

AN ABLATION MODEL FOR ULTRA HIGH TEMPERATURE CERAMICS

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1.0 Summary

Oxidation reactions for ZrB_2 and SiC are analyzed in order to establish the accuracy of a fundamental thermochemical database in order to use computational models based on thermodynamics to predict oxide phase formation under high temperature air oxidation. In order to understand the reactions that occur during the oxidation of ZrB_2 and SiC (which is described as the interaction of Zr-B-O and Si-C-O , respectively), the two systems must be modelled individually. The individual models for the systems provides the groundwork from which to develop an advanced model that can describe the composite oxidation interactions that also includes kinetics. Assumptions made for the development of the model will limit the reactions to molecular oxygen in the presence of air under atmospheric conditions, with high oxygen pressure (101kPa) and low oxygen pressure (1kPa), and laminar flow conditions that would feed into a diffusion limited oxidation kinetic rate model.

The goal of this project is to establish a fundamental framework for understanding the UHTC material microstructure response as a result of reactions with molecular oxygen at high temperature that can be predictive of the thermodynamics and kinetics and validated under prescribed experimental test conditions. The impact of this work will allow the predictive understanding of the oxidation microstructures that form as a function of high temperature environment. The following analysis focuses on validating the thermochemical phases formed from high temperature oxidation experiments and predicted thermochemical phase formations with a focus on also identifying un-validated or incomplete data that would be needed to be a predictive oxidation model.

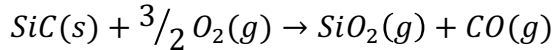
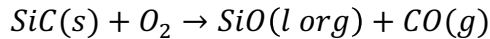
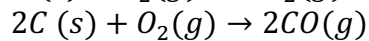
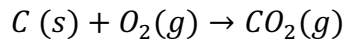
To validate the oxidation kinetics model a reliable test method for performing the high temperature oxidation studies that result in reproducible rate data is used called, dynamic non equilibrium thermal gravimetric analysis. The rate data is isothermal kinetics data that has been collected for a well characterize gas flow environment at high and low oxygen pressures. This fully integrated experimental and model approach eliminates the uncertainty when strictly developing predictive rate models from published results that use a range of materials and test facilities to develop rate data. The framework for the thermochemical model and identification of future work to build the kinetics model is summarized.

2.0 Introduction

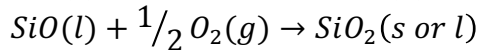
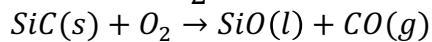
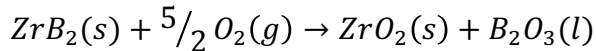
Ultra high temperature ceramics (UHTCs) such as zirconium diboride (ZrB_2) are promising material candidates for engineering applications especially in extreme environment owing to their high melting points ($>3000^\circ\text{C}$) and excellent capabilities at high-temperatures. Silicon carbide (SiC) is a common additive for ZrB_2 to improve densification (Akin et al. 2009), mechanical properties (Neuman, Hilmas, and Fahrenholtz 2013; Rosenberger, Stanciu, and Callegari 2015), as well as high temperature oxidation resistance (Fahrenholtz 2007). As the oxygen partial pressure increases under moderate heating conditions, the oxidation of SiC within the ZrB_2 matrix experiences active to passive transition and forms a desired silicon dioxide (SiO_2) layer instead of volatile SiO gas, and prevent further oxidation of the composite (Chen and Boyd 2019.).

Oxidation reactions for ZrB_2 and SiC are listed below in order to establish the accuracy of a fundamental thermochemical database for predicting oxide phase formation under high temperature air oxidation. Assumptions made will limit the reactions to molecular oxygen in the presence of air under atmospheric conditions, with high oxygen pressure (101kPa) and low oxygen pressure (1kPa), and laminar flow conditions that would feed into a diffusion limited oxidation kinetic rate model.

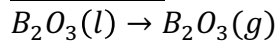
Solid $\rightarrow$ gas



Solid $\rightarrow$ liquid



Liquid $\rightarrow$ gas



The goal of this project is to establish a fundamental framework for understanding the UHTC material microstructure response as a result of reactions with molecular oxygen at high temperature that can be predictive if the thermodynamics and kinetics are analysis and validated under the conditions. The impact of this work will allow the predictive understanding of the oxidation microstructures that form as a function of high temperature environment. The following analysis focuses on validating the thermochemical phases formed from high temperature oxidation experiments and predicted thermochemical phase formations with a focus on also identifying incomplete phase equilibria and data that would be need to be acquired in order to fully develop the oxidation model.

3.0 Methods, Assumptions, and Procedures

The oxidation test reported here is done using a thermogravimetric analyzer (TGA) that allows the specimen to be heated in an inert gas environment that can be quickly switched to air once the isothermal test temperature is reached. In this case, the oxidation of the specimen is in the diffusion-controlled regime, where the diffusion of oxygen to the specimen surface is the slowest step under high temperature and low gas flow conditions. In order to experimentally investigate oxidation kinetics of $\text{ZrB}_2\text{-SiC}$ composite and use the testing results for future diffusion model (discussed later) verification, a given $\text{ZrB}_2\text{-25vol.\%SiC}$ test specimen of dimension $\sim 2\text{ mm} \times 7\text{ mm} \times 9\text{ mm}$ is placed directly on a ZrO_2 disk as shown in Figure 1 (a) inside the TGA furnace (Netzsch STA 449F3 Jupiter, Selb/Bavaria, Germany). Powder processing and densification methods of the specimen is described by (Walker, Pinc, and Corral 2012). The specimen is heated at $20^\circ\text{C}/\text{min}$ in ultra-high purity argon (UHP Ar) to the isothermal temperature (1600°C) with a flow rate of $100\text{ mL}/\text{min}$. Once the desired temperature is reached, the system is allowed to equilibrate for 2 min before the gas is switched to air ($200\text{ mL}/\text{min}$). After holding for 15 minutes, the gas is switched back to UHP Ar with a flow rate of $50\text{ mL}/\text{min}$ and allowed to cool freely. The purity of the UHP Ar is 99.999% with $\sim 1\text{ ppm}$ by volume of oxygen. The gas environment changed from inert to oxidizing in less than 4 s. The mass balance data acquisition rate is 600 points/min during the experiment, which gave a semi-continuous record of mass change with time. The digital resolution of the mass balance is $1\text{ }\mu\text{g}$. The free upper surface of the specimen and the lower one against the ZrO_2 support experienced different local environments in the upward flowing gas.

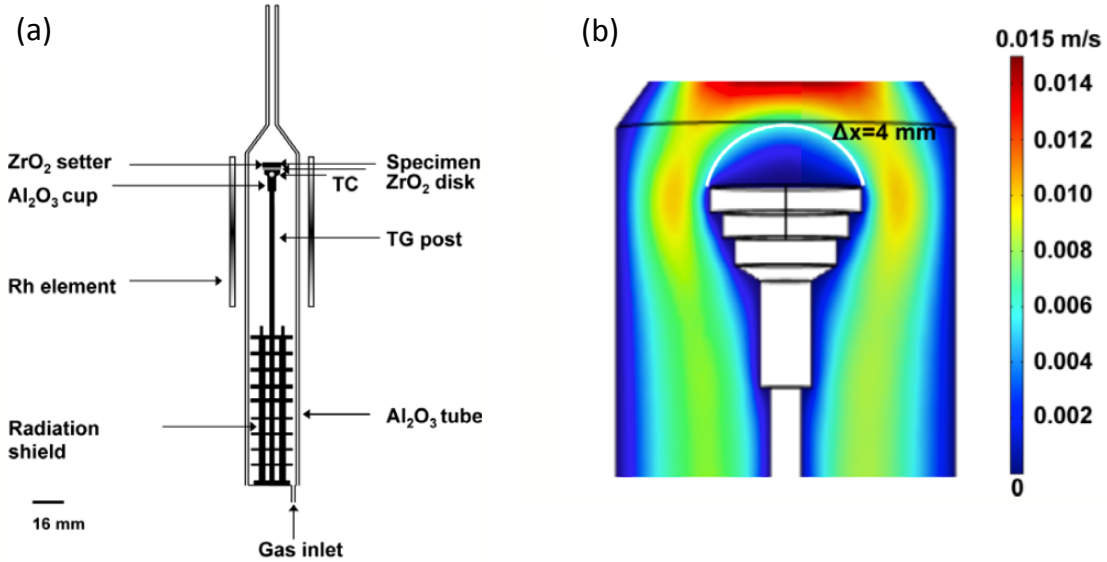


Figure 1: (a) Experimental setup for DNE-TGA used in isothermal oxidation at 1600°C . (b) The velocity map simulated by COMSOL of the gas flow of $200\text{ mL}/\text{min}$ (Miller-Oana, 2015).

Apart from the in-situ oxidation test in a TGA furnace, computational fluid dynamics (CFD) using a multiphysics software program (COSMOSOL, Inc., Los Angeles, CA) that solves the Navier–Stokes equation to model the gas flow inside the furnace is used to determine the boundary flow conditions around the specimen during testing. The model assumes that the temperature is isothermal (1600°C), the pressure is atmospheric, and the flow is laminar. In the TGA furnace, the gas is introduced through the bottom inlet with a flow of 0.8 m/s (200 mL/min) and exited the outlet at the top [Figure 1(a)]. The maximum inlet flow velocity using the current equipment configuration is 200 mL/min. High-temperature gas velocity maps are constructed in figure 1 (b) to show the local gas flow velocity and boundary layer thickness (4mm) around the specimen during the DNE-TGA testing at 1600 °C and 200 mL/ min inlet flow velocities. These results will be used as inputs for simulating oxygen diffusion and growth of oxide structure during the test, which will be discussed in recommendations for future work.

The current computational thermodynamic model for the Zr-B-C-O system was developed using the CALPHAD (CALculation of PHase Diagrams) method. The collected thermodynamic data has been assessed and verified to be correct up to 2200°C by cross-referencing experimental phase equilibria in the current literature. The accuracy of the database has been evaluated using a commercially available database Thermo-Calc SSUB5 (*Thermo-Calc Software SSUB5 SGTE Substance Database Version 5*) by simulating phase diagrams on the Si-C-O system. Through the development of the model, it is then possible to recalculate the phase equilibria of an entire system as a whole under various conditions.

4.0 Results and Discussion

Thermodynamic Evaluation of the Zr-B-O system: Oxidation of ZrB₂

In order to understand the reactions that occur during the oxidation of ZrB₂ and SiC (which is described as the interaction of Zr-B-O and Si-C-O, respectively), the two systems must be modelled individually. The individual models for the systems provides the groundwork from which to develop an advanced model that can describe the composite oxidation interactions. The Zr-B and Zr-O binary phase diagrams are shown in Figure 2. The accurate formation of ZrB₂ and zirconium oxides (ZrO₂) are of interest in these models. Both models are representative of the experimental data in the literature for Zr-B (H. M. Chen et al. 2009) and Zr-O (M. Chen, Hallstedt, and Gauckler 2004).

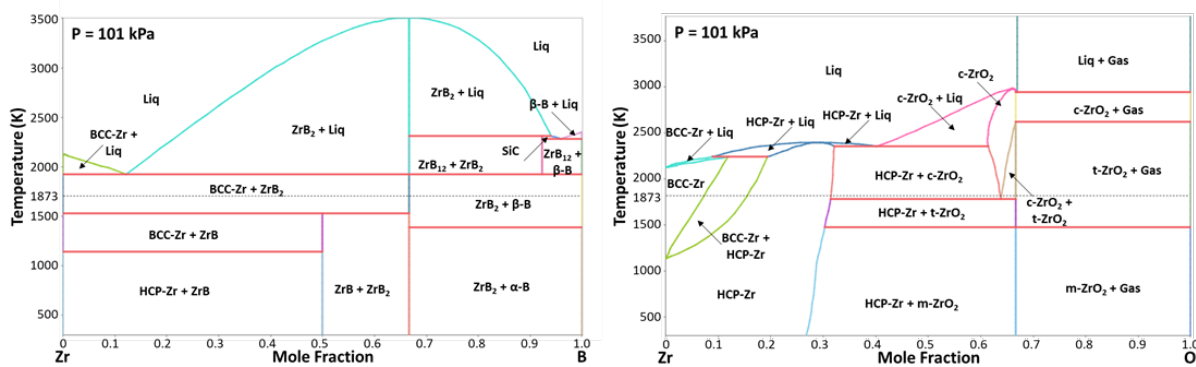


Figure 2: Thermodynamic models of the Zr-B and Zr-O binary phase diagrams calculated at atmospheric pressure.

In the case of the B-O binary system, thermochemical experimental data pertaining to the liquid phase regions (list the regions) are incomplete because the fundamental work has not been conducted experimentally on the given glass chemistries. The interaction parameters for the model were estimated from invariant temperature, congruent melting points and liquidus temperature for the temperature range of 1500°C to 1900°C (*Thermo-Calc Software SSUB5 SGTE Substance Database Version 5*). The resulting B-O binary model is shown in Figure 3. The B-O phase diagram was calculated for standard pressure (1 atm [101kPa]) and for a low oxygen partial pressure environment of 1kPa. It can be seen that by lowering the partial pressure of oxygen in the system, B₂O₃ liquid has a greater affinity to form the gaseous compound when pressure is lowered to 1kPa. The calculated phase diagrams at low pressure are currently not experimentally verified, but experiments can be performed to isolate the thermodynamic data that will feed accurate results to the thermochemical/kinetic model of oxidation.

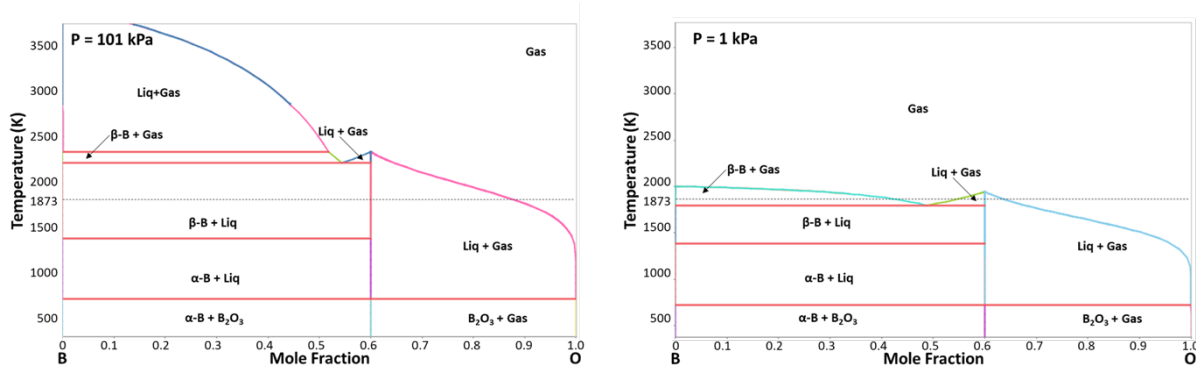


Figure 3: B-O binary phase diagrams calculated for standard pressure and 1kPa shows the increased favorability to form vapor species at 1600°C (1873K).

After development of the binary models, ternary interactions must be assessed. Ternary phase diagrams of the Zr-B-O system are calculated at standard pressure and 100Pa for 1600°C, shown in Figure 4. This provides thermodynamic information separate from the binary data where explicit data can be interpreted for the $\text{ZrB}_2 + \text{O}_2$ interaction. Drawing a line from the ZrB_2 phase to oxygen, under the two conditions results in different oxide being thermodynamically favorable. Under standard pressure, B_2O_3 liquid and ZrO_2 is formed. On the B-O line, the B_2O_3 liquid is not constrained to a single point, and instead shows solubility of ZrO_2 in the liquid phase. The ability for an oxide layer to prevent rapid oxidation of the substrate is dependent on limiting the ability for oxygen to diffuse. The properties for B_2O_3 to prevent oxidation are expected to be different than a $\text{B}_2\text{O}_3 \cdot \text{ZrO}_2$ liquid, which will have a higher viscosity (Karlsdottir, Halloran, and Grundy 2008). With the use of the thermodynamic model a more accurate representation of the formation of the oxide scale can be calculated. When the partial pressure of oxygen is reduced, the ternary phase diagram shows the gas phase of B_2O_3 is thermodynamically favored and there is no longer a liquid phase oxide interaction with B_2O_3 and ZrO_2 which is different than high pressure oxygen. Depending on the local environment in which the sample is exposed to high temperature molecular oxygen, two thermodynamic extremes are shown where a liquid oxide phase can develop, or there is a mass loss due to the vaporization of the B_2O_3 liquid phase. The thermodynamic models for the Zr-B-O system have been assessed and verified with experimental data from literature and in ZrB_2 powder processing work (Pham et al. 2016) (Pham et al. 2018). Verification in the case for the Zr-B-O model indicates that the predicted PEDs have been observed in material microstructures under identical experimental conditions for processing.

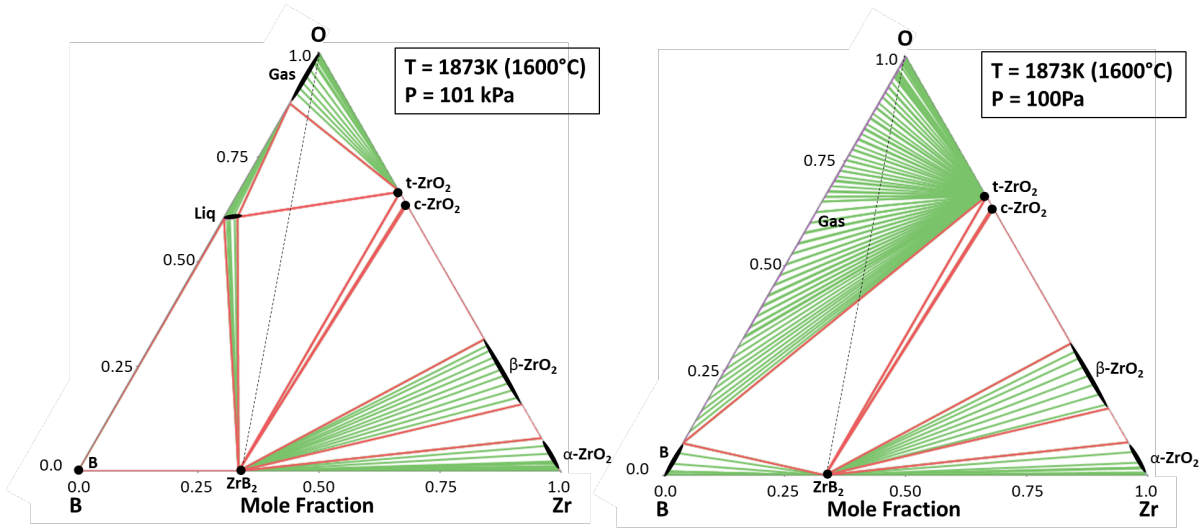


Figure 4: Calculated ternary diagrams for the Zr-B-O system under standard pressure and 100Pa, showing the change in the phase stability of B_2O_3 from liquid to gas.

Thermodynamic Evaluation of the Si-C-O system: Oxidation of SiC

Preliminary work has been performed on the Si-C-O system using a commercially available database from Thermo-Calc SSUB5 (*Thermo-Calc Software SSUB5 SGTE Substance Database Version 5*) by evaluating the accuracy of the database to experimental observation of phases formed during oxidation of SiC. The Si-C binary phase diagram shows the formation of SiC in Figure 5. The commercially available thermochemical database is experimentally accurate with literature results (Haase et al. 1985) at the temperature and composition of interest to form stoichiometric SiC. At high Si content and above 1600°C, the model requires further analysis to accurately show the formation regions for silicon liquid, noted in the dotted red line in the figure 5. In order to determine oxidation of as processed SiC materials that are made into fibers or bulk ceramics it is important to be able to accurately model oxidation of non-stoichiometric SiC that may result from microstructure related processing routes. Graphite rich material or Si rich material will result in different oxidation behavior of bulk SiC materials.

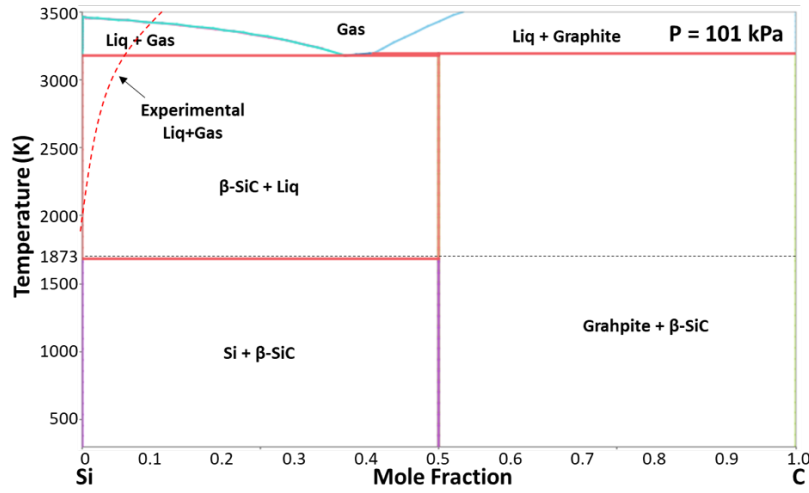


Figure 5: Preliminary Si-C calculated phase diagram.

For Si-O binary system, the same thermodynamic database (*Thermo-Calc Software SSUB5 SGTE Substance Database Version 5*) was used. Si-O binary phase diagrams were calculated at standard pressure and 1kPa for 1600°C, shown in Figure 6. SiO₂ is formed in the entire binary range, with excess oxygen present beyond 67mol% O. At standard pressure and 1600°C, SiO₂ can exist in the liquid state. The gas and liquid states are favorable at lower pressures which result in mass loss due to the volatilization of the oxides, rather than the deposition of a protective SiO₂ glass layer which limits the diffusion of oxygen to SiC and lowers oxidation rates. The Si-O binary system at standard pressure holds true with current experimental research, however, the data needs to be assessed at lower pressure to encapsulate the silicon liquid formation (Schnurre, Gröbner, and Schmid-Fetzer 2004).

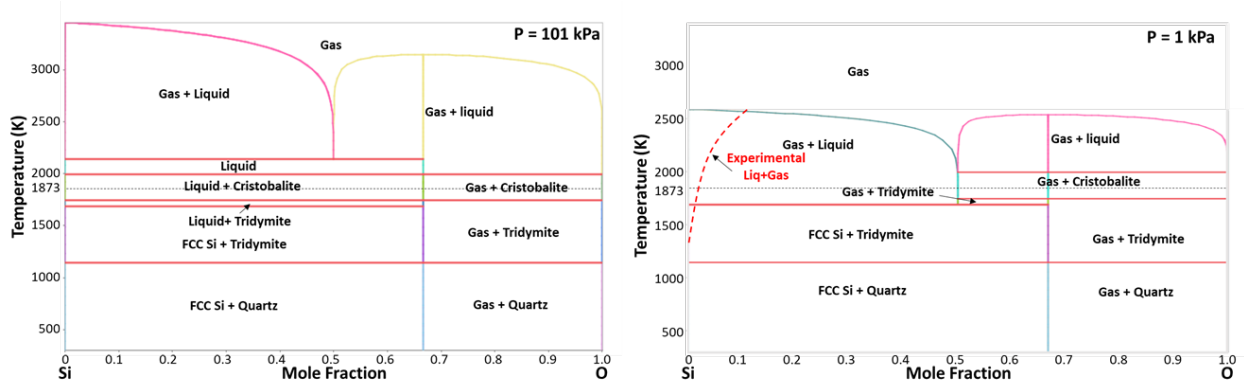


Figure 6: Si-O binary phase diagrams calculated for standard pressure and 1kPa shows the increased favorability to form vapor species at 1600°C (1873K).

The current binary models show there is insufficient data to accurately calculate the silicon liquid at low pressure. Knowing where the binary models need work, the ternary model can be graded to determine additional phase equilibria that needs to be improved or incorporated. Calculated ternary phase diagrams for the Si-C-O system are shown in Figure 7 at standard pressure and 100Pa for 1600°C. Under standard pressure, the Si-C-O ternary phase diagram shows

all phases are stable in the solid state. The gas region in the ternary is the oxygen phase as shown in the Si-O binary (Figure 5). Decreasing the pressure in the Si-C-O ternary shows greater favorability of forming the gas phase. As expected in the missing data in the binary diagrams, the ternary at low pressure does not show the $\text{Si}_{(l)}$ phase on the Si-C line. By addressing the discrepancy in the binary thermodynamic data, the ternary model will recalculate the correct phase equilibria. Specific ternary interactions that need to be addressed, is the incorporation of a silicon oxycarbide phase, which has a greater formation favorability at low pressure (Latournerie et al. 2006). The expected affected regions for this phase are noted in the phase diagram with $\text{SiC}_x\text{O}_{(1-x)}$. The SiCO phase is particularly important when modeling the oxidation of ZrB_2 composites with SiC fibers as this phase will already be present since they are a result of the production of fibers (Nagamori, Boivin, and Claveau 1995). Further development work on the thermodynamic database needs to contain these phase equilibria corrections. By accurately modeling the phases, the kinetic model will have the most accurate reactions with regards to the local partial pressure of species.

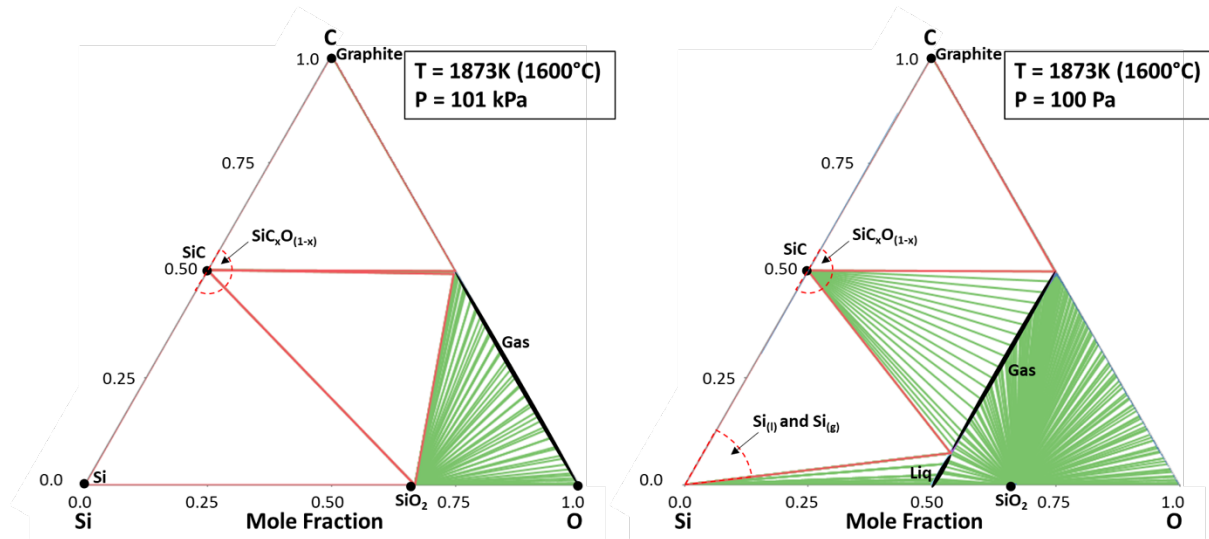


Figure 7: Si-C-O calculated phase diagrams at standard pressure and 100Pa for 1600°C.

Considerations for Nitride Reaction

In addition to the solid interactions above, the thermodynamic modeling can be used to encapsulate the formation of various gases products. During the oxidation of graphite in air, a mixture of oxygen and nitrogen, different gaseous species are formed. The formation of these species has been shown to affect the accuracy of kinetic models to model the ablation of graphite as gas-gas interactions occur (Keenan and Candler 1994). The following data is calculated from the SSUB5 thermochemical database and unverified with most recent literature, but shows the power in the modeling software to calculate gas equilibria. A graphical representation of a predominance diagram is shown in Figure 8 to show the trend in gas production of CO , CO_2 , NO and CN during graphite oxidation in air at 1600°C. In an atmosphere rich in oxygen and low in nitrogen (bottom right corner of the graph), the gas fractional gas composition is: 0.988 CO_2 , 0.0067 O_2 , 0.0056 CO , 3.2×10^{-10} NO . In a nitrogen rich environment (top left of the graph), the fractional gas composition is: 0.992 CO , 0.0067 N_2 , 0.0007 CO_2 , and 5.3×10^{-10} CN . To summarize the graphed space, with increasing oxygen content, CO_2 and NO is preferentially produced,

whereas increasing the nitrogen increases CO and CN production. By adding updated information to the thermodynamic database, more accurate simulations can be developed to qualitatively predict the gas species production during high temperature oxidation testing of materials. This provides more fundamental reaction data that is generally compensated for in kinetic models with fitting parameters that assume reaction rates to fit material loss or gain data.

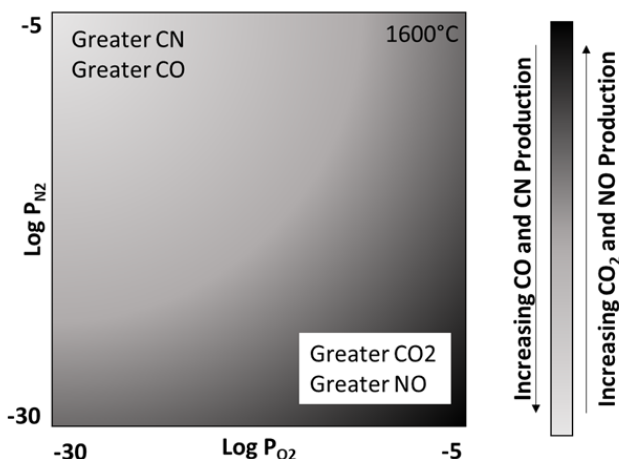


Figure 8: Graphical representation of a predominance diagram showing relative formation of CO, CO₂, NO and CN for graphite in varying partial pressure of O₂ and N₂ at 1600°C.

5.0 Conclusions and Recommendations for Future Work

Modification of Thermodynamic Database

On-going research on the oxidation behaviors of ZrB₂-SiC is being conducted. In addition to ZrO₂, B₂O₃ that are predicted in the aforementioned Zr-B-O ternary phase diagram, potential oxidation products also include SiO, SiO₂, CO, CO₂, and CN as we take the nitrogen gas (N₂) in air into account (Miller-Oana and Corral 2016). Therefore, modification and expansion of the current developed Zr-B-C-O quaternary thermodynamic database to incorporate silicon (Si) and nitrogen (N) is needed. An initial investigation into the Si thermodynamic data, the model needs to be modified to include the formation of silicon liquid at low pressures and the addition of SiCO into the equilibrium database. Multicomponent interactions such as SiO₂-B₂O₃-ZrO₂ need to be further evaluated from literature data and incorporated into the thermodynamic database and potential formation. The Zr-Si-B-C-O-N database will be limited to experimentally verified phases that are known to occur during oxidation of ZrB₂-SiC, as such there will be limited or no inclusion of zirconium silicides and solid nitride phases.

Kinetic Modeling with DICTRA

More importantly, a diffusion module with a kinetic database (i.e. Thermo-Calc_DICTRA) in addition to the thermodynamic database is required, in order to perform simulations on phase composition and thickness of the oxide structure as a function of oxygen partial pressure and exposure time. The schematics in Figure 9 demonstrates an example of oxide scale evolution at 1600 °C from 0 to 15 minutes in air, which results in the formation of a SiC-depleted layer, and gradually forms an intermediated layer that consists of SiO₂ and ZrO₂, and finally an outer oxide layer as time develops. With all layers including the base ZrB₂-SiC composite exhibit different oxidation rates; DICTRA is capable of predicting one-dimension diffusion controlled phase

transformation kinetics within each layer of the oxide scale with different chemical compositions. It is especially suitable for solving simulations that associated with a moving boundary, which allow us to predict the migrations of individual oxide interfaces (i.e. growth of oxide scale) as a function of time at various oxygen partial pressure results from the incoming air and various gaseous products such as CO, CO₂, CN, and B₂O₃ formed at each boundary layer. The multicomponent diffusion equations used for each oxide layer are solved under the assumption that thermodynamic equilibrium holds locally at all phase interfaces. Apart from the thermodynamic database for phase calculation in Thermo-Calc, diffusion simulations in DICTRA require an additional mobility (kinetics) database that contains information about the atomic mobility of individual components in various phases and is generated in a similar approach as the thermodynamic one through the CALPHAD methodology (“Diffusion Module (DICTRA) Documentation Set Thermo-Calc Version 2019a” 2019). Therefore, in order for us to gain more insight on oxidation of ZrB₂-SiC composite and be able to calculate the diffusion coefficients of various species in a specific oxide layer, development of a mobility database with experimental validation is needed.

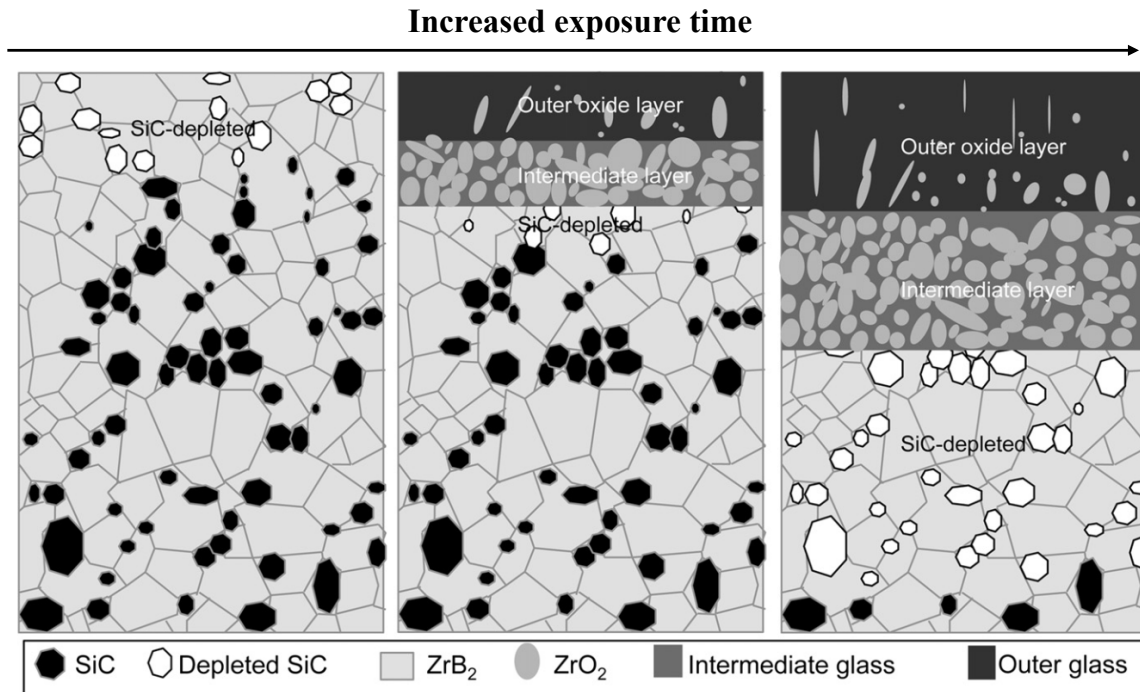


Figure 9: Schematics of an oxidized ZrB₂-SiC composite tested in a thermal gravimetric analyzer with the dynamic non-equilibrium method (DNE-TGA) at 1600°C in air (*Miller-Oana 2016*).

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