Oxidation behavior of non-stoichiometric (Zr,Hf,Ti) C_x carbide solid solution powders in air

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Abstract: Multi-component solid solutions with non-stoichiometric compositions are characteristics of ultra-high temperature carbides as promising materials for hypersonic vehicles. However, for group IV transition-metal carbides, the oxidation behavior of multi-component non-stoichiometric (Zr,Hf,Ti) C_x carbide solid solution has not been clarified yet. The present work fabricated four kinds of (Zr,Hf,Ti) C_x carbide solid solution powders by free-pressureless spark plasma sintering to investigate the oxidation behavior of (Zr,Hf,Ti) C_x in air. The effects of metallic atom composition on oxidation resistance were examined. The results indicate that the oxidation kinetics of (Zr,Hf,Ti) C_x are composition dependent. A high Hf content in (Zr,Hf,Ti) C_x was beneficial to form an amorphous Zr–Hf–Ti–C–O oxycarbide layer as an oxygen barrier to enhance the initial oxidation resistance. Meanwhile, an equiatomic ratio of metallic atoms reduced the growth rate of (Zr,Hf,Ti) O_2 oxide, increasing its phase stability at high temperatures, which improved the oxidation activation energy of (Zr,Hf,Ti) C_x .

Keywords: ultra-high temperature ceramics (UHTCs); (Zr,Hf,Ti) C_x carbides; oxidation behavior; oxidation resistance; free-pressureless spark plasma sintering

1 Introduction

Ultra-high temperature ceramics (UHTCs), including nitrides, diborides, and carbides consisted of groups IV and V transition-metals, are generally applied at hypersonic vehicle leading edges, nosetips, and the combustion chamber used for thermal protection

system [1–3], due to their high melting temperatures ($> 3000\text{ }^{\circ}\text{C}$), high hardness, and resistance to thermal shock [4,5]. However, among the carbides, the group IV transition-metal carbides (i.e., ZrC, HfC, and TiC) are prone to oxidation starting from a relatively low temperature. For instance, the oxidation of ZrC initiates at temperatures close to $277\text{ }^{\circ}\text{C}$ in oxygen partial pressure (1–50 kPa) environments [6]. Further, they are susceptible to rapid high-temperature oxidation [7–9], which restricts their potential applications in oxygen environments [10].

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Recently, novel single-phase multi-component (e.g., (Hf,Ta)C [11–15], (Zr,Nb,Ti)C [16], and $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{C}_{0.74}\text{B}_{0.26}$ [17]) or high-entropy [18,19] carbides have attracted considerable attention for their extremely high melting points ($\sim 3930^\circ\text{C}$) [20,21], high hardness [22,23], low thermal conductivity [24,25], and better oxidation resistance [15,26]. In particular, for high-entropy carbides (four or more principal metallic components), Tan *et al.* [27] investigated the oxidation behavior of (Zr,Ti,Hf,Nb,Ta)C at 1200°C in a water vapour atmosphere, and the parabolic rate constant of high-entropy carbide was almost two orders of magnitude lower than that of ZrC. Ye *et al.* [26,28] studied the oxidation behavior of $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})\text{C}$ at 1073–1773 K in air. The results show that the high-entropy carbide obtains a good oxidation resistance, which is ascribed to their high mixing entropy, creating a high-entropy effect on lattice deformation and the formation of a dense oxide to reduce the inward diffusion of O_2 [28] or H_2O [27]. Obviously, the addition of metallic elemental component into binary carbide will affect oxidation resistance. Prior work has shown that a multi-component carbide–carbon/carbon composite fabricated by the Hf, Zr, and Ti addition into carbon/carbon matrix via reactive melting infiltration possessed a superior ablation resistance at 2500°C [29]. Unfortunately, for (Zr,Hf,Ti)C carbide solid solution, as a medium entropy ceramic [30], a clear understanding of its oxidation behavior has not been achieved. It is noted that the metallic atoms in current high-entropy carbides are generally equimolar. The effects of variation in composition of metallic atoms on oxidation behavior and oxidation resistance of (Zr,Hf,Ti)C are also needed to be clarified.

Besides the effect from metallic component, carbon component also has an important effect on the oxidation resistance. The non-stoichiometric ZrC_x is stable over a wide compositional range with a C/Zr atom ratio of 0.6–1.0 [31], and the similarly wide compositional ranges also exist in HfC_x [32] and TiC_x [33]. The properties of MC_x (where M, C, and x represent the metallic cations, carbon, and the atom ratio of C/M, respectively), i.e., hardness [34], yield stress [35], radiation tolerance [36], oxidation resistance in water vapour atmosphere [37], and densification by reactive hot pressing [38–41], are generally sensitive to C/M atom ratio and ordering of carbon vacancies [42,43]. In fact, for binary carbide ceramics (i.e., ZrC, HfC, and TiC), the composition of the highest melting

point ceramic or the best high-temperature performance is usually not the stoichiometric ceramic with a C/M ratio of 1/1 [44,45]. For instance, the melting point of $\text{ZrC}_{0.81}$ is maximized, and the value ($\sim 3700^\circ\text{C}$) is higher than that $\sim 3150^\circ\text{C}$ of stoichiometric $\text{ZrC}_{1.0}$ [44]. The highest melting point of HfC_x presents in the $\text{HfC}_{0.85-0.95}$ region [32,46,47]. Similarly, the oxidation resistance of carbide solid solution consisted of Zr, Hf, and Ti components could be influenced by the carbon vacancies. To date, few reports focus on the oxidation behavior of non-stoichiometric $(\text{Zr,Hf,Ti})\text{C}_x$ ($x < 1$) carbides.

In this work, four kinds of non-stoichiometric $(\text{Zr,Hf,Ti})\text{C}_x$ carbide solid solution powders were fabricated via free-pressureless spark plasma sintering. The oxidation behaviors of $(\text{Zr,Hf,Ti})\text{C}_x$ were studied in air. The microstructures of oxide and oxidation kinetics of $(\text{Zr,Hf,Ti})\text{C}_x$ were investigated. The effect of metallic atom composition on oxidation behavior and oxidation resistance of $(\text{Zr,Hf,Ti})\text{C}_x$ was also discussed.

2 Experimental

2.1 Material preparation

Zr ($> 99.5\text{ wt\%}$, $\leq 50\text{ }\mu\text{m}$), Hf ($> 99.5\text{ wt\%}$, $\leq 50\text{ }\mu\text{m}$), Ti ($> 99.5\text{ wt\%}$, $\leq 50\text{ }\mu\text{m}$), and carbon (graphite, 99.95 wt%, 3 μm , Macklin Biochemical Co., Ltd., China) powders were mixed by a planetary ball mill (MITR-YXQM-2L, Changsha MITR Instrument and Equipment Co., Ltd., China), using agate balls, polytetrafluoroethylene vessel, and ethanol as media. Considering the melting point of HfC is higher than those of ZrC and TiC [31–33], this may be related to the good ablation resistance of (Zr,Hf,Ti)C–carbon/carbon composite [29], at which the (Zr,Hf,Ti)C owned a high Hf content among metallic atom composition (i.e., Hf:Zr:Ti = 0.5:0.3:0.2). Hence, first group specimens were designed with equal molar ratio of carbon and Ti in carbides to compare the effect of Zr and Hf on the oxidation resistance of carbide, including $\text{Zr}_{0.5}\text{Hf}_{0.25}\text{Ti}_{0.25}\text{C}_{0.7}$ and $\text{Zr}_{0.375}\text{Hf}_{0.375}\text{Ti}_{0.25}\text{C}_{0.7}$. The second group specimens included $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$ and $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ with an equal molar ratio of carbon and a close molar ratio of Zr to compare the effect of Ti and Hf on the oxidation resistance of carbide. The mass ratio of ethanol to powder was 1:1. The ball-to-powder mass ratio was 5:1. After milling for 3 h with a speed of

100 rpm, the milled powder was dried at 40 °C for 24 h. The morphologies of raw materials and samples after milling are shown in Fig. 1.

The milled powders were then sintered by a spark plasma sintering equipment (HP D 25-3, FCT System GmbH, Germany) with a designed graphite die with two T-shape punches, as shown in Ref. [48], for free-pressureless spark plasma sintering at 1600 °C for 15 min under vacuum (< 5 Pa) with a heating rate of 100 °C/min. After sintering, the porous ceramic bulks were ground into powders using an agate mortar. These powders after sintering are multi-component carbide powders and the morphologies of them are shown in Fig. 2.

Fig. 1 Scanning electron microscopy (SEM) images of raw materials and samples after milling: (a) Zr, (b) Hf, (c) Ti, (d) carbon, (e) $Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7}$, (f) $Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7}$, (g) $Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}$, and (h) $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$.

2.2 Oxidation test

Before testing thermogravimetry–differential scanning calorimetry (TG–DSC), carbide powders were sieved between 325 and 500 mesh to control its particle size to reduce the particle effect on oxidation kinetics analysis. The particle size distribution of carbides after sieving is shown in Fig. 3 and the distribution ranges of them are close. Dv(50) and Dv(90) mean the particle size below 50% and 90% of the sample volume, respectively. TG–DSC was performed in flowing dry air (a mixture of N_2/O_2 (80:20, vol/vol)) using a NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min. The rate of air flow was kept constant at 20 mL/min during heating. The mass of the powder sample used for oxidation experiment

Fig. 2 SEM images of multi-component carbide powders after sintering: (a) $Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7}$, (b) $Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7}$, (c) $Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}$, and (d) $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$.

Fig. 3 Particle size distribution of $(Zr,Hf,Ti)C_x$ carbides after sieving.

was ~20 mg. The weight loss, onset oxidation temperature, and peak oxidation temperature of carbide powder based on the data of TG–DSC were used to evaluate the oxidation resistance. Meanwhile, carbide powder (2 g) was heated in a muffle furnace at scheduled temperatures (200–1600 °C) in Al₂O₃ crucible for 1 h in air with a heating rate of 10 °C/min. The oxidized products were used to identify the phases.

2.3 Characterization

The X-ray diffraction (XRD) patterns were obtained by an Advance D8 X-ray diffraction meter (Bruker, Germany) using Cu K α radiation at a scanning rate of 0.5 (°)/min from 5° to 90° of 2 θ . The Rietveld refinement was carried out using the general structure analysis system (GSAS) software [49]. The morphologies were observed by a scanning electron microscope (SEM, FEI NOVA NanoSEM230, USA) with a X-ray energy-dispersive spectrometer (EDS) analyzer. The oxidized particles (particle size $\approx$ 10 μ m) were thinned by a focused-ion-beam (FIB) technique by FEI Helios Nanolab G3 UC and their microstructures were observed by a transmission electron microscope (TEM, FEI Tecnai G2 F20, USA). The oxygen content was analyzed by a Leco TCH-600 N/H/O analyzer and a Leco CS-600 analyzer was used to test the total carbon content. The free carbon (C_{free}) content was determined by methods for chemical analysis of Hardmetals–Determination of insoluble (free) carbon content–Gravimetric method (ISO 3908: 2009). The C_{free} means the carbon that had not reacted with metallic atoms to form carbide and the detailed test method was shown in Ref. [48]. The particle size distribution was determined by a Malvern Mastersizer 3000 system.

3 Results

3.1 Crystalline structure characterization of (Zr,Hf,Ti)C_x carbides

The obtained Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8} carbide has been characterized in Ref. [48], but we present the basic information in this section for the sake of clarity, and compare it to other three kinds of (Zr,Hf,Ti)C_x carbides in different compositions. Figure 4(a) shows that the XRD patterns of all (Zr,Hf,Ti)C_x contain only one set of diffraction peaks, indicating that Zr, Hf, Ti, and C basically react with each other as a carbide solid solution. The peak location of (Zr,Hf,Ti)C_x changes slightly, for Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7}, as observed for the (111) plane reflection found at 33.7° (Fig. 4(b)), higher than that 33.2° of ZrC (JCPDS 65-8837), which is attributed to the decrease in lattice parameters due to both the substitution of Zr by Hf, Ti [50], and sub-stoichiometric carbon content (i.e., C/M $\approx$ 0.7) [44]. α is the lattice constant. The α of ZrC (0.4667 nm, JCPDS 65-8837) are larger than those of HfC (0.4623 nm, JCPDS 65-8751) and TiC (0.4600 nm, JCPDS 74-1219). Compared with Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7}, the peak location of Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7} moves toward a higher angle due to its smaller α (0.4589 nm, Table 1) caused by more substitution of Zr by Hf. Since the molar ratio of Zr and C is almost equal in Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8} and Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}, respectively, the more Ti leads Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8} to a higher diffraction peak location. The Rietveld crystal structure parameters (Table 1) show that all (Zr,Hf,Ti)C_x carbides are generated in a single-phase of face-centered cubic (FCC) structure with a $Fm\bar{3}m$ space group. The values of the weighted profile residual factor (R_{wp}) and the profile residual factor (R_p) of (Zr,Hf,Ti)C_x (Table 1)

Fig. 4 XRD patterns of (a) (Zr,Hf,Ti)C_x carbides and the milled powder of Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8} before sintering and (b) the enlargement of XRD patterns from 32.5° to 35.5°.

Table 1 Crystal structure parameters of carbides from Rietveld refinement of XRD

Specimen	Space group	<i>a</i> (nm)	Volume (nm ³)	Density (g/cm ³)	Selected carbon–metal bond length (pm)	<i>R</i> _{wp} (%)	<i>R</i> _p (%)
Zr _{0.5} Hf _{0.25} Ti _{0.25} C _{0.7}	<i>Fm</i> $\bar{3}$ <i>m</i>	0.4606(1)	0.0978(1)	7.76	C1–Hf1 = 230.4(1) C1–Zr3 = 230.4(1) C1–Ti4 = 230.4(1)	4.95	3.86
Zr _{0.375} Hf _{0.375} Ti _{0.25} C _{0.7}		0.4589(0)	0.0966(1)	8.60	C1–Hf1 = 229.4(1) C1–Zr3 = 229.4(1) C1–Ti4 = 229.4(1)	4.98	3.79
Zr _{1/3} Hf _{1/3} Ti _{1/3} C _{0.8}		0.4575(0)	0.0958(0)	8.18	C1–Ti1 = 228.8(1) C1–Zr3 = 228.8(1) C1–Hf4 = 228.8(1)	4.81	3.76
Zr _{0.3} Hf _{0.5} Ti _{0.2} C _{0.8}		0.4637(1)	0.0997(1)	9.28	C1–Hf1 = 231.8(0) C1–Zr3 = 231.8(0) C1–Ti4 = 231.8(0)	4.08	3.21

are converged to a relatively low value, such as *R*_{wp} of 4.81% and *R*_p of 3.76% for Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}, indicating a close fit to the experimental data. It is noted that the carbon vacancies in (Zr,Hf,Ti)C_x are disordered, since no change in the crystal structure is caused by carbon vacancies in (Zr,Hf,Ti)C_x. The content of carbon vacancies depends on the carbon content (*x*) and equals to 1–*x*. That is, a high content of carbon in the carbide corresponds a low content of carbon vacancies.

Table 2 shows the total contents of carbon, *C*_{free}, and oxygen of the specimens. The carbon contents of Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7}, Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7}, and Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8} are 8.31, 7.51, and 9.00 wt%, respectively, all of which are slightly higher than the designed values. This is likely due to the diffusion of carbon element from the graphite die into the carbides during sintering. Meanwhile, the metal ratio of Zr:Hf:Ti in multi-component carbide (i.e., Zr_{0.3}Hf_{0.5}Ti_{0.2}) detected using the EDS is close to 0.3:0.5:0.2 for the designed values, as shown in Ref. [48]. The contents of oxygen and *C*_{free} of all (Zr,Hf,Ti)C_x are low, which are close to those of ZrC powder fabricated by self-propagating high-temperature synthesis with low oxygen (0.94 wt%) and *C*_{free} (0.38 wt%) [51]. The molar ratios of *C*_{free}/*C* of them are tiny, indicating that the reaction between metallic elements and carbon powder is almost completed. Therefore, the as-synthesized non-stoichiometric

(Zr,Hf,Ti)C_x is single-phase solid solution with FCC structure.

3.2 Oxidation behavior of (Zr,Hf,Ti)C_x carbides

Based on the TG curves of Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8} (Fig. 5(a)), a weight gain of 9.3 wt% is from ~450 to 700 °C with an exothermic DSC signal peak at 644 °C (Fig. 5(b)). A weight loss of 0.5 wt% occurs after the weight gain, which is related to oxidation of Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}. The weight gain during oxidation happens due to oxygen uptake and the weight loss due to carbon oxidation. During the oxidation of HfC, it is first oxidized to form HfC_xO_y oxycarbide and carbon phases below 600 °C [52]. Since this temperature is below the temperature at which carbon is oxidized to CO₂/CO (~600 °C), this formed carbon remains in the oxide layer as carbon precipitation. Similar to the oxidation of HfC, a carbon precipitation is produced during the oxidation of Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8} and is also considered to remain in the oxide layer. This carbon precipitation is removed until the formation of oxide, to react with oxygen above ~600 °C, leaving the system as CO/CO₂ [53], resulting in the weight loss. Compared to the weight loss of commercial HfC (6.1 wt%, Fig. 5(a)), the weight loss of (Zr,Hf,Ti)C_x carbides decrease. The weight loss of Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7} and Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7} is

Table 2 Elemental analyses data of carbides

Specimen	Designed values of C (wt%)	Elemental analyses (wt%)			Molar ratio	
		C	<i>C</i> _{free}	O	<i>C</i> _{free} / <i>C</i>	O/(C– <i>C</i> _{free})
Zr _{0.5} Hf _{0.25} Ti _{0.25} C _{0.7}	7.61	8.31	0.01	0.46	0.001	0.04
Zr _{0.375} Hf _{0.375} Ti _{0.25} C _{0.7}	6.93	7.51	0.01	0.77	0.001	0.08
Zr _{1/3} Hf _{1/3} Ti _{1/3} C _{0.8}	8.33	9.00	0.01	1.05	0.001	0.09
Zr _{0.3} Hf _{0.5} Ti _{0.2} C _{0.8}	7.08	7.53	0.02	0.62	0.003	0.06

Fig. 5 TG–DSC curves of (Zr,Hf,Ti) C_x carbides and commercial HfC: (a) TG and (b) DSC.

2.0 and 1.1 wt%, respectively. The weight loss of $Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}$ is 0.03 wt% even close to zero, which is attributed to its highest peak oxidation temperature of 716 °C (Table 3), which exceeds the temperature when the carbon precipitation reacts with oxygen. Thus, the oxidation of (Zr,Hf,Ti) C_x and the reaction of carbon precipitation are simultaneous, leading to no obvious weight loss after oxidation. The peak oxidation temperatures of (Zr,Hf,Ti) C_x are higher than that 509 °C of HfC, indicating that (Zr,Hf,Ti) C_x carbides exhibit better oxidation resistance.

(Zr,Hf,Ti) C_x carbides also show the delayed onset oxidation temperature in early oxidation stage (Table 3). The onset oxidation temperature of $Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7}$ is 396 °C, which is slightly higher than that of $Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7}$. Since the molar ratios of Ti and C are equal in these two carbides, a higher Hf content improves the onset oxidation temperature of (Zr,Hf,Ti) C_x carbides. This trend also exists in $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$ and $Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}$, since $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$ owns an onset temperature of 484 °C, whereas $Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}$ begins at 397 °C. Meanwhile, the onset oxidation temperature of HfC is 307 °C, which is lower than those of (Zr,Hf,Ti) C_x , indicating that (Zr,Hf,Ti) C_x owns an enhanced initial oxidation resistance.

According to the above-mentioned results, $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$ possesses the best initial oxidation resistance due to its largest onset oxidation temperature. Therefore, its oxidation process is investigated systematically. After being oxidized in air for 1 h, most of the diffraction peaks change slightly in the range from 200 to 500 °C (Fig. 6(a)). The oxidation produces a decrease in the intensity and broadening of the diffraction peaks, especially the (111) planes at 33.6° due to a decrease in crystallinity [54]. The crystallinity is used to quantify the progressive structural damage [55], defined as $C = B_0I/(I_0B) \times 100\%$, where C is the crystallinity, B_0 and B are the background intensities for original material and thermally treated material, respectively, I_0 and I are the peak intensities for original material and thermally treated material, respectively. The corresponding (111) plane crystallinity of $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$ at room temperature, 200, 300, 400, and 500 °C is 100%, 98.1%, 96.9%, 93.4%, and 58.8%, respectively. Two new peaks could be observed at 28.4° and 31.6° after being oxidized at 500 °C, which belong to the m -(Zr, Hf, Ti) O_2 , closed to m -HfO₂ (JCPDS 74-1506). The appearance of m -(Zr,Hf,Ti) O_2 indicates that the oxidation process starts from ~500 °C, which is consistent with TG–DSC results (Fig. 5). For 600 °C

Table 3 Onset oxidation temperatures, peak oxidation temperatures, and E values of carbides

Specimen	Onset oxidation temperature (°C) ^a	Peak oxidation temperature (°C)	E values calculated by Ginstling–Brounshtein (G–B) model (kJ/mol)	E values calculated by phase-boundary reaction-controlled equation (kJ/mol)
HfC (commercial)	307	509	130.1±3.3	—
$Zr_{0.5}Hf_{0.25}Ti_{0.25}C_{0.7}$	396	631	292.5±15.4	—
$Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7}$	365	669	269.8±17.4	53.7±5.2
$Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}$	397	716	155.8±1.0	121.6±2.7
$Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$	484	644	379.4±24.4	91.3±2.7

^a Onset oxidation temperatures are the temperatures when the weight gain is above 0.5 wt%. The temperature error is ±1 °C.

specimen, several new peaks observed at 17.6° , 34.2° , 41.2° , and 50.7° are also ascribed to $m\text{-(Zr,Hf,Ti)O}_2$. The intensity of $m\text{-(Zr,Hf,Ti)O}_2$ peaks gradually increases with the increase in temperature. For 1200°C specimen, one new weak peak is observed at 30.2° , which is assigned to $(\text{Zr,Hf})\text{TiO}_4$. Compared with HfTiO_4 (JCPDS 74-1287), this peak of $(\text{Zr,Hf})\text{TiO}_4$ shifts to a low angle (Fig. 6(c)) due to the solid solubility of Zr atoms. However, it disappears when

the temperature reaches to 1500°C , and it is inferred that $(\text{Zr,Hf})\text{TiO}_4$ redissolves with $m\text{-(Zr,Hf,Ti)O}_2$ with a slight peak shifting of (-111) plane (Fig. 6(c)). For 1400°C specimen, another new peak is observed at 27.1° , which is assigned to TiO_2 (JCPDS 80-1502). Therefore, $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ gradually transforms to $m\text{-(Zr,Hf,Ti)O}_2$ and TiO_2 with the increase in an oxidation temperature.

Figure 7 shows the morphologies of oxidation products

Fig. 6 XRD patterns of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ after being oxidized at different temperatures: (a) $200\text{--}900^\circ\text{C}$ and (b) $1000\text{--}1600^\circ\text{C}$; (c) the enlargement patterns of $1100\text{--}1600^\circ\text{C}$ from 28.0° to 31.0° .

Fig. 7 SEM images of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ after being oxidized at different temperatures: (a) 500°C and (b) 1200°C ; (c) element mapping of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ after being oxidized at 1200°C .

of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$. The surface of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ is smooth (Fig. 2(d)). When the temperature increases to 500 °C, some particles crack along the edge (Fig. 7(a)). The cracks are formed by the different lattice parameters between carbide and oxide, and the oxide has a large volume change [52]. When the temperature is 1200 °C, the carbide is completely oxidized (Fig. 7(b)). The uniform distribution of Zr, Hf, Ti, and O elements (Fig. 7(c)) indicates that the oxide retains a solid solution structure, described as $(\text{Zr,Hf,Ti})\text{O}_2$.

To further study the oxidation process and microstructure of oxide, one single $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ particle after being oxidized at 500 °C (particle size $\sim 10\ \mu\text{m}$) is thinned by FIB technique. The TEM results clearly show that the oxidized particle is consisted of two interfaces in zones c and d (Fig. 8(a)), which makes it divided into three layers. According to the EDS results (Fig. 8(b)), the center layer contains Zr, Hf, Ti, and C elements except O element (Spot C), whereas both the intermediate layer (Spot B) and the surface layer (Spot A) contain O element. Meanwhile, the intensity of C element in the surface layer is higher than that in the intermediate layer. Thus, three layers from center to surface are denoted as Zr–Hf–Ti–C layer, Zr–Hf–Ti–C–O layer, and Zr–Hf–Ti–O+C layer. The thickness of intermediate Zr–Hf–Ti–C–O layer is $\sim 200\ \text{nm}$, and that of surface Zr–Hf–Ti–O+C layer is

$\sim 130\ \text{nm}$. The appearance of bright electron diffraction (the inset in Fig. 8(c)) of Zr–Hf–Ti–C layer indicates that the center part of oxidized particle still maintains a carbide structure. The intermediate Zr–Hf–Ti–C–O layer is amorphous $(\text{Zr,Hf,Ti})\text{C}_x\text{O}_{1-x}$ oxycarbide, inducing a dispersed diffraction ring in its selected area electron diffraction (SAED) pattern (the inset in Fig. 8(e)). Similar to the formation mechanism of ZrC_xO_y in ZrC [6,56] and HfC_xO_y in HfC [52,57], respectively, the formation of amorphous $(\text{Zr,Hf,Ti})\text{C}_x\text{O}_{1-x}$ in $(\text{Zr,Hf,Ti})\text{C}_x$ could be attributed to the diffusion of superfluous oxygen atoms into the surface area of carbide [56]. The oxygen can occupy the carbon vacancies but can also be substituted to carbon on the octahedral site of the FCC lattice of metal atoms [57]. The oxycarbide layer is reported to form during the initial oxidation stage of ZrC [56], HfC [58], and TiC [59]. Unfortunately, for stoichiometric ZrC, Gasparrini *et al.* [8] reported that the oxycarbide layer had never been experimentally observed, perhaps as the ZrC crystal structure could accommodate up to 60% of oxygen in the crystal lattice without changing its structure [60]. Nevertheless, using the FIB technique, this oxycarbide layer can clearly be observed in the non-stoichiometric $(\text{Zr,Hf,Ti})\text{C}_x$, indicating that the carbon vacancies have helped to generate the oxycarbide layer and further increases the oxidation resistance.

Fig. 8 TEM observations of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ after being oxidized at 500 °C for 1 h in air: (a) TEM image, (b) EDS analysis of Spots A, B, and C in (a), (c) high resolution TEM (HRTEM) image of Zone c in (a), (d) enlargement of zone d in (a), and (e–g) HRTEM images of zones e–g in (d), respectively. The insets of (c, e, and g) are the corresponding SAED patterns.

The surface Zr–Hf–Ti–O+C layer is combined with (Zr,Hf,Ti)O₂ microcrystal and amorphous carbon precipitation (Fig. 8(f)). The size of (Zr,Hf,Ti)O₂ microcrystal is ~10 nm. The *d*-spacing of the (−111) and (111) lattice fringes of (Zr,Hf,Ti)O₂ is ~0.320 and ~0.286 nm, respectively, which are close to that of HfO₂ (0.325 nm for (−111) and 0.291 nm for (111), respectively, JCPDS 74-1506). The weak multiple electron diffraction rings (the inset in Fig. 8(g)) are ascribed to a low crystallinity of (Zr,Hf,Ti)O₂.

The carbon precipitation is confirmed by element mapping results (Figs. 9(a) and 9(c)), and it distributes with (Zr,Hf,Ti)O₂. A high content of carbon is combined with a low content of Hf, Zr, and Ti in the surface layer (the dashed part in Fig. 9(c)). Based on the line element distribution results (Fig. 9(b)), the carbon content increases from center to surface, meaning that the carbon element diffuses outward during oxidation. The oxygen content increases firstly and then decreases along the direction from surface to

center. This result shows that the diffusion rate of oxygen is limited by the intermediate Zr–Hf–Ti–C–O oxycarbide layer.

Therefore, the oxidation process of Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8} under 600 °C is depicted by the following reaction (assuming that the maximum solubility of oxygen in Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8} is 25% like HfC [61]):

The reaction temperatures of Reactions (1) and (2) are ~500 °C, and those of Reactions (3) and (4) are ~600 °C.

As a comparison, according to the TEM results (Fig. 10), Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8} particle after being oxidized

Fig. 9 EDS analysis of Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8} after being oxidized at 500 °C: (a) high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image, (b) element scanning along the line position in (a), and (c) element mapping of solid line area in (a).

Fig. 10 TEM observations of the $Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}$ after being oxidized at 500 °C for 1 h in air: (a, b) TEM images and (c–f) HRTEM images of zones h–k in (b), respectively. The insets of (c) and (d) are the corresponding SAED patterns.

at 500 °C (particle size $\sim 10 \mu m$) is also consisted of three layers from center to surface, namely, Zr–Hf–Ti–C layer, Zr–Hf–Ti–C–O layer, and Zr–Hf–Ti–C–O+C layer. The HRTEM image of zone h shows that the Zr–Hf–Ti–C–O layer is amorphous (Fig. 10(d)), whereas Zr–Hf–Ti–C layer still maintains a carbide structure (Fig. 10(c)). The thickness of Zr–Hf–Ti–C–O layer is ~ 180 nm, which is slightly thinner than that of $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$. The thickness of surface Zr–Hf–Ti–C–O+C layer is ~ 50 nm, which is consisted of amorphous $(Zr,Hf,Ti)C_xO_{1-x}$ and carbon precipitation (Figs. 10(e) and 10(f)). The carbon precipitation is confirmed by EDS analysis results (Figs. 11(c) and 11(d)), which is composed of ~ 95.5 at% carbon element (Sopt D). Compared with $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$, no $(Zr,Hf,Ti)O_2$ microcrystal is in the surface layer but amorphous $(Zr,Hf,Ti)C_xO_{1-x}$. Meanwhile, the oxygen content (Fig. 11(b)) firstly increases in the surface Zr–Hf–Ti–C–O+C layer, and then almost maintains in intermediate Zr–Hf–Ti–C–O layer, and eventually decreases at the interface between Zr–Hf–Ti–C–O layer and Zr–Hf–Ti–C layer, which is slightly different from the trend of oxygen diffusion in $Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}$ exhibiting a decreased oxygen content in the intermediate layer (Fig. 9(b)). It is suggested that the variation in composition of metallic

atoms affects the ability to inhibit the diffusion of oxygen by the Zr–Hf–Ti–C–O oxycarbide layer.

4 Discussion

4.1 Oxidation kinetics analysis

In the theory of non-isothermal oxidation processes, the dependence of the reaction rate on the temperature is commonly described by the Arrhenius equation. The kinetics studies are based on the following equation [62,63]:

$$da/dt = A \exp(-E/RT) f(\alpha) \quad (5)$$

where $f(\alpha)$ is the conversion function dependent on mechanism of reaction, da/dt is the conversion rate, A is the frequency factor, E is the apparent activation energy, T is the temperature, R is the gas constant, and α is the conversion degree.

In this work, Coats–Redfern method, an integral approach, is used to investigate the oxidation kinetics of $(Zr,Hf,Ti)C_x$ carbides, which is based on the following equation [62,64]:

$$\ln[g(\alpha)/T^2] = \ln[AR(1-2RT/E)/\beta E] - E/RT \quad (6)$$

where $g(\alpha)$ is the integral function form of kinetic model and β is the heating rate. During the kinetics analysis

Fig. 11 EDS analysis of $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$ after being oxidized at 500 °C: (a, c) HAADF-STEM images, (b) element scanning along the line position in (a), and (d) EDS analysis of Spot D in (c).

of oxidation processes, the appropriate form of the $g(\alpha)$ kinetic model is determined, and the parameters of Arrhenius equation (A and E) are calculated according to plotting by $\ln[g(\alpha)/T^2]$ against $1/T$. G-B model and phase-boundary reaction model have been successfully applied to analyze the oxidation kinetics of HfC [52] and ZrC [6]. The G-B model equals to $1-(2/3)\alpha-(1-\alpha)^{2/3}$ and it corresponds to a diffusion-controlled mechanism for taking into account the volumes of both the reactant and the product independently [6]. When the kinetics model equals to $1-(1-\alpha)^{1/3}$, it corresponds to a phase-boundary reaction controlled mechanism [62].

As a result, when $g(\alpha) = 1-(2/3)\alpha-(1-\alpha)^{2/3}$ or $g(\alpha) = 1-(1-\alpha)^{1/3}$, the following Coats-Redfern equation is obtained:

$$\ln\{[1-(2/3)\alpha-(1-\alpha)^{2/3}]/T^2\} = \ln[AR(1-2RT/E)/\beta E] - E/RT \quad (7)$$

$$\ln\{[1-(1-\alpha)^{1/3}]/T^2\} = \ln[AR(1-2RT/E)/\beta E] - E/RT \quad (8)$$

The graph of $\ln\{[1-(2/3)\alpha-(1-\alpha)^{2/3}]/T^2\}$ or $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$ versus $1/T$ shows the slope of straight line equal to $-E/R$ and the activation energy could be evaluated. The relationship between α and T in the oxidation weight gain process is used for the calculations (Table 4). The graphs of $\ln\{[1-(2/3)\alpha-$

$(1-\alpha)^{2/3}]/T^2\}$ and $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$ versus $1/T$ are shown in Fig. 12. The good linearity of $\text{Zr}_{0.5}\text{Hf}_{0.25}\text{Ti}_{0.25}\text{C}_{0.7}$ indicates that G-B model is the probable model for its whole oxidation weight gain process (Fig. 12(a)), suggesting that the diffusion of oxygen into the carbide is the predominant rate-determining step [6]. However, the kinetics of $\text{Zr}_{0.375}\text{Hf}_{0.375}\text{Ti}_{0.25}\text{C}_{0.7}$, $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$, and $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ can only be described by G-B model up to 50%, 60%, and 40% conversion degree, respectively. In this work, the oxidation process control by oxygen diffusion is described as the early oxidation stage, while the subsequent oxidation is described as the late oxidation stage. The late oxidation stages of them are found to be well described by the phase-boundary reaction-controlled equation (Fig. 12(b)).

The activation energies E are calculated in Table 3. The E values of $(\text{Zr,Hf,Ti})\text{C}_x$ calculated by G-B model are higher than those of HfC (130.1 ± 3.3 kJ/mol), ZrC (100 – 150 kJ/mol [6]), and TiC (125 – 150 kJ/mol [59]). When the activation energy E value is high, the oxidation reaction rate is slow, meaning that it is hard for oxygen to diffuse into the carbide. Therefore, the oxidation resistance of $(\text{Zr,Hf,Ti})\text{C}_x$ is better than those of their constituent binary carbides. Meanwhile, in the early oxidation stage, $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ has a strong oxidation resistance due to its high E value of

Table 4 Relationship between α and T of carbides

Specimen	T (K)									
	$\alpha = 10\%$	$\alpha = 20\%$	$\alpha = 30\%$	$\alpha = 40\%$	$\alpha = 50\%$	$\alpha = 60\%$	$\alpha = 70\%$	$\alpha = 80\%$	$\alpha = 90\%$	$\alpha = 100\%$
HfC (commercial)	666	703	728	746	762	777	792	808	828	878
Zr _{0.5} Hf _{0.25} Ti _{0.25} C _{0.7}	786	806	818	828	836	845	854	863	876	933
Zr _{0.375} Hf _{0.375} Ti _{0.25} C _{0.7}	795	821	836	849	863	878	894	924	946	970
Zr _{1/3} Hf _{1/3} Ti _{1/3} C _{0.8}	819	870	903	928	951	971	985	998	1014	1140
Zr _{0.3} Hf _{0.5} Ti _{0.2} C _{0.8}	829	841	852	864	875	888	902	919	935	977

Fig. 12 Activation energy calculations by Coats–Redfern method in the oxidation weight gain process ($\alpha = 0.2$ – 0.9) with (a) G–B model and (b) phase-boundary reaction controlled equation.

379.4±24.4 kJ/mol, and this brings a high onset oxidation temperature (484 °C). In the late oxidation stage, the oxidation resistance of Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8} is better due to its high E value (121.6±2.7 kJ/mol), leading to a high peak oxidation temperature (716 °C).

Interestingly, the various compositions in (Zr,Hf,Ti)C_x also affect the temperature changing from oxygen diffusion control to phase-boundary reaction control. Shimada and Ishi [60] reported a change in the oxygen diffusion mechanism of ZrC to phase boundary diffusion at 743 K due to the crystallization of ZrO₂ above 743 K. However, the actual temperature when this occurs has not been verified by others. Furthermore, some reports showed that the oxidation rate of ZrC is predominantly controlled by the phase boundary reaction with the presence of ZrO₂ crystals with a size of > 10 nm [65,66]. According to Fig. 12, the changing temperatures of Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}, Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}, and Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7} are 602, 712, and 605 °C, respectively. The grain size of (Zr,Hf,Ti)O₂ is calculated by Scherrer equation based on the XRD patterns of their oxides at corresponding changing temperature (Fig. 13). The grain size of their (Zr,Hf,Ti)O₂ is 11.6±0.2, 9.5±0.3, and 12.7±0.2 nm, respectively. Therefore, it is suggested that their oxidation processes are changed to be controlled from

Fig. 13 XRD patterns of the oxidation products of Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8}, Zr_{1/3}Hf_{1/3}Ti_{1/3}C_{0.8}, and Zr_{0.375}Hf_{0.375}Ti_{0.25}C_{0.7} after being oxidized at 602, 712, and 605 °C, respectively.

oxygen diffusion to phase-boundary reaction with the presence of (Zr,Hf,Ti)O₂ with a size of 9.5–12.7 nm, which is closed to the oxidation of ZrC with the presence of ZrO₂ crystals with a size of > 10 nm [65,66].

4.2 Oxidation mechanisms

The kinetics analysis shows that the rate-controlling mechanism changes among (Zr,Hf,Ti)C_x according to the composition. In this work, Zr_{0.3}Hf_{0.5}Ti_{0.2}C_{0.8} is used as an example to discuss the oxidation process in

detail.

In the early oxidation stage (below 40% oxidation), atomic oxygen could substitute for the carbon or occupy carbon vacancy sites [6,52,56–58], forming $(\text{Zr,Hf,Ti})\text{C}_x\text{O}_{1-x}$ oxycarbide. This process occurs rapidly, similar to the stoichiometric HfC and ZrC, forming $\text{HfC}_x\text{O}_{1-x}$ [52] and $\text{ZrC}_x\text{O}_{1-x}$ [6], respectively. The microstructure of oxycarbide layer is clearly observed, which indicates that the carbon vacancies help to generate this oxycarbide layer. Importantly, the diffusion rate of oxygen is decreased by the oxycarbide layer (Fig. 9(b)). Thus, the rate-determining step is the diffusion of oxygen through the oxycarbide layer. As oxidation proceeds, the carbon atom diffuses outward, and the $(\text{Zr,Hf,Ti})\text{C}_x\text{O}_{1-x}$ gradually transforms to $(\text{Zr,Hf,Ti})\text{O}_2$ (Reaction (2)). It is noted that the oxygen diffusion-controlled process is up to 40% oxidation (Fig. 12), corresponding to 864 K, and this temperature is below the reaction temperature of carbon to form CO/CO₂. Therefore, the carbon remains in the surface layer mixed with $(\text{Zr,Hf,Ti})\text{O}_2$.

In the late oxidation stage (above 40% oxidation), the temperature is beyond the carbon oxidation temperature. The previous compact surface Zr–Hf–Ti–C–O+C layer is broken by CO/CO₂, which weakens its oxygen barrier ability, accelerating the growth of $(\text{Zr,Hf,Ti})\text{O}_2$. The expansion stress increases due to the growth of $(\text{Zr,Hf,Ti})\text{O}_2$. To release this stress, cracking occurs along the grain boundaries [52], or the particles break up. Cracking is related to the change from oxygen diffusion control to phase-boundary reaction control, and it results in the rupture of the diffusion oxidized layers, including $(\text{Zr,Hf,Ti})\text{O}_2$ and $(\text{Zr,Hf,Ti})\text{C}_x\text{O}_{1-x}$, which provides a path for transport of oxygen. The easy diffusion of oxygen accelerates the reaction, generating a new oxidized product on the surface of $(\text{Zr,Hf,Ti})\text{C}_x$, and then rebuilds the diffusion oxidized layers. When the oxidized layer reaches a critical thickness, the imposed stress makes it break up another time. This cracking–rebuilding reaction process repeats in the late oxidation stage till complete oxidation. The oxidation rate measured in this process seems to be governed by oxide nucleation and the growth of oxide nuclei at the interface of $(\text{Zr,Hf,Ti})\text{O}_2/(\text{Zr,Hf,Ti})\text{C}_x\text{O}_{1-x}$. However, since the nucleation of $(\text{Zr,Hf,Ti})\text{O}_2$ is assumed to occur instantaneously, similar to the nucleation in the oxidation of HfC [52], the successive growth of nuclei determines the overall

rates. Thus, the activation energy for the phase-boundary reaction is dominated by the growth of $(\text{Zr,Hf,Ti})\text{O}_2$ nuclei in the late oxidation stage.

4.3 Effect of metallic atom composition of $(\text{Zr,Hf,Ti})\text{C}_x$ carbides on oxidation resistance

The oxidation resistances of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ and $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$ are affected by different metallic element composition. $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ exhibits a high onset oxidation temperature with a low E value in the late oxidation stage, while $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$ owns a low onset oxidation temperature and a high E value in the late oxidation stage (Table 3).

In the early oxidation stage, according to Figs. 8 and 10, $(\text{Zr,Hf,Ti})\text{O}_2$ microcrystal is easier to form in $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ than in $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$ after being oxidized at 500 °C. The Ellingham diagram (Fig. 14) shows that Hf has a high affinity for oxygen, whereas Ti has a low affinity. ΔG° indicates the standard free-energy change for a chemical reaction. Thus, $(\text{Zr,Hf,Ti})\text{O}_2$ microcrystal is easier to form in $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ due to its higher Hf and less Ti than in $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$. According to the EDS analysis (Figs. 9(b) and 11(b)), the ability to inhibit the inward diffusion of oxygen is not obvious in the surface layer. However, the diffusion rate of oxygen is limited by the intermediate Zr–Hf–Ti–C–O oxycarbide layer in both $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ and $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$, which is consistent with Barger *et al.* [9] suggesting that the oxygen diffusion coefficient of oxycarbide layer (i.e., Hf–C–O) in HfC is about 30 times lower than that of corresponding oxide (i.e., HfO₂). In addition, it is noted that the carbon–metal bond lengths (Table 1) in $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ are relatively longer than those in $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$, which makes them easier to break during oxidation. This is beneficial to oxygen to substitute for carbon to form oxycarbide layer and inhibits subsequent oxygen diffusion. Therefore, although a high Hf content leads to form $(\text{Zr,Hf,Ti})\text{O}_2$ microcrystal, the structure of carbide with a Zr:Hf:Ti ratio of 0.3:0.5:0.2 makes the oxycarbide layer easy to form and greatly inhibit the fast inward diffusion of oxygen, which increases the onset oxidation temperature. This trend also exists in the specimen group of $\text{Zr}_{0.5}\text{Hf}_{0.25}\text{Ti}_{0.25}\text{C}_{0.7}$ and $\text{Zr}_{0.375}\text{Hf}_{0.375}\text{Ti}_{0.25}\text{C}_{0.7}$, as $\text{Zr}_{0.5}\text{Hf}_{0.25}\text{Ti}_{0.25}\text{C}_{0.7}$ owns a higher onset oxidation temperature and longer carbon–metal bond length than $\text{Zr}_{0.375}\text{Hf}_{0.375}\text{Ti}_{0.25}\text{C}_{0.7}$.

Fig. 14 Ellingham diagram of metal–O and C–O system (data calculated from HSC Chemistry 6 software).

In the late oxidation stage, as the oxidation temperature increases, $(\text{Zr,Hf,Ti})\text{O}_2$ oxide grows quickly, leading to volume expansion, and eventually causes cracks. Based on the surface-energy theory [67,68], when the grain size of tetragonal ZrO_2 ($t\text{-ZrO}_2$) is larger than 10 nm, $t\text{-ZrO}_2$ will transform to stable monoclinic ZrO_2 ($m\text{-ZrO}_2$), and this will cause 3%–5% volume expansion. Similarly, this transformation is deduced to exist in $(\text{Zr,Hf,Ti})\text{O}_2$. When the grain size of $t\text{-}(\text{Zr,Hf,Ti})\text{O}_2$ is larger than 10 nm, it will spontaneously transform to the stable $m\text{-}(\text{Zr,Hf,Ti})\text{O}_2$. For $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$, the grain size of its oxide is 11.6 ± 0.2 nm at 602°C and it grows to 12.1 ± 0.1 nm at 700°C (calculated from Fig. 4), meaning that the grain size of oxide grows in an increasing temperature. For $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$, the grain size of its oxide is 9.5 ± 0.3 nm at 712°C , which is smaller than that 12.1 ± 0.1 nm of $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ oxidized at 700°C (close to 712°C). Thus, it is indicated that the growth rate of oxide with a Zr:Hf:Ti ratio of 1/3:1/3:1/3 is lower than that of 0.3:0.5:0.2. Meanwhile, the oxide with a Zr:Hf:Ti ratio of 1/3:1/3:1/3 could be stable in tetragonal crystal structure at a relative high oxidation temperature (above 712°C) due to its smaller grain size than 10 nm or the stabilization effect induced by the small amounts of free carbon as impurity [6], and the oxide with a Zr:Hf:Ti ratio of 0.3:0.5:0.2 has been already transformed to be monoclinic at 700°C (Fig. 6), meaning that the phase stability of oxide has been increased with an equiatomic ratio of metallic atoms. Wright and Luo [30] suggested that a high entropy value may increase phase stability for the high-symmetry phase in high-entropy or compositionally complex ceramics. In other words, in comparison with

their low-entropy counterparts, the high-symmetry phase may be stabilized to lower temperatures. According to the calculation of molar configurational entropy [69], the entropy value of $(\text{Zr,Hf,Ti})\text{O}_2$ achieves the maximum when its metallic atoms are in equiatomic ratio. Hence, the low grain growth rate and high phase stability of $(\text{Zr,Hf,Ti})\text{O}_2$ caused by an equiatomic ratio of Zr:Hf:Ti in carbide could weaken the phase-boundary reaction, which improves its activation energy in late oxidation stage. In addition, when the oxidation temperature is 605°C , the gain size of oxide of $\text{Zr}_{0.5}\text{Hf}_{0.25}\text{Ti}_{0.25}\text{C}_{0.7}$ is calculated to be 16.4 ± 0.7 nm, which is larger than that 12.7 ± 0.2 nm of $\text{Zr}_{0.375}\text{Hf}_{0.375}\text{Ti}_{0.25}\text{C}_{0.7}$. It is inferred that the oxygen diffusion controls the whole oxidation process of $\text{Zr}_{0.5}\text{Hf}_{0.25}\text{Ti}_{0.25}\text{C}_{0.7}$ due to its high grain growth rate of oxide.

5 Conclusions

In this work, the oxidation behaviors of four kinds of non-stoichiometric $(\text{Zr,Hf,Ti})\text{C}_x$ carbide solid solution powders are studied in air. The oxidation kinetics is demonstrated to be composition dependent: $\text{Zr}_{0.5}\text{Hf}_{0.25}\text{Ti}_{0.25}\text{C}_{0.7}$ obeys oxygen diffusion control in the whole process of oxidation, while $\text{Zr}_{0.375}\text{Hf}_{0.375}\text{Ti}_{0.25}\text{C}_{0.7}$, $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$, and $\text{Zr}_{0.3}\text{Hf}_{0.5}\text{Ti}_{0.2}\text{C}_{0.8}$ obey oxygen diffusion control in the early oxidation stage and phase-boundary reaction control in the late oxidation stage. A high Hf content in metallic atomic composition was beneficial to form an amorphous Zr–Hf–Ti–C–O oxycarbide layer as an oxygen barrier to increase the onset oxidation temperature in the early oxidation stage. An equiatomic ratio of metallic atoms in $\text{Zr}_{1/3}\text{Hf}_{1/3}\text{Ti}_{1/3}\text{C}_{0.8}$ reduces the growth rate of $t\text{-}(\text{Zr,Hf,Ti})\text{O}_2$, increasing its phase stability at high temperatures, which improves the activation energy in the late oxidation stage. The results herein provide the fundamental information for designing advanced oxidation-resistant non-stoichiometric $(\text{Zr,Hf,Ti})\text{C}_x$ carbide ceramics.

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