

Growth-front complexions deliver stacking faults and $\Sigma 2$ grain boundaries

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Abstract

WC-Co cemented carbides usually exhibit high fractions of $\Sigma 2$ boundaries, yet their origin remains unresolved. Here we capture the WC/liquid-Co growth front by HVOF thermal spraying followed by ultrafast quenching, which preserves an amorphous binder and maintains the interfacial configuration at the WC dissolution-reprecipitation front. Two facet-dependent growth-front states are resolved: P-I facets are stabilized by a BCC-type trilayer complexion that enforces registry and epitaxial constraint (symmetry protecting), whereas P-II facets exhibit a clean-type complexion with reduced constraint, under which stacking selection becomes unstable and directly injects planar faults. These faults undergo a trigger-evolve-recover cycle, transforming among single-, double-, and triple-layer faults and nanoscale $\Sigma 2$ -like motifs. Under cooperative conditions, the nanoscale motifs can evolve toward a continuous $\Sigma 2$ boundary, stabilized by a step-partial-dislocation geometry that partitions interfacial mismatch. Together, these results identify the WC/Co growth front as a key $\Sigma 2$ source and suggest an interfacial-engineering strategy to tailor stacking-fault-type planar defects (e.g., twins) in multicomponent ceramic systems.

Introduction

WC-Co cemented carbides are being pushed toward increasingly demanding combinations of strength, toughness and environmental robustness^{1,2}. Because the boundary network governs their plastic accommodation^{3,4}, crack-path selection and fracture resistance⁵, and transport-assisted degradation^{6,7}, interfacial design—particularly grain-boundary engineering—has become central^{8,9}. Low-energy Σ boundaries, especially $\Sigma 2$ ⁴, have been linked to improved performance through enhanced resistance to dislocation transfer², crack deflection/energy dissipation via nanoscale $\Sigma 2$ -related motifs¹⁰, and—when interfacial chemistry remains comparatively “clean”, reduced corrosion-assisted penetration and Co infiltration along interfaces^{6,7,11,12}. Therefore, introducing high-density $\Sigma 2$ boundaries in a controllable manner has become a central objective in grain boundary engineering of cemented carbides.

Yet $\Sigma 2$ regulation remains largely empirical (grain refinement¹³, growth inhibitors¹⁴, binder-content tuning¹⁵), and alternative densification routes such as spark plasma sintering^{16,17}, and a unified mechanism for $\Sigma 2$ formation and regulation is still lacking. Two representative routes have been proposed. The first is a liquid-phase-driven “rotation-matching” pathway¹⁸: WC grains are predominantly terminated by basal (B) and prismatic (P) planes, and capillary forces from the liquid cobalt (Co) binder during sintering may drive grain rotation/rearrangement, promoting CSL (Coincidence Site Lattice) relationships such as $\Sigma 2$ (P on P). High-resolution microscopy further suggests that $\Sigma 2$ boundaries often adopt twist configurations and share local structural motifs with stacking-fault-like units^{19–21}. The second is a “primary inheritance” pathway²²: Mo-marker studies in WC-Mo₂C-Co model systems indicate that, although most WC boundaries are infiltrated and reconstructed by the liquid binder, a fraction of special boundaries remains uninfiltrated and retained, implying inheritance of GBs such as $\Sigma 2$ from the starting powder.

However, several observations remain difficult to reconcile within these frameworks. Reported $\Sigma 2$ fractions can be unusually high and exhibit strong additive sensitivity^{14,15}, for instance, in WC-10 wt.% Co, Cr doping raises the $\Sigma 2$ fraction from 12.8% to 14.8%. Such a high population of a single CSL type—together with systematic differences among V-, Cr-, and Ti-containing alloys prepared from identical starting powders—is hard to account for by either a rotation-based route (which should largely scale with rotation probability) or an inheritance-based route alone, or even by their simple combination. This is particularly true because these additives do not substantially alter the dominant WC exposed facets, which remain primarily basal and prismatic¹⁸.

These inconsistencies suggest that high $\Sigma 2$ fractions may arise from multiple sources. In addition to rotation and inheritance, we propose a third pathway in which $\Sigma 2$ -related structures are triggered and evolve in situ at the WC-Co liquid-phase growth front (LGF) during carbide growth. Testing this hypothesis requires capturing the growth-front configuration before binder crystallization and interfacial reconstruction erasing it—necessitating an ultrafast quench that preserves Co in an amorphous state. Here we employ high-velocity oxygen-fuel (HVOF) thermal spraying²³ to provide an ultrafast quench ($\sim 10^5$ - 10^6 K.s⁻¹) that effectively “freezes” the high-temperature growth-front configuration (from $> 2500^\circ\text{C}$) and retains the binder in an amorphous state. In this process, semi-molten WC/Co particles impact the pretreated substrate at high velocity and rapidly spread into ultrathin splats, enabling microsecond-millisecond heat extraction. This quasi-in-situ access allows us to test whether defect injection at the growth front generates dense fault populations that evolve into $\Sigma 2$ -related structures, thereby offering structural insight into the origin of high $\Sigma 2$ fractions and opening opportunities for controllable defect and grain-boundary engineering.

Results

Ultrafast quenching captures defect-rich fronts and $\Sigma 2$ boundaries

Supplementary Fig. 1 illustrates the quenched microstructure of the as-sprayed WC-Co coating, where cross-sectional lamellae were prepared by focused ion beam (FIB). In bright-field (BF, Fig. 1a) image and its schematic counterpart (Fig. 1b), WC grains (bluish gray) show pronounced diffraction contrast and a relatively regular size distribution (~ 300 - 500 nm), while the surrounding Co phase (warm gray) appears uniform contrast and devoid of discernible crystallites. The architecture is notably distinct from conventional cemented carbides: rather than being compartmentalized by a contiguous WC framework, the binder here forms large, continuously interconnected pools that separate dispersed WC grains. Yet, the WC grains remain sharply faceted, with triangular or rectangular cross-sections that are consistent with a trigonal-prismatic habit retained at high temperature (estimated $> 2500^\circ\text{C}$). Such faceting implies a stable, low-index-plane-controlled growth front and points to a stepwise, layer-by-layer mode of interface advance. Diffuse amorphous rings in the Co-pool diffraction pattern (Fig. 1c) corroborate an amorphous binder and EDS (energy dispersive X-ray spectroscopy) data reveals substantial W solubility in the quenched Co pools. Taken together, these observations suggest that ultrafast quenching locks in

the binder as an amorphous phase, retaining the interfacial configuration of the WC dissolution-precipitation front.

TKD (Transmission Kikuchi Diffraction) mapping of the same area (Fig. 1d) further reveals a relatively high fraction of $\Sigma 2$ boundaries (green lines, fraction: 22.8%). The enlarged view (Fig. 1e) shows a $\Sigma 2$ boundary separating a grain oriented near $\langle 0001 \rangle$ (#1) from one near $\langle 2\bar{1}10 \rangle$ (#2), with their trigonal-square orientations summarized in Fig. 1f. Importantly, this $\Sigma 2$ boundary is not expressed as a faceted interface. Instead, it adopts a curved morphology on the microscale, departing from the idealized flat Σ -boundary geometry often assumed. TEM (Transmission Electron Microscopy) imaging (Fig. 1g) reveals, beyond the curved $\Sigma 2$ boundary itself, dense arrays of parallel intragranular contrasts. Notably, at the LGF front, particularly on the #1 side, these defects are especially abundant and align with the local growth front. Their occurrence at the advancing front (Fig. 1h) suggests that at least a substantial fraction of the fault population—particularly that associated with the growth front of grain #1—was introduced during high-temperature growth and subsequently preserved by ultrafast quenching before later relaxation.

Interfacial complexions govern fault injection and evolution

Aberration-corrected microscopy reveals that the as-quenched WC grains host dense, crystallographically-organized planar defects. A WC grain viewed along $[0001]$ (Fig. 2a) exhibits a truncated-triangular outline bounded by asymmetric $\{10\bar{1}0\}$ facets: long P-I segments (~ 200 - 300 nm) and short P-II segments at the truncated corners¹⁸ (~ 50 - 100 nm). The grain interior is threaded by elongated line contrasts parallel to $\{10\bar{1}0\}$ (Fig. 2b), which intensify toward the P-II corners and are reflected by the elongation of the three equivalent $\{10\bar{1}0\}$ diffraction spots (Fig. 2c). These stacking-fault traces parallel to the prismatic planes were also identified in another example along the $[0001]$ zone axis (Supplementary Fig. 2), as well as in two additional cases observed along the $[2\bar{1}10]$ and $[2\bar{1}\bar{1}3]$ zone axes, respectively (Supplementary Figs. 3 and 4). Beyond the prominent fault traces, the boxed region in Fig. 2a contains finer nanoscale faults (Fig. 2d) that can terminate within the crystal or intersect, forming locally darker overlap segments.

At the atomic scale (Fig. 2e), defect-free WC is composed of triangular motifs with ABABAB stacking along the $\{10\bar{1}0\}$ plane, whereas some defected regions display rectangular motifs, marking a local rearrangement of stacking. Accordingly, three fault types are resolved (Fig. 2, f-h). The single-layer fault (1L-SF, purple) retains ABABAB on both sides but shows a local displacement that produces an ABA|A(B)|ABA configuration. The double-layer fault (2L-SF, blue) corresponds to AB|AA|BA, while the triple-layer fault (3L-SF, green) extends the faulted zone to AB|AAA|BA. Upon tilting the crystal to the $[2\bar{1}10]$ zone axis, abundant stacking faults with different sample thicknesses were also observed within the grain interior (Supplementary Fig. 5). Faults frequently interact with one another (Supplementary Fig. 6), producing atomic-scale kinks, where no discernible elemental segregation is detected (Supplementary Fig. 7). Some defects emerge within the grain interior as an embryonic state (Supplementary Fig. 8), whereas others terminate or appear locally healed, consistent with a dynamic defect population during growth. A statistical assessment over ten high-resolution regions gives a defect density of $2.3 \times 10^{15} \text{ m}^{-2}$

(total fault length per unit volume), far exceeding that typically observed after conventional cooling. The prevalence of finer faults parallel to prismatic planes further points to insufficient structural relaxation under rapid cooling and implicates atomic stacking at the WC (prismatic)-Co growth front as a likely origin.

Guided by the intragranular defect signatures, we turned to the carbide/binder interface to interrogate the atomic structure of the WC growth front. The rapidly-quenched specimens preserve the interfacial front in a near-growth configuration, enabling us to assess whether the defect-rich WC interiors are seeded at the advancing interface. A representative WC grain viewed along [0001] is shown in Fig. 3a, where WC adjoins an amorphous Co binder. The leading front is enclosed by three long P-I type facets and three shorter P-II type facets. At low magnification, P-I fronts remain comparatively smooth, whereas P-II fronts—although straight in overall contour—exhibit distinct curvature concentrated near the lower corners. Upon magnification (Fig. 3b), the P-II front resolves into atomic-height steps and appears markedly rough, while the neighboring P-I front remains atomically smooth.

At the atomic scale, P-I and P-II fronts diverge in their termination and stacking responses. iDPC (integrated differential phase contrast) imaging of the P-I front (Fig. 3c) reveals a predominantly W-terminated interface accompanied by a finite-thickness transition zone (~ 2 -3 atomic layers). Within this zone, interlayer spacing and C-site configurations deviate from bulk WC, and progressive C-site depletion toward the amorphous binder is evident—features consistent with a BCC-type Co-enriched interfacial complexion that stabilizes the growth front. In contrast, the P-II front exhibits two competing stacking outcomes (Fig. 3, d and e). One retains the normal ABAB sequence along the $\{10\bar{1}0\}$ plane, supporting defect-free epitaxial advance. The other undergoes a local ABAB $\rightarrow$ AAA transition, creating a faulted segment at the front and indicating fault nucleation at P-II. The absence of a clear transition layer at P-II, in contrast to P-I, points to distinct interfacial growth modes.

Notably, the stacking can revert to ABAB after the insertion of faulted layers (Fig. 3e), indicating a local recovery of the stacking sequence. This alternation in stacking modes appears to drive the local transformation between square-like and triangular structural units, which in turn accounts for the apparent roughening of the P-II facet. Together, these observations indicate a stacking mode transition at the P-II growth front, potentially serving as a source of stacking faults in WC. The stacking follows two accessible pathways—normal ABAB stacking or a defect-enabled perturbation route involving a near-90° reorientation of the structural unit (Fig. 3f)—ultimately giving rise to the nanoscale fault configurations observed in Fig. 2.

Fig. 4 further reveals a growth front that is structurally heterogeneous: faulted and fault-free segments coexist along the same advancing interface, particularly at the P-II-type front. Large-area stitched HAADF (high-angle annular dark-field) imaging (Supplementary Fig. 9) further shows that these faults permeate the grain interior and interconvert across thicknesses, underscoring that stacking faults in WC function as dynamic structural units during growth rather than static defects.

In a representative [0001] dataset (Figs. 4, a and b, pairs of HAADF and iDPC images), ABAB stacking dominates, interrupted by localized faulted segments. The upper region links a fault embryo to a triple-layer fault, whereas the lower region contains short single-layer fault embryos generated by local layer displacement from ABAB stacking. These single-layer segments are intrinsically finite in length, typically confined to ~2-10 nm (Fig. 4e), consistent with facile triggering and limited persistence. Viewed along $\langle 2\bar{1}10 \rangle$ (Fig. 4, c and d), similar behavior is observed, with faults captured as they extend and disappear.

Length statistics from stitched images (Supplementary Fig. 9) separate three regimes in Fig. 4e: single-layer faults are the shortest (mean ~5 nm), double-layer faults are intermediate (mean ~10 nm), and triple-layer faults are the longest (most probable ~10-20 nm, mean ~30-40 nm), occasionally traversing grains. The triple-layer faults appear as a more stable fault configuration, consistent with a nanoscale $\Sigma 2$ -like motif informed by Fig. 3.

Molecular dynamics (MD) simulation results (Fig. 4f) support thickness-dependent stability: the single-layer faults are lowest in energy; double-layer faults are highest in energy; and triple-layer faults drop below the double-layer case. Together with Fig. 3, these results indicate that the P-II front serves as a potential source of fault injection. The W-terminated, “clean”-type interface exposes a near-square local geometry ($a=2.90$ vs. $c=2.84$ Å), introducing quasi-fourfold symmetry ($\sim L^4$) and rendering two stacking pathways nearly competitive (Fig. 4g): normal ABAB epitaxy or an $\sim 90^\circ$ reoriented alternative stacking mode. Under high-velocity impact and rapid cooling during thermal spraying, these two pathways may dynamically switch, producing and preserving interconvertible faults of different thicknesses, thereby explaining the abundant stacking faults and nanoscale $\Sigma 2$ -like structures observed at the P-II front and within WC grains.

Cooperative defect integration into a macroscopic $\Sigma 2$ boundary

Fig. 5 shows that nanoscale stacking faults (nano $\Sigma 2$ -related motifs) are not necessarily local and transient: under appropriate conditions, they can integrate cooperatively into a macroscopically visible $\Sigma 2$ boundary. The example in Fig. 5a combines a near-rectangular lower grain with a truncated-triangular upper grain joined by a curved interface, consistent with a near- $\Sigma 2$ relationship inferred from their projected zone-axis characteristics (upper near [0001], lower near $[2\bar{1}10]$).

The boundary in Fig. 5b is segmented rather than perfectly planar, alternating between straight, curved and inclined stretches. Denoting the upper and lower grains as WC-#1 and WC-#2, diffraction (inset) confirms [0001] (#1) $\parallel$ $[2\bar{1}10]$ (#2) and parallel $(10\bar{1}0)$ planes, supporting assignment of a $\Sigma 2$ orientation relationship. At the atomic scale, a locally straight segment resolves into repeated steps of ~1-2 atomic layers (Fig. 5c). GPA (Geometric Phase Analysis) concentrates strain at step corners, identifying dislocation cores, and Burgers-circuit analysis reveals dissociation into partial dislocations ($\vec{b}=\langle 11\bar{2}\bar{3} \rangle/6$). The NCS model (Fig. 5d) shows that partial cores are systematically coupled to steps (or termed as disconnection), implying that steps are functional elements of mismatch relaxation, enabling Burgers-vector partitioning. CSL/DSCL (displacement shift complete lattice) modeling (top view in

Supplementary Fig. 10) provides a geometric basis: Along the $\Sigma 2$ orientation, periodically alternating well-matched and mismatched regions emerge. The mismatch is accommodated cooperatively by partial dislocations and steps, instead of a single perfect dislocation, enabling local coherency to be maintained with smaller Burgers vector displacements and lower elastic energy. Consistently, the DSCL model and iDPC imaging of the stepped region (Figs. 5, e and f) indicate that steps are introduced to minimize local mismatch and thus act as required structural units for stabilizing the $\Sigma 2$ boundary.

Together with Figs. 3-5, these results suggest a continuous evolution from nanoscale $\Sigma 2$ -related faults to a macroscopic $\Sigma 2$ boundary. In certain growth windows, the P-II front can trigger dense, similarly oriented faults that couple and merge into a continuous $\Sigma 2$ interface, more typically, faults remain short-range and locally interconverting, persisting as high-density nanoscale defects (Fig. 2). Thus, Fig. 5 represents a high-cooperativity endpoint of the same fault-generation mechanism established in Figs. 2-4.

Discussion

This work identifies a growth-front control principle: the formation of an interfacial complexion at the carbide/binder front—and the geometric constraint that accompanies it—reprograms interfacial coordination, thereby enabling stacking-fault injection and, under suitable conditions, $\Sigma 2$ -related structures formation. This provides a structural basis for the unusually high $\Sigma 2$ fractions in cemented carbides and leads to three implications.

First, spray-assisted ultrafast quenching allows the WC-Co liquid-growth front to be captured in a near-growth configuration. The P-I-terminated front exhibits an atomically smooth transition layer, here manifested as a BCC-type trilayer complexion²⁴, which imposes a constrained coordination environment. In contrast, the P-II-terminated front is effectively a clean-type complexion^{25–28}, presenting a segregation-free interface.

Second, we uncover a dynamic defect pathway at the nonequilibrium growth front: stacking faults are repeatedly triggered, evolve in thickness, and can locally recover. Rapid undercooling drives the growth front into a defect-rich regime, where stacking faults and $\Sigma 2$ -related nanoscale motifs emerge in abundance—signatures seldom accessible in conventional microstructures—and high-velocity impact may further strengthen this effect. Direct observations at the P-II fronts connect fault evolution to the $\Sigma 2$ boundaries commonly reported in cemented carbides. Accordingly, beyond facet-rotation models¹⁸, inheritance/retention pathways inferred from Mo marker experiments²², growth-front fault evolution at the P-II interface could be considered an additional contribution to $\Sigma 2$ formation.

The relative weights of these routes are likely chemistry-dependent. For example, our prior observation of abundant stacking faults in V-containing WC-Co²⁹ suggests that V-rich precipitate segregation may promote the initialization and subsequent merging of independently developed WC micro-pillars, potentially introducing another pathway that elevates $\Sigma 2$ fractions in V-doped alloys. More broadly, the

emergence of macroscopic $\Sigma 2$ boundaries may involve an early formation window during the spray stage—possibly associated with higher W solubility in the binder—during which dense faults can interact and integrate into microscopically continuous $\Sigma 2$ boundaries. At later and more common stages, defects are retained primarily as nanoscale stacking faults or $\Sigma 2$ -related motifs. Pinning down this early formation window, and its compositional sensitivity, will be an important direction of our ongoing work.

Third, our results establish complexions as symmetry-protecting (or orienting) elements at the growth front. At the P-I front, the trilayer complexion exhibits near registry with the underlying WC lattice, strengthening geometric constraint and biasing epitaxial advance toward the parent orientation. In contrast, the clean-type P-II front has enhanced coordination freedom, exposing two near-competitive stacking pathways and thereby facilitating faulting and $\Sigma 2$ -related motifs. Interfacial coordination thus emerges as a decisive control parameter for defect generation during growth.

In closing, we shift $\Sigma 2$ tuning from a macroscopic outcome to an atomistic lever at the WC/Co phase boundary. Whereas prior approaches have primarily targeted additive chemistry¹⁴ and grain-shape engineering¹³, we propose that termination- and coordination-level engineering at the P-II-type front can program fault injection and, under suitable conditions, steer its evolution toward continuous $\Sigma 2$ boundaries. This viewpoint also reframes additive effects: alloy chemistry may tune $\Sigma 2$ fractions by stabilizing a quasi-fourfold symmetric ($\sim L^4$) complexion state (e.g., clean complexion), thereby modulating defect injection and evolution. Our findings thus unify nanoscale faulting and $\Sigma 2$ enrichment within a single growth-front complexion mechanism and suggest a practical route for programming special-boundary populations: engineering termination, coordination, and complexion state at the WC/Co phase boundary to control defect injection and its subsequent evolution. In a broader sense, pseudo-fourfold ($\sim L^4$) complexion symmetry acts as a stacking selector that steers $\Sigma 2$ -type growth defects, offering a general principle to program stacking-fault-derived planar defects (e.g., twins) in multicomponent ceramic growth systems.

Materials and Methods

Fabrication of WC-Co cemented carbide

Commercially available WC powder (0.8 μm) and 17 wt.% Co powder (0.8 μm) were mixed by wet ball milling for 20 hours using ethyl alcohol as the milling medium. After drying, the WC-17Co powder was mechanically blended with 3 wt.% polyethylene glycol (PEG) and 35 wt.% deionized water to form a stable slurry. The slurry was then subjected to centrifugal spray drying, followed by subsequent vacuum heat-treatment at 1200 °C for 90 min. After sieving, the WC-17Co feedstock powder with a particle size range of 15–45 μm for the high velocity oxy-fuel (HVOF) thermal spraying was obtained. Detailed information on the morphology of the feedstock powder can be found in our previous study²³. Prior to spraying, the substrate was pretreated by grit blasting and cleaning to improve the interfacial bonding strength between the coating and the substrate. A JP5000 HVOF spraying system was used to deposit

the feedstock powder onto a mild steel substrate (0.45 wt.% C). During spraying, the powder was injected into the flame and heated to a semi-molten state in the high-temperature ($> 2500\text{ }^{\circ}\text{C}$), high-velocity gas stream. These particles subsequently impacted the substrate at high speeds and rapidly spread into thin splats. Owing to the high thermal conductivity of the substrate and the ultrathin geometry of the splats, heat dissipation occurred within microseconds to milliseconds, resulting in an extremely high cooling rate on the order of $10^5\text{-}10^6\text{ K.s}^{-1}$.

Material characterization

After rapid cooling, the as-quenched samples were polished and subsequently characterized by scanning electron microscopy (SEM) to examine the microstructural morphology. TEM lamella was extracted by a Helios G4 CX focused ion beam (FIB) system (Thermofisher Scientific) equipped with a gallium ion source. The crystallographic orientation of WC grains was obtained using a Transmission Kikuchi Diffraction (TKD) mode (Oxford Aztec). The acquisition parameters were set as follows: accelerating voltage: 30 kV, working distance: 4mm, sample tilt of -20° . TKD data was further analyzed using Oxford AZtecCrystal software for grain sizes (equivalent circle diameter)³⁰ and orientation analysis. Selected area electron diffraction (SAED) pattern was collected from a Transmission Electron Microscope (TEM, Talos F200s, 200kV). HAADF (high-angle annular dark-field), iDPC (integrated differential phase contrast) imaging and EDS (energy-dispersive X-ray spectroscopy) mapping were performed on the aberration-corrected scanning transmission electron microscopy (AC-STEM, Themis Z, 300 kV). A collection semi-angle of 60–200 mrad was used for HAADF imaging, and a probe current of 80 pA was applied during EDS mapping for sufficient X-ray signals.

CSL/NCS-based analysis of interfacial structure and dislocation geometry

The near-coincidence site (NCS) and coincidence site lattice (CSL) models were employed to analyze the interfacial structure of $\Sigma 2$ grain boundary. Based on the experimentally determined orientation relationship, the distribution of near-coincidence sites, and the corresponding displacement shift complete (DSC) lattice³¹ were constructed to determine the possible Burgers vectors, which is compared with the Burgers circuits of interfacial partial dislocations, as well as their association with interfacial steps for mismatch accommodation.

Molecular dynamics simulation

All simulations were performed using the LAMMPS software package³². Interatomic interactions were computed via the DeePMD-kit interface by employing the DPA-1 machine-learned potential, which is specifically developed for transition metal carbides³³. This potential has demonstrated excellent performance in simulating properties related to heterogeneous interfaces, such as melting point, grain

boundary energy, and stacking fault energy. For the stacking fault models of the WC systems with different compositions (WC-monolayer (1L-SF), WC-bilayer (2L-SF), and WC-trilayer (3L-SF)), we constructed supercells containing 864, 792, and 864 atoms, respectively. Structural relaxation was conducted using the conjugate gradient algorithm, with convergence criteria set to an energy change of less than 1×10^{-12} eV and a force tolerance below 1×10^{-8} eV/Å. After relaxation, the stacking fault energy (γ) was calculated as

$$\gamma = \frac{E_f - E_o}{A}$$

where E_o denotes the initial energy of the fault-free WC system (1L-SF: -9692.4384 eV; 2L-SF: -8884.7352 eV; 3L-SF: -9692.4384 eV), E_f is the energy after stacking fault formation (1L-SF: -9686.5432 eV; 2L-SF: -8862.9072 eV; 3L-SF: -9683.8735 eV), and A is the slip-plane area (1L-SF: 298.7993 Å^2 ; 2L-SF: 299.1389 Å^2 ; 3L-SF: 298.3842 Å^2). The resulting stacking fault energies are 0.0197, 0.0730, and 0.0287 eV/Å² for the 1L-SF, 2L-SF, and 3L-SF systems, respectively.

Declarations

Competing interests

The authors declare no competing interests.

Author contributions

X.Y.Y., H.B.W., X.Y.S., and Z.Y.Y. conceived the research and designed the experiments. H.B.W. and H.H.H. fabricated the samples. X.Y.Y. and H.L.C. carried out the characterization with assistance from L.L.Z. and C.Y.X.. X.F.G. guided the CSL/NCS-based analysis. X.Y.L. and F.Z.D. conducted the MC-MD calculations. X.Y.Y. and H.L.C. analyzed the data and drafted the manuscript. X.Y.Y., H.L.C., H.B.W., X.Y.S., and Z.Y.Y. revised the manuscript. H.B.W., X.Y.S., and Z.Y.Y. supervised the research. All authors discussed the results and commented on the manuscript.

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Data Availability Statement

All the data supporting the findings of this study are available within this article and its Supplementary Information. Any additional information can be obtained from corresponding authors upon request.

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Figures

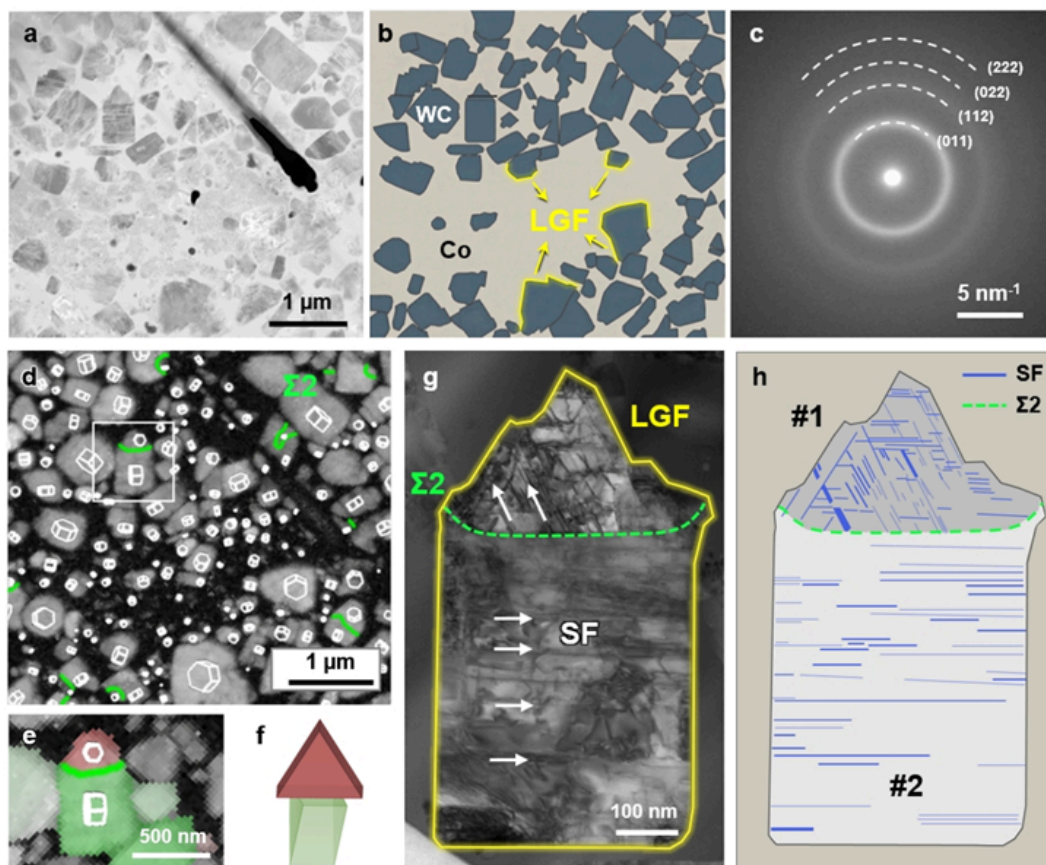


Fig. 1 | Quenched microstructure of a thermally sprayed WC-Co coating. **a** Bright-field image showing faceted WC grains (dark) within an interconnected Co matrix (bright). **b** Schematic of (a) (WC: bluish gray, Co pools: warm gray), with the quenched WC liquid-growth front marked (yellow lines). **c** Diffraction pattern of the Co-binder region in (b) showing amorphous rings. **d** Transmission Kikuchi diffraction map highlighting $\Sigma 2$ boundaries ($\langle 10\bar{1}0 \rangle 90^\circ$, green). **e** Boxed region from (d) with IPF (inverse pole figure) over band contrast, identifying a $\Sigma 2$ boundary between grains near $\langle 0001 \rangle$ and $\langle 2\bar{1}\bar{1}0 \rangle$. Their orientation is schematically shown in (f). **(g-h)** Transmission electron microscopy image and schematic of the same $\Sigma 2$ boundary showing abundant intragranular stacking-fault contrasts (faults in blue, boundary in green).

Figure 1

See image above for figure legend.

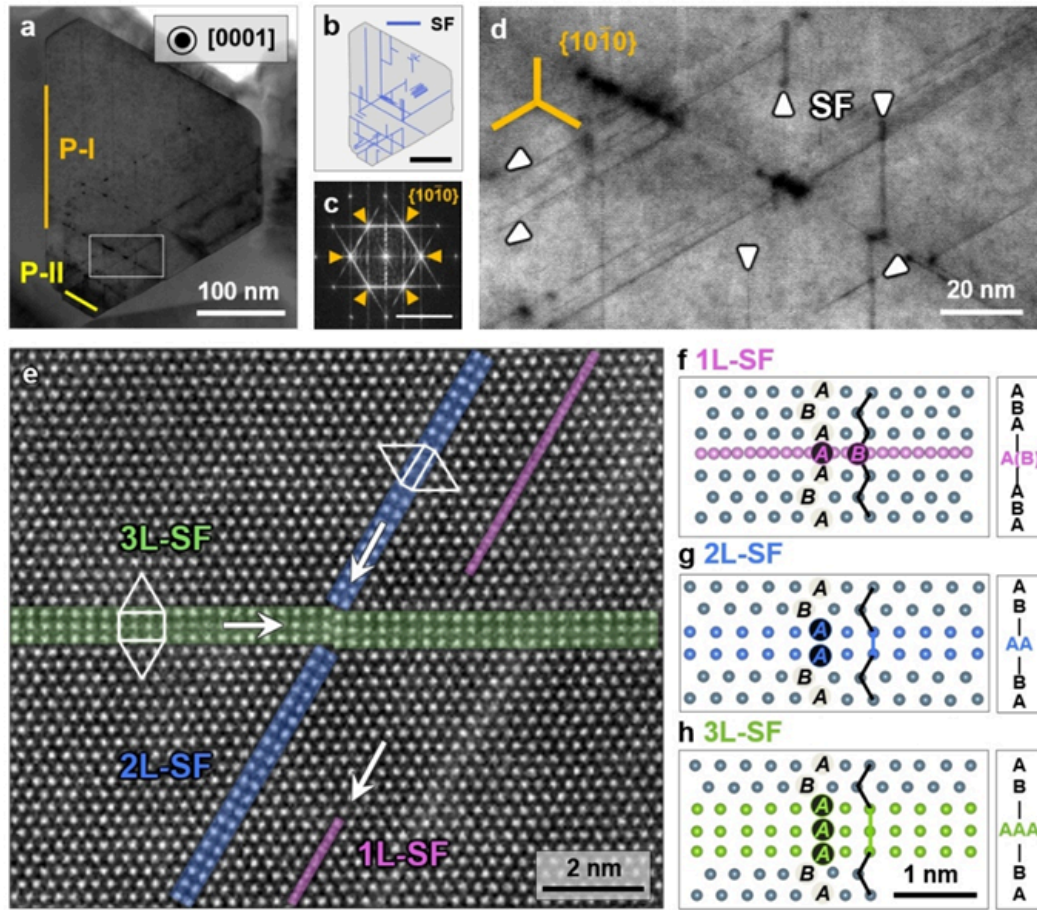


Fig. 2 | Stacking faults in a rapidly-quenched WC grain (viewed along $[0001]$ axis). Low-magnification BF image **(a)** and corresponding schematic **(b)** highlighting intragranular defect traces. **(c)** FFT (Fast Fourier Transform) from an intragranular region, where yellow arrows indicate diffraction spots of the symmetry-equivalent $\{10\bar{1}0\}$ planes. **(d)** Magnified view of the boxed region in **(a)**. Stacking-fault traces are marked by white arrows and yellow lines indicate the three equivalent $\{10\bar{1}0\}$ planes. **(e)** Atomic-resolution image showing single-layer (1L-SF, purple), double-layer (2L-SF, blue), and triple-layer (3L-SF, green) stacking faults. **(f-h)** Crystallographic models corresponding to the three fault configurations.

Figure 2

See image above for figure legend.

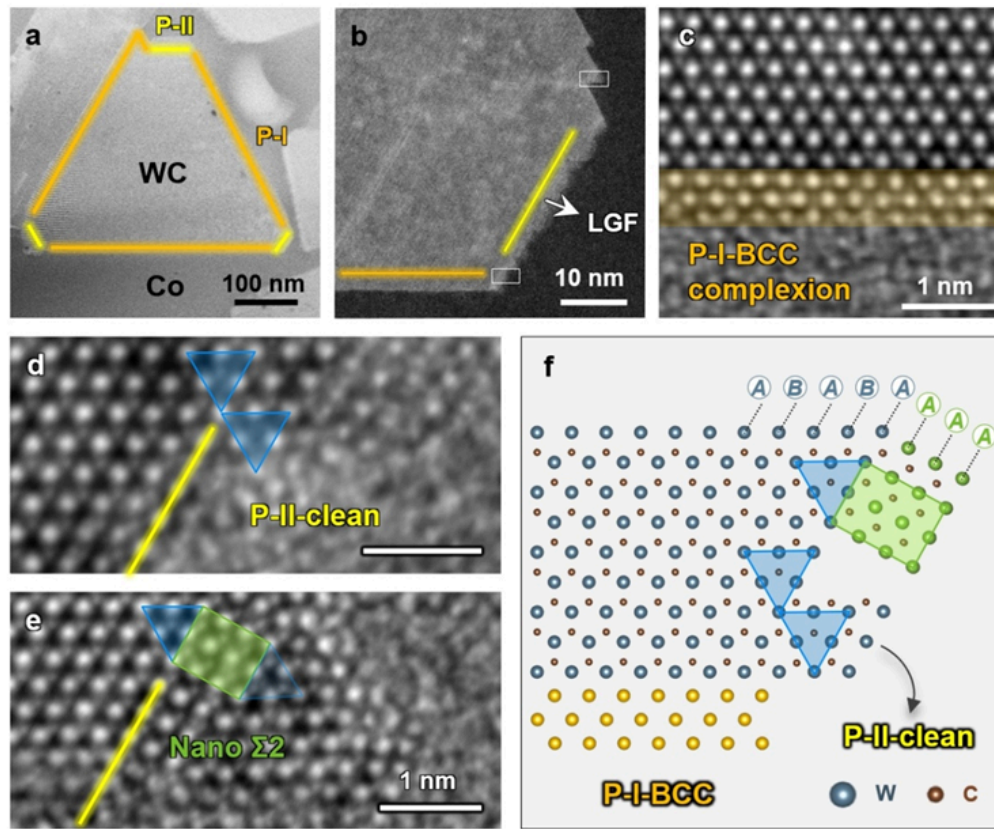


Fig. 3 | WC/Co growth front as the atomistic origin of planar defects in quenched WC grains. **a** Representative WC grain viewed along $[0001]$, with P-I (golden yellow) and P-II (yellow) facets annotated. **b** Zoomed view of the bottom-right region in (a), contrasting adjacent P-I and P-II-terminated growth fronts. The liquid-growth front was highlighted by the white arrow. **c** iDPC (integrated differential phase contrast) image of the P-I-terminated front identifying W (bright) and C (weaker) columns. The interfacial complex transition zone is highlighted by golden yellow. **d-e** Two stacking outcomes at the P-II-terminated front: either ABAB stacking is preserved during advance into the amorphous Co binder, or a local ABAB $\rightarrow$ AAA transition occurs to generate a nanoscale faulted region. The stacking can subsequently recover to ABAB, highlighting the P-II front as both a defect source and a locally self-healing interface. **f** Atomic model showing different stacking behaviors on P-I and P-II growth front (W: bluish gray, C: brown, transitional complex zone : golden yellow, nano- $\Sigma 2$ W: green).

Figure 3

See image above for figure legend.

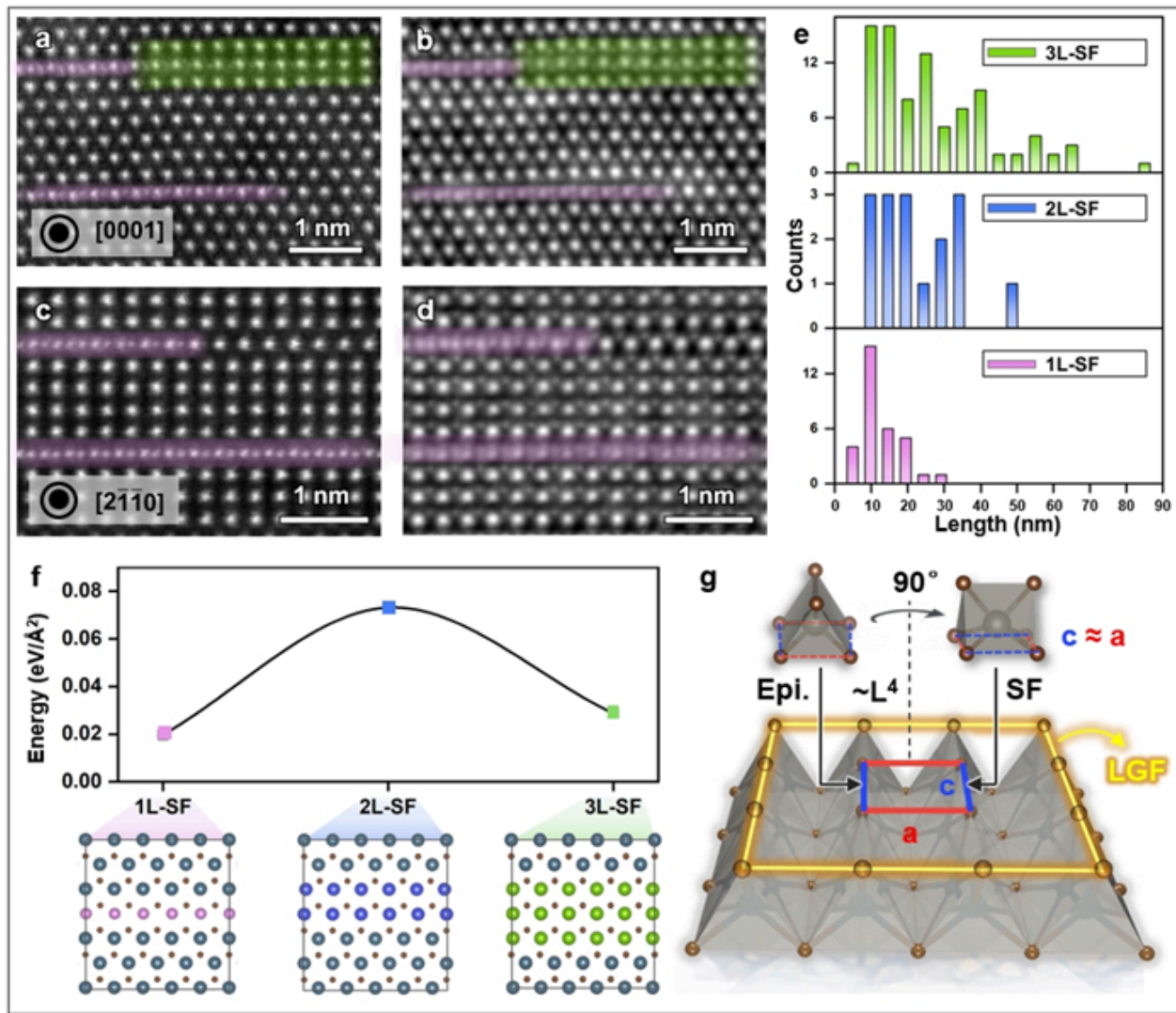


Fig. 4 | Nucleation, evolution, and stabilization of stacking faults in WC. **a-b** HAADF (high-angle annular dark-field) and iDPC imaging along [0001] showing single-layer fault annihilation and conversion toward a triple-layer fault. **c-d** $\langle 2\bar{1}\bar{1}0 \rangle$ atomic-resolution images capturing nucleation, extension, and annihilation of single-layer faults. **e** Distributions of fault length and occurrence for 1L-, 2L-, and 3L-SF. **f** Stacking fault energies of different faulted configurations. **g** Schematic of fault formation at the WC(P-II) growth front. Epi.=Epitaxial.

Figure 4

See image above for figure legend.

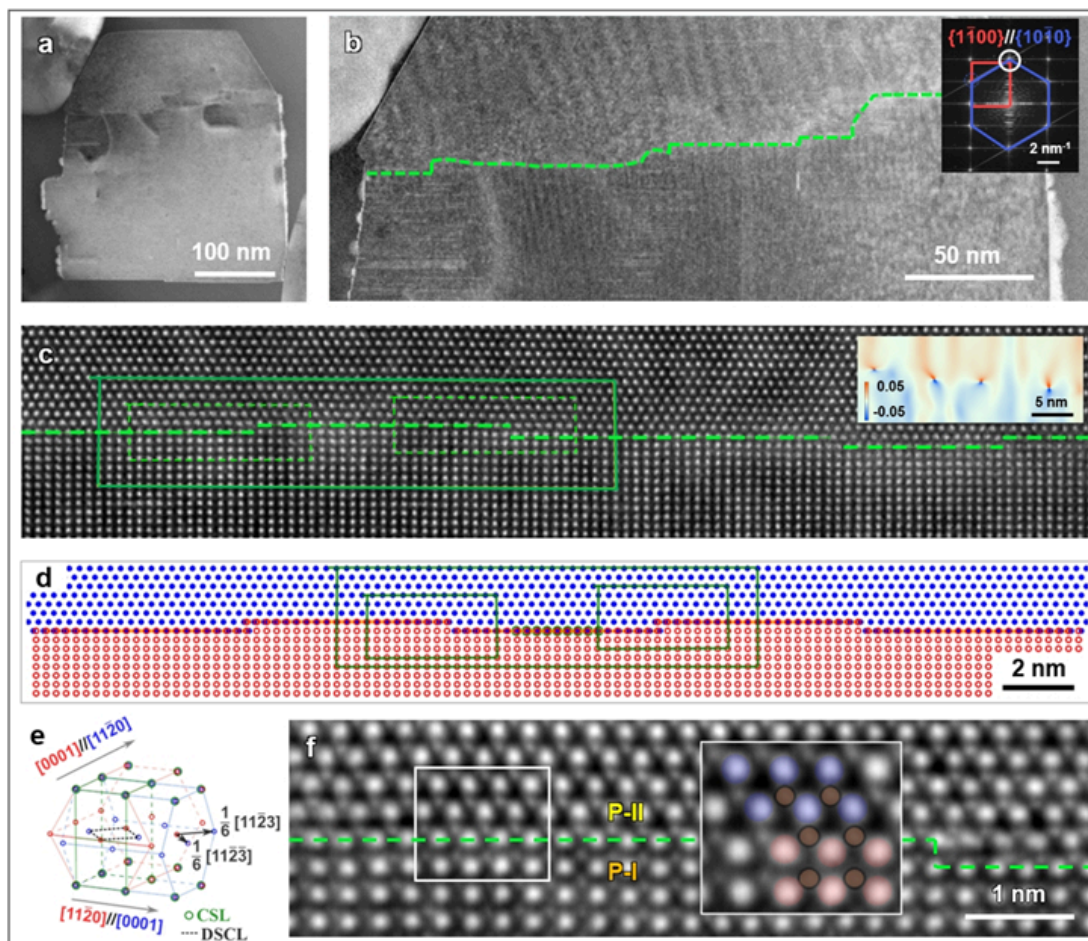


Fig. 5 | Cooperative evolution of nanoscale defects into a macroscopic $\Sigma 2$ grain boundary in WC. **a-b** HAADF overview and enlargement of a $\Sigma 2$ boundary in WC (trace in green). Inset: interfacial FFT, with blue and red marking the fundamental diffraction units for $[0001]$ and $[2\bar{1}\bar{1}0]$, respectively. **c** Atomic-resolution HAADF image of a straight $\Sigma 2$ segment revealing periodic step arrays. GPA (geometric phase analysis, inset) highlights strain localization at dislocation cores. **d** NCS (near coincidence site) model showing the coherence in the interface and the Burgers circuits for the interfacial partial dislocations associated with the interfacial steps. **e** The lattice correspondence between $\Sigma 2$ oriented grains forming the CSL/DSCL (displacement shift complete lattice). **f** iDPC image showing step-partial-dislocation cooperation in mismatch compensation.

Figure 5

See image above for figure legend.

Supplementary Files

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