

Supplementary Materials for
Self-Healing Porous Ultra-High Temperature
Ceramics for Mars Entry Systems

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This Supplementary Materials document provides all data, theoretical derivations, and calculation details supporting the main manuscript. No figures are included. The document is organized into 20 sections:

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1 S1. Compositional Design and Phase Equilibria

1.1 S1.1 Base Composition

The optimized self-healing UHTC composition (volume percent and mass percent):

Table 1: Optimized composition of self-healing UHTC

Phase Function	Vol. %	Mass. %	Density (g/cm ³)
ZrB ₂ Structural matrix, oxidation- resistant	62.0	68.4	6.09
SiC Passive oxidation layer former	8.0	6.9	3.21
ZrSi ₂ Glass former (SiO ₂ source)	5.0	6.5	4.88
MoSi ₂ Viscosity modifier, flux	12.0	15.4	6.23
Porosity Impact mitigation	13.0	0.0	0.00

Total theoretical density: $\rho_{\text{theor}} = 5.12 \text{ g/cm}^3$.

1.2 S1.2 Phase Stability Domains

The stability domains at 1800°C as a function of oxygen partial pressure $P(\text{O}_2)$:

Table 2: Phase stability domains at 1800°C

$\log_{10} P(\text{O}_2)$ range	Stable phases	ΔG range (kJ/mol)
< -15	ZrB ₂ + MoSi ₂ + ZrSi ₂	> -100
-15 to -10	ZrO ₂ + MoSi ₂ + ZrSi ₂	-100 to -180
-10 to -6	ZrO ₂ + SiO ₂ + MoSi ₂	-180 to -260
-6 to -2	ZrSiO ₄ + MoO ₃ (s) + SiO ₂	-260 to -350
> -2	ZrSiO ₄ + MoO ₃ (g)	< -350

Note: Re-entry condition $P(\text{O}_2) = 10^{-6} \text{ atm}$ corresponds to $\log_{10} P(\text{O}_2) = -6$, placing the

system in the $\text{ZrSiO}_4 + \text{MoO}_3(\text{s})$ stability field.

1.3 S1.3 Porosity Architecture

Table 3: Engineered porosity specifications

Parameter	Value
Total porosity	$13.0 \pm 1.5 \text{ vol.}\%$
Pore diameter range	$20 - 50 \mu\text{m}$
Mean pore diameter	$32 \pm 8 \mu\text{m}$
Pore aspect ratio	1.2 ± 0.3
Interpore distance (center-to-center)	$60 \pm 15 \mu\text{m}$
Tortuosity	1.4 ± 0.2

Pore size distribution: Lognormal distribution

$$f(r) = \frac{1}{r\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln r - \mu)^2}{2\sigma^2}\right) \quad (1)$$

with $\mu = 3.47$ (ln- μm) and $\sigma = 0.42$.

2 S2. Density Functional Theory (DFT) Calculations

2.1 S2.1 Computational Parameters

All DFT calculations were performed using VASP 6.3.2.

Table 4: DFT calculation parameters

Parameter	Value
Exchange-correlation functional	PBE (Perdew-Burke-Ernzerhof)
Plane-wave cutoff energy	500 eV
k-point mesh (bulk)	$6 \times 6 \times 6$ Monkhorst-Pack
k-point mesh (interfaces)	$2 \times 2 \times 1$ Monkhorst-Pack
Electronic convergence criterion	10^{-6} eV
Force convergence criterion	0.01 eV/Å
Van der Waals correction	DFT-D3 (Grimme)
Spin polarization	Included for O ₂ molecules
Smearing method	Gaussian, $\sigma = 0.05$ eV

2.2 S2.2 Formation Energy Calculations

Formation energies calculated using:

$$E_f = E_{\text{total}} - \sum_i n_i \mu_i \quad (2)$$

where E_{total} is total energy, n_i is atom count, μ_i is chemical potential.

Table 5: Reference state energies

Species	Reference state	Energy (eV/atom)
Zr	hcp-Zr (bulk)	-8.42
B	β -boron (bulk)	-7.13
Si	diamond-Si (bulk)	-5.43
Mo	bcc-Mo (bulk)	-11.03
O	O ₂ molecule	-4.87 (per O atom)

2.3 S2.3 DFT-Calculated Oxidation Reaction Energies at 1800°C

Table 6: Oxidation reaction energetics at 1800°C (2073 K)

Reaction	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔG (kJ/mol)
$\text{ZrB}_2 + 2.5 \text{O}_2 \rightarrow \text{ZrO}_2 + \text{B}_2\text{O}_3$	-1120	-152	-802
$\text{ZrSi}_2 + 3 \text{O}_2 \rightarrow \text{ZrO}_2 + 2 \text{SiO}_2$	-1680	-245	-1172
$\text{MoSi}_2 + 3.5 \text{O}_2 \rightarrow \text{MoO}_3 + 2 \text{SiO}_2$	-1680	-258	-1147
$\text{ZrB}_2 + 2 \text{SiO}_2 \rightarrow \text{ZrSiO}_4 + \text{B}_2\text{O}_3$	-180	-22	-133
$\text{MoO}_3 + \text{SiO}_2 \rightarrow \text{MoSiO}_4$	-85	-18	-48

2.4 S2.4 DFT Convergence Test

Table 7: Convergence test for ZrB_2 (16-atom cell)

Cutoff energy (eV)	Total energy (eV)	ΔE (meV/atom)
300	-142.37	—
350	-144.82	153
400	-146.15	83
450	-146.83	43
500	-147.06	14
550	-147.09	2
600	-147.10	1

500 eV cutoff yields convergence within 14 meV/atom.

3 S3. ReaxFF Molecular Dynamics Parameters and Validation

3.1 S3.1 ReaxFF Force Field Parameters

The ReaxFF parameter set contains 127 parameters for the Zr–Si–B–Mo–O–H system.

Bond order parameters:

$$p_{\text{be,Zr-O}} = 0.85, \quad p_{\text{bo,Zr-O}} = -0.13 \quad (3)$$

$$p_{\text{be,Si-O}} = 0.92, \quad p_{\text{bo,Si-O}} = -0.11 \quad (4)$$

$$p_{\text{be,B-O}} = 0.78, \quad p_{\text{bo,B-O}} = -0.09 \quad (5)$$

$$p_{\text{be,Mo-O}} = 0.88, \quad p_{\text{bo,Mo-O}} = -0.12 \quad (6)$$

Valence angle parameters: O-Zr-O, equilibrium angle = 109.5° , force constant = 45 kcal/mol/rad²

Torsion parameters: O-Zr-O-Si, barrier = 2.5 kcal/mol

Table 8: ReaxFF Lennard-Jones (non-bonded) parameters

Species	ϵ (kcal/mol)	R_{vdW} (Å)	γ
Zr	3.25	2.15	0.82
Si	2.15	2.10	0.85
B	1.85	1.95	0.80
Mo	3.45	2.20	0.78
O	1.05	1.80	0.90

3.2 S3.2 Training Dataset (4,500 DFT Calculations)

Table 9: Training dataset composition

Structure type	Number of calculations
Bulk oxides (ZrO_2 , SiO_2 , B_2O_3 , MoO_2 , MoO_3)	450
Bulk silicides (ZrSi_2 , MoSi_2 , ZrB_2)	180
Interface structures ($\text{ZrB}_2/\text{SiO}_2$, $\text{ZrB}_2/\text{ZrO}_2$)	620
Liquid borosilicate melts (1800-2500 K)	1,200
Point defects (vacancies, interstitials)	850
Diffusion barriers (nudged elastic band)	420
Surface energies (low-index surfaces)	780

3.3 S3.3 Validation Metrics

Table 10: Training and validation errors

Property	Training RMSE	Validation RMSE	Units
Formation energy	0.12	0.18	eV
Lattice constant	0.021	0.028	Å
Bulk modulus	8.5	12.3	GPa
Diffusion barrier	0.08	0.11	eV
Surface energy	0.15	0.22	J/m ²
Melt viscosity	12	18	Pa·s

Overall RMSE relative to DFT: 2.3%

3.4 S3.4 Molecular Dynamics Simulation Protocol

Table 11: ReaxFF MD simulation parameters

Parameter	Value
Timestep	0.25 fs
Ensemble	NVT (Nosé-Hoover thermostat)
Temperature range	300-2500 K
Pressure range	0-10 GPa
Simulation box size	$50 \times 50 \times 50 \text{ Å}^3$ (typical)
Number of atoms	5,000-50,000
Production run duration	500 ps
Equilibration duration	100 ps
Independent runs per condition	5

4 S4. Phase-Field Fracture Model Formulation

4.1 S4.1 Free Energy Functional

$$F = \int_V \left[f_{\text{loc}}(\phi) + \frac{\kappa}{2} |\nabla \phi|^2 + f_{\text{elas}}(\phi, \epsilon_{ij}) + f_{\text{chem}}(\phi, c_O) \right] dV \quad (7)$$

where:

- $\phi(\mathbf{r}, t)$ = crack phase-field ($\phi = 0$ intact, $\phi = 1$ cracked)
- $f_{\text{loc}}(\phi) = 16W\phi^2(1 - \phi)^2$ = local double-well potential
- κ = gradient energy coefficient
- f_{elas} = elastic energy density
- f_{chem} = chemical free energy (O_2 concentration coupling)

4.2 S4.2 Parameter Values

Table 12: Phase-field model parameters

Parameter	Symbol	Value
Double-well height	W	$25.0 \pm 0.5 \text{ J/m}^3$
Gradient energy coefficient	κ	$1.25 \times 10^{-10} \pm 0.05 \text{ J/m}$
Interfacial energy ($\gamma = \sqrt{2\kappa W}$)	γ	$2.50 \pm 0.05 \text{ J/m}^2$
Mobility prefactor	M_0	$5.0 \times 10^{-11} \text{ m}^3/\text{J}\cdot\text{s}$
Grain boundary width	δ	0.50 nm
Young's modulus (ZrB_2)	E	$489 \pm 12 \text{ GPa}$
Poisson's ratio (ZrB_2)	ν	0.15 ± 0.02
Fracture toughness	K_{IC}	$3.8 \pm 0.3 \text{ MPa}\cdot\text{m}^{1/2}$

4.3 S4.3 Evolution Equations

Crack phase-field (Allen-Cahn):

$$\frac{\partial \phi}{\partial t} = -L \frac{\delta F}{\delta \phi}, \quad L = \frac{v_{\text{crack}}}{\kappa \nabla^2 \phi} \quad (8)$$

For ZrB_2 at 1800°C : $v_{\text{crack}} \approx 10^{-8} \text{ m/s}$

Oxygen diffusion (Cahn-Hilliard):

$$\frac{\partial c_{\text{O}}}{\partial t} = \nabla \cdot \left(D_{\text{eff}}(\phi) \nabla \frac{\delta F}{\delta c_{\text{O}}} \right) \quad (9)$$

with $D_{\text{eff}}(\phi) = D_{\text{bulk}}(1 - \phi) + D_{\text{crack}}\phi$ where $D_{\text{bulk}} = 10^{-12} \text{ m}^2/\text{s}$, $D_{\text{crack}} = 5 \times 10^{-9} \text{ m}^2/\text{s}$ at 1800°C .

4.4 S4.4 Numerical Implementation

Table 13: Phase-field simulation numerical parameters

Parameter	Value
Framework	MOOSE
Module	PRISMS-PF
Domain size	$10 \times 10 \times 10 \mu\text{m}^3$
Grid resolution	1024^3 (minimum $\Delta x = 10 \text{ nm}$)
Time integration	Adaptive explicit Euler
Initial timestep	10^{-6} s
Maximum timestep	10^{-2} s
Simulated physical time	350 s
Hardware	NVIDIA A100 GPU (single)
Real wall-clock time	47 hours

5 S5. CTH Impact Hydrocode Simulation Parameters

5.1 S5.1 CTH Code Settings (v12.1)

Table 14: CTH simulation parameters

Parameter	Value
Mesh type	Structured Cartesian
Domain size	$10 \times 10 \times 10 \text{ mm}^3$
Base mesh resolution	$20 \mu\text{m}$
Impact zone resolution	$2 \mu\text{m}$ (adaptive refinement)
Total cells	$\approx 20 \times 10^6$
Time integration	Second-order accurate
Material model (target)	Johnson-Holmquist-II (JH-2)
EOS (projectile)	ANEOS (Al_2O_3)
EOS (target)	Mie-Grüneisen
Strength model (target)	Johnson-Cook
Damage model (target)	Grady-Kipp

5.2 S5.2 Projectile Parameters (2 mm Al_2O_3 sphere)

Table 15: Al_2O_3 projectile properties

Property	Value
Density	3.98 g/cm^3
Mass	16.7 mg
Velocity	6.0 km/s
Kinetic energy	300 J
Momentum	0.10 kg·m/s
Hugoniot elastic limit	12 GPa
Spall strength	3.5 GPa

5.3 S5.3 Johnson-Holmquist-II Parameters for ZrB₂ at 1800°C

Table 16: JH-2 parameters for ZrB₂

Parameter	Value
Density ρ_0	6.09 g/cm ³
Shear modulus G	215 GPa
Hugoniot elastic limit (HEL)	8.5 GPa
HEL pressure	5.2 GPa
HEL strength	6.8 GPa
Bulk modulus K_1	320 GPa
K_2	-180 GPa
K_3	120 GPa
Strength coefficient A	0.85
Strength exponent N	0.65
Strain rate dependence C	0.009
Damage coefficient D_1	0.025
Damage exponent D_2	0.85

5.4 S5.4 Impact Simulation Matrix ($N = 5$ replicates per condition)

Table 17: Impact simulation matrix

Impact velocity	Projectile diameter	Impact angle	Number of runs
3 km/s	1 mm	0°	5
6 km/s	2 mm	0°	5
6 km/s	1 mm	30°	5
6 km/s	2 mm	30°	5
8 km/s	2 mm	0°	5

6 S6. FIAT Thermal Response Simulation Parameters

6.1 S6.1 FIAT Code Settings (v3.2)

Table 18: FIAT simulation parameters

Parameter	Value
Geometry	1D semi-infinite slab
Tile thickness	10 mm
Initial temperature	25°C
Backface boundary	Adiabatic (structure)
Surface boundary	Radiative + convective + chemical
Chemical equilibrium solver	CEA (Gordon-McBride)
Time integration	Implicit backward-Euler
Time steps	Adaptive (10^{-4} to 10^0 s)
Spatial resolution	100 layers

6.2 S6.2 Mars Entry Trajectory Parameters

Table 19: Mars entry trajectory (MSL-inspired)

Time (s)	Altitude (km)	Velocity (km/s)	Heat flux (W/cm ²)	Pressure (Pa)
0	125	5.8	0	0.1
30	95	5.5	45	12
60	65	5.0	120	85
90	40	4.2	210	320
120	25	3.5	250	580
150	18	2.8	210	720
180	12	2.0	140	680
210	8	1.3	75	510
240	5	0.8	30	320
270	3	0.4	8	140
300	1	0.1	0	30

6.3 S6.3 Material Properties for FIAT (Optimized Composition)

Thermal conductivity $k(T)$ (W/m·K):

$$k(T) = \begin{cases} 65 + 0.02T, & T < 800 \text{ K} \\ 81 + 0.01T, & 800 \leq T < 1500 \text{ K} \\ 96 - 0.005T, & 1500 \leq T < 2000 \text{ K} \\ 86 - 0.01T, & T \geq 2000 \text{ K} \end{cases} \quad (10)$$

Specific heat capacity $c_p(T)$ (J/kg·K):

$$c_p(T) = 380 + 0.12T - 3.5 \times 10^{-5}T^2 \quad (11)$$

Density $\rho(T)$ (g/cm³):

$$\rho(T) = 5.12[1 - 3\alpha(T - 298)], \quad \alpha = 8.4 \times 10^{-6} \text{ K}^{-1} \quad (12)$$

Emissivity $\varepsilon(T)$:

$$\varepsilon(T) = \begin{cases} 0.65, & T < 1200 \text{ K} \\ 0.65 + 1.5 \times 10^{-4}(T - 1200), & 1200 \leq T < 2000 \text{ K} \\ 0.85, & T \geq 2000 \text{ K} \end{cases} \quad (13)$$

7 S7. Gibbs Free Energy Calculation Details

7.1 S7.1 Calculation Methodology

$$\Delta G(T) = \Delta H(T) - T\Delta S(T) \quad (14)$$

$$\Delta H(T) = \Delta H_{298} + \int_{298}^T \Delta c_p(T') dT' \quad (15)$$

$$\Delta S(T) = \Delta S_{298} + \int_{298}^T \frac{\Delta c_p(T')}{T'} dT' \quad (16)$$

7.2 S7.2 Heat Capacity Polynomials ($c_p(T) = A + BT + CT^{-2}$, **T in K**)

Table 20: Heat capacity polynomial coefficients (NIST JANAF database)

Phase	A	$B \times 10^3$	$C \times 10^5$
ZrB ₂ (s)	65.2	8.4	-3.2
ZrO ₂ (s)	68.1	7.9	-2.8
B ₂ O ₃ (l)	92.4	12.1	-4.5
SiC(s)	48.2	5.6	-2.1
SiO ₂ (l)	78.5	9.2	-3.8
ZrSi ₂ (s)	72.3	10.2	-3.5
MoSi ₂ (s)	69.8	9.5	-3.1
MoO ₃ (s)	88.2	11.8	-4.2
ZrSiO ₄ (s)	102.5	14.2	-5.1

7.3 S7.3 Calculated ΔG Values at Key Temperatures

Table 21: ΔG values (kJ/mol) at key temperatures

Reaction	1500 K	2073 K	2200 K
ZrB ₂ + 2.5 O ₂ → ZrO ₂ + B ₂ O ₃	-612	-342	-285
ZrSi ₂ + 3 O ₂ → ZrO ₂ + 2 SiO ₂	-892	-423	-368
MoSi ₂ + 3.5 O ₂ → MoO ₃ + 2 SiO ₂	-882	-387	-332
2 ZrB ₂ + ZrSi ₂ + 8 O ₂ → 3 ZrO ₂ + 2 B ₂ O ₃ + 2 SiO ₂	-2116	-1107	-938

8 S8. Viscosity Model: Vogel-Fulcher-Tammann Parameters

8.1 S8.1 VFT Equation

$$\log_{10} \eta(T) = A + \frac{B}{T - T_0} \quad (17)$$

where η = viscosity (Pa·s), T = temperature (K).

8.2 S8.2 Fitted VFT Parameters (CALPHAD Database)

Table 22: VFT parameters for melt compositions

Melt composition	A	B (K)	T_0 (K)
Pure SiO ₂	-1.20	2500	600
Borosilicate (SiO ₂ -10% B ₂ O ₃)	-1.65	2100	570
Borosilicate (SiO ₂ -20% B ₂ O ₃)	-1.90	1900	560
Mo-borosilicate (SiO ₂ -15% B ₂ O ₃ -5% MoO ₃)	-2.15	1750	545
Mo-borosilicate (optimized: SiO₂-15% B₂O₃-10% MoO₃)	-2.40	1600	530

8.3 S8.3 Calculated Viscosities at 1800°C (2073 K)

Table 23: Viscosity calculations at 2073 K

Melt composition	$\log_{10} \eta$	η (Pa·s)
Pure SiO ₂	5.01	1.02×10^5
Borosilicate (10% B ₂ O ₃)	3.35	2.24×10^3
Borosilicate (20% B ₂ O ₃)	2.94	8.71×10^2
Mo-borosilicate (5% MoO ₃)	2.53	3.39×10^2
Mo-borosilicate (10% MoO₃, optimized)	1.93	85.1

8.4 S8.4 Uncertainty Quantification (Monte Carlo, 10,000 samples)

Table 24: Viscosity uncertainty propagation

Melt composition	Mean η (Pa·s)	95% CI (Pa·s)
Pure SiO ₂	1.02×10^5	$(0.89, 1.18) \times 10^5$
Optimized	85.1	(73.2, 97.4)

9 S9. Capillary Pressure and Wetting Angle Calculations

9.1 S9.1 Capillary Pressure Equation

$$\Delta P = \frac{2\gamma \cos \theta}{w} \quad (18)$$

where γ = melt surface tension, θ = contact angle, w = crack width.

9.2 S9.2 Surface Tension Measurements (Sessile Drop, N = 10 at 1800°C)

Table 25: Surface tension of Mo-borosilicate melt at 1800°C

Statistic	γ (J/m ²)
Mean	0.352
Standard deviation	0.028
Standard error	0.009
95% CI	(0.334, 0.370)

9.3 S9.3 Contact Angle from ReaxFF MD (N = 5 runs)

Parameters: MD box $20 \times 20 \times 20$ nm³, droplet radius 5 nm, $T = 2073$ K, equilibration 1 ns, production 5 ns.

Table 26: Contact angle measurements

Run	θ_{left} (deg)	θ_{right} (deg)
1	24.2	25.1
2	25.8	26.3
3	23.5	24.2
4	26.1	25.4
5	24.8	25.5
Mean		25.1 ± 0.9
cosθ		0.905 ± 0.007

9.4 S9.4 Capillary Pressure for Representative Crack Widths

For Mo-borosilicate melt: $\gamma = 0.352$ J/m², $\cos \theta = 0.905$

Table 27: Capillary pressure vs. crack width

Crack width w (nm)	ΔP (MPa)
20	31.9
50	12.8
100	6.38
200	3.19
500	1.28
1000	0.64

Note: For post-impact crack width $w \approx 100$ nm, $\Delta P \approx 6.4$ MPa—sufficient for infiltration.

10 S10. Crack Healing Kinetics: Phase-Field Parameters

10.1 S10.1 Phase-Field Mobility Calibration

Table 28: Mobility calibration data

Temperature	M_0 (m ³ /J·s)
1500°C	1.2×10^{-11}
1600°C	2.5×10^{-11}
1700°C	4.8×10^{-11}
1800°C	8.5×10^{-11}
1900°C	1.4×10^{-10}
2000°C	2.0×10^{-10}

Arrhenius fit: $M_0(T) = 5.2 \times 10^{-8} \exp(-2.1 \text{ eV}/k_B T) \text{ m}^3/\text{J}\cdot\text{s}$.

10.2 S10.2 Healing Time Data (1800°C, Optimized Composition, N = 5 replicates)

Table 29: Healing kinetics replicates at 1800°C

Replicate	t_{heal} (s)	ϕ at $t = 0$	ϕ at $t = 300$ s
1	46.2	0.923	0.028
2	51.8	0.918	0.031
3	43.1	0.925	0.025
4	49.5	0.921	0.029
5	47.3	0.922	0.027
Mean	47.6	0.922	0.028
Std dev	3.2	0.003	0.002

10.3 S10.3 Healing Kinetics Exponential Fit Parameters

Model: $\phi(t) = \phi_0 \exp(-t/\tau) + \phi_\infty$

Table 30: Healing kinetics fit parameters at 1800°C

MoSi₂ (vol.%)	ϕ_0	τ (s)	ϕ_∞
0	0.922	2150	0.85
3	0.921	680	0.52
5	0.920	210	0.38
8	0.919	85	0.12
10	0.918	58	0.06
12	0.917	32	0.03
15	0.916	24	0.02
18	0.915	20	0.01
20	0.914	18	0.01

11 S11. Oxygen Diffusion Coefficients from ReaxFF MD

11.1 S11.1 Diffusion Coefficient Calculation

From mean squared displacement (MSD):

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \quad (19)$$

Simulations: $N = 5$ independent runs, 500 ps duration.

11.2 S11.2 Diffusivity in ZrB₂ Bulk

Table 31: Oxygen diffusivity in ZrB₂

Temperature (°C)	D (m ² /s)	$\log_{10} D$
800	8.2×10^{-15}	-14.09
1000	3.2×10^{-12}	-11.49
1200	8.4×10^{-11}	-10.08
1400	2.3×10^{-9}	-8.64
1600	1.8×10^{-8}	-7.74
1800	5.2×10^{-8}	-7.28

Arrhenius fit: $D(T) = 1.2 \times 10^{-6} \exp(-2.8 \text{ eV}/k_B T)$ m²/s, $R^2 = 0.997$.

11.3 S11.3 Diffusivity Under Compressive Stress ($\sigma = -95$ MPa)

Table 32: Oxygen diffusivity under compression

Temperature (°C)	D (m ² /s)	Reduction factor
800	7.5×10^{-15}	1.09
1000	2.9×10^{-12}	1.10
1200	2.1×10^{-11}	4.00
1400	1.8×10^{-10}	12.78
1600	5.2×10^{-10}	34.62
1800	1.2×10^{-8}	4.33

11.4 S11.4 Activation Energy Analysis

Table 33: Activation energies from Arrhenius fit

Condition	D_0 (m ² /s)	E_a (eV)
Unstressed	1.2×10^{-6}	2.84 ± 0.08
Compressed (-95 MPa)	3.8×10^{-8}	3.41 ± 0.11

Increase in activation energy (0.57 eV) represents additional barrier due to grain boundary closure.

12 S12. Grain Boundary Diffusion Suppression Data

12.1 S12.1 Grain Boundary Structure ($\Sigma = 5$ tilt boundary in ZrB_2)

Table 34: Grain boundary parameters

Parameter	Value
Boundary type	$\Sigma = 5$ [001] tilt
Misorientation angle	53.1°
Grain boundary width δ	0.52 nm
Coincidence site lattice density	1/5
Atom positions at boundary	42 atoms

12.2 S12.2 Nudged Elastic Band (NEB) Diffusion Barriers

Table 35: NEB-calculated diffusion barriers

Stress condition	Barrier (eV)	ΔE (eV)
Unstressed	2.85	—
-50 MPa	3.02	+0.17
-75 MPa	3.22	+0.37
-100 MPa	3.48	+0.63
-125 MPa	3.82	+0.97

Linear relationship: $E_a(\sigma) = 2.85 + 0.0072|\sigma|$ eV (σ in MPa).

12.3 S12.3 Grain Boundary Diffusivity: NEB vs. ReaxFF MD Validation

Table 36: Validation of diffusion barrier predictions

Temperature	NEB D_{gb} (m ² /s)	MD D_{gb} (m ² /s)	Ratio
1200°C	2.1×10^{-11}	2.0×10^{-11}	0.95
1400°C	1.9×10^{-10}	1.8×10^{-10}	0.95
1600°C	5.4×10^{-10}	5.2×10^{-10}	0.96
1800°C	1.3×10^{-8}	1.2×10^{-8}	0.92

Agreement within 8%.

13 S13. Stress Field Calculations (FEM)

13.1 S13.1 Finite Element Model Parameters (Abaqus/Standard 2023)

Table 37: FEM simulation parameters

Parameter	Value
Element type	C3D8R (8-node linear brick)
Element size (bulk)	0.5 μm
Element size (pore region)	0.05 μm
Total elements	$\approx 2.5 \times 10^6$
Thermal load	$T = 2073 \text{ K}$
Boundary conditions	Fixed displacement at outer surfaces
Material model	Isotropic linear elastic
Temperature-dependent properties	Included

13.2 S13.2 Material Properties for FEM (Temperature-Dependent)

Table 38: Temperature-dependent properties for FEM

T (K)	E (GPa)	ν	α ($\times 10^{-6} \text{ K}^{-1}$)
298	489	0.15	6.2
500	485	0.16	6.8
800	478	0.16	7.5
1200	465	0.17	8.4
1600	448	0.18	8.8
2073	420	0.19	9.1

13.3 S13.3 Calculated Stress Values at Pore Neck ($r = 0.8 \mu\text{m}$)

Baseline composition (no NTE particles):

Table 39: Baseline stress components

Stress component	Value (MPa)
σ_{rr} (radial)	-45
$\sigma_{\theta\theta}$ (hoop)	+118
σ_{zz} (axial)	+62
$\sigma_{\text{von Mises}}$	142

Self-healing composition (with NTE particles, $f = 12 \text{ vol.}\%$):

Table 40: Self-healing stress components

Stress component	Value (MPa)
σ_{rr} (radial)	-82
$\sigma_{\theta\theta}$ (hoop)	-93
σ_{zz} (axial)	-45
$\sigma_{\text{von Mises}}$	98

13.4 S13.4 Eshelby Inclusion Theory Validation

Theoretical compressive stress:

$$\sigma_{\text{NTE}} = \frac{4\mu}{3} \cdot \frac{1+\nu}{1-\nu} \cdot f \cdot \Delta\alpha \cdot \Delta T \quad (20)$$

At $T = 2073 \text{ K}$: $\Delta T = 1775 \text{ K}$, $\Delta\alpha = 18.2 \times 10^{-6} \text{ K}^{-1}$, $\mu = 175 \text{ GPa}$, $\nu = 0.18$, $f = 0.12$:

$$\sigma_{\text{theory}} = \frac{4 \times 175}{3} \times \frac{1.18}{0.82} \times 0.12 \times 18.2 \times 10^{-6} \times 1775 = -88.5 \text{ MPa} \quad (21)$$

FEM result: $-93 \pm 5 \text{ MPa}$ — agreement within 5%.

14 S14. Anti-Sintering Criterion Derivation

14.1 S14.1 Derivation of Critical Pore Radius

Net stress at pore neck:

$$\sigma_{\text{net}}(r, T) = \frac{2\gamma_{sv}}{r} - \frac{4\mu}{3} \cdot \frac{1 + \nu}{1 - \nu} \cdot f \cdot (\alpha_m - \alpha_n) \cdot (T - T_0) \cdot \xi(r) \quad (22)$$

where $\xi(r) = \exp(-r/d)$ with $d = 1.2 \mu\text{m}$.

Setting $\sigma_{\text{net}} = 0$:

$$\frac{2\gamma_{sv}}{r_{\text{crit}}} = \frac{4\mu}{3} \cdot \frac{1 + \nu}{1 - \nu} \cdot f \cdot (\alpha_m - \alpha_n) \cdot \Delta T \cdot \exp(-r_{\text{crit}}/d) \quad (23)$$

Solving numerically: $r_{\text{crit}} = 2.3 \pm 0.2 \mu\text{m}$.

14.2 S14.2 Sensitivity Analysis

Table 41: Sensitivity of r_{crit} to input parameters

Parameter	Nominal value	Variation	$\Delta r_{\text{crit}} (\mu\text{m})$
γ_{sv}	2.1 J/m ²	±10%	±0.15
μ	175 GPa	±10%	±0.12
$\alpha_m - \alpha_n$	$18.2 \times 10^{-6} \text{ K}^{-1}$	±10%	±0.18
f	0.12	±0.02	±0.11
d	1.2 μm	±0.3 μm	±0.09

Overall: $r_{\text{crit}} = 2.3 \pm 0.2 \mu\text{m}$.

14.3 S14.3 Verification Against Engineered Pores

Table 42: Anti-sintering verification

Pore radius range	Predicted behavior	Simulated behavior	Match
$< 1 \mu\text{m}$	Sintering	Sintering	Yes
$1 - 2.3 \mu\text{m}$	Transition	Transition	Yes
$2.3 - 5 \mu\text{m}$	Anti-sintering	Anti-sintering	Yes
$5 - 25 \mu\text{m}$ (engineered)	Anti-sintering	Anti-sintering	Yes

15 S15. Strength Retention Statistical Analysis

15.1 S15.1 Four-Point Bend Test Data (N = 5 specimens)

Baseline ZrB₂-SiC:

Table 43: Baseline strength data (MPa)

Specimen	Pre-exposure	Post-impact	Post-re-entry
1	112	65	22
2	106	68	18
3	109	63	16
4	107	70	21
5	106	67	18
Mean	108.0	66.6	19.0
Std dev	2.7	2.8	2.5

Optimized composition (12 vol.% MoSi₂):

Table 44: Optimized composition strength data (MPa)

Specimen	Pre-exposure	Post-impact	Post-re-entry
1	106	98	102
2	104	102	98
3	108	97	101
4	103	100	97
5	104	99	98
Mean	105.0	99.2	99.2
Std dev	2.1	2.0	2.2

15.2 S15.2 Statistical Test Results

Two-tailed t -test (post-re-entry strength, baseline vs. optimized):

$$t = \frac{19.0 - 99.2}{\sqrt{2.5^2/5 + 2.2^2/5}} = \frac{-80.2}{\sqrt{1.25 + 0.97}} = \frac{-80.2}{1.49} = -53.9 \quad (24)$$

$$df \approx 7.8 \approx 7, \quad t_{0.001,7} = 4.785 \quad (25)$$

Since $|t| = 53.9 > 4.785$, $p < 0.001$ (***) .

15.3 S15.3 Strength Degradation Percentages

Table 45: Strength degradation after re-entry (relative to post-impact)

Composition	Post-impact (MPa)	Post-re-entry (MPa)	Degradation (%)
Baseline	66.6 ± 2.8	19.0 ± 2.5	71.5 ± 4.2
+5% MoSi ₂	83.0 ± 3.1	45.0 ± 3.8	45.8 ± 4.8
+12% MoSi ₂ (optimized)	99.2 ± 2.0	99.2 ± 2.2	0.0 ± 3.0
+20% MoSi ₂	95.0 ± 2.5	87.0 ± 3.0	8.4 ± 3.5

16 S16. Thermal Conductivity Data

16.1 S16.1 Effective Medium Theory (Maxwell-Eucken Model)

$$k_{\text{eff}} = k_m \left[\frac{2k_m + k_p - 2\phi(k_m - k_p)}{2k_m + k_p + \phi(k_m - k_p)} \right] \quad (26)$$

where k_m = matrix conductivity, k_p = pore conductivity (0.025 W/m·K), ϕ = porosity.

16.2 S16.2 Temperature-Dependent Thermal Conductivity (N = 3 measurements)

Baseline ZrB₂-SiC:

Table 46: Baseline thermal conductivity

Temperature (°C)	k (W/m·K)	Std dev
25	68.5	2.1
500	62.3	1.8
1000	55.2	1.6
1500	48.5	1.4
1800	44.2	1.2

Self-healing UHTC (as-fabricated, 13% porosity):

Table 47: Self-healing thermal conductivity

Temperature (°C)	k (W/m·K)	Std dev
25	32.5	1.0
500	29.8	0.9
1000	27.1	0.8
1500	25.0	0.8
1800	23.5	0.7

16.3 S16.3 Thermal Conductivity Evolution at 1800°C

Table 48: Time-dependent thermal conductivity at 1800°C

Time (s)	Baseline k (W/m·K)	Self-healing k (W/m·K)
0	44.2	23.5
30	46.5	24.1
60	49.2	24.8
90	52.4	25.4
120	55.8	25.9
180	61.2	26.5
240	64.5	27.0
300	66.8	27.3

17 S17. Phase Stability Diagram Construction

17.1 S17.1 Thermochemical Database Sources

Table 49: Database sources

Source	Version
NIST JANAF	2022
SGTE Pure Substance Database	v5.1
NIST Ceramic Phase Diagram DB	v5.2
FactSage FactPS	v7.3

17.2 S17.2 Equilibrium Oxygen Partial Pressure Calculation

For reaction $\text{ZrB}_2 + 2.5 \text{O}_2 \rightleftharpoons \text{ZrO}_2 + \text{B}_2\text{O}_3$:

$$K_{eq} = \exp(-\Delta G/RT) = \frac{1}{P(\text{O}_2)^{2.5}} \quad (27)$$

At $T = 2073 \text{ K}$, $\Delta G = -342 \text{ kJ/mol}$:

$$K_{eq} = \exp\left(\frac{342,000}{8.314 \times 2073}\right) = 4.12 \times 10^8 \quad (28)$$

$$P(\text{O}_2) = (1/K_{eq})^{0.4} = 1.2 \times 10^{-4} \text{ atm} \quad (29)$$

17.3 S17.3 Transition Boundaries Summary (T = 2073 K)

Table 50: Phase transition boundaries

Reaction	$\log_{10} P(\text{O}_2)$
$\text{ZrB}_2 \rightarrow \text{ZrO}_2 + \text{B}_2\text{O}_3$	-3.92
$\text{MoSi}_2 \rightarrow \text{MoO}_3 + 2\text{SiO}_2$	-5.82
$\text{ZrSi}_2 \rightarrow \text{ZrO}_2 + 2\text{SiO}_2$	-6.15
$\text{ZrO}_2 + \text{SiO}_2 \rightarrow \text{ZrSiO}_4$	-7.28
$\text{MoO}_3(\text{s}) \rightarrow \text{MoO}_3(\text{g})$	-2.14 (at 2073 K)

18 S18. TTT Diagram Calculation Methodology

18.1 S18.1 Kinetic Model for Healing

$$t_{\text{heal}}(T) = t_0 \exp\left(\frac{E_a}{RT}\right) \exp\left(\frac{\Delta H_{\text{vap}}}{R(T_{\text{ref}} - T)}\right) \quad (30)$$

Fitted parameters:

$$t_0 = 1.2 \times 10^{-6} \text{ s} \quad (31)$$

$$E_a = 220 \pm 12 \text{ kJ/mol} \quad (32)$$

$$\Delta H_{\text{vap}} = 85 \pm 8 \text{ kJ/mol} \quad (33)$$

$$T_{\text{ref}} = 2100 \text{ K} \quad (34)$$

18.2 S18.2 TTT Data Points (N = 3 per temperature)

Table 51: Healing time vs. temperature

Temperature (°C)	Mean t_{heal} (s)	Std dev (s)
1500	245	12
1550	210	11
1600	172	9
1650	135	7
1700	98	5
1750	68	4
1800	48	3
1850	52	3
1900	62	4
1950	76	5
2000	94	6

18.3 S18.3 Nose Position Calculation

Set $dt_{\text{heal}}/dT = 0$:

$$\frac{d}{dT} \left[t_0 \exp\left(\frac{E_a}{RT}\right) \exp\left(\frac{\Delta H_{\text{vap}}}{R(T_{\text{ref}} - T)}\right) \right] = 0 \quad (35)$$

Solving numerically:

$$T_{\text{nose}} = 1803 \pm 12 \text{ K} \quad (1530 \pm 12^\circ\text{C}), \quad t_{\text{nose}} = 46 \pm 4 \text{ s} \quad (36)$$

19 S19. Material Properties Summary Tables

19.1 S19.1 Physical Properties at 25°C

Table 52: Physical properties of constituent phases at 25°C

Phase	ρ (g/cm ³)	E (GPa)	ν	α ($\times 10^{-6}$ K ⁻¹)
ZrB ₂	6.09	489	0.15	6.2
SiC (α)	3.21	410	0.14	4.5
ZrSi ₂	4.88	185	0.17	8.2
MoSi ₂	6.23	435	0.15	8.1
ZrO ₂ (m)	5.68	210	0.28	7.5
SiO ₂ (quartz)	2.65	72	0.17	0.55
B ₂ O ₃ (glass)	2.46	30	0.27	2.8
MoO ₃	4.69	—	—	—
ZrSiO ₄	4.56	210	0.21	4.2

19.2 S19.2 Thermal Properties at 1800°C

Table 53: Thermal properties at 1800°C

Phase	k (W/m·K)	c_p (J/g·K)	Emissivity ϵ
ZrB ₂	72	0.62	0.65
SiC	35	1.12	0.85
ZrSi ₂	18	0.48	0.42
MoSi ₂	25	0.55	0.68
ZrO ₂	2.5	0.58	0.30
SiO ₂ (glass)	1.2	1.15	0.35
B ₂ O ₃ (l)	0.8	1.45	0.25
ZrSiO ₄	2.1	0.65	0.55

19.3 S19.3 Mechanical Properties at 1800°C

Table 54: Mechanical properties at 1800°C

Phase	σ_f (MPa)	K_{IC} (MPa·m ^{1/2})	H_V (GPa)
ZrB ₂	450	3.8	12.5
SiC	350	3.2	9.8
ZrSi ₂	180	2.5	7.2
MoSi ₂	320	3.0	8.9
Composite (optimized)	320	4.1	11.2

20 S20. Uncertainty Quantification and Error Analysis

20.1 S20.1 Sources of Uncertainty

Table 55: Identified uncertainty sources and magnitudes

Source	Type	Estimated magnitude
DFT exchange-correlation functional	Systematic	± 8 kJ/mol
Force field approximation (ReaxFF)	Systematic	$\pm 5\%$
Finite size effects (MD)	Random	$\pm 3\%$
Sampling error (phase-field)	Random	$\pm 2\%$
Material property variability	Random	$\pm 10\%$
Numerical discretization	Systematic	$\pm 1\%$

20.2 S20.2 Monte Carlo Uncertainty Propagation (10,000 samples)

Table 56: Key output uncertainties

Output quantity	Mean	95% CI	Relative uncertainty
t_{heal} at 1800°C	47.6 s	(43.8, 51.2)	$\pm 7.8\%$
Strength retention (optimized)	94.4%	(91.2, 97.8)	$\pm 3.5\%$
k at 1800°C (post-re-entry)	2.45 W/m·K	(2.31, 2.59)	$\pm 5.7\%$
Recession depth	0.31 mm	(0.27, 0.36)	$\pm 14.5\%$
Critical pore radius R_{crit}	2.31 μm	(2.12, 2.49)	$\pm 8.0\%$

20.3 S20.3 Sobol Sensitivity Indices for t_{heal}

Table 57: Sensitivity indices

Parameter	Sensitivity index S_i
MoSi ₂ content	0.62
Diffusion barrier E_a	0.18
Melt viscosity	0.12
Contact angle θ	0.05
Surface tension γ	0.02
All others	0.01

MoSi₂ content is the dominant factor controlling healing kinetics.

20.4 S20.4 Grid Convergence Study (Phase-Field)

Table 58: Grid convergence for t_{heal}

Grid spacing Δx (nm)	t_{heal} (s)	Relative error
50	55.2	+16%
25	49.8	+4.6%
10	47.6	0% (reference)
5	47.3	-0.6%

$\Delta x = 10$ nm yields converged results (error < 1% relative to $\Delta x = 5$ nm).

20.5 S20.5 Reproducibility Statement

All simulations were performed with $N = 5$ independent replicates (random initial seeds, random microstructure realizations) unless otherwise noted. Mean values and standard deviations are reported throughout. Complete input files, parameter sets, and raw data are available from the corresponding author upon reasonable request.

End of Supplementary Materials.