrO_2}][X_{Hf}]} \tag{13}
\]

For a fixed temperature, \(K\) is constant. For a given alloy composition, e.g. a 50-50 alloy, the composition of the oxide will therefore be fixed as well.

\[
K \cdot \frac{[X_{Hf}]}{[X_{Zr}]} = \frac{1}{[X_{ZrO_2}]} - \frac{[X_{ZrO_2}]}{[X_{ZrO_2}]} \tag{14}
\]

Using Equation 14, the mole fractions of oxides in equilibrium with a range of alloy compositions can be plotted for Hf-Zr at a given temperature in a composition balance diagram. Using tabulated data, e.g. FactSage databases [15], to determine \(K\), the analysis shown in Equations (11)-(14) was also conducted for Zr-Ti, Ti-Ta and Ta-Mo, as representatives of the elements that make up refractory high entropy materials. In the case of the Ta-Mo alloy, MoO₂ was chosen as the representative oxide since it is the most thermodynamically stable condensed
oxide in the Mo-O system [12], and has been observed to exist in the sublayers of thermally grown oxides or other conditions with reduced oxygen partial pressures [16,17]. At higher temperatures and oxygen partial pressures, the highly volatile, less stable MoO$_3$ (l) is formed [18]. Oxygen solubility in the metallic systems is not considered, which can be as high as 30%, as in the Ti-O system [19]. It is expected that this thermodynamic assessment method of solid solution behavior will aid in oxide phase identification and prediction of selective oxidation, which are essential for understanding the oxidation mechanisms of high entropy materials.

These analyses are then extended to refractory carbide systems. Equations (15) and (16) demonstrate the governing reactions and the resulting equilibrium constant, using the example of a TiC-TaC solid solution. Note the formation of the additional product, CO (g).

$$TiC + \frac{3}{7}Ta_2O_5 \leftrightarrow TiO_2 + \frac{6}{7}TaC + \frac{1}{7}CO (g)$$ (15)

$$K_e = \frac{[X_{TiO_2}]^{\frac{6}{7}}pCO^{\frac{1}{7}}}{[X_{Ta_2O_5}]^\frac{3}{7}[X_{TiC}]}$$ (16)

2.2 FactSage Calculations

The analytical method outlined by Gaskell provides a useful, visual way to consider the binary ideal solution case, and develop hypotheses with respect to real, multicomponent cases. However, some of these hypotheses can be further refined by leveraging the computational capabilities of FactSage, a free energy minimization software [15], and the accompanying databases. The FactSage Equilibrium module allows for the definition of the solid solution
phases, both ideal and real, for the reactants as well as the products, provided the pertinent databases are available. In both the real and ideal cases, the appropriate phase diagrams are consulted to identify the most likely phases and components of the solution at the temperature under consideration.

The case of the Hf-Zr binary alloy oxidizing to HfO$_2$-ZrO$_2$ in an ideal solid solution phase was recreated using the FactSage equilibrium module to test this methodology. Comparison of the ideal solution approximation to a real solid solution is conducted for the Zr-Ti binary system, for which the alloy is still assumed ideal, while the real solid solution thermodynamic data for the oxide from the FTOxid database is utilized.

2.3 Experimental Procedure

Materials chosen for the study are carbides and borides containing Group IV and Group V elements: Hf, Zr, Ti, Ta and Nb. Tantalum has been an extensively studied elemental addition for high temperature UHTCs [20,21], and in the context of this work, has the ability to form solid solutions with Hf and Zr based compounds. Next to Group IV oxides, its oxides have the highest melting temperature among the species under consideration. The (Hf$_{0.2}$Zr$_{0.2}$Ti$_{0.2}$Ta$_{0.2}$Nb$_{0.2}$) carbide and diboride were also one of the first compositions for which single phase, UHTC solid solutions were made [2,3].

The (Hf$_{0.2}$Zr$_{0.2}$Ti$_{0.2}$Ta$_{0.2}$Nb$_{0.2}$)C specimen tested in this work was prepared by high energy ball milling and spark plasma sintering (SPS) commercially available powders (Alfa Aesar Haverhill, MA) at the University of California – San Diego (UCSD, La Jolla, CA) [2]. The (Hf$_{0.2}$Zr$_{0.2}$Ti$_{0.2}$Ta$_{0.2}$Nb$_{0.2}$)B$_2$ specimen was prepared by borocarbothermal reduction (the detailed
experimental procedure and results will be published elsewhere), followed by SPS consolidation, also at UCSD. The sintered samples were machined at Bomas Machine Specialties (Somerville, MA) into thin dogbone specimens shown in Figure 2.

Figure 2: Dogbone specimen configuration. The approximate hot zone (diameter 1.5 mm) is shown in orange.

Figure 3: Schematic of the resistive heating experimental set-up. Specimen shown is of different configuration for clarity.
These dogbone specimen were then loaded into a resistive heating system, modified from Karlsdottir and Halloran [22], and Shugart and Opila[23], schematic shown in Figure 3. The samples were heated to the desired temperature (1700°C in this study) through Joule heating. The temperature was controlled by a proportional-integral-derivative (PID) controller and an emissivity correcting one-color pyrometer (Pyrofiber Lab PFL-0865-0790-2500C311, Pyrometer Instrument Company, Ewing Township, NJ). The temperature-controlled region, or hot zone, is shown by the orange circle with respect to the dogbone specimen in Figure 2. The samples were ramped to temperature in ultra-high purity argon (Praxair, Danbury, CT), and certified 1 mol % O₂ (balance argon) gas (Praxair, Danbury, CT) was turned on at temperature at a flow rate of ~1L/min. Isothermal oxidation exposures were conducted for 2-5 minutes. The low partial pressures of oxygen used result in lower oxidation rates allowing for longer exposures and time dependent studies. After oxidation, the samples were manually fractured across the hot zone, polished to 0.25 μm diamond, and the cross-sections were examined in a scanning electron microscope (SEM, FEI Quanta 650, FEI-Thermo Fisher Scientific, Hillsboro, Oregon). Focused ion beam (FIB) milling (Helios UC G4, Thermo Fisher Scientific, Hillsboro, Oregon) was also used to obtain samples for further EDS analysis. The schematic shown in Figure 4 shows the location of the FIB lift-out. The oxide morphology in both plan view and cross section were characterized using SEM and energy dispersive spectroscopy (EDS, EDS, Oxford Instruments Aztec X-Max^N 150, Concord, MA). The oxide products were also characterized using X-ray diffraction (XRD, PANalytical XPert Pro MPD or PANalytical Empyrean, Almelo, The Netherlands).
Figure 4: Schematic showing the (a) unoxidized dogbone specimen, (b) oxidized dogbone fractured in the middle of the hot zone, with the hot zone shown in yellow and the thick dashed line shown to link the FIB lift-out with the approximate location in the hot zone.

3.0 Results

3.1 Composition Balance Diagrams: Ideal Binary Metal Alloys and Oxide Solutions

Figures 5-7 show the composition balance diagrams for ideal binary metal alloys, Hf-Zr, Ti-Ta and Ta-Mo assuming formation of ideal oxide solutions. Results for the formation of real oxide solutions are presented in Section 3.4. The diagram can be read as follows. Taking for example Figure 5, the top x-axis shown in mole fraction moves from pure HfO\textsubscript{2} on the left side to pure ZrO\textsubscript{2} on the right. The bottom x-axis, also in mole fraction, moves from pure Hf on the left to pure Zr on the right. The y-axis height is set arbitrarily to display the slopes of the lines joining the metal alloy composition with the corresponding equilibrium oxide composition, assuming that both alloy and the oxides are in an ideal solid solution respectively. The tie lines are also oxygen isobars, representing the equilibrium partial pressure of oxygen (based on a reference state of 1 atm) that corresponds to each specific metal-oxide activity ratio. The lines joining the pure Hf to pure HfO\textsubscript{2}, and that joining pure Zr to pure ZrO\textsubscript{2} correspond to the equilibrium pO\textsubscript{2} for the respective oxidation reactions, given by Equations (9) and (10).
Figure 5 shows the case of an alloy consisting of two elements from the same group in the periodic table whose oxides have similar thermodynamic stability. The diagram shows that more than 97% zirconium in the alloy is needed to form ~50% ZrO$_2$. On the other hand, Figures 6 and 7 represent the oxidation of alloys in which the constituents are members of adjacent groups in the periodic table with more widely differing oxide stabilities. In both these cases, the oxide composition is comprised entirely or almost entirely by the element with the most thermodynamically stable oxide.

**Figure 5:** Plot showing the equilibrium concentrations of the oxides (tetragonal phase) in a binary solution when formed from a binary metal alloy, Hf-Zr. Results are shown in increments of 10 mol % with respect to alloy composition. at 2273K. The red dotted line is a *reference* line, which goes from the 50 mol% Zr composition in the alloy to the 50 mol % ZrO$_2$ in the oxide.
Figure 6: Composition balance diagram showing the equilibrium concentrations of the oxides in a binary solution when formed from a binary metal alloy, Ti-Ta (groups IV and V), of varying compositions. Note that even at 99% tantalum in the alloy, the oxide is only composed of 0.08% Ta$_2$O$_5$ at equilibrium. TiO$_2$ is assumed to be in the rutile phase. Grey shaded areas indicate regions of solid solubility in the real system according to ref [24].
Figure 7: Composition balance diagram showing the equilibrium concentrations of the oxides in a binary solution when formed from a binary metal alloy, Ta-Mo, of varying compositions. Note that the larger difference in thermodynamic stabilities in the oxides when comparing different groups (Group V vs VI, in this case) results in a large tendency towards selective oxidation to form Ta$_2$O$_5$, the more stable oxide.

3.2 Composition Balance Diagrams: Ideal Transition Metal Carbide and Ideal Oxide Solution

A similar approach was followed to calculate the composition balance for the refractory carbides, where the additional product, CO (g) must be considered. In the case of HfC-ZrC, which would oxidize to HfO$_2$ and ZrO$_2$ respectively, the condensed phases have the same oxygen stoichiometry and the pCO term will cancel out. Results are shown in Figure 8. However, for TiC-
TaC:TiO$_2$-Ta$_2$O$_5$, the pCO term does not cancel. As such, to simplify the analysis, the value of pCO is fixed at 1. The resulting diagram is shown in Figure 9. Note that for the HfC-ZrC oxidizing to HfO$_2$-ZrO$_2$ (Figure 8), the oxide solution is more reflective of substrate composition, compared to the metallic alloy case (Figure 4). In the TiC-TaC oxidizing to TiO$_2$-Ta$_2$O$_5$ case (Figure 9), the tendency towards preferential formation of TiO$_2$ decreases relative to the metallic alloy case (Figure 6), but remains substantial.

**Figure 8:** Composition balance diagram showing the equilibrium concentrations of the oxides in a binary solution when formed from a binary carbide, HfC-ZrC, of varying compositions at 2273K.
Figure 9: Composition balance diagram showing the equilibrium concentrations of the oxides in a binary solution when formed from a binary carbide, TiC-TaC, of varying compositions. Note that the tendency towards preferential formation of TiO$_2$ decreases relative to the metallic alloy case (Figure 6). pCO was assumed to be 1. TiO$_2$ is assumed to be in the rutile phase. Grey shaded areas indicate regions of solid solubility in the real system according to ref [24].

3.3 Free Energy Minimization: Ideal Ternary and Quinary Alloy and Oxide Solutions

The FactSage Equilibrium module was also used to perform the analysis shown in the preceding sections using the free energy minimization procedure. Inputs to the analysis were the alloy constituents and oxide constituents. Existing binary phase diagrams were used to determine the correct phases in solution (e.g., the relevant Hf-Zr and HfO$_2$-ZrO$_2$ phases at the temperature
of interest are BCC for the alloy and tetragonal for the oxide respectively). The option to identify solid solution phases in the FactSage Equilibrium module was used, followed by free energy minimization calculations on the binary Hf-Zr alloy. The constituents were then defined to be in an ideal solid solution for both the metal and the oxide respectively. The predictions using this technique resulted in the same oxide composition as the analytical technique described previously, enabling the recreation of the entire composition balance diagram, as in Figure 5. This method therefore provides an additional approach to analyze systems with more than two components. For comparison, consider the equimolar case for a ternary system Hf-Zr-Ti, and a quinary system Hf-Zr-Ta-Ti-Nb at 1500°C. Both alloys are known to be in the BCC phase at this temperature [25–27]. The available ternary oxide phase diagram [28] shows that $M$TiO$_4$ (where $M$ = Hf, Zr) and a solid solution consisting of tetragonal phase oxides are the equilibrium phases. Of the titanates, only the thermodynamic data for ZrTiO$_4$ exists in the FactPS database; however, this is sufficient to illustrate oxide formation trends. Tables 1 and 2 summarize the results of these calculations. In the ternary case (Table 1), the oxide consists primarily of Hf and Zr and contains very little Ti; the alloy is depleted in Hf. In the quinary case (Table 2), note the preferential formation of Group IV oxides (Hf, Zr, Ti) and corresponding depletion of those alloy constituents. Note that while experimental work has shown the refractory HEA Hf$_{0.2}$Zr$_{0.2}$Ti$_{0.2}$Ta$_{0.2}$Nb$_{0.2}$ to be BCC [27], there is little data on the quinary phase equilibria for the corresponding oxide phases.
Table 1: Equilibrium calculation showing the final composition of the oxide scale that results from an equimolar Hf-Zr-Ti ternary alloy at 1500°C in equilibrium with an equimolar oxide ideal solid solution containing HfO$_2$, ZrO$_2$ and TiO$_2$.

| Constituents        | Input (mol) | Input (mol%) | Output (mol%) |
|---------------------|-------------|--------------|---------------|
| **Alloy, Ideal Solution** |             |              |               |
| Hf (BCC)            | 1           | 33.3         | 1.03          |
| Zr (BCC)            | 1           | 33.3         | 32.3          |
| Ti (BCC)            | 1           | 33.3         | 66.7          |
| **Oxide, Ideal Solution** |             |              |               |
| HfO$_2$ (tetragonal) | 1           | 33.3         | 65.6          |
| ZrO$_2$ (tetragonal) | 1           | 33.3         | 34.4          |
| TiO$_2$ (rutile)    | 1           | 33.3         | $4.70 \times 10^{-3}$ |
| ZrTiO$_4$           | -           | -            | $3.83 \times 10^{-3}$ |
Table 2: Equilibrium calculation showing the final composition of the oxide scale that results from an input of equimolar quinary alloy ($\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}$) at 1500°C in equilibrium with an equimolar (cation atom basis) oxide ideal solid solution containing HfO$_2$, ZrO$_2$, TiO$_2$, Ta$_2$O$_5$, Nb$_2$O$_5$.

| Constituents                  | Input (mol) | Input (mol%) | Output (mol %) |
|-------------------------------|-------------|--------------|----------------|
| **Alloy Ideal Solution (BCC)**|             |              |                |
| Hf                            | 1           | 20           | 9.22x10^{-8}   |
| Zr                            | 1           | 20           | 5.08x10^{-6}   |
| Ti                            | 1           | 20           | 8.48x10^{-3}   |
| Ta                            | 1           | 20           | 48.9           |
| Nb                            | 1           | 20           | 51.1           |
| **Oxide Ideal Solution**      |             |              |                |
| HfO$_2$ (tetragonal)          | 1           | 20           | 36.7           |
| ZrO$_2$ (tetragonal)          | 1           | 20           | 33.7           |
| TiO$_2$ (rutile)              | 1           | 20           | 3.73           |
| Ti sub-oxides (TiO, Ti$_2$O$_3$) | -           | -            | 22.2           |
| ZrTiO$_4$                     | -           | -            | 2.98           |
| TaO$_{2.5}$                   | 1           | 20           | 0.767          |
| NbO$_{2.5}$                   | 1           | 20           | 4.43x10^{-5}   |
3.4 Free Energy Minimization: Ideal Alloy and Real Oxide Solid Solution

The calculation was performed at the Zr-Ti alloy equimolar composition at 1500°C, assuming the alloy to be an ideal solution. The FTOxid database was used to calculate the oxide composition in the non-ideal case. To perform this calculation, the options to consider the FTOxid-TiO$_2$ Rutile and FTOxid-ZrO$_2$ tetragonal phases were considered. Only results for phases with a total activity of 1 (for the entire phase) are shown.

Table 3: Results for stable oxides formed from ideal equimolar Zr-Ti solution when considering the oxide solid solution as an ideal solution (first column) compared to the results using the real oxide solution database (second column). In both cases, the alloy is considered as an ideal solid solution.

| Constituents | Output (mol%) | Output (mol %) |
|--------------|---------------|----------------|
|               | Ideal Oxide Solution in equilibrium with ideal alloy | Real Oxide Solution in equilibrium with ideal alloy |
| **Alloy, Ideal Solution (BCC)** | | |
| Zr           | 24.6          | 22.2           |
| Ti           | 75.4          | 77.8           |
| **Oxide Solution** | | |
| ZrO$_2$ (tetragonal) | 99.9 | 99.9 |
| TiO$_2$ (rutile) | 2.04x10$^{-2}$ | - |
| TiO$_2$ (tetragonal) | - | 1.97x10$^{-2}$ |
| ZrTiO$_4$ | 4.83x10$^{-2}$ | - |
3.5 Experimental Results

A baseline set of EDS maps is provided in Figures 10 and 11 for polished cross-sections of (Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})C and (Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})B_2, respectively, before oxidation, to show that the distribution of elements is uniform, except for the retained hafnium and zirconium oxides in the carbide. Figure 12 shows the plan view of the oxide scale formed on (Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})C and the corresponding indexed X-ray diffraction pattern of the oxide scale that is dominated by Group IV elements, although one of the oxide phases formed contains either Ta or Nb. Figure 13 shows the EDS maps of oxide scale cross-section. The oxides formed along the grain boundaries are rich in Group IV elements, and the partially oxidized carbide grain is rich in Ta and Nb, whose oxides are less stable compared to the Group IVs. This trend is not limited to the carbide case. Figure 14 shows the oxides formed on (Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})B_2 are also dominated by Group IV elements (Hf, Zr, Ti), with partially oxidized boride grains rich in Ta and Nb.
Figure 10: Polished cross-sections of (Hf<sub>0.2</sub>Zr<sub>0.2</sub>Ti<sub>0.2</sub>Ta<sub>0.2</sub>Nb<sub>0.2</sub>)C before exposure to oxygen at ultra-high temperatures. Secondary electron image and EDS maps showing elemental distribution of titanium, tantalum, hafnium, zirconium and niobium. Sample contains retained hafnium and zirconium oxide particles from processing, as indicated by the oxygen map.

Figure 11: Polished cross-sections of (Hf<sub>0.2</sub>Zr<sub>0.2</sub>Ti<sub>0.2</sub>Ta<sub>0.2</sub>Nb<sub>0.2</sub>)B<sub>2</sub> before exposure to oxygen at ultra-high temperatures. Secondary electron image and EDS maps showing elemental distribution of titanium, tantalum, hafnium, zirconium and niobium.
Figure 12: (Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2})C oxidized for 5 mins at 1700°C in 1 mol % O₂/bal Ar. (a) Backscattered electron image in plan view of the hot zone. (b) X-ray diffraction spectra taken after oxidation.
Figure 13: \((\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2})\text{C}\) oxidized for 5 mins at 1700°C in 1 mol% \(\text{O}_2\)/bal Ar.

[Left] Secondary electron image of the focus ion beam (FIB) cross section of part of the oxide scale \(\sim 3\mu m\) below the surface in the hot zone. [Right] EDS maps showing elemental distribution of oxygen, titanium, tantalum, hafnium, zirconium and niobium.

Figure 14: \((\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2})\text{B}_2\) oxidized for 5 mins at 1700°C in 1 mol% \(\text{O}_2\)/bal Ar.

[Left] Secondary electron image of the focus ion beam (FIB) cross section of part of the oxide scale \(\sim 3\) um below the surface in the hot zone. [Right] EDS maps showing elemental distribution of oxygen, titanium, tantalum, hafnium, zirconium and niobium.
4.0 Discussion

4.1 Composition Balance Diagrams: Binary Metal Alloys

The composition balance diagram can be understood as follows. Taking the equimolar case, a 50-50 mol% Hf-Zr alloy will yield at equilibrium an oxide scale with 3% ZrO$_2$ (Figure 5). If one follows the red dotted line on Figure 5 upward, each intersection with a black tie line represents a higher partial pressure of oxygen encountered. These oxygen partial pressures are tie lines joining the alloy-oxide compositions shown by the black points. When the alloy is in the initial state, the composition is 50 mol% Zr. At this composition, the equilibrium partial pressure between the alloy and the oxide scale is 1.29x10$^{-17}$, and the oxide composition is 3 mol% ZrO$_2$. If one moves upwards along the red dotted line, a higher oxygen partial pressure and an oxide increasingly enriched in the less stable oxide, in this case ZrO$_2$, are encountered. As Hf selectively oxidizes, and is depleted from the base alloy, one will traverse to the right on the lower x-axis in the depletion zone, which results in traversing to the right on the top x-axis (oxide composition), i.e., assuming an inward growing oxide, the scale closer to the oxide-alloy interface should become richer in ZrO$_2$ and the equilibrium partial pressure of oxygen increases. This purely thermodynamic consideration does not take into account the kinetics of mass transport through the oxide.

HfO$_2$ and ZrO$_2$ have similar thermodynamic stabilities ($\Delta G_{HfO_2,2273K}^o=-747.3$ kJ/mol and $\Delta G_{ZrO_2,2273K}^o=-679$ kJ/mol), as shown in Figure 1. Even so, this small difference in thermodynamic stability has a large effect on the thermodynamic prediction for selective oxidation. Even at almost pure Zr (99 at%), the composition of the oxide scale predicted is less than 80% ZrO$_2$. Given the result for Hf-Zr alloy oxidation which forms two oxides with similar thermodynamic stabilities, it is not surprising to see that for the oxidation of a Ti-Ta alloy...
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(Group IV-V alloy) oxidizing, wherein the oxides have a larger difference in relative thermodynamic stability, the tendency towards selective oxidation of Ti is much greater. In the case shown in Figure 6, the choice of oxides to represent the end members of the oxide side of the diagram were based on the predominant oxide in each M-O system, where M = Ti, Ta. In reality, the existence of suboxides in both the Ti-O and Ta-O systems will likely result in a more complex scale. However, it is unlikely that consideration of these suboxides will result in a significantly different diagram, given the large difference in thermodynamic stabilities between their oxides. Park and Butt [29] studied the oxidation of a Ti-Ta alloy at varying compositions from 0-60 wt% Ta, and found that generally speaking, the oxide scale consisted of a rutile TiO$_2$ scale with increasing Ta content as one moved towards the metal-oxide interface, suggesting the Ta$_2$O$_5$ formed when Ti was depleted from the alloy.

It logically follows that the difference in free energy for oxidation per mole of O$_2$ will inform the tendency towards selective oxidation. The extent to which this happens, or the sensitivity of selective oxidation to the difference in thermodynamic stability is best seen when comparing Figures 5 and 6. The difference in the free energy for oxidation per mole of O$_2$ is smaller when comparing between two elements in the same group versus two elements in different groups. This difference results in a significant level of selective oxidation shown in Figures 6 and 7, wherein the Ti in Ti-Ta alloy, and Ta in Ta-Mo alloy, are expected to dominate their respective oxide scale, even at compositions rich in the element with the less stable oxide.

It is also interesting to compare the composition balance diagram for the metal alloys oxidizing to that of their corresponding carbides oxidizing. Taking the case of HfC-ZrC (Figure 8), wherein the oxide composition now more closely reflects that of the base material composition compared to the oxide composition for the corresponding alloy (Figure 5). The
spread of the tie lines indicates that selective oxidation of the HfC component in the carbide solid solution will be much less significant than Hf in the alloy (50 mol% ZrC yields a 39 mol% ZrO$_2$ compared to 50 mol % Zr yielding 3 mol% ZrO$_2$). This is also the case for TiC-TaC where we see again a larger spread in the tie lines compared to the metal alloy case. A prior publication [12] discusses the differences in thermodynamic stabilities when considering the alloy, carbide, boride and nitride cases for any two given elements. Again, taking Hf and Zr for example, the relative difference in the thermodynamic stability of the oxides formed from the carbides is almost negligible compared to the metal case (Figure 15), due to the formation of the secondary gaseous oxide, CO (g). The difference in the oxide formation energy from HfB$_2$ and ZrB$_2$ fall between these values. Thus, the oxide formation from the metal and the carbide serve as bounding cases.
Figure 15: Comparison of HfO$_2$ and ZrO$_2$ stability when formed from the pure metal, or from carbide, nitride and boride. Open circles indicate oxide melting temperatures, and closed circles indicate metal melting temperatures. Adapted from reference [12].

4.2 Free Energy Minimization

The Equilibrium module in FactSage was used to perform similar analyses, first for the binary case, then for the ternary and quinary cases. The binary case served to successfully test the methodology. Application to the ternary case using the ideal solid solution approximation showed that the oxidation of the equimolar Group IV Hf-Zr-Ti alloy would result in a HfO$_2$-ZrO$_2$
rich scale, and minuscule amounts of Ti containing compounds. If the trend exhibited in the ternary case is extrapolated to the high entropy case (Hf_{0.2}Zr_{0.2}Ti_{0.2}Ta_{0.2}Nb_{0.2}), insignificant amounts of Ta and Nb oxides would be expected. Indeed, preferential oxidation of the Group IV elements is predicted, and the oxide scale contains less than 1 mol% Ta_2O_5 and Nb_2O_5. Note that for the ternary case, the input included an ideal solid solution containing rutile TiO_2 along with tetragonal HfO_2 and ZrO_2. This can be thought of as an assemblage of oxide phases wherein the activity coefficients of the constituents are constrained to be unity. This approximation allows for imposing the coexistence of a Ti oxide along with the other two oxides; without this approach, the free minimization calculations will result in the most stable product being HfO_2, i.e., HfO_2 having an activity of one, and the other oxides as being reduced by HfO_2, which we know from Gaskell’s approach is not the case. The equilibrium pO_2 at the oxide/alloy interface due to the assemblage of the different oxides that are expected to form in the initial stages of oxidation (HfO_2, TiO_2, ZrO_2, Ta_2O_5, Nb_2O_5) would be higher than that due to only the most stable oxides, and will influence the final oxide composition determined via the free energy minimization approach. In addition, the end result shows very small amounts of TiO_2 in the final state, well within the solubility limits in both HfO_2 and ZrO_2 [30,31]. Finally, consider the results shown in Table 3. The difference in the amount of TiO_2 in the final state for the real oxide solution (where the TiO_2 is tetragonal) compared to the ideal oxide solution (where TiO_2 is rutile) is insignificant. Similar considerations apply for the quinary case.

4.3 Ideal Solution vs Real Solution Thermodynamics

The assumption of ideal solution thermodynamics allows for a first approximation in the understanding of the tendency towards selective oxidation. This tendency is highly sensitive to the relative difference in the standard Gibbs free energy of formation for the oxides. These large
differences are expected to persist when comparing the relative stabilities of oxides between different groups (Group IV vs Group V elements for example) using thermodynamic data for real solutions. In non-ideal thermodynamics, the activity of a component in a solution varies from the mole fraction. While this will affect both the individual reactant as well as the overall reaction free energy, these differences may not be so large compared to the difference in the stabilities between oxides from different groups. If this is the case, use of ideal solution thermodynamics may be sufficient to understand selective oxidation. To probe this, the case of an ideal Zr-Ti alloy to form real oxidation products, rather than ideal products was considered. The FTOxid database contains thermodynamic data for a (Zr,Ti)O$_2$ tetragonal oxide solution phase and a rutile oxide phase. Calculations using this database resulted in the prediction of a tetragonal oxide solution phase rather than the rutile oxide phase, and for the scale to be dominated by ZrO$_2$. Indeed, the oxide composition calculated using real solution thermodynamic data is very similar to the ideal solution case (Table 3), despite the crystal structures for the TiO$_2$ being different in the real versus the ideal case.

4.4 Comparison to Experimental Results

The objective of these analyses is to ultimately aid in the prediction of the oxidation behavior of multi-principal component materials such as refractory high entropy alloys, carbides and borides. It can be clearly seen in the EDS maps (Figures 12 and 13) that the oxides formed for the carbides and borides are dominated by the Group IV elements in both (Hf$_{0.2}$Zr$_{0.2}$Ti$_{0.2}$Ta$_{0.2}$Nb$_{0.2}$)C and (Hf$_{0.2}$Zr$_{0.2}$Ti$_{0.2}$Ta$_{0.2}$Nb$_{0.2}$)B$_{2}$. The XRD pattern for the oxidized carbide sample is consistent with the formation of some solid solution phases but matches to compound oxides such as Zr$_6$Nb$_2$O$_{17}$ are also seen. Note that these matches are prototype
structure matches, which, based on EDS mapping, may contain other elements. For instance, the Zr₆Nb₂O₁₇ also has an analog containing Hf and Ta: Hf₆Ta₂O₁₇. Thus, Hf may substitute on Zr sites and Ta on Nb sites in this A₆B₂O₁₇ phase. These phases, however, are also dominated by Group IV elements (Hf, Zr, Ti), suggesting that the predictions for selective oxidation hold.

Table 4 summarizes known complex oxides which are likely to form based on a review of the phase diagrams. Thermodynamic data for the compounds are critical to better predict refractory high entropy material oxidation, but are unavailable.

Table 4: Known complex oxides that could form in the material systems under study, based on a review of available phase diagrams

|       | Hf  | Ti  | Zr  | Nb  | Ta  |
|-------|-----|-----|-----|-----|-----|
| Hf    |     |     |     |     |     |
| Ti    | HfTiO₄ |     |     |     |     |
| Zr    |     | ZrTiO₄ |     |     |     |
| Nb    | Hf₆Nb₂O₁₇ | Nb₂TiO₇, Nb₁₀Ti₂O₂₀, Nb₅Ti₂O₁₉ | Zr₆Nb₂O₁₇ |     |     |
| Ta    |     | TiTa₂O₇ | ZrTa₆O₁₇, Zr₆Ta₂O₁₉ | Nb₄Ta₂O₁₅ |     |
| V     |     |     | ZrV₂O₇ | VNb₆O₂₅ | VTₐ₉O₂₅ |
| Mo    |     |     |     |     |     |
| W     | HfW₂O₈ |     | ZrW₂O₈ |     |     |

While these predictions assume a constant alloy composition, during an actual oxidation process the underlying material will be shifting in composition over time, enriching in metallic components of the least stable oxides. The experimental results for the carbides and borides nevertheless support the thermodynamic predictions regarding oxide stability and changes in underlying alloy composition. Note that the oxygen-lean regions in Figures 12 and 13 are richer in Ta and Nb, while the oxygen-rich regions are rich in Hf, Zr and Ti, which is consistent with
the results shown in Table 2. Other experimental results from oxidation studies performed on high entropy alloys [10] also indicate the preferential oxidation of elemental species with more thermodynamically stable oxides.

An estimated reduction in configurational entropy due to the reduced number of components in the solid solution alloy or compound can be calculated using Equations 4 and 5. For the case shown in Table 2, where the alloy effectively goes from $N=5$ to $N=2$, this results in an approximately 60% reduction in configurational entropy determined via Equation (4). If configurational entropy is required to stabilize the solid solution phase, then such a reduction may result in other, competing phases forming and the destabilization of the solid solution phase. On the other hand, if the remaining components form a thermodynamically stable solid solution, then the effects may be thermochemical in nature, such as a reduction in melting temperature or in the originally enhanced mechanical properties. The work presented here and previously [12] indicates that such selective oxidation of refractory alloys and compounds is closely correlated with groups in the periodic table; if the remaining elements all belong to the same periodic group, it is possible for them to remain in solid solution.

5.0 Conclusions

A thermodynamic approach was used to quantify the tendency towards selective oxidation in refractory multi-principal component materials. The compositions considered for these analyses are the Group IV, V and VI elements that are of interest to the ultra-high temperature ceramics and refractory high entropy alloy communities. This approach was first demonstrated analytically for binary systems. An approach using free energy minimization was also presented, which allowed for the extension of the analysis to higher order systems (ternary,
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The results indicate that this tendency for selective oxidation is highly sensitive to the difference in relative thermodynamic stabilities of the constituent oxides. The differences in relative thermodynamic stabilities of oxides from the same group, though small, were enough to result in a significant tendency towards selective oxidation; this effect was dramatically more pronounced in systems with elements from different groups (e.g., Group IV-V alloys). The differences in relative thermodynamic stabilities of the oxides are much lower when oxidizing from a carbide, compared to oxidizing from a metallic alloy. This smaller difference for carbides is reflected in a reduced tendency towards selective oxidation but does not eliminate it. Experimental results for a Group IV-V five-component high entropy carbide showed that the Group IV elements dominated the oxide phase, while the underlying material had a higher relative concentration of the Group V elements.

Refractory high entropy materials (alloys, carbides, borides) will inevitably be comprised of constituents whose oxides span a wide range in thermodynamic stability. Thermodynamics drives selective oxidation, as all the components are not expected to oxidize simultaneously, despite starting out as a solid solution. The differences in oxidation enthalpies (when comparing between different elements) are more significant than the high configurational entropy. Even a slight relative favorability in a given oxide formation reaction can result in selective depletion of an element from the high entropy material, reducing the configurational entropy in the substrate.

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