

Kinetic Role of Carbon in Solid-State Synthesis of Zirconium Diboride using Nanolaminates: Nanocalorimetry Experiments and First-Principles Calculations

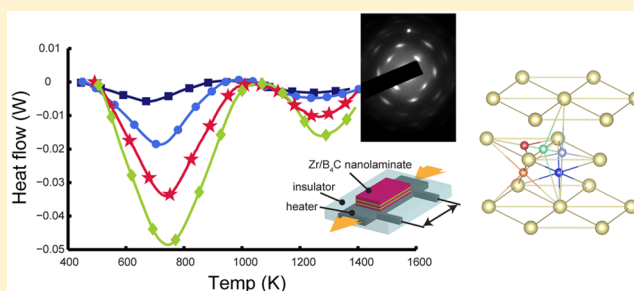
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ABSTRACT: Reactive nanolaminates afford a promising route for the low-temperature synthesis of zirconium diboride, an ultrahigh-temperature ceramic with metallic properties. Although the addition of carbon is known to facilitate sintering of ZrB_2 , its effect on the kinetics of the formation reaction has not been elucidated. We have employed a combined approach of nanocalorimetry and first-principles theoretical studies to investigate the kinetic role of carbon in the synthesis of ZrB_2 using $\text{B}_4\text{C}/\text{Zr}$ reactive nanolaminates. Structural characterization of the laminates by XRD and TEM reveal that the reaction proceeds via interdiffusion of the B_4C and Zr layers, which produces an amorphous $\text{Zr}_3\text{B}_4\text{C}$ alloy. This amorphous alloy then crystallizes to form a supersaturated $\text{ZrB}_2(\text{C})$ compound. A kinetic analysis shows that carbon lowers the energy barriers for both interdiffusion and crystallization by more than 20%. Energetic calculations based on first-principles modeling suggest that the reduction of the diffusion barrier may be attributed to the stronger bonding between Zr and C as compared to the bonding between Zr and B.

KEYWORDS: Zirconium diboride, carbon, reactive nanolaminate, nanocalorimetry, first-principles calculation



Zirconium diboride (ZrB_2), a high-performance ceramic with metallic properties, exhibits a unique combination of physical, chemical, and structural properties, making it a material of interest for a broad range of applications. Examples include its use as a substrate for group III nitride semiconductors in optoelectronic devices,^{1–5} as support material for low-temperature fuel cells,^{6,7} and as a hydrogen storage medium.⁸ Difficulties associated with synthesis, however, have hindered broad adoption of the material; production of high-density ZrB_2 typically requires both extremely high temperature and pressure⁹ because of its high melting point and stability. Viable synthesis methods of ZrB_2 have been a topic of intense investigation for decades.^{5,9,10} Additives such as carbon have been shown to improve the processability of ZrB_2 . It has been reported that carbon promotes removal of surface oxides in ZrB_2 powders and limits grain growth, thus enhancing its sinterability.^{11–14} The beneficial role of carbon in the formation of ZrB_2 -based compounds, however, is not fully understood and few studies have been conducted at the nano- to atomistic scales.¹³

Recent experiments¹⁵ have demonstrated low-temperature synthesis of highly textured crystalline ZrB_2 coatings through use of reactive nanolaminates (RNLs) that consist of alternating layers of Zr and B. The synthesis is facilitated by the formation of an intermediate amorphous phase that allows fast transport of B.^{15,16} The notion that the addition of carbon may further facilitate synthesis of ZrB_2 motivated us to investigate the phase evolution in reactive nanolaminates that

contain Zr, B, and C. In this report, we combine nanocalorimetry and ab initio simulations to study the energetics and kinetics of phase evolution in $\text{Zr}/\text{B}_4\text{C}$ RNLs.

We demonstrate that, as temperature increases, the crystalline Zr and amorphous B_4C layers of the RNLs intermix to form an amorphous compound. In a subsequent step, this amorphous compound crystallizes to form a textured ZrB_2 coating that is supersaturated with carbon. A kinetics analysis of the nanocalorimetry results reveals that the activation energies of both diffusion and crystallization are reduced by more than 20% compared to the reaction in RNLs without carbon. Ab initio calculations on α -Zr with a C atom at various interstitial sites reveal that Zr and C bond more strongly than Zr and B, thus facilitating interdiffusion of B. The finding suggests that C doping may be an effective strategy to facilitate ZrB_2 synthesis.

The micromachined nanocalorimetry sensors used in this study have been described in detail elsewhere in the literature;^{15,17–19} a brief description of the sensors and experimental details are provided in **Methods**. RNLs consisting of alternating Zr and B_4C layers were sputter deposited directly onto the nanocalorimetry sensors as illustrated schematically in the inset of **Figure 1a**. The thickness of each layer was determined to ensure a stoichiometric composition; as-

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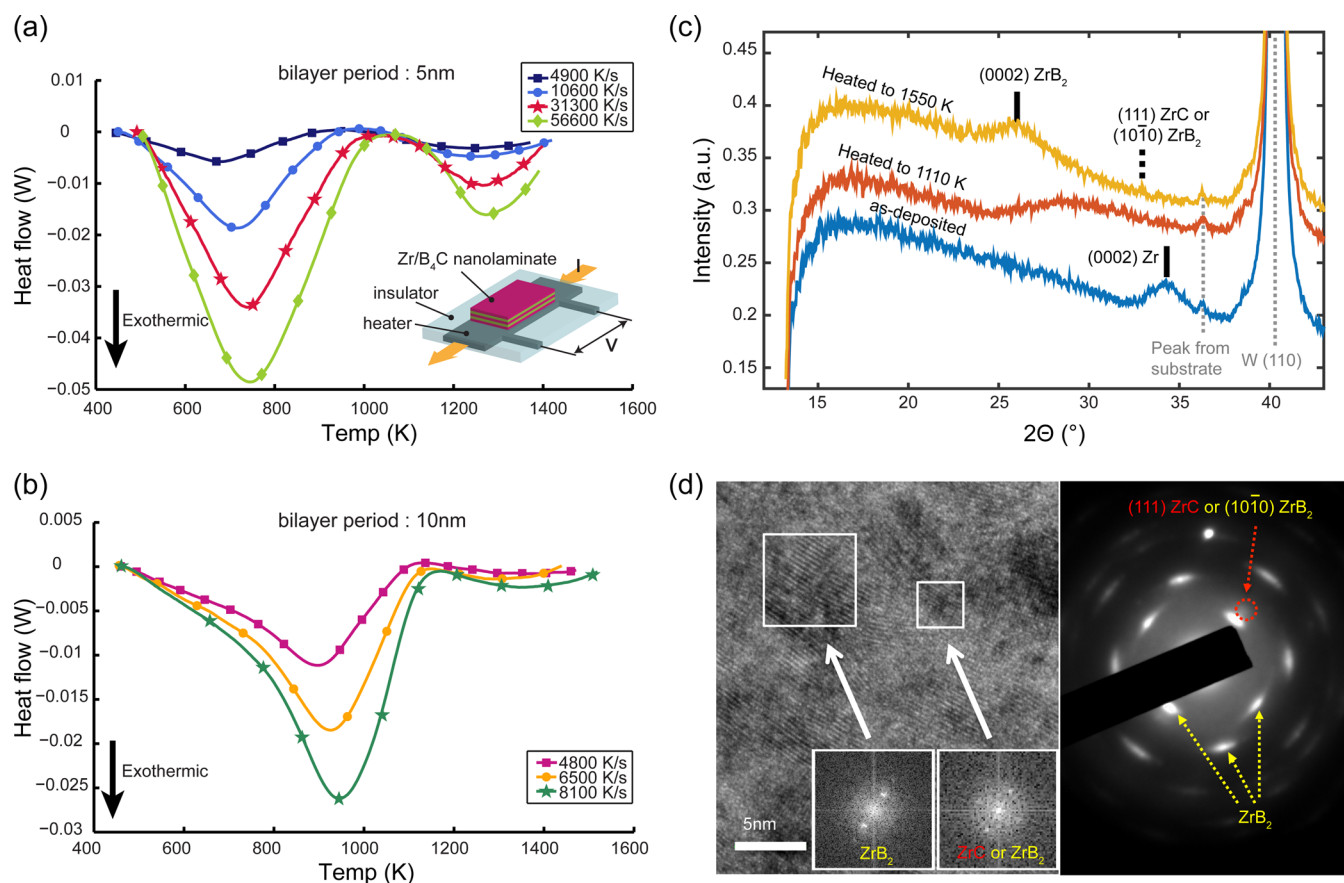


Figure 1. Heat flow versus temperature for Zr/B₄C nanolaminates with bilayer periods of (a) 5 nm and (b) 10 nm measured using nanocalorimetry. Nanocalorimetry heating rates are indicated in the insets of the figures (c) XRD results for an as-deposited nanolaminate (bilayer period, 10 nm), and for nanolaminates heated to 1110 and 1550 K (scanning rate, 8100 K/s). (d) Cross-sectional TEM micrographs for a nanolaminate heated to 1550 K: (left) bright-field image with Fourier transform analyses for selected regions and (right) diffraction pattern.

deposited samples had a 3:1 molar ratio of Zr/B₄C, to produce a 2:1 molar ratio of ZrB₂/ZrC after reaction. Figure 1 shows, as a function of temperature, the heat flow produced by Zr/B₄C nanolaminates with bilayer periods of (a) 5 nm and (b) 10 nm. In order to characterize the kinetics of the reaction, scanning rates were varied from 4800 to 56 600 K/s as indicated in the figures.

The heat flow curves in Figure 1a,b clearly show that the reaction in the Zr/B₄C RNLs proceeds in two distinct stages, each represented by an exothermic peak. The stage that corresponds to the first exotherm starts around 400–500 K for all samples tested. This stage of the reaction is complete at temperatures below 1000 K for the samples with a 5 nm bilayer period and below 1150 K for the samples with a 10 nm period. Faster heating rates and larger bilayer periods result in higher peak temperatures. The second stage is completed at approximately 1400 K for the samples with a 5 nm bilayer period, and at 1550 K for the 10 nm samples. Again, faster heating rates and larger bilayer periods shift the peak temperatures to higher values but the effect is less pronounced than for the first stage.

To determine the phase evolution of the RNLs during the two stages of the reaction, X-ray diffraction (XRD) was performed on RNLs with a 10 nm bilayer period in the as-deposited state, heated to an intermediate temperature (1110 K) and quenched after completion of the second exothermic reaction (1550 K). As shown in Figure 1c, the as-deposited sample has a diffraction peak corresponding to crystalline Zr

with a (0002) fiber texture (Powder Diffraction File #050665). No other reflections are identified, indicating that the as-deposited RNL consists of crystalline Zr and amorphous B₄C. The intermediate sample has a broad peak corresponding to an amorphous structure. This result implies that the first exothermic peak in the calorimetric signal is caused by the intermixing and amorphization of the Zr and B₄C layers in the laminate, explaining the shift to higher temperatures of the first calorimetry peak as the bilayer period, and thus the diffusion distance, increases. The sample heated to 1550 K has a strong diffraction peak corresponding to the (0002) ZrB₂ reflection (Powder Diffraction File #340423) and a very small peak caused by the (10 $\bar{1}$ 0) ZrB₂ or the (111) ZrC (Powder Diffraction File #350784) reflections; evidently, the second stage in the reaction corresponds to the crystallization of the amorphous phase to form a supersaturated, crystalline ZrB₂ phase with possibly a small amount of ZrC. The XRD results suggest that the crystallographic texture of the ZrB₂ films is composed primarily of a (0002) fiber texture. Transmission electron microscopy (TEM) performed on the same sample confirms the XRD findings as shown in Figure 1d. This texture, together with the small crystallite size, suggests that the crystalline phase nucleates preferentially at the original interfaces of the RNLs¹⁵ or that remanent concentration gradients at these interfaces induce a preferred nucleus orientation. These arguments are further supported by the observation that the peak crystallization temperature decreases

with decreasing bilayer period, that is, with increasing density of original interfaces.

The total reaction enthalpy is calculated by integrating the heat flow curves in Figure 1a,b with respect to time. The reaction enthalpy is independent of the heating rate but varies with the bilayer period of the RNLs because of a small amount of intermixing that occurs during sputter-deposition of the nanolaminates; samples with a 5 nm period released $392 \pm 72 \mu\text{J}$, while 10 nm period samples produced $784 \pm 117 \mu\text{J}$, respectively 19.7 ± 3.6 and $39.5 \pm 5.9\%$ of the theoretical enthalpy for the reaction of $3\text{Zr} + \text{B}_4\text{C} \rightarrow 2\text{ZrB}_2 + \text{ZrC}$.²⁰ The enthalpies associated with the first stage of the reaction are 295 ± 55 and $727 \pm 93 \mu\text{J}$, respectively. Given that the total thickness of the two sets of laminates is the same and that the total volume of initially intermixed material is two times larger for the samples with the 5 nm period than for the samples with the 10 nm period, the thickness of the intermixed layer can be estimated as approximately 1.9 nm per interface. This estimate is based on the assumption that the intermixed layers are fully intermixed, that is, they release no enthalpy on heating other than during the crystallization process. After correcting for the presence of the intermixed layers, the enthalpy of formation of the amorphous phase is found to be $1160 \pm 190 \mu\text{J}$, approximately 60% of the enthalpy of formation of pure crystalline ZrB_2 and ZrC in a 2:1 molar ratio.

The sequence of interdiffusion and crystallization in the $\text{Zr}/\text{B}_4\text{C}$ RNLs is similar to the sequence observed in RNLs that consist of alternating Zr and amorphous B¹⁵ layers. Thus, we adopt the diffusion model developed for the Zr/B system to characterize the first exothermic reaction in the $\text{Zr}/\text{B}_4\text{C}$ RNLs.¹⁵ According to this model, there exists a simple relationship between the rate at which enthalpy is produced during the reaction and the rate of interdiffusion: $(H + H_0)dH/dt$ at a given temperature is proportional to the diffusivity at that temperature. Here, H is the enthalpy released during the exothermic reaction and H_0 is the enthalpy that corresponds to the initially mixed $\text{Zr}/\text{B}_4\text{C}$ interface layers. Figure 2a shows graphs of $\ln((H + H_0)dH/dt)$ versus $1/k_B T$ over the temperature range of the first exotherm for several samples. The graphs are nearly linear and have a slope of $0.37 \pm 0.08 \text{ eV}$, regardless of bilayer period or heating rate. This slope is the activation energy for the interdiffusion process.^{15,21,22}

The kinetics of the crystallization step can be characterized using a Kissinger analysis²³ of the crystallization peak temperature, yielding an activation energy of $1.85 \pm 0.34 \text{ eV}$ (Figure 2b). This value is much larger than the activation energy for interdiffusion, which is consistent with the observation that the crystallization peak temperature is less sensitive to the heating rate than the interdiffusion peak (Figure 1a,b). The activation energies for diffusion and crystallization obtained for the $\text{Zr}/\text{B}_4\text{C}$ RNLs are approximately 20% smaller than the values for the Zr/B RNLs.¹⁵ Because the nanolaminates were synthesized in high vacuum without any exposure to air, our results suggest that carbon enhances the formation of ZrB_2 , not by the removal of surface/interfacial oxides as observed in the sintering of ZrB_2 powders,^{11–14} but by lowering the energy barriers associated with the formation reactions.

The formation of amorphous phases in both $\text{Zr}/\text{B}_4\text{C}$ and Zr/B ¹⁵ nanolaminates upon intermixing can be explained by the large differences in the atomic sizes of the constituent atoms (atomic radius of Zr, B, and C are 1.62, 0.90, and 0.77 Å, respectively²⁴), the low solubility of B and C in Zr, and the

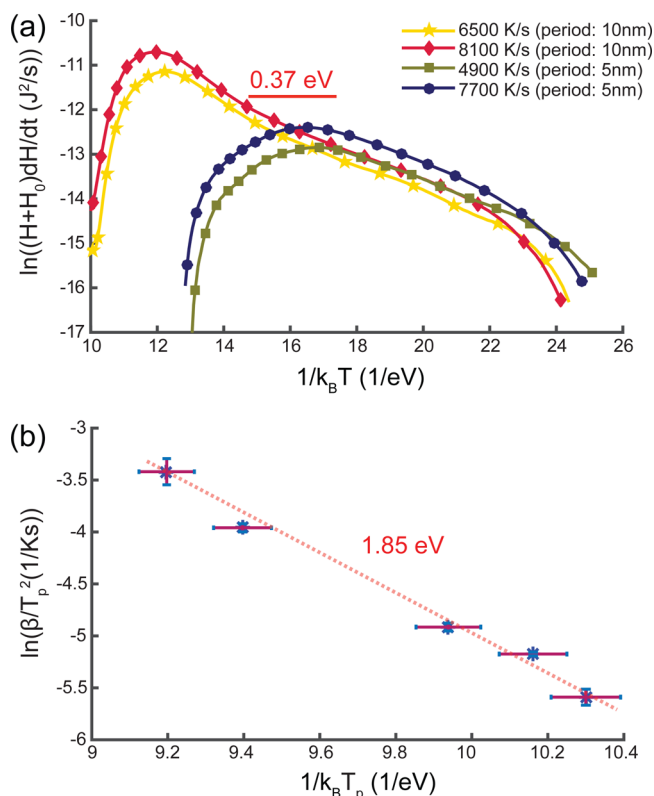


Figure 2. Kinetic analyses of the reactions in $\text{Zr}/\text{B}_4\text{C}$ RNLs: (a) $\ln((H + H_0)dH/dt)$ versus $1/k_B T$ over the temperature range of interdiffusion between Zr and B_4C . (b) Kissinger analysis of the crystallization peaks of the nanolaminates with a 5 nm bilayer period.

steep concentration gradients at the interfaces of the RNLs, which suppress nucleation of the crystalline phase.^{25–29} However, the lower activation energies for interdiffusion and crystallization in the $\text{Zr}/\text{B}_4\text{C}$ system compared to the Zr/B system are somewhat surprising because the addition of more elements to a compound typically enhances its glass forming ability and lowers the diffusivity of its constituent atoms.^{26,30–32}

In order to gain a better understanding of the mechanism responsible for lowering the activation energies for interdiffusion and crystallization, we have performed first-principles calculations on $\alpha\text{-Zr}$ ($P6_3/mmc$, $a = b = 3.23 \text{ Å}$, and $c = 5.17 \text{ Å}$ ^{33,34}) containing C atoms at various interstitial sites. We only consider stable or metastable sites where the C atom is stabilized at the initial interstitial position upon energetic relaxation.¹⁶ These sites include the octahedral site (Oct), the crowdion site (Cd), the basal bond center site (Bc), the hexagonal site (Hex), and the plane center (Pc) site. Positions and local environments of the sites are depicted in Figure 3. We also consider the substitutional site (Sub) as a reference. To determine the thermodynamic stability, the formation energy per C atom can be calculated for each interstitial site using the following expression

$$E_{\text{IC}}(n) = \frac{[E_{\text{nC-Zr}} - (54 - m)E_{\text{Zr}} - nE_{\text{C}}]}{n} \quad (1)$$

We take the energies of a Zr atom (E_{Zr}) and a C atom (E_{C}) in bulk form as reference energies, with $E_{\text{nC-Zr}}$ the total energy of a system containing n C atoms in a supercell that contains $(54 - m)$ Zr atoms ($m = 0$, except when C is at the Sub site, in which case $m = 1$).

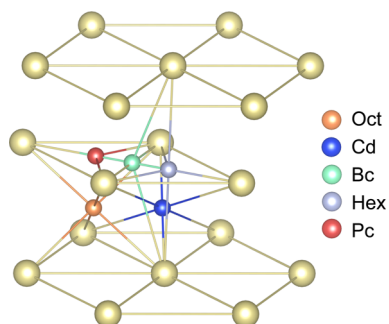


Figure 3. Positions and local environments of the interstitial sites in Zr.

Table 1 lists calculated values for E_{IC} at various sites. CN represents the coordination number, which is calculated using a cutoff length of 110% of the Zr–C bond length in crystalline ZrC (2.36 Å). We also list the formation energy per B atom (E_{IB}) at each interstitial site in Zr for comparison.¹⁶ The most stable site for C in Zr is the Oct site, which is also the most stable site for B in Zr. The Sub site is energetically very costly for both C and B atoms, indicating that both B and C are transported in the Zr lattice via an interstitial rather than a substitutional mechanism.

The values in parentheses in the last two columns of Table 1 represent the static energy barrier (ΔE_s), a measure of the energy barrier for a given diffusion path.^{16,35} ΔE_s can be estimated by subtracting E_{IC} or E_{IB} for each interstitial site from that of the most stable site (Oct). Interestingly, the Oct–Bc–Oct transition yields the lowest value for C ($\Delta E_s = 1.48$ eV), while B has a preferred diffusion path of Oct–Cd–Oct ($\Delta E_s = 1.12$ eV). These results suggest that C diffuses faster along the *c*-axis, while B diffuses preferentially within the basal plane. Note that the barrier for diffusion in Zr is larger for C than for B, for most of the cases considered. Thus, the enhanced interdiffusion between Zr and B in the presence of C is not caused by the intrinsic diffusion properties of C in Zr. Instead, we submit that it arises because the interaction between Zr and C is stronger than between Zr and B; as shown in Table 1, C has a lower energy in all interstitial sites of Zr than B. The stronger bonding between Zr and C enhances the amorphization of the Zr lattice in the course of intermixing and thus facilitates the transport of B through the resulting amorphous phase. The presence of C decreases the equilibrium concentration of B at the amorphous $\text{ZrB}_x\text{C}_y/\alpha\text{-Zr}$ phase boundary compared to Zr/B RNLs. Previous *ab initio* simulations¹⁶ have shown that the diffusion activation energy decreases with decreasing B concentration in ZrB_x , $0 < x \leq 1$, which is in line with our observation here.

Carbon also reduces the activation energy for crystallization. We believe that this is not the result of enhanced mobility of the constituent atoms; on the contrary, we would expect the presence of C in a homogeneous amorphous ZrB_2 alloy to

reduce the mobility of all atoms.^{26,30,31} Our experimental results show that the enthalpy of crystallization is larger for Zr/ B_4C than for Zr/B RNLs.¹⁵ This observation suggests that the reduced activation energy for crystallization may be caused by a larger free energy difference between the amorphous phase and the crystalline product. According to classical nucleation theory,³⁶ a larger free energy difference increases the thermodynamic driving force for crystallization and lowers the nucleation barrier, resulting in a reduced activation energy for the crystallization process.

In conclusion, we have studied the thermodynamics and kinetics of the interdiffusion and crystallization of Zr/ B_4C RNLs by combining nanocalorimetry and first-principles calculations. Nanocalorimetry and structural characterization reveal intermixing of the two constituent layers of the RNLs upon heating, followed by crystallization to form a ZrB_2 phase that is supersaturated with C. A diffusion model for a multilayered system with crystalline and amorphous phase boundaries and a Kissinger analysis reveal that the Zr/ B_4C RNLs have lower energy barriers for both interdiffusion and crystallization than Zr/B RNLs. First-principles calculations suggest that the lower energy barrier for interdiffusion is not caused by the diffusional properties of C in the Zr lattice, but rather by the stronger interactions between Zr and C. The reaction thermodynamic and kinetics discussed in this work can provide guidance for optimizing the fabrication process of ZrB_2 coatings.

METHODS

Each micromachined nanocalorimetry sensor consists of a 100 nm Ti–W alloy four-point electrical probe that serves both as a resistance thermometer and as a Joule heater. The element is encapsulated and is supported by a freestanding 300 nm Si_3N_4 membrane. The Si_3N_4 membrane serves to isolate sample and sensor from the ambient. Details of the operating principles and sensor fabrication procedures can be found elsewhere.^{15,18,19}

Zr/ B_4C nanolaminate samples were magnetron sputter deposited (ATC 1800, AJA Int.) on the measurement section of the nanocalorimetry sensors using 99.99% Zr (DC 80W, 5 nm/min) and 99.95% B_4C (RF 150W, 0.4 nm/min) targets (Kurt J. Lesker Company). The thickness of each layer was determined to ensure a stoichiometric composition: 3:1 molar ratio of Zr/ B_4C in the as-deposited samples to produce a 2:1 molar ratio of ZrB_2/ZrC after the reaction. Nanolaminate samples with bilayer periods of 5 and 10 nm, and a total thickness of 80 nm were used in this work. The area of the sample was defined using a custom-made Si-shadow mask during the sputter-deposition process.

All nanocalorimetry measurements were performed inside a high-vacuum furnace with a base pressure better than 5×10^{-6} Torr. The samples were heated to approximately 1550 K at heating rates from 4800 to 56 600 K/s. The power input and

Table 1. Structural and Energetic Features of a Single C or B Atom at Various Sites in the Zr Lattice

interstitial sites	position	CN	E_{IC} (eV)	E_{IB} (eV) ¹⁶
octahedral (Oct)	(0.33, 0.67, 0.25)	6	−1.53	−0.53
crowdion (Cd)	(0.83, 0.17, 0.25)	6	0.029 (1.56)	0.59 (1.12)
basal bond center (Bc)	(0.67, 0.83, 0.50)	6	−0.046 (1.48)	0.82 (1.35)
hexahedral (Hex)	(0.00, 0.00, 0.50)	5	0.303 (1.83)	1.45 (1.98)
plane center (Pc)	(0.33, 0.67, 0.50)	3	2.16 (3.69)	2.18 (2.71)
substitutional (Sub)	(0, 0, 0)	12	3.98	1.86

the temperature data were utilized to determine the reactive heat flow of the nanolaminate sample following the procedures established in our previous work.¹⁷

X-ray diffraction (XRD) measurements were performed on both the as-deposited sample and on the samples heated to 1110 and 1550 K (D8 Discover, Bruker). TEM images were acquired for the sample heated to 1550 K using JEOL 2100 system. The TEM sample was prepared using a typical in situ lift-out technique (INLO)³⁷ in an focused ion beam system (Zeiss NVision 40 Dual-Beam). The samples that were heated for XRD and TEM studies were quenched with a fast cooling rate ($\sim 15\,000$ K/s) to freeze in the structure before performing XRD or TEM.

Density functional theory calculations were performed using the Vienna ab initio simulation package (VASP).³⁸ The projected-augmented-waves (PAW)³⁹ with the Perdew–Burke–Ernzerhof (PBE)⁴⁰ exchange–correlation potentials were adopted. For Zr, the valence states were treated using a Zr_sv ($4s^2 4p^6 5s^2 4d^2$) pseudopotential. The C ($2s^2 2p^2$) pseudopotential was employed for carbon. The cutoff energy for plane waves was set to 400 eV, and forces were converged to within 0.02 eV/Å. We used a 54-atom Zr supercell ($3 \times 3 \times 3$) and one C atom for the simulations to identify the interstitial sites. A $6 \times 6 \times 4$ k -point mesh in the Monkhorst–Pack scheme was employed for Brillouin zone sampling.

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Notes

The authors declare no competing financial interest.

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