Contents lists available at ScienceDirect



## Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original article

# Thermodynamic assessment of the group IV, V and VI oxides for the design of oxidation resistant multi-principal component materials



Journal of the

### Lavina Backman\*, Elizabeth J. Opila

University of Virginia, Department of Materials Science and Engineering, Charlottesville, VA 22904, United States

above 1700°C.

ARTICLE INFO	A B S T R A C T
Keywords: Ultra-high temperature ceramics High entropy Oxidation Ellingham	Multi-principal component materials (MPCMs) are currently being investigated for use in high and ultra-high temperature environments. The design of oxidation resistant multi-component materials requires as input the oxidation behavior of each of the components. FactSage free energy minimization software and databases were used to calculate the equilibrium oxide phases and free energies of formation for the oxides of the Group IV, V and VI refractory metals, and their carbides, nitrides and borides. The results are summarized in Ellingham diagrams. Periodic trends were noted; Group IV elements form the most stable oxides with the highest melting
	temperatures $(1_m)$ , Group V elements form oxides with low $1_m$ , and Group VI elements form gaseous oxide species. Oxygen diffusion data from literature for some of these oxides were also reviewed and summarized. The
	results are utilized to identify strategies for optimizing oxidation resistance of MPCMs for service at temperatures

#### 1. Introduction

Multi-principal component materials (MPCM), including high entropy alloys, oxides, carbides, borides and nitrides, are the subject of active research for high temperature applications [1,2], and most recently ultra-high temperature applications (> 1700°C) [3,4]. Design considerations for high temperature oxidation resistant materials has typically relied on Al and Si additions to promote formation of slow growing Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> scales. However, the use of components such as Si and Al has been shown to not be a viable strategy for oxidation resistance at ultra-high temperatures, especially for hypersonic applications [5–8]. The large composition space afforded by MPCMs provides new opportunities to design for oxidation resistance.

The determination of the equilibrium phases that form during an oxidation reaction is a necessary step in the design of a multi-component system with a focus on ultra-high temperature oxidation resistance. 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 [9]. At longer times, the equilibrium oxide products that form are governed by their relative thermodynamic stability and oxidation kinetics.

The Ellingham diagram [10] is a useful and straightforward predictive tool, enabling the comparison of the relative thermodynamic stabilities of the oxides that form in a multi-component system. An Ellingham diagram, in the context of oxidation, plots the change in negative free energy of an oxidation reaction, normalized to one mole of oxygen, as a function of temperature. Each reaction is a straight line in this plot, wherein the slope is the negative of the entropy of the oxidation reaction, and the intercept is the enthalpy of the reaction. The lower the line is on the plot, the more thermodynamically stable the oxide, relative to the other oxides. While several Ellingham diagrams have been calculated and published [11-17] that include some members of the Group IV, V and VI columns of the periodic table, the work here is the first to (a) comprehensively review and select the relevant oxidation reactions in the Group IV, V and VI metal and ceramic systems for plotting on an Ellingham diagram, (b) compare the oxidation reactions for all Group IV, V and VI early transition metals and their carbides, borides and nitrides, and (c) provide insight into how the diagrams for the ceramic compounds (carbides, borides and nitrides) vary in a predictable manner from the metals. All of these elements are not only of significant interest to the design of oxidation resistant Ultra-High Temperature Ceramics (UHTCs), but also to existing studies that seek to promote improved oxidation behavior of refractory high entropy alloys (HEAs) [1,2,18-20]. The objectives of this study are therefore to (1) develop Ellingham diagrams for component M, MC,  $MB_2$  and MN, where M = Group IV, V and VI transition metals, and (2) provide a framework for using this information in the design of high temperature and ultra-high temperature MPCMs, particularly UHTCs.

\* Corresponding author.

E-mail address: lb2ty@virginia.edu (L. Backman).

https://doi.org/10.1016/j.jeurceramsoc.2018.11.004

Received 23 June 2018; Received in revised form 25 October 2018; Accepted 2 November 2018 Available online 10 November 2018 0955-2219/ © 2018 Elsevier Ltd. All rights reserved.

#### 2. Methodology

The Fe-O system was used to test the chosen methodology as the oxidation behavior of iron is well understood [17]. FactSage [21], a free energy minimization software package, was used for all the thermodynamic calculations. A two-step calculation method was employed. First, the equilibrium module was used with the Fact Pure Substance (FactPS) database to determine the equilibrium assemblage of reactants and oxide products that represented the minimum free energy of the system. Calculations were performed from 100°C-3000°C in 100°C increments at a pressure of one atm. The activities of the oxide species that formed were tabulated for each temperature increment. It was found that an input of one mol each of Fe and O resulted in an activity of less than unity for iron once the calculation was complete, indicating that the high stability of the oxides tends towards complete oxidation of the metal. The calculation was conducted again, fixing the activity of iron at one to ensure the Fe reactant was not depleted. This strategy of fixing the metal activity at one in performing the equilibrium calculations with a 1:1 M:O ratio of reactants was thus utilized to identify potential product oxide phases for other metal-oxygen systems.

The oxides that formed or had a potential of forming, as determined by the equilibrium calculation, in the Fe-O system were FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, as expected from previous studies [17,22]. The oxide formation reactions on a per mol O<sub>2</sub> basis are as shown by Reactions (i)–(iii) below

$$2Fe(s) + O_2(g) = 2FeO(s, l)$$
 (i)

$$\frac{3}{2}Fe(s) + O_2(g) = \frac{1}{2}Fe_3O_4(s, l)$$
(ii)

$$\frac{4}{3}Fe(s) + O_2(g) = \frac{2}{3}Fe_2O_3(s)$$
(iii)

In the second step, these oxidation reactions were used as inputs in calculating the standard free energies of formation using the reaction module in FactSage for the temperature range of 100°C–3000°C and a pressure of 1 atm. The values of  $\Delta G^{\circ}$  thus obtained were plotted versus temperature providing an Ellingham diagram.

This approach, confirmed with the well-known Fe-O system, was then used to study the metal-oxygen systems of each of the Group IV, V and VI early transition metals, as well as for the carbides, nitrides and borides of the same elements. In addition, where available, previously published observations of metal oxide products and their kinetics of formation are reviewed and discussed in the context of these diagrams. Finally, strategies are identified for optimizing design of high temperature MPCMs, particularly high entropy UHTCs, for oxidation resistance above 1700°C.

#### 3. Results

#### 3.1. Validation of methods using Fe-O system

The reactions for the formations of the stable oxides in the Fe-O system, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeO, normalized to 1 mol O<sub>2</sub>(g) are summarized in the Ellingham diagram in Fig. 1.

Points of interest have been labeled on the Ellingham diagram; namely, "M" indicates the melting point of the metal, "O" indicates the melting point of the oxides and "B" indicates the boiling point of the metal. The order of thermodynamic stability demonstrated by the diagram corresponds with the order of layering of the oxides shown in Fig. 1 (Bottom) from the work of Pujilaksono et al [22], in accordance with the equilibrium activities of oxygen at each interface, an observation that has previously been noted [17]. The free energy-temperature space occupied by a given metal-oxide equilibrium system can thus be thought of as a band on an Ellingham diagram, enveloping multiple oxidation reactions.

The kinetics of the oxidation reaction must be considered in



**Fig. 1.** (Top) Ellingham diagram showing the formation reactions of Fe oxides, normalized to 1 mol  $O_2$ . Closed circles indicate melting point of the metal, open circles that of the oxide. Closed squares indicated boiling point of the metal; (Bottom) Layered oxide formed on Fe oxidized in dry  $O_2$  at 600°C for 24 hours, from Pujilaksono et al. [22] [reprinted with permission].

conjunction with thermodyanamics, as it can influence the observation of the predicted equilibrium phases. An expression has been derived [17,23] establishing a relationship between the relative thicknesses of the different oxides formed and their parabolic oxidation rate constants. Specifically, the ratio of the thicknesses of two oxides that form in the case of a bilayered oxide is proportional to the square root of the ratio of their respective rate constants. The oxidation rate constant is related to diffusivity by Wagner's equation [24] shown by Equation 1. In this equation,  $k'_p$  is the parabolic rate constant,  $p_{O_2}$  is the partial pressure of oxygen, and  $D_M$  and  $D_O$  are the diffusivities of the metal species and oxygen respectively. The prime ('and ") modifiers on  $p_{O_2}$  indicate the maximum and minimum values governed by the fixed oxygen activities at the relevant interface, and  $z_c$  and  $z_a$  are the valences of the cations and anions respectively.

$$k'_{p} = \frac{1}{2} \int_{p'_{02}}^{p'_{02}} (\frac{z_{c}}{|z_{c}|} D_{M} + D_{O}) d\ln p_{O2}$$
(1)

This is highlighted by the differences in thicknesses of the different oxide layers on Fe, wherein FeO with the highest defect concentration and highest diffusivities forms the thickest layer [22,25,26]. This combined consideration of thermodynamic stability and kinetics becomes important in the analysis of some of the metal-oxygen systems presented later, particularly that of Ti-O.



**Fig. 2.** Summary of equilibrium calculations showing the thermodynamically stable products for each temperature range up to 3000°C. Blue bars with diagonal lines indicate solid oxides, orange bars with cross-hatched lines indicate liquid oxides and black bars indicate gaseous oxides (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

#### 3.2. Oxidation of group IV, V and VI metals

The equilibrium oxide products and relative thermodynamic stabilities of the oxides formed from the Group IV, V and VI metals under consideration as components for high temperature MPCMs were determined and are summarized in Fig. 2.

The most thermodynamically stable reaction in each M–O system was then identified and plotted on a comparative Ellingham diagram for the metal-oxide reactions shown in Fig. 3.

Identification of the lower bound for the formation of the oxides of the Group IV and V metals was relatively straightforward, as the most thermodynamically stable product did not change across the temperature range of interest. However, the stable oxide products of the Group VI metals were more complex. Fig. 4 shows the Mo-O system as an example.

The most thermodynamically stable oxide of Mo transitions from  $MoO_2$  (s) to  $(MoO_3)_3$  (g), at 2052°C and then transitions to  $MoO_2$  (g) at 2980°C. The lower bound of the Mo-O oxide formation band, shown in the bottom diagram in Fig. 4, therefore, consists of different oxides. The transition at 2052°C is from a solid oxide to a different, gaseous oxide. Such transitions also necessitated the use of new symbols, which are shown in Fig. 3, namely the open triangle and open square. The open triangle indicates transition from a solid oxide to a different oxide in the liquid phase,  $T_L$ , while the open square indicates a transition from a solid oxide to a different oxide in the liquid phase,  $T_V$ .



**Fig. 3.** Ellingham diagram showing the formation reactions of the Group IV, V and VI early transition metals. 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 ( $T_V$ ).

#### 3.3. Oxidation of transition metal carbides, borides and nitrides

The development of diagrams for the oxidation of the refractory carbides, borides and nitrides was primarily conducted with the oxides of Hf and Zr, given that these M–O systems are relatively less complex, each consist of one oxide, and can therefore serve as model systems to understand how the free energy of oxide formation from the  $M + O_2$  reaction differs from that formed from the MX +  $O_2$  reaction (where X stands for C, N, B or B<sub>2</sub>). The results are presented in Fig. 5. Generalized oxidation reactions for carbides, borides and nitrides are shown below by Reactions (iv)–(vi), respectively.

$$\frac{2}{b+1}MC + O_2(g) \leftrightarrow \frac{2}{b+1}MO_b + \frac{2}{b+1}CO(g)$$
(iv)

$$\frac{2}{b+3}MB_2 + O_2(g) \leftrightarrow \frac{2}{b+3}MO_b + \frac{2}{b+3}B_2O_3(l,g)$$
(v)

$$\frac{2}{b}MN + O_2(g) \leftrightarrow \frac{2}{b}MO_b + \frac{1}{b}N_2(g)$$
(vi)

The *relative* thermodynamic stability of  $HfO_2$  and  $ZrO_2$ , whether formed from the metal, boride, carbide or nitride, is largely unchanged in all temperature regimes. The only exception is the Hf and Zr carbideoxygen systems, wherein the lines for  $HfO_2$  and  $ZrO_2$  are barely distinguishable from each other at lower temperatures (< 2000°C). The enthalpic contributions to the free energies of oxide formation for oxides formed from the carbides, borides and nitrides are all within a range of ~ 200 kJ/mol O<sub>2</sub>, and are much less negative than that formed from the pure metals. The entropic contributions for oxide formation are lower for the oxides formed from carbides and nitrides, as can be seen by the shallower slopes.

#### 4. Discussion

The constructed Ellingham diagram in Fig. 3 shows clear periodic trends. Lines for the Group IV, V and VI metals, respectively are clustered within their group, demonstrating the similarity in the enthalpies of formation (y-intercept at 0 K) for their most thermodynamically stable oxides. Group IV oxides are the most thermodynamically stable, while those of Group VI are the least thermodynamically stable. If the same logic described for the Fe-O system were to be applied, it would be expected that, for oxidation of systems containing multiple transition metals and ignoring kinetic effects, the Group VI oxides would be found



**Fig. 4.** [Top] Ellingham diagram showing oxides formed from the oxidation of Mo. [Bottom] Ellingham diagram showing the delineation of the "lower bound" of the Mo-O system (bold, green line) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

at the oxide/gas interface, while the Group IV oxides would be found at the metal/oxide interface.

The Group IV metals also tend to form oxides with melting temperatures higher than the melting temperature of the metal. On the other hand, Group V metals form oxides with low melting temperatures, lower than the metal itself. The Group VI metal oxides are primarily gaseous at high temperatures. This trend is important to note as dimensional stability is required for many high temperature applications. For example, in hypersonic vehicle wing leading edges and rocket nozzles, the form of the structure is critical to their function. A system that forms a solid oxide at these high temperatures is more desirable than one that forms liquid oxides that can easily shear away or volatilize during operation.

Changes in the slope of the line on an Ellingham diagram represent the negative of the change in entropy, and are largely dominated by changes due to the consumption or production of the number of gas molecules in the oxidation reaction. The slopes for the carbide and nitride reactions are much shallower than that for the metal reactions due to formation of gaseous products (Reactions (iv) and (vi)). A



**Fig. 5.** 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, closed circles indicate metal melting temperatures, and half-filled squares indicates the boiling temperature for boria.

similarly shallow slope is observed in the boride reaction lines at high temperatures, as boria is now forming as a gas (Reaction (v)). These shallower slopes indicate a reduced temperature dependence for the oxidation reactions, allowing for the extrapolation of oxidation behavior at 2000°C, to temperatures as high as 3000°C.

The Ellingham diagrams also indicate thermodynamically stable oxides that are not always observed at oxidizing temperatures and atmospheric pressure, such as TiO. The Fact Pure Substance database used to calculate these diagrams is a collection of data from standard compilations as well as additional data evaluated from the literature. The values for the enthalpy and entropy of formation used in these calculations at high temperatures (typically  $T > 1200^{\circ}C$  for most oxides) were extrapolated by FactSage from lower temperature data where thermodynamic data at those temperatures for these materials were not available. In addition, these thermodynamic calculations do not account for oxidation kinetics. It is therefore useful to compare these predictions to oxide phases observed in prior studies from the literature.

#### 4.1. Group IV elements

Hafnium is reported to only have one oxide, HfO2 [25,27,28]. Likewise, although the JANAF database has thermochemical data for ZrO(g),  $ZrO_2$  is considered the only oxide of import [25,27,29,30] in the oxidation of zirconium. In the Ti-O system, the most thermodynamically stable oxide according to the calculations in this study is TiO, but TiO<sub>2</sub> is primarily observed in oxidation studies of titanium [25]. TiO formation on titanium has been observed at temperatures less than 1000°C at near atmospheric pressures. Kofstad et al [31] have reported that at low partial pressures of oxygen, the oxides of titanium form in a layered manner, similar to the Fe-O system. The generally limited observations of TiO may be attributed to the relative kinetics of oxygen transport in TiO and TiO<sub>2</sub>, as suggested by Yurek et al.'s work [23], and similar analysis by Smeltzer and Young [17]. TiO is likely not always observed due to the transport of oxygen in TiO<sub>2</sub> being much faster [25,32,33]. It is well known that TiO<sub>2</sub> is highly nonstoichiometric relative to its suboxides and that the large oxide defect concentration should result in rapid oxidation kinetics. Kinetics can therefore play a large role in what is observed versus what is predicted by thermodvnamics.



Fig. 6. Diffusivities of oxygen in the oxides of Group IV, V and VI transition metals, from data available in literature:  $TiO_2$  [61,68];  $ZrO_2$  [60];  $VO_2$  [42,43];  $V_2O_5$  [62];  $Nb_2O_5$  [63],  $Ta_2O_5$  [64–66];  $WO_3$  [54].

#### 4.2. Group V elements

Thermochemical analyses [34] and oxidation studies of tantalum [35] have shown that  $Ta_2O_5$  is the only stable condensed phase in the Ta-O system, which is reflected in the calculated Ellingham diagram in Fig. 3. Gulbransen's analysis [34] shows TaO<sub>2</sub> to be the major volatile species in that system, with an additional volatile species being TaO, and this is likewise reflected in our calculations (Fig. 2). Similarly, Gulbransen reports Nb<sub>2</sub>O<sub>5</sub> as being the stable condensed oxide formed on niobium at high temperatures and near atmospheric pressures, and the suboxides being present as volatile species [34]. Oxidation studies of niobium have shown the formation of the sub-oxides, particularly NbO<sub>2</sub> [35-37] forming at lower temperatures (< 500°C) and then subsequently oxidizing to Nb<sub>2</sub>O<sub>5</sub> [35]. The sub-oxides have also been observed at lower pressures. Kofstad and Espevik [37], in their study of the oxidation of niobium spanning the temperature range of 1200-1700°C, reported the formation of NbO and NbO2 at low pressures, with NbO<sub>2</sub> subsequently oxidizing to Nb<sub>2</sub>O<sub>5</sub>. This observation suggests that NbO is the most thermodynamically stable oxide, consistent with our representation of the Nb-O system in Fig. 3. Studies of the oxidation of vanadium [38-43] up to 1050°C at varying pressures show that the pentoxide, V<sub>2</sub>O<sub>5</sub>, readily forms. Mukherjee reports that VO<sub>2</sub> forms at low pressures and above 500°C [43]. Both Westman [44], and Stringer and Price [39] have reported on the formation of VO on vanadium at varying pressures and temperatures above 500°C. Specifically, Stringer and Price reported the formation of VO in an experiment where a fixed volume of O<sub>2</sub> was admitted into the system, and the pressure drop from the gas consumption was measured with time. The computations performed in this study predict that VO is the most thermodynamically stable oxide, followed by VO2 and V2O5. It can thus be expected that similarly to Ta and Nb, VO will oxidize to VO2 and V<sub>2</sub>O<sub>5</sub>. In the case of Nb and V, the sub-oxides are chosen to represent their respective M–O systems in Fig. 3 because these condensed oxides have been previously observed, and are thermodynamically favored relative to M2O5.

#### 4.3. Group VI elements

Studies of the oxidation of molvbdenum [34,45–50] and tungsten [47,51–56] show that gaseous oxide species dominate the high temperature oxidation behavior of these metals, which is consistent with the results of this study (Fig. 2). Note that most of the high temperature data available were collected at low total pressures. Pressure is a significant variable as it affects both the equilibrium partial pressure and transport of the volatile species through the gas boundary layer [34]. Gulbransen et al. [34,46] found that the temperature at which the oxide will volatilize as fast as it forms on the metal changes with total pressure. Below this transition, both condensed and volatile species coexist.  $MoO_3(c)$  is reported to be the primary condensed phase oxide formed on molybdenum, especially at higher pressures, but MoO<sub>2</sub>(s) has also been observed [49], usually as an inner layer in the thermally grown oxide scale at lower temperatures. This is consistent with the calculations in this study (that indicate the most thermodynamically stable oxide will be located at the metal/oxide interface), as shown in Fig. 3. Similarly, the condensed oxides of tungsten form in a layered manner, consisting primarily of the trioxide [34,35]. The dioxide has been reported [57], but Kellett and Rogers [56] have suggested that what was previously reported as WO<sub>2</sub>(c) is defective or non-stoichiometric  $WO_3(c)$ . The difference between the free energies of formation for  $WO_3(c)$  and  $WO_2(c)$  lines was found to be insignificant, and the presence of a condensed oxide layer at high temperatures is negligible to non-existent.

#### 4.4. Kinetic considerations

The role of kinetics in the high temperature oxidation of MPCMs, as mentioned earlier, cannot be ignored. Existing reviews of kinetics parameters [58,59] do not consider all the available data for oxygen diffusion in the oxides of Group IV, V and VI. As such, an updated review of the diffusivity data in literature [42,43,54,60–66,68] for the oxides of interest was conducted and summarized in Fig. 6. Most of the data shown are for oxygen diffusion in the oxide; oxidation in these strongly bonded materials tends to be controlled by oxygen diffusion inward. The available data were obtained at low or intermediate temperatures (relative to a maximum of  $3000^{\circ}$ C). Data for some of the oxides of the group IV, V and VI oxides are not available, such as the sub-oxides of titanium, or the condensed oxides of molybdenum. Consideration of the highest temperature data available shows that diffusion in zirconia, which is among the more thermodynamically stable oxides, is rapid. Therefore, it can be expected that ZrO<sub>2</sub>, which has a high melting temperature will readily form if included in the material. Similar conclusions may be drawn for the formation of Ta<sub>2</sub>O<sub>5</sub>. Oxygen diffusion in Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> is slower than the former two oxides. Thus, if a material containing Zr, Ta, Ti and Nb were to form a layered oxide scale, the ZrO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> layers would be expected to be thicker than the oxides of the other two elements.

The formation of complex oxides are extremely likely, based on the similar diffusivities of the Group IV and V oxides, the respective phase diagrams showing the solubility of Group IV and V oxides in each other, and the existence of mixed stoichiometric oxides such as  $Hf_6Ta_2O_{17}$  [67]. As far as the authors are aware, there are no data available for the diffusivities of oxygen in the complex oxides.

#### 4.5. Implications for high temperature MPCMs

This study has only considered the thermodynamic stabilities and kinetics of binary oxides of individual reactants and has not considered the complex oxides. Given the requirement for the formation of a solid oxide, Hf, Zr, or Ti, or a combination of them, should be primary components of a high temperature MPCM. Both the thermodynamics and kinetics suggest that oxidation of these components is more favorable among the Group IV, V and VI elements; therefore, using them as the basis for an MPCM, especially for ultra-high temperature applications, is a viable strategy. Group V containing compounds should be minimized, as they both exhibit rapid kinetics of formation, are next in the order of thermodynamic stability, and have low melting temperatures. In addition, their phase diagrams indicate the potential for the formation of low melting oxide eutectics [25], e.g. a eutectic in the ZrO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> [69] is noted at 665°C, which is dramatically lower than the melting temperature of ZrO2 (~2700°C). Group VI element additions can be expected to promote the formation of oxides with high vapor pressures, which may result in porosity in the oxide. This may not be an issue with carbides and nitrides, which already form porous oxides. Small amounts of Group VI additions such as WC have previously been explored as a method to promote oxidation resistance [70]; however, recent research [71] has shown that at temperatures above 1650°C, the volatility of W oxides precludes any protection.

#### 5. Conclusions

A primary step in the design of high temperature Multi-Principal Component Materials (MPCMs) that exhibit good oxidation resistance requires an understanding of the oxidation behavior of each of its constituents. In this study, the relative thermodynamic stabilities of the oxides of the elements of interest were evaluated. FactSage was used to calculate the change in standard Gibbs free energy of the relevant oxidation reactions. These calculations were summarized in Ellingham diagrams to enable a comparison of relative thermodynamic stabilities of the oxides that may form in a multi-component material. Periodic trends in the thermodynamic stability and melting temperatures of the oxides were noted. In the context of ultra-high temperatures, the group IV oxides are the most thermodynamically stable, have the highest melting temperatures, forming solid oxides up to nearly 3000°C, and for this reason are the desired constituents of a ultra-high temperature MPCMs. The group V oxides, which are next in stability, have low melting temperatures, forming liquid oxides below 2000°C, and lead to formation of low melting eutectics at even lower temperatures. These

oxides are detrimental to the formation of a solid, adherent, protective oxide. The group VI metals form the least thermodynamically stable oxides, and are gaseous, which may result in porosity in the oxide scale.

This work suggests that in the compositional design of an ultra-high temperature MPCM for oxidation resistance, Group IV elements are the best option as primary components. The rapid formation of the group IV oxides will be beneficial in establishing a solid scale at high temperatures. On the other hand, their rapid formation will likely lead to excessive consumption of the substrate. Further studies are needed to optimize the additions of Group V (which form oxides with low melting temperatures) and Group VI elements (which form gaseous oxides). Kinetic considerations do not provide substantial guidance for compositional choices, as oxygen transport in all the group IV, V and VI oxides considered here are rapid. The kinetics involving the formation of complex oxides are poorly understood in the literature.

#### Acknowledgments

This work is supported by the U.S. Office of Naval Research MURI program (grant no. N00014-15- 1-2863) and the Virginia Space Grant Fellowship.

#### References

- [1] B. Gorr, F. Mueller, H.-J. Christ, T. Mueller, H. Chen, A. Kauffmann, M. Heilmaier, High temperature oxidation behavior of an equimolar refractory metal-based alloy 20Nb-20Mo-20Cr-20Ti-20Al with and without Si addition, J. Alloys Compd. 688 (2016) 468–477.
- [2] B. Gorr, M. Azim, H.-J. Christ, T. Mueller, D. Schliephake, M. Heilmaier, Phase equilibria, microstructure, and high temperature oxidation resistance of novel refractory high-entropy alloys, J. Alloys. Compd. 624 (2015) 270–278.
- [3] E. Castle, T. Csanádi, S. Grasso, J. Dusza, M. Reece, Processing and properties of high-entropy ultra-high temperature carbides, Sci. Rep. 8 (2018) 8609.
- [4] J. Gild, Y. Zhang, T. Harrington, S. Jiang, T. Hu, M.C. Quinn, et al., High-entropy metal diborides: a new class of high-entropy materials and a new type of ultrahigh temperature ceramics, Sci. Rep. (2016) 37946.
- [5] E. Wuchina, E. Opila, M. Opeka, W. Fahrenholtz, I. Talmy, UHTCs: ultra-high temperature ceramic materials for extreme environment applications, Electrochem. Soc. Interface 16 (4) (2007) 30.
- [6] M.M. Opeka, I.G. Talmy, J.A. Zaykoski, Oxidation-based materials selection for 2000°C + hypersonic aerosurfaces: theoretical considerations and historical experience, J. Mater. Sci. 39 (19) (2004) 5887–5904.
- [7] W.G. Fahrenholtz, G.E. Hilmas, Oxidation of ultra-high temperature transition metal diboride ceramics, Int. Mater. Rev. 57 (2012) 61–72.
- [8] P. Hu, X.-H. Zhang, J.-C. Han, X.-G. Luo, S.-Y. Du, Effect of various additives on the oxidation behavior of ZrB<sub>2</sub>-Based ultra-high-Temperature ceramics at 1800°C, J. Am. Ceram. Soc. 93 (2010) 345–349.
- [9] D.J. Young, first edition), High Temperature Oxidation and Corrosion of Metals 1 Elsevier, 2008 p. ix.
- [10] H.J.T. Ellingham, Reducibility of oxides and sulfides in metallurgical processes, J. Soc. Chem. Ind. 63 (1944) 125–133.
- [11] B. Gleeson, 1.09 Thermodynamics and Theory of External and Internal Oxidation of Alloys. Shreir's Corrosion, (2010), pp. 182–184.
- [12] S.R. Shatynski, The thermochemistry of transition metal carbides, Oxid. Met. 13 (1979) 105–118.
- [13] K. Ishizaki, Phase diagrams under high total gas pressures—Ellingham diagrams for hot isostatic press processes, Acta Metall Mater. 38 (1990) 2059–2066.
- [14] S. Howard, Ellingham Diagrams: Standard Gibbs Energies of Formation for Oxides. SD Sch Mines Technol Rapid City SD, (2006).
- [15] N. Birks, G.H. Meier, F.S. Petiti, Introduction to the High Temperature Oxidation of Metals, Cambridge University Press, 2006, p. 351.
- [16] W.B. Hillig, Prospects for ultra-high-temperature ceramic composites, Tailoring
- multiphase and composite ceramics, Springer, Boston, MA, 1986, pp. 697–712.[17] W.W. Smeltzer, D.J. Young, Oxidation properties of transition metals, Prog Solid State Chem. (1975) 17–54.
- [18] O.N. Senkov, G.B. Wilks, D.B. Miracle, C.P. Chuang, P.K. Liaw, Refractory highentropy alloys, Intermetallics 18 (2010) 1758–1765.
- [19] O.N. Senkov, J.M. Scott, S.V. Senkova, F. Meisenkothen, D.B. Miracle, C.F. Woodward, Microstructure and elevated temperature properties of a refractory TaNbHfZrTi alloy, J. Mater. Sci. 47 (2012) 4062–4074.
- [20] O.N. Senkov, S.V. Senkova, C. Woodward, Effect of aluminum on the microstructure and properties of two refractory high-entropy alloys, Acta Mater. 68 (2014) 214–228.
- [21] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, K. Hack, I.H. Jung, Y.B. Kang, J. Melançon, A.D. Pelton, C. Robelin, S. Petersen, FactSage thermochemical software and databases - recent developments, Calphad 33 (2009) 295–311.
- [22] B. Pujilaksono, T. Jonsson, M. Halvarsson, J.-E. Svensson, L.-G. Johansson,

Oxidation of iron at 400–600 $^\circ C$  in dry and wet O2, Corros. Sci. 52 (2010) 1560–1569.

- [23] G.J. Yurek, J.P. Hirth, R.A. Rapp, The formation of two-phase layered scales on pure metals, Oxid. Met. 8 (5) (1974) 265–281.
- [24] C. Wagner, Contribution to the theory of formation of oxidation films, Z Phys. Chem. B 21 (1933) 25.
- [25] P. Kofstad, High Temperature Corrosion, Elsevier Applied Science ; Sole distributor in the USA and Canada, Elsevier Science Pub. Co., London; New York; New York, NY, USA, 1988 pp. 8, 289–319.
- [26] R.Y. Chen, W.Y.D. Yeun, Review of the high-temperature oxidation of iron and carbon steels in air or oxygen, Oxid. Met. 59 (2003) 433–468.
- [27] G.R. Wallwork, A.E. Jenkins, Oxidation of titanium, zirconium, and hafnium, J. Electrochem. Soc. 106 (1959) 10–14.
- [28] P. Kofstad, S. Espevik, Kinetic study of high-temperature oxidation of hafnium, J. Common Met. 12 (1967) 382–394.
- [29] J. Belle, M.W. Mallett, Kinetics of the high temperature oxidation of zirconium, J. Electrochem. Soc. 101 (1954) 339–342.
- [30] D. Cubicciotti, The oxidation of zirconium at high temperatures, J. Am. Chem. Soc. 72 (1950) 4138–4141.
- [31] P. Kofstad, High-temperature oxidation of titanium, J. Common Met. 12 (1967) 449–464.
- [32] P. Kofstad, P.B. Anderson, O.J. Krudtaa, Oxidation of titanium in the temperature range 800–1200°C, J. Common Met. 3 (1961) 89–97.
- [33] D.E. Poland, A.K. Kuriakose, J.L. Margrave, The oxidation of titanium monoxide at high temperatures, J. Phys. Chem. 69 (1965) 158–160.
- [34] E.A. Gulbransen, Thermochemistry and the oxidation of refractory metals at high temperature, Corrosion 26 (1970) 19–28.
- [35] O. Kubaschewski, B.E. Hopkins, Oxidation mechanisms of niobium, tantalum, molybdenum and tungsten, J. Common Met. 2 (1960) 172–180.
- [36] J.T. Clenny, C.J. Rosa, Oxidation kinetics of niobium in the temperature range of 873 to 1083 K, Metall Trans A 11 (1980) 1385–1389.
- [37] P. Kofstad, S. Espevik, Low-pressure oxidation of niobium at 1200°–1700°C, J. Electrochem. Soc. 112 (1965) 153–160.
- [38] J. Stringer, The vanadium-oxygen system—a review, J. Common Met. 8 (1965) 1–14.
- [39] W.R. Price, J. Stringer, The oxidation of vanadium at high temperatures, J. Common Met. 8 (1965) 165–185.
- [40] W.R. Price, J. Stringer, Oxidation of vanadium in the liquid oxide region, Nature 212 (1966) 1356.
- [41] W.R. Price, S.J. Kennett, J. Stringer, The oxidation of vanadium in the temperature range 700°-1000°C: the non-linear rate law, J. Common Met. 12 (1967) 318–325.
- [42] A. Mukherjee, S.P. Wach, Kinetics of the oxidation of vanadium in the temperature range 350–950°C, J Common Met. 92 (1983) 289–300.
- [43] A. Mukherjee, S.P. Wach, An investigation of the kinetics and stability of VO<sub>2</sub>, J. Common Met. 132 (1987) 107–113.
- [44] S. Westman, On the lower oxides of vanadium, Acta Chem. Scand. 17 (3) (1963) 749–752.
- [45] R.W. Bartlett, Molybdenum oxidation kinetics at high temperatures, J. Electrochem. Soc. 112 (1965) 744–746.
- [46] E.A. Gulbransen, K.F. Andrew, F.A. Brassart, Oxidation of Molybdenum 550° to 1700°C, J. Electrochem. Soc. 110 (1963) 952–959.
- [47] J.B. Berkowitz-Mattuck, A. Büchler, J.L. Engelke, S.N. Goldstein, Mass-spectrometric investigation of the oxidation of molybdenum and tungsten, J. Chem. Phys. 39 (1963) 2722–2730.

- [48] D.E. Rosner, H.D. Allendorf, Kinetics of high-temperature oxidation of molybdenum by dissociated oxygen, J. Chem. Phys. 40 (1964) 3441–3442.
- [49] E.S. Jones, C.J.F. Mosher, R. Speiser, J.W. Spretnak, The oxidation of molybdenum, Corrosion 14 (1958) 20–26.
- [50] R.C. Peterson, W. Fassell Jr, High Pressure Oxidation of Metals. Molybdenum in Oxygen, Utah University, Salt Lake City, Department of Metallurgy, 1954.
- [51] E.A. Gulbransen, K.F. Andrew, Kinetics of the oxidation of pure tungsten from 500° to 1300°C, J. Electrochem. Soc. 107 (1960) 619–628.
- [52] E.A. Gulbransen, K.F. Andrew, F.A. Brassart, Kinetics of oxidation of pure tungsten, 1150°-l615°C, J. Electrochem. Soc. 111 (1964) 103–109.
- [53] F.J. Harvey, High temperature oxidation of tungsten wires in O<sub>2</sub>-Ar mixtures, Metall Trans. 4 (1973) 1513–1517.
- [54] V.K. Sikka, C.J. Rosa, The oxidation kinetics of tungsten and the determination of oxygen diffusion coefficient in tungsten trioxide, Corros. Sci. 20 (1980) 1201–1219.
- [55] P.O. Schissel, O.C. Trulson, Mass-spectrometric study of the oxidation of tungsten, J. Chem. Phys. 43 (1965) 737–743.
- [56] E.A. Kellett, S.E. Rogers, The structure of oxide layers on tungsten, J. Electrochem. Soc. 110 (1963) 502–504.
- [57] W.W. Webb, J.T. Norton, C. Wagner, Oxidation of tungsten, J. Electrochem. Soc. 103 (1956) 107–111.
- [58] E.L. Courtright, Engineering Property Limitations of Structural Ceramics and Ceramic Composites Above 1600°C, Proceedings of the 15th Annual Conference on Composites and Advanced Ceramic Materials: Ceramic Engineering and Science Proceedings, John Wiley & Sons, Ltd., 2008, pp. 1725–1744.
- [59] E.L. Courtright, H.C. Graham, A.P. Katz, R.J. Kerans, Ultrahigh Temperature Assessment Study: Ceramic Matrix Composites, Battelle Pacific Northwest Labs Richland WA, Battelle Pacific Northwest Labs Richland WA, 1992ADA262740.
- [60] C.J. Rosa, Oxidation of zirconium—a critical review of literature, J. Common Met. 16 (1968) 173–201.
- [61] R. Haul, G. Dümbgen, Sauerstoff-selbstdiffusion in Rutilkristallen, J. Phys. Chem. Solids 26 (1965) 1–10.
- [62] R. Kapoor, S.T. Oyama, Measurement of solid state diffusion coefficients by a temperature-programmed method, J. Mater. Res. 12 (1997) 467–473.
- [63] W.K. Chen, R.A. Jackson, Diffusion of oxygen in near-stoichiometric α-Nb<sub>2</sub>O<sub>5</sub>, J. Chem. Phys. 47 (1967) 1144–1148.
- [64] J. Giber, H. Oechsner, Dissolution of anodic Ta<sub>2</sub>O<sub>5</sub> layers into polycrystalline tantalum, Thin Solid Films 131 (1985) 279–287.
- [65] J.E. Stroud, W.C. Tripp, J.M. Wimmer, Defect structure of Ta<sub>2</sub>O<sub>5</sub>, J. Am. Ceram. Soc. 57 (1974) 172–175.
- [66] R. Chandrasekharan, I. Park, R.I. Masel, M.A. Shannon, Thermal oxidation of tantalum films at various oxidation states from 300 to 700°C, J. Appl. Phys. 98 (2005) 114908.
- [67] R. Roth, L. Coughanour, Phase equilibrium relations in the systems titania-niobia and zirconia-niobia, J. Res. Bur. Stand. 55 (4) (1955) 209–213.
- [68] C.J. Rosa, Oxygen diffusion in alpha and beta titanium in the temperature range of 932° to 1142°C, Metall Trans. 1 (9) (1970) 2517–2522.
- [69] M.K. Reser (Ed.), Phase Diagrams for Ceramists 1969, The American Ceramic Society, Columbus, OH, 1969 Supplement, Fig. 2405.
- [70] S.C. Zhang, G.E. Hilmas, W.G. Fahrenholtz, Improved oxidation resistance of zirconium diboride by tungsten carbide additions, J. Am. Ceram. Soc. 91 (2008) 3530–3535.
- [71] L. Silvestroni, D. Sciti, F. Monteverde, K. Stricker, H.-J. Kleebe, Microstructure evolution of a W-doped ZrB<sub>2</sub> ceramic upon high-temperature oxidation, J. Am. Ceram. Soc. 100 (2017) 17.