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Predicting Thermal Stability of Advanced Thermal/Environmental Barrier Coating (T/EBC) for Gas Turbine Engines

by Sophia R Cooper, Marcus L Young, Samir M Aouadi, Andrey Voevodin, Anindya Ghoshal, Muthuvel Murugan, and Luis Bravo Robles

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14. ABSTRACT Thermal/environmental barrier coatings (T/EBCs) are a high-temperature corrosion/oxidation-resistant solution used to improve the mechanical properties and lifespan of many high-strength bulk metals and ceramics. The recent development of high-entropy ceramics shows promising properties that prove them to be potential replacements for T/EBC applications. High-entropy materials are a revolutionary group of materials known for their unique tailorable properties—specifically, to perform as T/EBCs. They also possess remarkable mechanical properties for high temperature (>1000 °C) applications. These materials exhibit high strength and fracture toughness at high temperatures compared to conventional ceramics. In this study, we performed a theoretical examination of high-entropy ceramics for high-temperature applications. We selected the coating systems based on modified Hume–Rothery “rules” for determining single-phase high-entropy materials. The HfO ₂ -Al ₂ O ₃ -SiO ₂ system satisfied the modified Hume–Rothery rules with values of 70.85, 2.05%, and 5.09 for the entropic, atomic size, and valence electron considerations, respectively. The metal equivalent system, Hf-Al-Si system, was also examined to better understand the HfO ₂ -Al ₂ O ₃ -SiO ₂ system. Thermo-Calc CALPHAD software was used to build binary and ternary phase diagrams to determine the high-temperature stable phases of the Hf-Al-Si system, identify the phase changes that occur, and calculate the properties of the stable phases at 1300, 1350, and 1400 °C. At every temperature, the Hf-Al-Si system exhibited consistent thermal resistance values of 1.00E+20 mK/W. These are promising results for the oxide high-entropy ceramic system as a T/EBC solution.					
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1. Introduction

Military vehicles, especially military aircraft, are powered by their unique engine design. Gas turbine engines are intended to propel vehicles through a complex process. Fuel is sprayed into a pressurized air stream within the combustor. This fuel is ignited before entering the turbine to produce a high-temperature pressurized gas. As this high-temperature pressurized gas flows through the engine, it powers the compressor while propelling the actual machinery.¹ This intricate process is a revolutionary method for converting thermal energy into mechanical propulsion for high-power/high-speed vehicles. Given the high-temperature/high-pressure mechanics of this process, the smallest debris can cause catastrophic engine failure. In many instances, a small particle such as sand can lead to this failure and present a major safety hazard.¹

Small sand particles infiltrating military vehicles and aircraft can lead to catastrophic engine failure. The CaO-MgO-Al₂O₃-SiO₂ system, otherwise known as CMAS, is used to simulate this sand in a research-based lab environment. CMAS, which is typically blasted at high temperatures toward the material of interest, in this case the thermal/environmental barrier coating (T/EBC), can melt onto and eat away at the surface of the material. High temperatures, up to 2500 °C, are used to simulate the high operating temperatures experienced in these engines. CMAS is usually the main cause of material degradation for these applications and is used to understand specific material degradation due to CMAS attack, especially since this attack can diminish the material's desirable thermal and mechanical properties. This can also lead to engine failure, reduce engine lifespan, and hinder routine mechanical movement. Therefore, the need for a high-temperature T/EBC that can withstand CMAS attack is necessary for proper engine function, extended engine lifespan, and the safety of the Soldiers, which is the highest priority.

While there is a constant search for innovative ideas and technologies, modern technology uses yttria stabilized zirconia (YSZ) as the primary coating material for the base metal, typically nickel-based superalloys, of gas turbine engines. Some gas turbine engines also use a ceramic matrix composite (CMC) material as the base material, specifically SiC-SiC CMCs. This is a composite material made up of SiC fibers within a SiC matrix.² YSZ was initially considered the prime coating material for metal-based gas turbine engine components in the 1970s. It was first studied as a suitable material for engine coatings by Curt Liebert at the NASA John H. Glenn Research Center.³ It was more notably studied in 1978 by Dr Stephan Stecura, a former NASA employee.³ As noted in Smialek and Miller,³ Stephan Stecura defined the ideal composition for YSZ as a successful T/EBC as 6–8 mol.% yttria; thus, YSZ with 7 mol.% yttria became the most dominant YSZ composition for

plasma spray T/EBCs. In the 1990s, 7 mol.% YSZ gained popularity and is now considered the standard inert tough ceramic material for high-temperature applications.

To ensure the safety of Soldiers and reduce the mechanical malfunctions of their vehicles, there is a great need to create advanced T/EBCs for the gas turbine engines used in these vehicles—ideally, a high-temperature coating that may withstand temperatures up to approximately 2500 °C. A potential materials solution is the use of high-entropy ceramics (HECs) as T/EBC. While high-entropy alloys (HEAs), which are multicomponent solid solution materials with near equiatomic composition (anywhere from 5 to 35 at.%), have been extensively researched recently,^{4–9} HECs, which are similarly defined but with ceramic components rather than metals, have grown more slowly.⁴ The near equiatomic makeup of both HEAs and HECs means that there is no primary component. These materials are also known for their large entropies of mixing, which help to reduce the overall Gibbs free energy of the system. The lack of published HEC research means there are few methods for predicting their phase diagrams, phase changes, and thermodynamic and mechanical properties. As a first step toward developing HECs as T/EBCs, we evaluated the equivalent HEA using the TCHEA4 database in Thermo-Calc CALPHAD, which is a computational software that can predict a material's properties to better understand its behavior in various environments or when used for any desired application. CALPHAD is used to build the phase diagrams, predict the thermodynamic properties, and determine which phases are stable at high operating temperatures for these alloys and, in turn, provide insight into the equivalent ceramic coatings. The use of CALPHAD reduces the time and cost that it might take to find comparable experimental results and draw similar conclusions. Results from these calculations are compared with the CMAS system.

2. Computational Methods

The following process was used chronologically to characterize and evaluate the $\text{HfO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ HEC T/EBC system for gas turbine engine applications:

- (1) Apply modified Hume–Rothery rules for HEAs.
- (2) Analyze and compare the HEC descriptor data to the HEA predictors.
- (3) Build binary phase diagrams with the elements that make up the multicomponent ceramic material.
- (4) Build ternary phase diagrams of main elemental components (Hf, Al, and Si).

- (5) Predict phase changes and thermodynamic properties of multicomponent ceramic T/EBC with Thermo-Calc CALPHAD software.
- (6) Analyze those binary and ternary phase diagrams to down-select and identify ranges of potential compositional variations that meet Army-specific requirements.

CALPHAD allows us to build these binary and ternary phase diagrams, which are used to calculate and predict the thermodynamic properties of the phases and the overall system as well as the phase changes that occur at various compositions, temperatures, and pressures.

The following section explains how we use modified Hume–Rothery rules for HEAs to predict these material properties and aid in determining the viability of using $\text{HfO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ as an HEC for T/EBCs. For HEAs, the modified Hume–Rothery rules are based on three parameters: entropic consideration (Ω), atomic size consideration (δ), and valence electron consideration (VEC).^{10,11} To solve for the entropic consideration, the following four equations (Eqs. 1–4) are necessary¹⁰:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (1)$$

$$T_m = \sum_{i=1}^n c_i (T_m)_i \quad (2)$$

$$\Delta S_{mix} = -R \sum_{i=1}^n c_i \ln c_i \quad (3)$$

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n 4\Delta H_{AB}^{mix} c_i c_j \quad (4)$$

where T_m represents the melting temperature of the element or species, ΔS_{mix} is the change in the entropy of mixing, ΔH_{mix} is the change in enthalpy of mixing, c_i is the composition of the element or species, R is the universal gas constant, and ΔH_{AB}^{mix} is the mixing enthalpy of element A with element B .

To solve for the atomic size consideration, Eq. 5 is used¹⁰:

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r}{\sum_{i=1}^n c_i r_i}\right)^2} \quad (5)$$

where r is the atomic radius of the specific element.

To solve for the valence electron consideration, Eq. 6 is used¹¹:

$$\text{VEC} = \sum_{i=1}^n c_i V_i \quad (6)$$

where V_i is the valence of the element.

These three parameters, commonly referred to as the descriptor approach, apply specifically to HEAs.^{10–12} Very little research exists for using the descriptor

approach in designing HECs.¹²⁻¹⁶ The calculations proposed by Sarker et al.¹⁴ for the entropic forming ability (EFA) and by Liu et al.¹³ for atomic size consideration are defined in the following equations (Eqs. 7 and 8)¹²:

$$EFA = \left(\sqrt{\frac{\sum_{i=1}^n g_i (\Delta H - \Delta H_{mix})^2}{(\sum_{i=1}^n g_i) - 1}} \right)^{-1} \quad (7)$$

$$\delta = \frac{R^* (\Delta R^*)^2}{Z} (G) \quad (8)$$

where g_i is the number of degeneracies in the system, R^* is the effective lattice constant, and Z is the number of formula units per unit cell.¹²⁻¹⁴

Due to the limited amount of research on HECs, we use the same descriptor approach for HEAs and apply it to HECs with some modifications. It is also important to note that solid solution is predicted when $\Omega > 1.1$ and $\delta < 6.6\%$ and single-phase stability within the system is predicted when $VEC \leq 4.4.1$.^{10,11}

After computing preliminary data to aid in the elemental selection of this HEC T/EBC, Thermo-Calc CALPHAD, a thermodynamic software with the TCHEA4 database, is used to build binary phase diagrams for the elements of interest and ternary isothermal phase diagrams of the Hf-Al-Si HEA system. These phase diagrams are created using the graphical mode in CALPHAD. The temperature for each isothermal phase diagram is set (in our case, 1300, 1350, and 1400 °C) along with the composition of the HEA system (in the case, 33.33 at.%) for each element of the specific three-component HEA. These simulated phase diagrams provide information regarding the stable phases and phase changes that occur with variations in composition and temperatures. The Property Model calculator is then used to measure the Gibb's free energy, enthalpy, entropy, thermal resistance, and thermal conductivity of the stable phases and system as a whole. This calculation can be completed by defining the range of temperatures, properties to be calculated, their units, and the desired number of data points. The Property Model calculator is also used to calculate the temperature at which a phase transition occurs. This calculation requires a few input parameters, which include a range of temperatures of interest, the composition of the specific HEA, and the stable phases to track.

3. Results and Discussion

Table 1 shows the results from calculations from the modified Hume–Rothery rules using Eqs. 1, 5, and 6 for the Hf-Al-Si HEA system.

Table 1 Calculations from the modified Hume–Rothery rules for the Hf-Al-Si system

Hf (at.%)	Al (at.%)	Si (at.%)	T (C) ¹⁷	ρ_{avg} (g/cm ³)	Ω	δ (%)	VEC
33.33	33.33	33.33	1617.67	6.10	105.21	1.72	3.66

Tables 2 and 3 show the results from calculations from the modified Hume–Rothery rules for the HfO₂-Al₂O₃-SiO₂ and CaO-MgO-Al₂O₃-SiO₂ systems, respectively. These systems vary considering the introduction of oxygen into the system, electroneutrality considerations, and the differences in bonding (i.e., metallic bonding in the HEA and ionic and covalent bonding in the HEC). Despite these differences, high-entropy materials all depend on modified Hume–Rothery rules, although the VEC defined for HEAs may need modifications given the importance of electroneutrality in ceramics.

Table 2 Calculations from the modified Hume–Rothery rules for the HfO₂-Al₂O₃-SiO₂ system

HfO2 (at.%)	Al2O3 (at.%)	SiO2 (at.%)	T _m (C) ¹⁷	ρ_{avg} (g/cm ³)	Ω	δ (%)	VEC
33.33	33.33	33.33	2179.98	5.43	70.85	2.05	5.09

Table 3 Calculations from the modified Hume–Rothery rules for the CaO-MgO-Al₂O₃-SiO₂ system

CaO (at.%) ¹⁸	MgO (at.%) ¹⁸	Al2O3 (at.%) ¹⁸	SiO2 (at.%) ¹⁸	T _m (C) ¹⁷	ρ_{avg} (g/cm ³)	Ω	δ (%)	VEC
40.51	7.48	2.33	49.68	2153.04	3.03	64.54	2.35	4.67

These results all satisfy the prediction parameters for solid solution and single-phase stability ($\Omega > 1.1$, $\delta < 6.6\%$, $\text{VEC} \leq 4.4$), although the HfO₂-Al₂O₃-SiO₂ system shows values that highly satisfy the entropic and atomic size considerations. These values directly correlate to the properties of the material—the solid solution improving strength and the melting temperature and entropic consideration contributing to improved thermal resistance and stability. The sandphobic properties of the HEC can also be predicted. Given the high amount of SiO₂ in both systems and the greater amount of Al₂O₃ in the HEC, acceptable sandphobic properties can be expected. It is also important to note the differences in density. The HEC system is denser than the CMAS. Although the CMAS is transported at high velocities after infiltrating the gas turbine engine,^{19–25} coating the engine or engine blades in a slightly denser material may help decrease the material degradation caused by CMAS.

The binary oxide phase diagrams for these main elemental components, Hf, Al, and Si, are shown in Figs. 1–3. Figure 1 shows stable monoclinic and tetragonal phases for HfO_2 , Fig. 2 shows a stable Al_2O_3 phase with gas, and Fig. 3 shows a stable SiO_2 and liquid phase from 1000 to 2000 °C. These diagrams are used to predict the thermal stability of the overall HEC oxide in comparison to the Hf-Al-Si HEA pictured in Figs. 4–6. The melting temperatures of Hf, Al, and Si are 2233, 933, and 1687 °C, respectively.¹⁷ The melting temperatures of HfO_2 , Al_2O_3 , and SiO_2 are approximately 2700, 2050, and 1725 °C, respectively. Comparatively, these values, which can be derived from their binary phase diagrams in Figs. 1–3, are significantly higher with the addition of oxygen. Specifically, Fig. 1 shows approximately a 500 °C increase in melting temperature between Hf and HfO_2 , Fig. 2 shows an 1100 °C increase in melting temperature between Al and Al_2O_3 , and Fig. 3 shows a 50 °C increase between Si and SiO_2 . The increase in melting temperature shown in Figs. 1–3 for each of the binaries support the basic principle of ceramics—thermal stability of the system at higher temperatures. These binary phase diagrams can be used to predict properties and behaviors that may occur within the high-entropy materials with and without the oxide. This also ensures that the HEA ternary phase diagrams built using Thermo-Calc CALPHAD and their use as prediction tools for the HEC counterparts are correct.

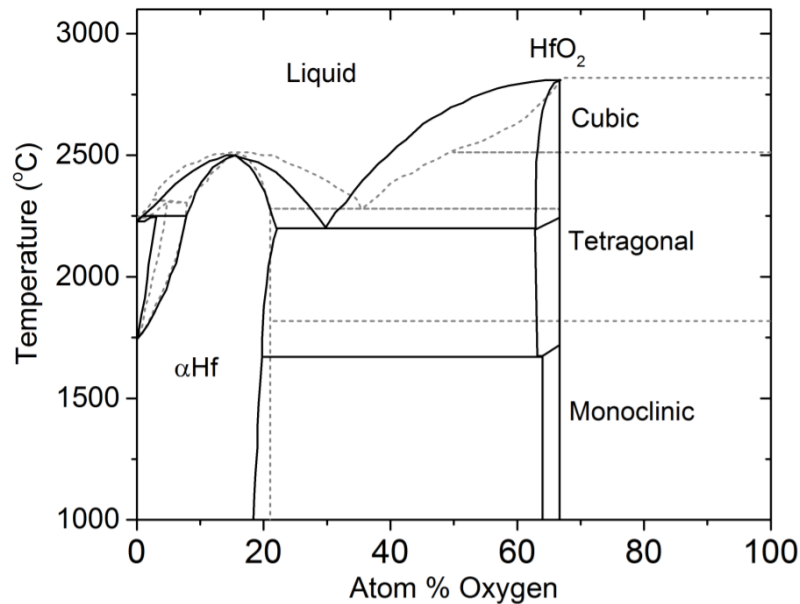


Fig. 1 Hf-O binary phase diagram²⁶

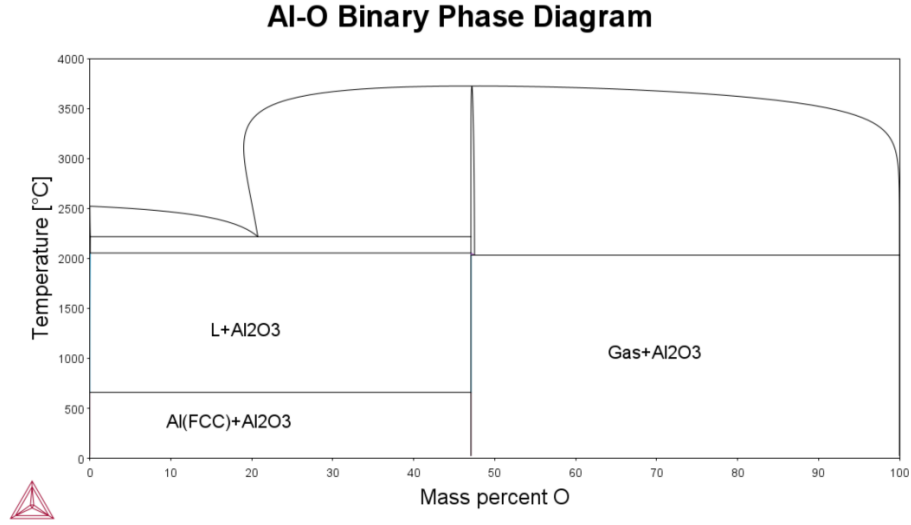


Fig. 2 Al-O binary phase diagram (calculated using CALPHAD)

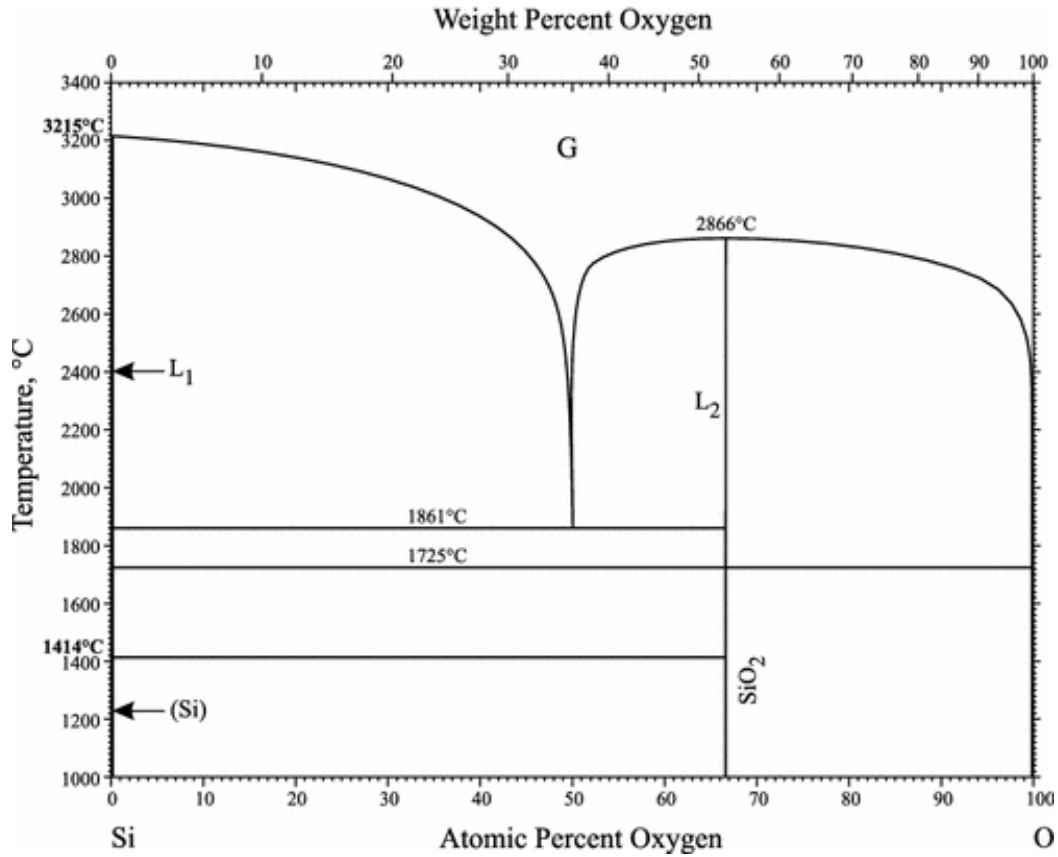


Fig. 3 Si-O binary phase diagram²⁷

The phase diagrams for the Hf-Al-Si HEA at 1300, 1350, and 1400 °C are shown in Figs. 4–6, respectively. Their corresponding thermodynamic properties at these temperatures are listed in Tables 4–6.

Hf-Al-Si Ternary Phase Diagram at 1300°C

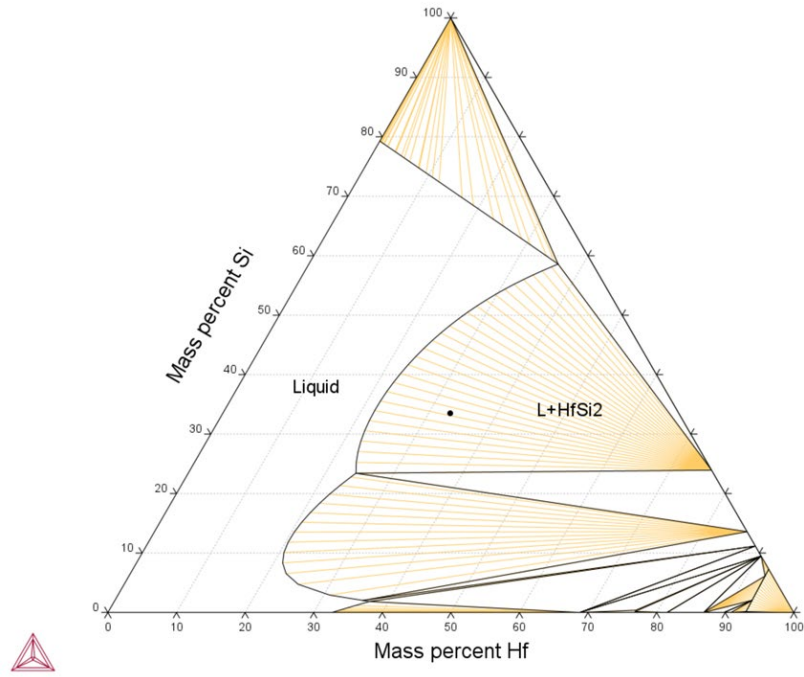


Fig. 4 Ternary phase diagram of Hf-Al-Si at 1300 °C

Table 4 Thermodynamic properties of the L+HfSi₂ phase and Hf-Al-Si system at 1300 °C

	T (K)	G (kJ)	H (kJ/mol)	S (J/K)	K (W/mK)	R (mK/W)
L+HfSi ₂	1573.15	-13.87	-40.19	6.19	0.00	1.00E+20
System	1573.15	-99.17	45.70	92.09	0.00	1.00E+20

Hf-Al-Si Ternary Phase Diagram at 1350°C

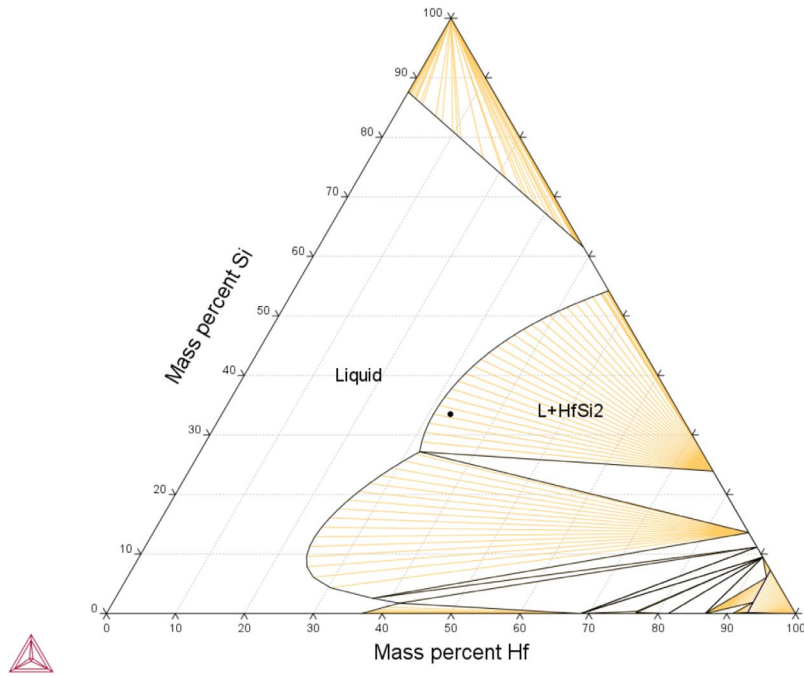


Fig. 5 Ternary phase diagram of Hf-Al-Si at 1350 °C

Table 5 Thermodynamic properties of the L+HfSi₂ phase and Hf-Al-Si system at 1350 °C

	T (K)	G (kJ)	H (kJ/mol)	S (J/K)	K (W/mK)	R (mK/W)
L+HfSi ₂	1623.15	-3.91	-38.62	1.74	0.00	1.00E+20
System	1623.15	-103.88	52.24	96.18	0.00	1.00E+20

Hf-Al-Si Ternary Phase Diagram at 1400°C

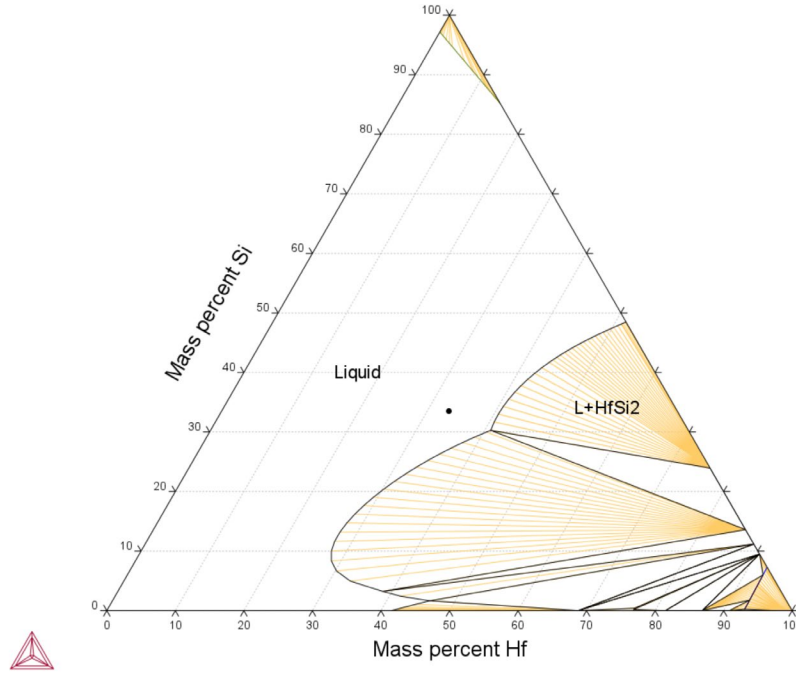


Fig. 6 Ternary phase diagram of Hf-Al-Si at 1400 °C

Table 6 Thermodynamic properties of the L+HfSi₂ phase and Hf-Al-Si system at 1400 °C

	T (K)	G (kJ)	H (kJ/mol)	S (J/K)	K (W/mK)	R (mK/W)
L+HfSi ₂	1673.15	−0.00	−37.05	0.00	0.00	1.00E+20
System	1673.15	−108.76	55.68	98.28	0.00	1.00E+20

The ternary isothermal phase diagrams of the Hf-Al-Si system shown in Figs. 4–6 show the transition of the material from the L+HfSi₂ phase to the liquid phase as the temperature increases from 1300 to 1400 °C. Figure 4 clearly shows the 0.33Hf-0.33Al-0.33Si HEA stable within the L+HfSi₂ phase at 1300 °C. Figure 5 shows a shift in the L+HfSi₂ phase at 1350 °C although the HEA is still stable within this phase as long as there are not any compositional variations. The HEA stable in the liquid phase is pictured in Fig. 6. This phase transition is also illustrated by the change in thermodynamic properties from 1300 to 1400 °C as depicted in Tables 4–6. The overall Gibb’s free energy (G) of the system decreases with this temperature change from −99.17 kJ to −108.76 kJ while the enthalpy (H) and entropy (S) of the system increase from 45.70 kJ/mol to 55.68 kJ/mol and 92.09 J/K to 98.28 J/K, respectively. This is explained by the liquid phase consuming the material system with increasing temperature—the system is reaching an

equilibrium that causes the Gibbs free energy to decrease while the transition from solid to liquid increases the disorder of the system and produces energy (heat), increasing both the entropy and enthalpy. The thermodynamic properties of the L+HfSi₂ phase are opposite in trend compared to the system. Since the L+HfSi₂ phase becomes less prominent with increasing temperature, the Gibbs free energy of the phase increases while the enthalpy and entropy of the phase decrease.

Tables 4–6 also list values for the thermal conductivity (K) and thermal resistivity (R) of the L+HfSi₂ phase and system at these varying temperatures. These values are consistent between the phase and system for all temperatures, with the thermal conductivity measuring 0.00 W/mK and the thermal resistivity measuring 1.00E+20 mK/W. These values are the inverse of each other; however, since the measurement for thermal conductivity is so small, it is noted as 0.00 W/mK. These values are promising given the high-temperature resistance needed for T/EBCs. Thermo-Calc CALPHAD was also used to identify the temperature at which the L+HfSi₂/liquid phase change occurs. This calculation determined a phase transition at 1363.69 °C, which agrees with the changes observed in the ternary isothermal phase diagrams for 1300, 1350, and 1400 °C. Ceramics, unlike metals, care about what positions their atoms sit in. Each atom has a fixed position in its crystal structure and resists changing these positions with increased temperatures. This resistance is a result of higher bond strengths. This means that ceramic bonds only break when an even higher stress or temperature, compared to metals, is applied. This results in higher melting temperatures and increased stability at high temperatures.^{28–33} Given this nature of ceramics, the phase change of this HEA at 1363.69 °C will occur at even higher temperatures for the HfO₂-Al₂O₃-SiO₂ HEC system.

4. Conclusions

High-entropy ceramics offer great potential as new materials solutions for thermal/environmental barrier coatings for gas turbine engines. After applying the modified Hume–Rothery rules for HEAs to the HfO₂-Al₂O₃-SiO₂ HEC and CaO-MgO-Al₂O₃-SiO₂ CMAS systems, it was determined that both satisfy the solid solution parameters $\Omega > 1.1$ and $\delta < 6.6\%$ and single-phase stability parameter $VEC \leq 4.4$ with values of $\Omega = 70.85$, $\delta = 2.05\%$, $VEC = 5.09$ and $\Omega = 64.54$, $\delta = 2.35\%$, $VEC = 4.67$, respectively. These values predict high-temperature stability of the HfO₂-Al₂O₃-SiO₂ HEC as compared to CMAS. The ternary isothermal phase diagrams of the Hf-Al-Si HEA also show L+HfSi₂ phase stability until the phase transition to liquid at 1363.69 °C. At 1300, 1350, and 1400 °C, this HEA also showed a consistent thermal resistivity of 1.00E+20 mK/W in both the L+HfSi₂ phase and the material system. The thermal resistance, high T_m , and phase stability

of this HEA promise increased thermal resistance, T_m , and phase stability for the $\text{HfO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ HEC, making it a promising candidate as an advanced T/EBC material.

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List of Symbols, Abbreviations, and Acronyms

Ω	entropic consideration
δ	atomic size consideration
c_i	composition
CMAS	CaO-MgO-Al ₂ O ₃ -SiO ₂ system
CMC	ceramic matrix composite
EFA	entropy forming ability
G	Gibb's free energy
g_i	number of degeneracies
H	enthalpy
H_{AB}^{mix}	enthalpy of mixing for A-B solution
H_{mix}	enthalpy of mixing
HEA	high-entropy alloy
HEC	high-entropy ceramic
NASA	National Aeronautics and Space Administration
R	universal gas constant
R^*	effective lattice constant
r	atomic radius
S	entropy
S_{mix}	entropy of mixing
T/EBC	thermal/environmental barrier coating
T_m	melting temperature
VEC	valence electron consideration
V_i	valence
YSZ	yttria stabilized zirconia
Z	number of formula units per cell

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