Thermodynamics of the oxidation of ZrB<sub>2</sub>–TiB<sub>2</sub>, ZrB<sub>2</sub>–SiC and ZrB<sub>2</sub>–B<sub>4</sub>C ceramics

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Abstract. The thermodynamics of the oxidation of three-high temperature ZrB<sub>2</sub>-based ceramics (ZrB<sub>2</sub>–TiB<sub>2</sub>, ZrB<sub>2</sub>–SiC and ZrB<sub>2</sub>–B<sub>4</sub>C) has been studied in order to find the stability domain of zirconium diboride, in terms of temperature, partial pressure of oxygen and composition, in which it is protected against oxidation. In the case of the ZrB<sub>2</sub>–TiB<sub>2</sub> binary system, a plot of log<br><sub><i>p</sub><sup>O</sup><sub>2</sub></sub> vs. 1/<sub><i>T</sub></sub> in the temperature range of 500–2000 K and another plot of <sub><i>p</sub><sup>O</sup><sub>2</sub></sub> (×10<sup>14</sup>) vs. <sub><i>x</i><sup>TiB<sub>2</sub></sub></sub> for <sub><i>T</i></sub> = 2000 K are made taking into account the two-extreme possibilities of no solubility and 100% solid solubility between ZrB<sub>2</sub> and TiB<sub>2</sub>, respectively. A plot of log<br><sub><i>p</sub><sup>CO</sup></sub> vs. log<br><sub><i>p</sub><sup>O</sup><sub>2</sub></sub> is made for 1773 K for the systems ZrB<sub>2</sub>–SiC and ZrB<sub>2</sub>–B<sub>4</sub>C. It was found that the ZrB<sub>2</sub>–TiB<sub>2</sub> ceramics does not have sufficient oxidation resistance in the temperature range of 500–2000 K. ZrB<sub>2</sub> of ZrB<sub>2</sub>–SiC ceramics can be protected under 1 atmosphere oxygen or in air if the liquid borosilicate (with the chosen composition, 70% B<sub>2</sub>O<sub>3</sub>–30% SiO<sub>2</sub>), which is an intermediate product, provides a kinetic barrier to the continuation of oxidation by forming an impervious layer on the exposed surfaces. In contrast, the ZrB<sub>2</sub>–B<sub>4</sub>C ceramics does not produce the borosilicate upon oxidation. In view of the volatility of pure liquid B<sub>2</sub>O<sub>3</sub>, it is recommended that the ZrB<sub>2</sub>–B<sub>4</sub>C ceramics can be used at a lower temperature, perhaps below 1373 K, when the vapour pressure of B<sub>2</sub>O<sub>3</sub> is significantly small.

Keywords. Thermodynamics; stability diagram; oxidation; ZrB<sub>2</sub>-based ceramics.

1. Introduction

Of all ultra-high temperature ceramics, zirconium diboride possesses unique combination of low density, high-melting temperature, high hardness and strength and good electrical and thermal conductivity [<sup>1</sup>–<sup>4</sup>]. These properties make it suitable for leading edges in aircraft and re-entry vehicles, as well as for high-temperature structural applications. Moreover, ZrB<sub>2</sub> does not undergo any phase transformation during high-temperature use, and its oxide also withstands high temperature. The oxidation resistance of ZrB<sub>2</sub>, alone or in combination with SiC or other borides/carbides, has been reported by many investigators [<sup>5</sup>–<sup>11</sup>]. Notably, Peng and Speyer [<sup>10</sup>] studied the oxidation resistance of pore-free pressureless-sintered and post-hot isostatic pressed ZrB<sub>2</sub>–B<sub>4</sub>C (with varying concentrations of SiC) ceramics with the help of scanning thermogravimetry, over a range of temperatures. Specimens were heated in flowing air (flow rate of 0.1 l min<sup>−1</sup>) from room temperature (298 K) at 50° min<sup>−1</sup> to 1223 K, 30° min<sup>−1</sup> to 1343 K, 10° min<sup>−1</sup> to 1373 K, 5° min<sup>−1</sup> to 1423 K and finally 3° min<sup>−1</sup> to 1823 K. Crystalline phases in the oxidized samples were identified by X-ray diffraction and their microstructures were examined by scanning electron microscopy. Guo and Zhang [<sup>11</sup>] studied the oxidation behaviour of ZrB<sub>2</sub>–SiC ceramics containing 10 and 30 vol% SiC in air at 1773 K for 0.5–10 h. The post-oxidation microstructural features were examined. The oxidation kinetics was analysed on the basis of weight gain, glass (borosilicate) layer thickness and the extended SiC-depleted layer thickness. The kinetics of oxidation has also been extensively studied in several other research groups [<sup>12</sup>–<sup>16</sup>]. Even so, a complete thermodynamic analysis of the oxidation of ZrB<sub>2</sub>-based ceramics has not been available in the literature so far. Particularly, the construction of stability diagrams showing the stability domains of different phases as a function of temperature, oxygen pressure and composition (of the solid solution of two borides, say) has not been given due importance. These diagrams furnish the equilibrium products of oxidation as well as the condition under which no oxidation may occur. The objective of the present work is, accordingly, to draw such stability diagrams for each of three important ZrB<sub>2</sub>-based systems, ZrB<sub>2</sub>–TiB<sub>2</sub>, ZrB<sub>2</sub>–SiC and ZrB<sub>2</sub>–B<sub>4</sub>C, and to find the conditions under which ZrB<sub>2</sub> is protected in an oxygen environment.

2. Construction of the stability diagrams

The following data [<sup>17</sup>] for the standard free-energy changes as a function of temperature are used for the construction of
the stability diagrams for the systems ZrB2–TiB2, ZrB2–SiC and ZrB2–B4C:

\[
\begin{align*}
ZrB_2(s) + 5/2O_2(g) &\rightleftharpoons ZrO_2(s) + B_2O_3(s); \\
\Delta G^o &\rightleftharpoons -2,016,897 + 403.6T J, \quad (1) \\
ZrB_2(s) + 5/2O_2(g) &\rightleftharpoons ZrO_2(s) + B_2O_3(l); \\
\Delta G^o &\rightleftharpoons -1,992,839 + 370.3T J, \quad (2) \\
TiB_2(s) + 5/2O_2(g) &\rightleftharpoons TiO_2(s) + B_2O_3(s); \\
\Delta G^o &\rightleftharpoons -1,909,369 + 400.4T J, \quad (3) \\
TiB_2(s) + 5/2O_2(g) &\rightleftharpoons TiO_2(s) + B_2O_3(l); \\
\Delta G^o &\rightleftharpoons -1,885,311 + 367.1T J, \quad (4) \\
SiC(s) + 3/2O_2(g) &\rightleftharpoons SiO_2(l) + CO(g); \\
\Delta G^o &\rightleftharpoons -937,593 + 77.23T J, \quad (5) \\
B_4C(s) + 7/2O_2(g) &\rightleftharpoons 2B_2O_3(l) + CO(g); \\
\Delta G^o &\rightleftharpoons -2,530,567 + 118.67T J. \quad (6)
\end{align*}
\]

2.1 **System ZrB2–TiB2**

Two extreme cases are considered regarding the solid solubility of ZrB2 and TiB2: (i) no solid solubility and (ii) 100% solid solubility. The data given in equations (1)–(4) are utilized to draw the stability diagrams.

2.1a **No solid solubility:** By using the thermodynamic relation \(\Delta G^o = -RT \ln K\) (where \(R\) is the universal gas constant, \(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\); \(T\), the temperature (Kelvin) and \(K\), the equilibrium constant in terms of activities), equation (1) yields the relation:

\[
-2,016,897 + 403.6T = 5/2RT \ln p_{O_2}.
\]

(7)

It may be noted that \(K = (a_{ZrO_2} \cdot a_{B_2O_3})/(a_{ZrB_2} \cdot (p_{O_2})^{5/2})\), in which the activities \((a)\) of pure condensed phases such as ZrB2(s), ZrO2(s) and B2O3(s) are unity and \(a_{O_2} = p_{O_2}\).

Equation (7) is used to plot \(\log p_{O_2}\) vs. \(1/T\) as line AB, which is extended over the temperature range of 500–723 K (melting point of B2O3) in figure 1. Above line AB, ZrO2(s) and B2O3(s) are stable, and below it, ZrB2(s) is stable. In an exactly similar manner, line BC is drawn in the temperature range of 723–2000 K by plotting the following relation, obtained from equation (2):

\[
-1,992,839 + 370.3T = 5/2RT \ln p_{O_2}.
\]

(8)

Above line BC, ZrO2(s) and B2O3(l) are stable, and below line BC, ZrB2(s) is stable.

The oxidation of TiB2 is shown by lines EF (in the temperature range of 500–723 K) and FG (in the temperature range of 723–2000 K), which are drawn by using the following two relations, obtained from equations (3 and 4), respectively:

\[
-1,909,369 + 400.4T = 5/2RT \ln p_{O_2},
\]

(9)

2.1b **100% Solid solubility:** Because the composition of the ZrB2–TiB2 solid solution is a variable in the present case, the stability diagram (figure 2) is constructed in a different way. A plot of \(p_{O_2}\) vs. \(x_{TiB_2}\) (\(x\) represents mole fraction) at 2000 K generates the curves HK and LK. The curve HK represents the equilibrium given by equation (2) and the curve LK represents the equilibrium given by equation (4). Assuming that ZrB2 and TiB2 form ideal solid solution (\(a_i = x_i\),
Figure 3. Stability diagram of the ZrB2–SiC system showing the stability fields of the oxide, boride and carbide mixtures at 1773 K, considering 70 mol% B2O3 in liquid borosilicate. The dotted isobaric curve abcd for p\textsubscript{total} = p\textsubscript{O2} + p\textsubscript{CO} = 1 atm, represents the thermodynamic progress of the oxidation, shown by arrows, of the ceramic ZrB2–SiC under 1 atm O2 at 1773 K; similarly, the dotted isobaric curve ghjkln for 5 atm O2 at 1773 K.

equations (2 and 4), at 2000 K, yield the following two relations:

\[
\begin{align*}
5.08 \times 10^{32} &= 1/(x\text{ZrB}_2 \cdot p\text{O}_2^{5/2}), \\
1.16 \times 10^{30} &= 1/(x\text{TiB}_2 \cdot p\text{O}_2^{5/2}).
\end{align*}
\]

Solving these two equations, with \(x\text{ZrB}_2 = 1 - x\text{TiB}_2\), the value of \(x\text{TiB}_2\) is found to be 0.998 and \(p\text{O}_2\) is 9.43 \times 10^{-13} \text{ atm}. These two values represent point K. Above line MKN, the boride mixture is fully converted into oxides. In the area enclosed by MK and HK, ZrB2 is partially oxidized and in the area enclosed by NK and LK, which is negligibly small, TiB2 is partially oxidized.

2.2 System ZrB2–SiC

Because two of the oxidation products of this system, namely B2O3 and SiO2, enter into a liquid phase (borosilicate) formation, the stability diagram (figure 3) is drawn, by plotting log \(p\text{CO}\) vs. \(p\text{O}_2\), for \(T = 1773\) K and for a particular liquid composition of 70 mol% B2O3–30 mol% SiO2 in view of the reported [11] superior oxidation resistance of ZrB2–30 vol% SiC (ZB30S). The equilibrium constant of equation (5) at 1773 K gives \(K = 3.88 \times 10^{23} = (a\text{SiO}_2 \cdot p\text{CO})/(a\text{SiC} \cdot p\text{O}_2^{3/2})\), which yields, after substituting \(a\text{SiO}_2 = x\text{SiO}_2\) (assuming ideal solution) = 0.3 and \(a\text{SiC} = 1\) (pure), the following equilibrium relation representing line PRQ:

\[
\begin{align*}
\log p\text{CO} &= 3/2 \log p\text{O}_2 + 24.1. \\
\log p\text{O}_2 &= −15.81.
\end{align*}
\]

Above line PRQ, SiC is stable and below it, impure SiO2 (l) is stable. Similarly, on the left of line SRT, ZrB2 is stable and on its right, ZrO2 and impure B2O3 (l) are stable. Two-isobaric curves (abcdef and ghjkln) representing the total pressure \(p\text{O}_2 + p\text{CO}\) of 1 and 5 atm, respectively, are superimposed on the stability diagram to show the course of oxidation of the ZrB2–SiC mixture under 1 and 5 atm oxygen pressure.

2.3 System ZrB2–B4C

Because the oxidation products, in this case, include pure liquid B2O3, besides solid ZrO2, the construction of the stability diagram (figure 4), drawn for 1773 K, is simpler. The equilibrium constant of equation (6) at 1773 K gives \(K = 2.28 \times 10^{68} = ((a\text{B}_2\text{O}_3)^2 \cdot p\text{CO})/(a\text{B}_4\text{C} \cdot p\text{O}_2^{7/2})\), which yields, after substituting each activity \((a)\) as 1, the following equilibrium relation representing line UWV:

\[
\begin{align*}
\log p\text{CO} &= 7/2 \log p\text{O}_2 + 68.36. \\
\log p\text{O}_2 &= −15.75.
\end{align*}
\]
Above line UWV, $\text{B}_2\text{C}$ is stable and below it, $\text{B}_2\text{O}_3$ is stable. Similarly, on the left of line XWY, $\text{ZrB}_2$ is stable and on its right, $\text{ZrO}_2$ and $\text{B}_2\text{O}_3$ are stable. The isobaric curve (abcdef) representing the total pressure ($p\text{O}_2 + p\text{CO}$) of 1 atm is superimposed on the stability diagram to show the course of oxidation of the $\text{ZrB}_2$–$\text{B}_4\text{C}$ mixture under 1 atm oxygen pressure.

3. Discussion

3.1 System $\text{ZrB}_2$–$\text{TiB}_2$

3.1a No solid solubility: In figure 1, line BC presents a greater protective range for $\text{ZrB}_2$ than line AB in terms of partial pressure of oxygen, as a function of temperature ($T > 723$ K). Similarly, line FG presents a greater protective range for $\text{TiB}_2$ than line EF in terms of partial pressure of oxygen, as a function of temperature ($T > 723$ K). Below these two lines, $\text{ZrB}_2$ and $\text{TiB}_2$, respectively, are free from oxidation. However, these protective limits of oxygen pressure, say $10^{-13}$ atm at 2000 K for $\text{ZrB}_2$, are far too small, compared to the atmospheric oxygen. Accordingly, $\text{ZrB}_2$ will oxidize in air forming the two oxides $\text{ZrO}_2$ and $\text{B}_2\text{O}_3$. It is required to be seen that if the consideration of 100% solid solubility between the two borides will give any greater oxidation protection for the two borides, particularly $\text{ZrB}_2$.

3.1b 100% Solid solubility: As the thermodynamic activity (and hence the mole fraction) of $\text{ZrB}_2$ in solid solution with $\text{TiB}_2$ progressively decreases from 1, along line HK in figure 2, the equilibrium partial pressure of oxygen for the oxidation of $\text{ZrB}_2$, according to equation (2), progressively increases and reaches the maximum value of about $10^{-12}$ atm at point K. The composition of the solid alloy corresponding to point K is 99.8 mol% $\text{TiB}_2$ and 0.2 mol% $\text{ZrB}_2$. Thus, the protective $p\text{O}_2$ limit for the oxidation of $\text{ZrB}_2$ increases at the most by about a factor of 10 when $\text{ZrB}_2$ is brought in solution with $\text{TiB}_2$. This value is much higher than the atmospheric oxygen and the oxidation of the borides is inevitable. It is to be noted that at a temperature $\approx 2000$ K, the protection range of oxygen partial pressure is even lowered. If only the temperature of the system is $> 2000$ K, which is uncommon, the equilibrium partial pressure for oxidation, and hence the protection range, will somewhat increase. So, it can be concluded that there is not much scope for the prevention of oxidation of $\text{ZrB}_2$–$\text{TiB}_2$ ceramics.

3.2 System $\text{ZrB}_2$–$\text{SiC}$

Zirconium diboride is protected, as shown in figure 3, in the domain PRS as well as in the domain enclosed by TRP (above line PR and on the left of line TR). According to the equilibrium diagram, the $\text{ZrB}_2$–$\text{SiC}$ composite should be fully oxidized to $\text{ZrO}_2$ (s) and $\text{B}_2\text{O}_3$–$\text{SiO}_2$ (l) under 1 atm oxygen pressure. The thermodynamic path of oxidation of the $\text{ZrB}_2$–$\text{SiC}$ (s) mixture to $\text{ZrO}_2$ (s) and $\text{B}_2\text{O}_3$–$\text{SiO}_2$ (l) under 1 atm oxygen pressure can be tracked by moving from $a$ to $f$ along the line abcdef drawn for 1 atm total pressure ($p\text{O}_2 + p\text{CO} = 1$) and superimposed on the stability diagram of figure 3. The relevance of this curve is that when the $\text{ZrB}_2$–$\text{SiC}$ mixture is exposed to 1 atm $\text{O}_2$, the resulting gas composition will contain the product gas CO and the unreacted $\text{O}_2$ at the total pressure of 1 atm, satisfying the equilibrium constant of reaction (5). Therefore, an isobaric line for 1 atm ranging from 100% $\text{CO}$ to 100% $\text{O}_2$ will cover all the possibilities of equilibrium gas composition when the $\text{ZrB}_2$–$\text{SiC}$ composite is exposed to 1 atm oxygen. For example, point b represents the equilibrium of reaction (5), which is the first stage of oxidation, with equilibrium values $p\text{CO} ≈ 1$ atm and $p\text{O}_2 ≈ 10^{-16}$ atm. Upon complete conversion of $\text{ZrB}_2 + \text{SiC}$ into $\text{SiO}_2$ (dissolved in liquid $\text{B}_2\text{O}_3$) + $\text{ZrB}_2$ (unreacted), according to equation (5), with continued oxidation, the second stage of oxidation (point c) involves the oxidation of $\text{ZrB}_2$ into $\text{ZrO}_2$ and $\text{B}_2\text{O}_3$ (in solution with $\text{SiO}_2$). One way of preventing the oxidation of $\text{ZrB}_2$ is to dissociate the oxygen environment from the ceramics, if possible, before the second stage of oxidation commences. Alternatively, and more practically, one can take advantage of the kinetic barrier offered to the continuation of oxidation by the liquid $\text{B}_2\text{O}_3$–$\text{SiO}_2$ (borosilicate, 70 mol% $\text{B}_2\text{O}_3$–30 mol% $\text{SiO}_2$) layer covering the exposed surfaces. The role of borosilicate layer in the oxidation resistance of $\text{ZrB}_2$–$\text{SiC}$ ceramics has been reported in many previous studies [5–7,10,11]. Even if $\text{B}_2\text{O}_3$ tends to evaporate off, owing to its high vapour pressure (boiling point, 2316 K), the $\text{SiO}_2$-rich layer provides effective oxidation protection [7].

Notably, the preceding discussion is equally valid, if not more, for the oxidation of $\text{ZrB}_2$–$\text{SiC}$ ceramics in air ($p\text{O}_2 = 0.21$ atm), rather than in 1 atm $\text{O}_2$. This is because air is less oxidizing than pure oxygen. To follow the thermodynamic stages of oxidation, a similar isobar of 0.21 atm, which will lie below and parallel to the 1 atm isobar (line abcdef) is to be drawn (figure 3).

The 5-atm isobar (line ghjklnm) presents a different picture. The first stage of oxidation involves the oxidation of $\text{ZrB}_2$ itself along with the formation of liquid borosilicate. Even if liquid borosilicate provides oxidation resistance to the remaining unoxidized $\text{ZrB}_2$, the partial oxidation of the zirconium diboride may spoil its high-temperature properties.

The experimental results of Peng and Speyer [10] support the preceding thermodynamic predictions. Specimens containing $\text{ZrB}_2$ and $\text{SiC}$ formed an amorphous, protective borosilicate coating when heated in flowing air at 1733 K. Increasing $\text{SiC}$ additions improved the oxidation resistance of the ceramics over an expanding range of temperatures. Guo and Zhang [11] also found that the oxidation of the ceramic $\text{ZrB}_2$–30 vol% $\text{SiC}$ was superior to that of the $\text{ZrB}_2$–10 vol% $\text{SiC}$. The oxidation of the $\text{ZrB}_2$–30 vol% $\text{SiC}$ followed a cubic kinetics while the $\text{ZrB}_2$–10 vol% $\text{SiC}$ followed a...
parabolic kinetics. The improved oxidation resistance in the ZrB$_2$–30 vol% SiC was attributed to the viscosity increase of the glassy (borosilicate) layer.

3.3 System ZrB$_2$–B$_4$C

The stability diagram of the system ZrB$_2$–B$_4$C and the superimposed 1-atm isobar (abcdef), in figure 4, present almost a similar situation to the system ZrB$_2$–SiC, except for the fact that there is no borosilicate formation. Accordingly, after the first stage of oxidation (point b), during which ZrB$_2$ is not oxidized, the product is B$_2$O$_3$ liquid (pure) plus ZrB$_2$ (unreacted). In view of the volatility of liquid B$_2$O$_3$, it is uncertain how much oxidation resistance this type of ceramics may have. The only recommendation would be to use this ceramics at a lower temperature, perhaps below 1373 K, when the vapour pressure of B$_2$O$_3$ is significantly small. In agreement with this, Peng and Speyer [10] reported a poor oxidation resistance of ZrB$_2$–13.5 vol% B$_4$C, especially beyond a temperature of 1573 K which marked the onset of accelerated oxidation.

4. Conclusions

The thermodynamics of the oxidation of three-binary ZrB$_2$-based high temperature ceramics (ZrB$_2$–TiB$_2$, ZrB$_2$–SiC and ZrB$_2$–B$_4$C) was studied with the help of four-stability diagrams constructed. It was found that the ZrB$_2$–TiB$_2$ ceramics does not have sufficient oxidation resistance in the temperature range of 500–2000 K. ZrB$_2$ of ZrB$_2$–SiC ceramics can be protected under 1 atm O$_2$ or in air if liquid borosilicate (with chosen composition, 70 mol% B$_2$O$_3$–30 mol% SiO$_2$), which is an intermediate product, provides a kinetic barrier to the continuation of oxidation by forming an impervious layer on the exposed surfaces. In contrast, the ZrB$_2$–B$_4$C ceramics does not produce the borosilicate because of the absence of SiO$_2$. In view of the volatility of pure liquid B$_2$O$_3$, it is uncertain how much oxidation resistance this type of ceramics may have. The only recommendation would be to use the ZrB$_2$–B$_4$C ceramics at lower temperature, perhaps below 1373 K, when the vapour pressure of B$_2$O$_3$ is significantly small.

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