

Supplementary Material for

**High-entropy diborides - Silicon carbide composites by reactive and non-reactive spark
plasma sintering: a comparative study**

Ekaterina Pakhomova, Giacomo Cao, Roberto Orrù,

Sebastiano Garroni, Paolo Ferro, Roberta Licheri

Supplementary **Figures S1-S5** and **Tables S1- S4**

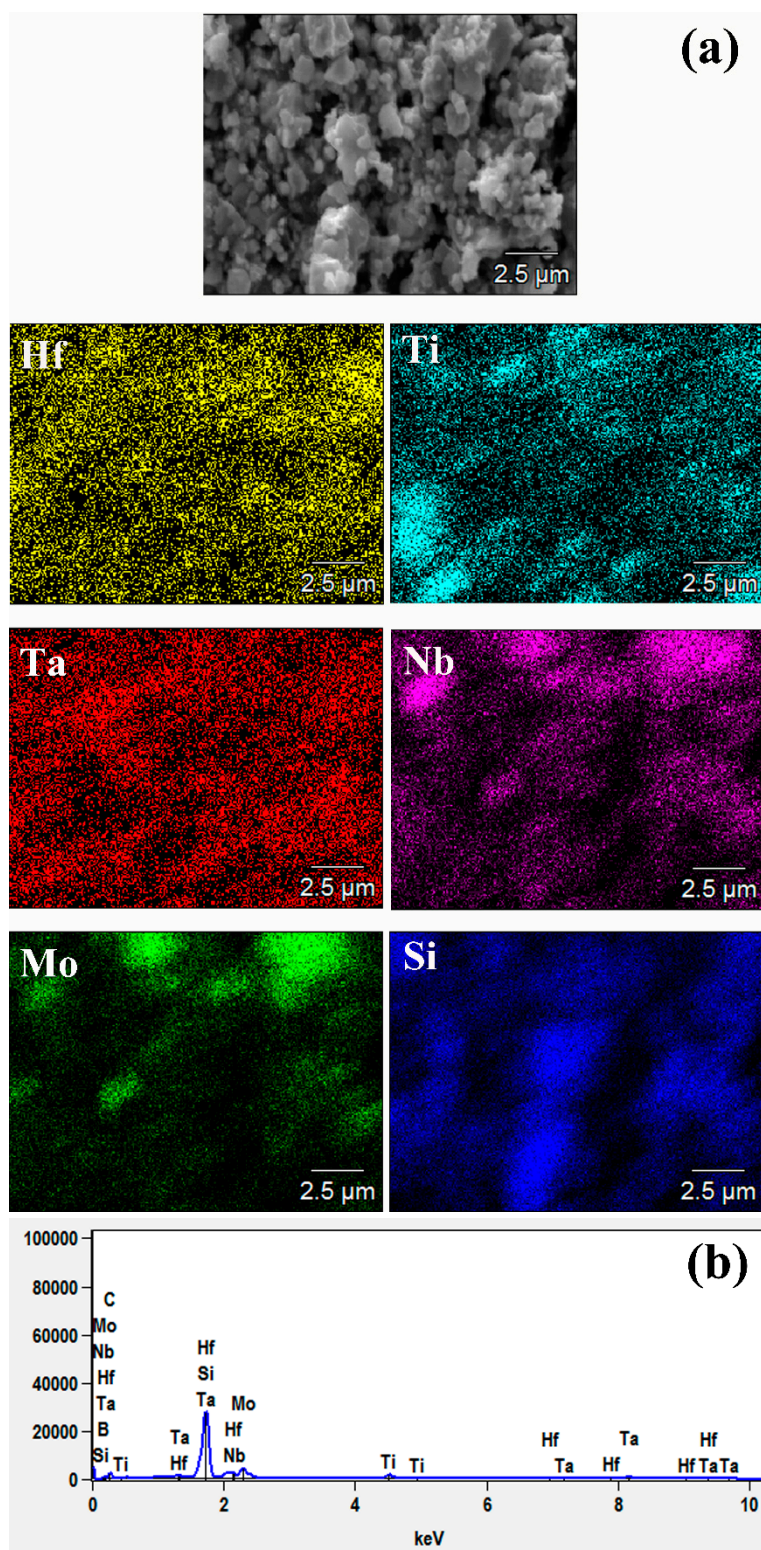


Figure S1. (a) SEM micrograph along with the corresponding EDS elemental maps, and (b) X-EDS pattern of HEB_Nb-SiC powders synthesized by SHS

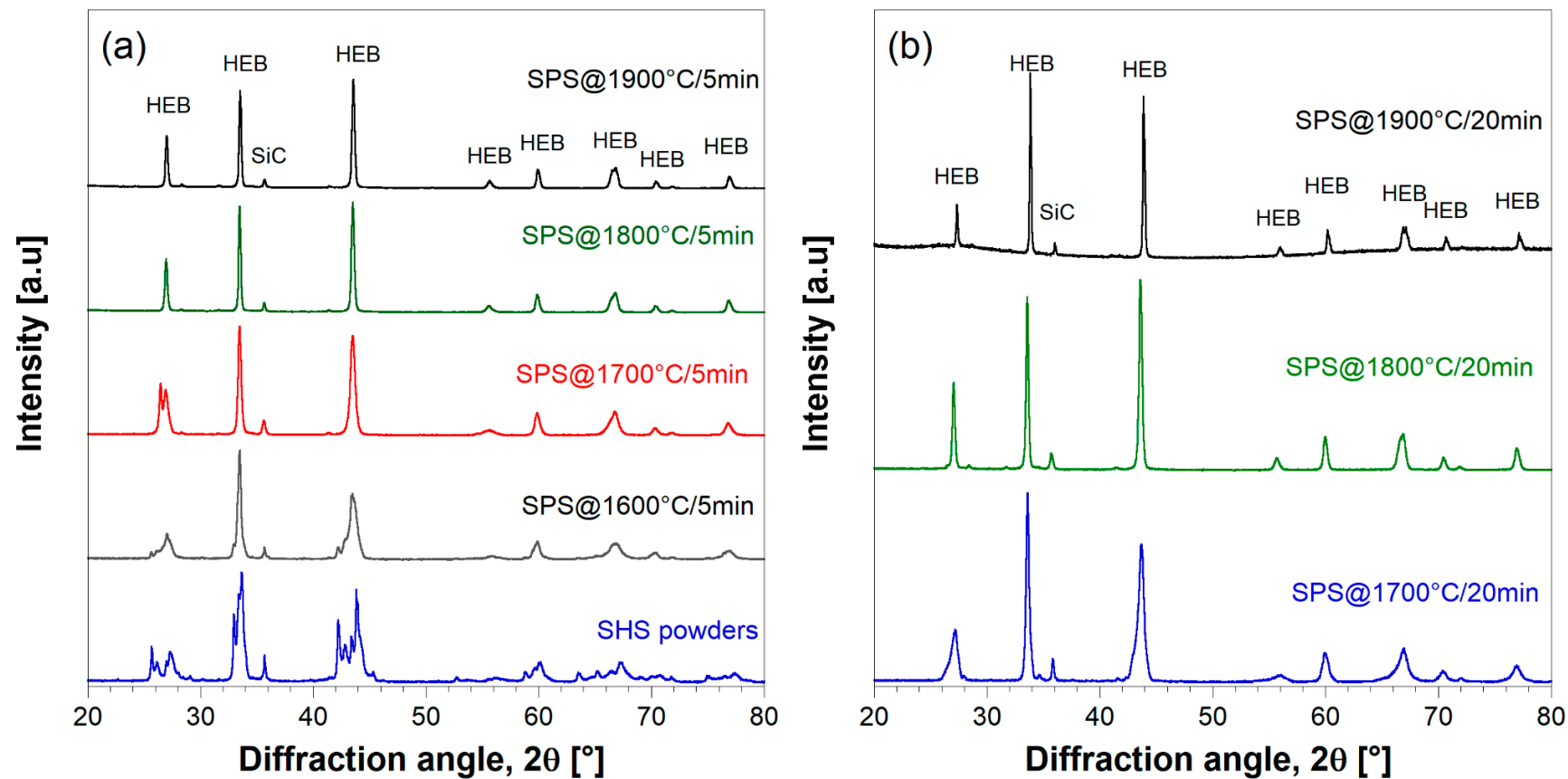


Figure S2. XRD patterns of HEB_Nb-SiC products obtained by SHS-SPS at different T_D values: (a) $t_D = 5$ min, (b) $t_D = 20$ min. The XRD pattern of SHS powders is also included, for comparison.

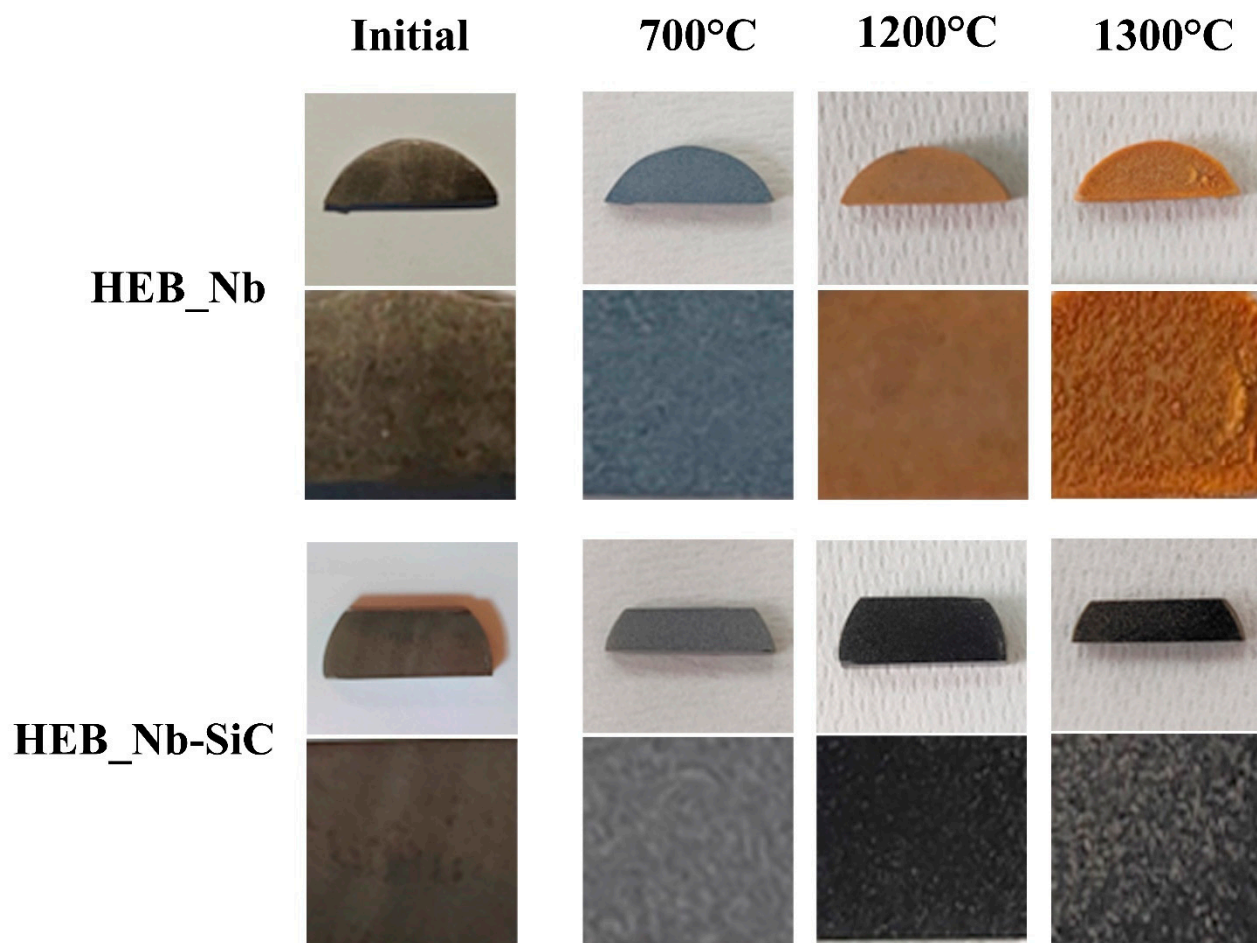


Figure S3. Optical images (complete and detailed view) showing the surface changes of $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2})\text{B}_2$ and $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2})\text{B}_2\text{-SiC}$ samples after oxidation experiments in air furnace at different temperatures.

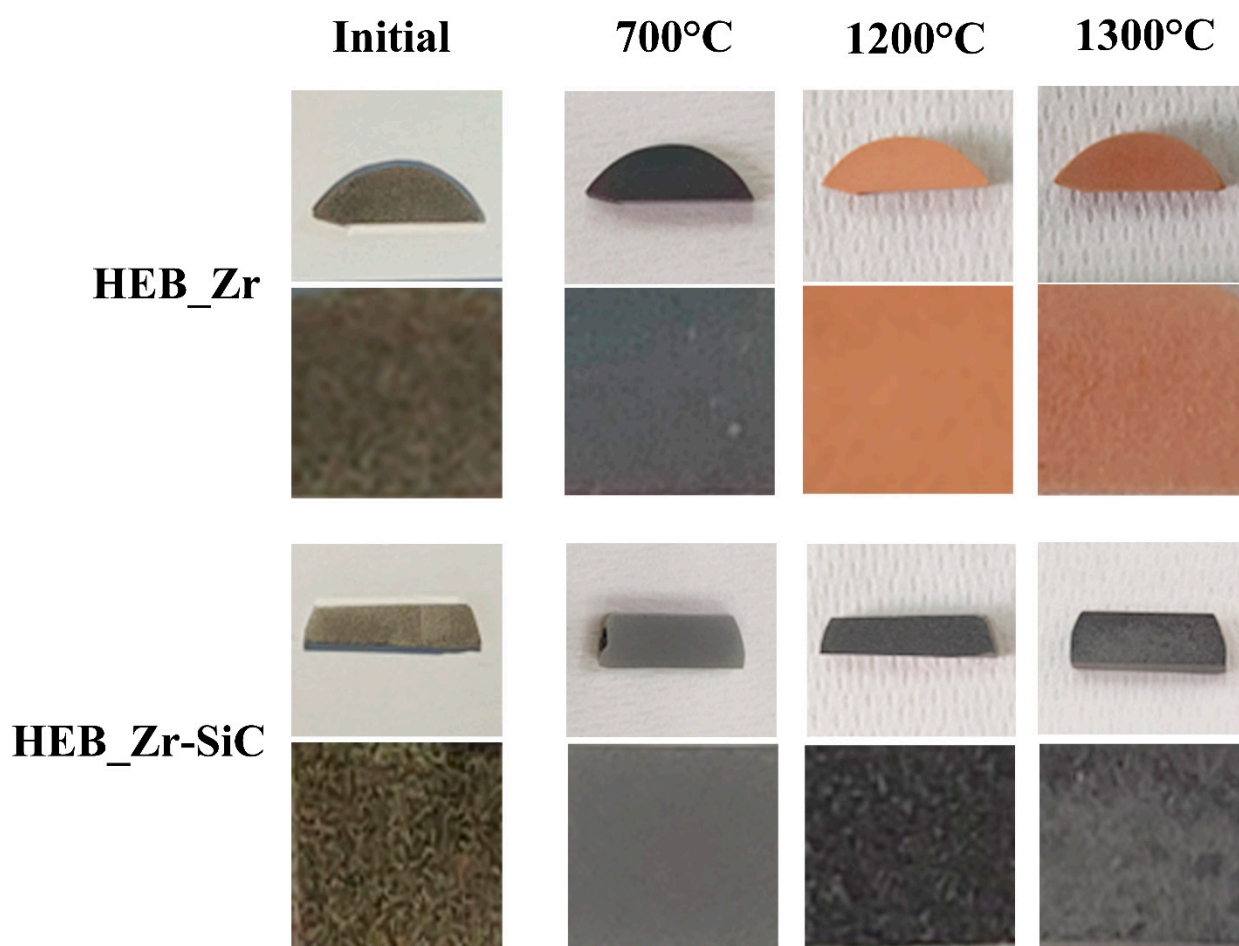


Figure S4. Optical images (complete and detailed view) showing the surface changes of $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{Zr}_{0.2})\text{B}_2$ and $(\text{Hf}_{0.2}\text{Mo}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{Zr}_{0.2})\text{B}_2\text{-SiC}$ samples after oxidation experiments in air furnace at different temperatures.

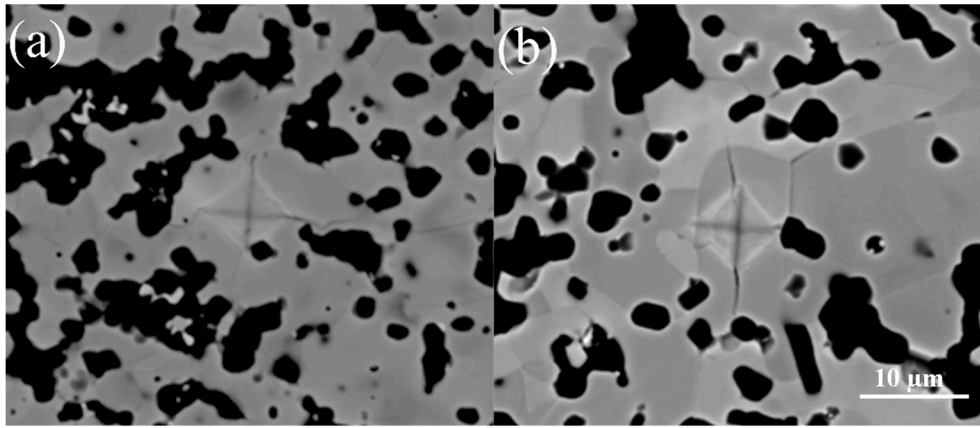


Figure S5. Example of SEM images showing the cracks propagated from the indent tips used to evaluate the fracture toughness of (a) the HEB_Nb-SiC, and (b) HEB_Zr-SiC samples.

Table S1-S4

Cif files from the Crystallography Open Database (COD) available at <https://www.crystallography.net/cod/index.php>, have used for the Rietveld refinement [37].

Bragg reflections belonging to the HEB_Nb and HEB_Zr solid solution phases have been interpolated modifying the cif file used for the system reported in the manuscript of Tallarita et al. [38].

For each phase the COD references are here below reported:

SiC: #1011031, MoB₂: #1510765, (Ta_{0.5}Ti_{0.5})B₂: #1510835, NbB₂: #1510778, TaB₂: #1510843, TiB₂: # 2002799, HfB₂: # 1510711, (MoTi)B₄: # 1510760, MoSi₂: # 1010282, C: # 1200017, SiO₂: # 1532513, Si: # 1526655, B₄C: # 4124697, HfO₂: # 1528988, ZrB₂: # 1510856.

Table S1. Phases and quantitative phase analysis results of the **HEB_Nb-SiC** product obtained by Reactive SPS. (SS): Solid Solution

R-SPS (2000°C, 20 min)									
Phase	wt. (%)	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	Space Group	Crystallite size (Å)	Microstrain
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Nb _{0.2})B ₂ (SS)-1	20.4	3.0974	-	3.3196	-	Hexagonal	P6/mmm	1104	4.59 E-4
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Nb _{0.2})B ₂ (SS)-2	20.3	3.0904	-	3.3032	-	Hexagonal	P6/mmm	1092	1.14 E-3
SiC	12.8	4.3529	-	3.3196	-	Cubic	F-43m	>1500	1.24 E-3
MoB ₂	16.7	3.1030	-	3.2118	-	Hexagonal	P6/mmm	988	1.53 E-4
NbB ₂	15.1	3.0746	-	3.2620	-	Hexagonal	P6/mmm	1006	1.82 E-3
(Ta _{0.5} Ti _{0.5})B ₂	14.7	3.0496	-	3.2381	-	Hexagonal	P6/mmm	991	1.58 E-4

Table S2. Phases and quantitative phase analysis results of the **HEB_Nb-SiC** product obtained by SHS

SHS									
Phase	wt. (%)	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	Space Group	Crystallite size (Å)	Microstrain
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Nb _{0.2})B ₂	14.9	3.1051	-	3.4182	-	Hexagonal	P6/mmm	845	4.93 E-3
SiC	11.5	4.3614	-	-	-	Cubic	F-43m	>1500	3.09 E-3
TaB ₂	14.6	3.0769	-	3.2720	-	Hexagonal	P6/mmm	1125	2.15 E-3
TiB ₂	13.4	3.0566	-	3.2437	-	Hexagonal	P6/mmm	1382	4.21E-3
NbB ₂	12.8	3.1014	-	3.3110	-	Hexagonal	P6/mmm	1265	1.58 E-3
MoB ₂	9.5	2.9870	-	3.1920	-	Hexagonal	P6/mmm	1038	5.56 E-3
HfB ₂	9.0	3.1412	-	3.4739	-	Hexagonal	P6/mmm	1227	1.21 E-3
(MoTi)B ₄	3.9	3.2788	-	2.6036	-	Hexagonal	P6/mmm	799	1.46 E-3
MoSi ₂	2.9	3.2088	-	7.8529	-	Tetragonal	I4/mmm	1077	9.54 E-4
C	2.9	2.4646	-	6.7332	-	Hexagonal	P63mc	1030	1.28 E-3
SiO ₂	1.7	7.0669	12.3077	7.1960	120.4	Monoclinic	C2/c:b1	896	1.34 E-3
Si	1.6	5.4375	-	-	-	Cubic	Fd-3m:1	972	1.43 E-3
B ₄ C	1.3	5.6010	-	12.2410	-	Trigonal	R-3m:H	978	1.1 E-4

Table S3. Phases and quantitative phase analysis results of the **HEB_Nb-SiC** products obtained by SPS, at different operating conditions, from SHS powders.

SPS (1800°C, 20 min)									
Phase	wt. (%)	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	Space Group	Crystallite size (Å)	Microstrain
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Nb _{0.2})B ₂	83.1	3.0887	-	3.3035	-	Hexagonal	P6/mmm	1089	1.33 E-3
SiC	13.6	4.3605	-	-	-	Cubic	F-43m	>1500	1.43 E-3
HfO ₂	2.4	5.1201	5.1748	5.2851	99.1	Monoclinic	P21/c:b1	974	3.33 E-3
C	0.9	2.4584	-	6.7480	-	Hexagonal	P63mc	1005	2.72E-4

SPS (1900°C, 5 min)									
Phase	wt. (%)	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	Space Group	Crystallite size (Å)	Microstrain
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Nb _{0.2})B ₂	85.6	3.0887	-	3.3035	-	Hexagonal	P6/mmm	1319	1.52 E-4
SiC	13.0	4.3605	-	-	-	Cubic	F-43m	>1500	1.03 E-3
HfO ₂	1.4	5.1201	5.1748	5.2851	99.1	Monoclinic	P21/c:b1	993	6.05 E-4

SPS (1900°C, 20 min)									
Phase	wt. (%)	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	Space Group	Crystallite size (Å)	Microstrain
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Nb _{0.2})B ₂	85.2	3.0891	-	3.3027	-	Hexagonal	P6/mmm	1517	1.04 E-4
SiC	13.7	4.3611	-	-	-	Cubic	F-43m	>1500	1.31 E-3
HfO ₂	1.1	5.1248	5.1777	5.2948	99.3	Monoclinic	P21/c:b1	1069	1.21 E-4

Table S4. Phases and quantitative phase analysis results of the **HEB_Zr-SiC** products obtained by SHS, and SPS.

SHS									
Phase	wt. (%)	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	Space Group	Crystallite size (Å)	Microstrain
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Zr _{0.2})B ₂	11.9	3.1091	-	3.4226	-	Hexagonal	P6/mmm	1032	5.28 E-3
(MoTi)B ₄	3.4	3.2902	-	2.5892	-	Hexagonal	P6/mmm	845	3.66 E-3
ZrB ₂	13.7	3.0969	-	3.3188	-	Hexagonal	P6/mmm	1430	3.52 E-3
TaB ₂	15.2	3.0758	-	3.2806	-	Hexagonal	P6/mmm	1197	2.67 E-3
HfB ₂	10.7	3.1405	-	3.4731	-	Hexagonal	P6/mmm	1275	2.45 E-3
SiC	10.9	4.3613	-	-	-	Cubic	F-43m	>1500	5.55 E-4
MoB ₂	10.8	2.9741	-	3.1920	-	-	P6/mmm	1039	2.69 E-3
TiB ₂	14.6	3.0567	-	3.2424	-	-	P6/mmm	1383	4.17E-3
MoSi ₂	2.6	3.2086	-	7.8408	-	-	I4/mmm	1062	1.24 E-3
SiO ₂	1.9	7.0685	12.3074	7.1961	120.4	Monoclinic	C2/c:b1	799	7.45 E-3
C	1.8	2.4677	-	6.7188	-	Hexagonal	P63mc	1030	1.17 E-3
Si	1.3	5.4378	-	-	-	Cubic	Fd-3m:1	972	2.32 E-3
B ₄ C	1.2	5.6005	-	12.2459	-	Trigonal	R-3m:H	999	7.86 E-4

SPS (1800°C, 20 min)									
Phase	wt. (%)	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	Space Group	Crystallite size (Å)	Microstrain
(Hf _{0.2} Mo _{0.2} Ti _{0.2} Ta _{0.2} Zr _{0.2})B ₂	84.4	3.0976	-	3.3628	-	Hexagonal	P6/mmm	1229	8.30 E-4
SiC	14.1	4.3593	-	-	-	Cubic	F-43m	>1500	4.50 E-4
HfO ₂	1.5	5.1958	5.2193	5.3845	99.2	Monoclinic	P21/c:b1	1069	1.21 E-4