

Mechanisms of Surface Degradation and Mechanical Property Deterioration in Haynes 230 Under High-Temperature Ultrahigh-vacuum

Shuting Yuan

China Institute of Atomic Energy

Wanhuan Yang

yangwanhuan@cnnmail.cn

China Institute of Atomic Energy

Jichun Zou

China Institute of Atomic Energy

Jiandong Kang

Nanchang University

Binlin Hua

Nanchang University

Yurui Chen

China Institute of Atomic Energy

Shen Li

Nanchang University

Weihua Zhong

China Institute of Atomic Energy

Wen Yang

China Institute of Atomic Energy

Research Article

Keywords: Haynes 230 alloy, High-temperature volatilization, Microstructural evolution, Tensile properties, Oxidation behavior

Posted Date: September 29th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11005889/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Mechanisms of Surface Degradation and Mechanical Property

Deterioration in Haynes 230 Under High-Temperature

Ultrahigh-vacuum

Shuting Yuan ^a, Wanhuan Yang ^{a*}, Jichun Zou ^a, Jiandong Kang ^{a,b}, Binlin Hua ^{a,b}, Yurui Chen ^a, Shen Li ^{b*}, Weihua Zhong ^{a*}, Wen Yang ^a

^a Division of Reactor Engineering Technology Research, China Institute of Atomic Energy, Beijing 102413, China

^b School of Advanced Manufacturing, Nanchang University, Nanchang 330031, China

*Corresponding authors. yangwanhuan@cnnmail.cn (W. Yang), li_shen130@163.com (S. Li), zhongwh@cnnmail.cn (W. Zhong)

Abstract: Haynes 230 alloy is widely used as a high-temperature structural material in hot-end components. To investigate the mechanisms underlying surface-defect evolution and mechanical-property degradation under high-temperature ultrahigh-vacuum conditions, exposure tests were conducted for up to 2000 h. Tensile tests were performed on as-received and exposed specimens at room temperature and 900 °C. Scanning electron microscopy (SEM) revealed selective volatilization of alloying elements from the material surface at high temperature, accompanied by M₆C carbide precipitation and grain-boundary sinking. Voids were also observed beneath the M₆C carbide precipitates, while M₂₃C₆ carbides precipitated along internal grain boundaries. After exposure, the yield strength and elongation decreased slightly at room temperature. This degradation was primarily attributed to preferential cracking of brittle M₆C carbides and debonding of M₂₃C₆ carbides from the matrix during loading, both of which promoted microcrack initiation. By contrast, pronounced mechanical degradation occurred during tensile testing at 900 °C. Cr depletion inhibited the formation of a protective oxide scale, leaving the surface susceptible to continued oxidation. Concurrently, local stress concentrations associated with grain-boundary sinking promoted preferential cracking along grain boundaries. Once initiated, the cracks propagated readily, while oxygen diffused rapidly along the grain boundaries; together, these processes severely degraded the overall mechanical performance of the alloy.

Keywords: Haynes 230 alloy, High-temperature volatilization, Microstructural evolution, Tensile properties, Oxidation behavior

1 Introduction

Typical Ni-based high-temperature structural alloys, including Haynes 230 [1, 2], Inconel 718 [3-5], Hastelloy N [6], and Inconel 617 [7, 8], face substantial challenges in terms of long-term microstructural stability and service life under extreme conditions combining temperatures of up to 900 °C with ultrahigh-vacuum ($<10^{-6}$ Pa) [9]. Such environments can cause pronounced thermal-vacuum volatilization. Previous studies have shown that Ni-based superalloys exposed to these conditions undergo substantial elemental volatilization, leading to compositional depletion, microstructural degradation, and secondary-phase precipitation

[10, 11]. During normal operation, high-power ground test facilities can maintain a closed high-vacuum environment, in which elemental volatilization is a primary mode of material degradation. Under off-design conditions, however, such as leakage or cooling-system failure, the vacuum may no longer be maintained. Critical component materials may then undergo oxidation after prolonged vacuum-induced elemental depletion. The synergistic failure mechanism arising from oxidation superimposed on volatilization-induced pre-damage remains poorly understood and therefore requires targeted experimental investigation.

The continuous volatilization of alloying elements in a high-temperature vacuum involves the loss of metal atoms from the surface in the gas phase, resulting in uniform thinning of the effective load-bearing cross-section. This process resembles the matrix consumption caused by high-temperature corrosion because both mechanisms degrade alloy performance through cross-sectional loss and surface deterioration. High-temperature oxidation and molten-salt hot corrosion are two common corrosion modes in Ni-based alloys. Sun et al. investigated the effects of high-temperature oxidation on the mechanical properties of a Ni-based alloy, while Meng et al. reported the formation of oxide scales and sulfides after molten-salt corrosion and their effects on tensile properties [12, 13]. Other studies have examined the evolution of carbides, Cr-Ni-enriched phases, and α -W phases in Ni-based alloy matrices during long-term thermal aging, together with the associated mechanisms of mechanical degradation [14-17]. Although both volatilization and corrosion cause substrate thinning, their underlying damage mechanisms differ fundamentally. During corrosion, a passivating film forms on the metal surface and can impede further penetration of the corrosive species. By contrast, volatilization involves continuous, unidirectional elemental depletion from the surface and therefore produces a distinct form of mechanical degradation. Long-term vacuum exposure has likewise been reported to alter the mechanical properties of Ni-based alloys, including Inconel 617, Haynes 230, and Haynes 188[18-20]. Their strengths decreased after exposure, whereas ductility depended on both the exposure and test temperatures. For example, the elongation of Haynes 230 decreased after vacuum exposure at 1093 K but increased when the exposure temperature was raised to 1173 K.

Haynes 230 is a solid-solution- and carbide-strengthened Ni-based superalloy with favorable high-temperature properties and high creep-rupture strength. Previous studies have shown that selective volatilization of active elements occurs at and near the surface of Haynes 230 under high-temperature, ultra-high-vacuum conditions, particularly for Cr, a key element governing oxidation resistance [21, 22]. This process redistributes elements within the surface and subsurface regions and produces a Cr-depleted transition zone in which the Cr concentration increases gradually with depth [23, 24]. The formation and long-term stability of a continuous protective Cr_2O_3 scale require an adequate Cr supply. Consequently, surface Cr depletion may suppress the development of effective oxidation protection, accelerate oxidation during subsequent exposure to an oxidizing environment, and ultimately impair the high-temperature mechanical properties of the alloy[25, 26].

Accordingly, this study investigates elemental volatilization, microstructural degradation, and the resulting changes in the mechanical properties of Haynes 230 under high-temperature ultrahigh-vacuum conditions. Thermal-vacuum exposure tests were conducted, followed by tensile testing and microstructural characterization of the exposed specimens. The objective was to clarify the microstructural evolution induced by prolonged volatilization and the

associated microscopic damage mechanisms governing tensile behavior. The results provide an experimental basis for evaluating the mechanical performance of Haynes 230 after long-term volatilization and for assessing the service performance and lifetime of key load-bearing components under accidental air-ingress conditions in high-power ground test facilities. They may also inform the design of alloys with improved resistance to volatilization.

2 Experimental Procedure

2.1 Materials and specimen preparation

The chemical composition of the Haynes 230 alloy investigated in this study is given in Table 1. Dog-bone tensile specimens were cut from sheet material by electrical discharge machining (EDM). The specimens were 0.750 mm thick, with a gauge width of 1.500 mm, a gauge length of 5.000 mm, and an overall length of 16.000 mm, as shown in Fig. 1(a). The thermal-vacuum exposure apparatus is shown in Fig. 1(b). Each specimen was placed on a holder inside a vacuum furnace. A chiller and circulating cooling water were used to cool the heating electrodes, molecular pump, and furnace body and thereby prevent overheating. Before exposure, the specimen surfaces were vibration-polished to ensure surface flatness. The specimens were then exposed for 2000 h at 900 °C under a pressure of $\leq 5 \times 10^{-6}$ Pa. The as-received specimens are hereafter designated NVT (non-volatilization-treated), and those subjected to high-temperature vacuum exposure are designated VT (volatilization-treated).

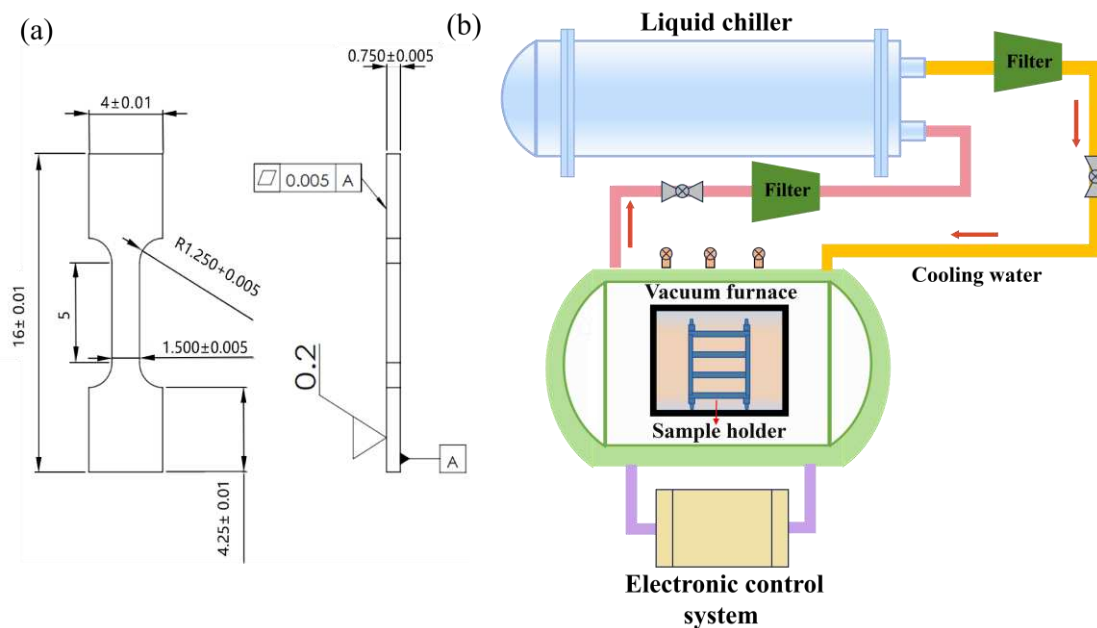


Fig. 1. (a) Geometry of the tensile specimen and (b) thermal-vacuum exposure apparatus.

Table 1. Chemical composition of Haynes 230 (wt.%).

Ni	Cr	W	Mo	Fe	Mn	Si	Al	Co	C	La	Cu	B	P	Ti	S
60.31	22.19	13.73	1.27	1.12	0.47	0.33	0.28	0.14	0.1	0.024	0.03	0.03	0.006	< 0.01	< 0.002

2.2 Tensile testing

Tensile tests were performed in air on both NVT and VT specimens at room temperature and 900 °C using a Zwick/Roell universal testing machine. For the high-temperature tests, the furnace was heated to 900 °C at 10 °C min⁻¹, and the specimens were held at this temperature

for 30 min before loading.

2.3 Microstructural characterization

Microstructural characterization and compositional analysis were performed using a field-emission scanning electron microscope (FE-SEM, ZEISS SUPRA55) equipped with an energy-dispersive X-ray spectrometer (EDX). Secondary-electron images were acquired at an accelerating voltage of 5 kV. Phase identification was performed by X-ray diffraction (XRD). Metallographic specimens were ground to a 2000-grit finish, polished using 3 and 1 μm diamond suspensions, and etched in aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$) for 15 s. Changes in surface morphology before and after exposure were examined using a laser confocal microscope (Sensofar S neox 090). Crack widths and areas were measured using ImageJ.

3 Result

3.1 Microstructural evolution under high-temperature, ultra-high-vacuum conditions

Figure 2 shows the grain-boundary morphology of the NVT alloy. In the solution-annealed condition, the material exhibits a uniform equiaxed grain structure with clean, well-defined grain boundaries and no continuous grain-boundary carbide precipitation. Numerous carbides of various sizes are distributed within the grains and along the grain boundaries. Previous studies have identified these precipitates as W-rich M_6C carbides. The elemental-distribution maps obtained by electron probe microanalysis (EPMA) are shown in Fig. 2, and the corresponding EDX results in Table 2 further support this identification. After thermal-vacuum exposure, pronounced grain-boundary sinking is observed in the VT material (Fig. 3(a)). Compared with those in the NVT material, the grain boundaries are more diffuse and less distinct. Numerous newly formed carbides are present on the surface, including fine intragranular particles and coarse blocky particles at grain boundaries (Fig. 3(b)). EDX analysis identifies the newly formed grain-boundary particles as M_6C carbides. The laser confocal microscopy images in Fig. 4(a, b) further demonstrate grain-boundary sinking in the VT material and thus reflect the volatilization-induced surface evolution [27]. In the confocal images, the grain boundaries appear blue, indicating greater material loss and the formation of distinct depressions, whereas the second-phase particles appear red because they protrude above the surrounding grain surfaces. Nine randomly selected surface regions were examined, yielding an average grain-boundary recession depth of 4.38 μm . Deep pores are also observed at the interfaces between grain-boundary second-phase particles and the matrix (Fig. 3(b)). The two profiles across a single grain boundary in Fig. 4(a), one intersecting a grain-boundary carbide and the other not, show more severe material loss where the carbide is present. Similarly, the profile across an intragranular carbide in Fig. 4(b) shows enhanced material loss at the carbide/matrix interface. Figure 4(c) compares the recession depths at grain-boundary carbide sites, carbide-free grain-boundary regions, intragranular carbide/matrix interfaces, and the surrounding matrix. Both grain boundaries and carbide/matrix interfaces therefore undergo preferential volatilization and exhibit greater depths of material loss.

The cross-sectional microstructures are shown in Fig. 3(c–e). Carbides precipitate continuously along grain boundaries within the matrix (Fig. 3(c, d)). A narrow carbide-free zone is also present near the surface of the VT material (Fig. 3(e)). Previous studies have shown that grain-boundary segregation in Ni-based superalloys becomes more pronounced with increasing thermal-exposure time. The relative concentrations of Cr, W, and Mo affect

the types of secondary carbides that form. According to the empirical criterion in Ref. [28], the carbide type can be predicted using the parameter C_R , defined as follows:

$$C_R = \frac{Cr \text{ at } \%}{(Cr + Mo + 0.7W) \text{ at } \%} \quad (1)$$

When $C_R > 0.82$, only Cr-rich $M_{23}C_6$ carbides precipitate. The nominal composition of the Haynes 230 alloy used here gives a C_R value of 0.867, exceeding the threshold of 0.82. Together with the EDX results in Table 3, this value identifies the carbide phase as Cr-rich $M_{23}C_6$.

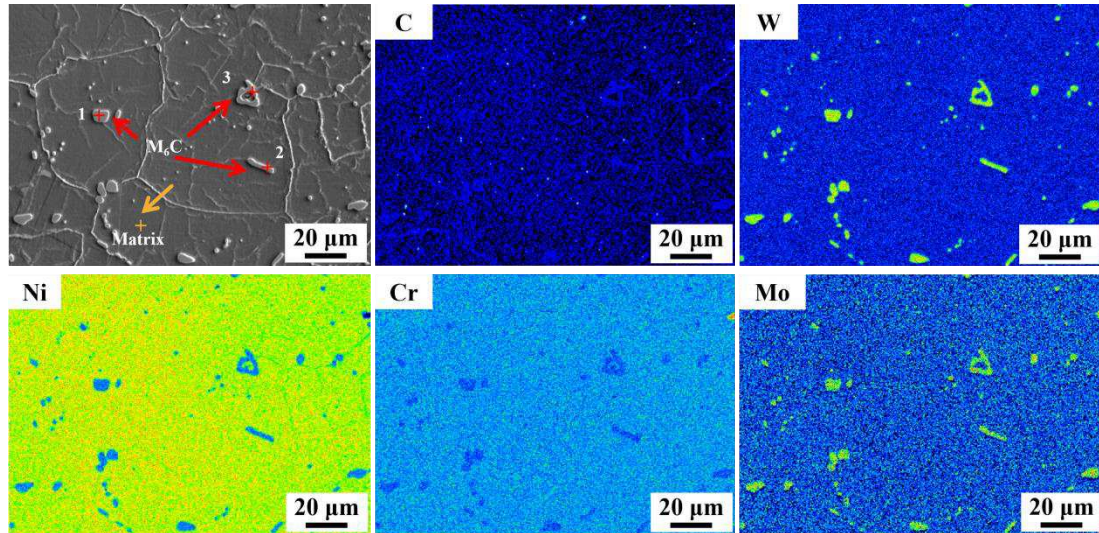


Fig. 2. SEM images and EPMA elemental-distribution maps of the NVT material.

Table 2. EDX results for the locations marked in Fig. 2

Location	Elements composition (at%)					Type of carbides
	Ni	W	C	Cr	Mo	
1	31.28	31.06	8.49	22.51	4.32	M_6C
2	30.75	31.50	9.05	22.21	4.04	M_6C
3	30.71	31.15	8.32	22.81	4.53	M_6C

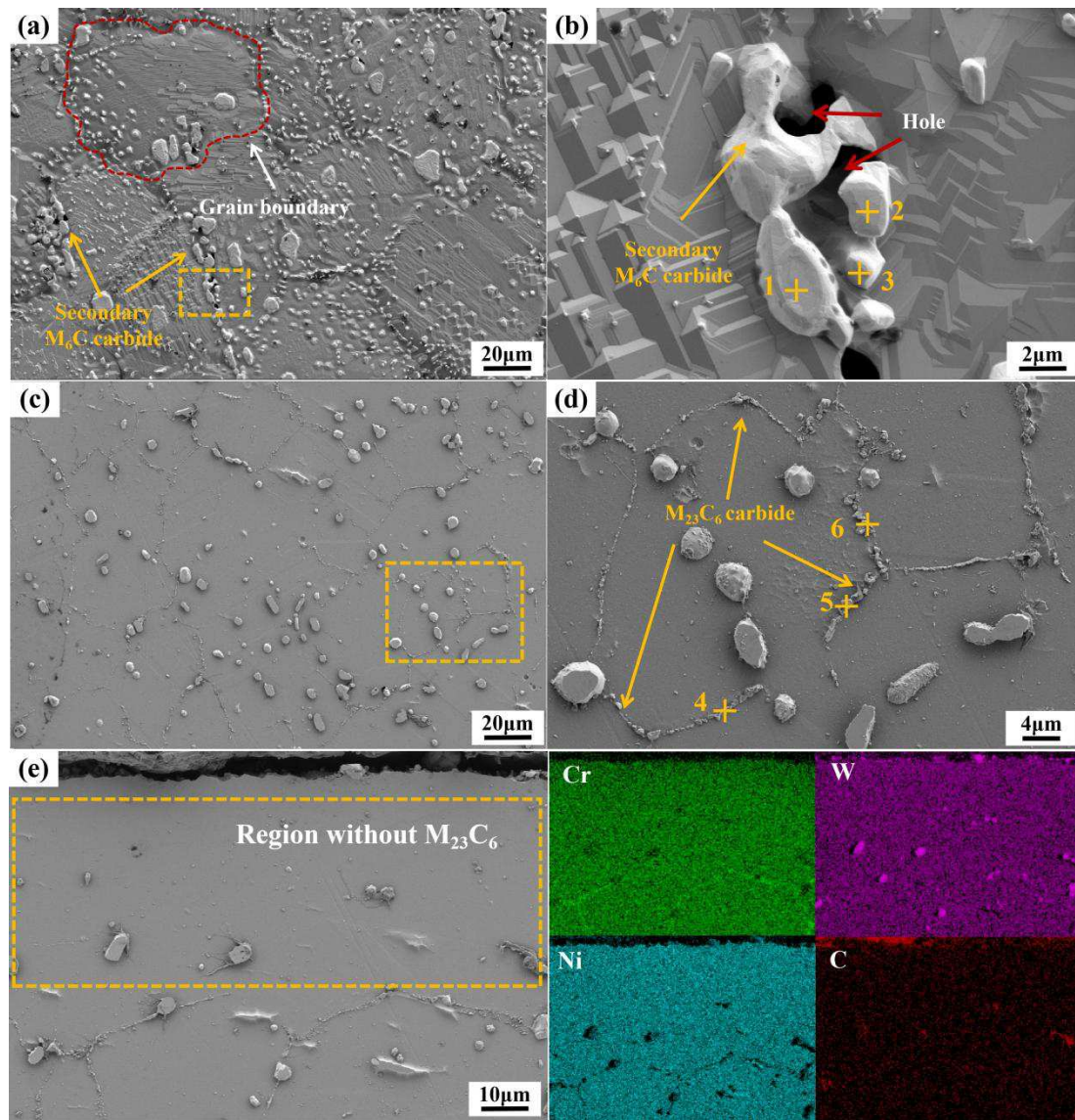


Fig. 3. (a) SEM image of the surface microstructure of the VT material; (b) enlarged view of the grain-boundary pores in (a); (c) cross-sectional SEM image of the VT material; (d) enlarged view of the yellow-boxed region in (c); and (e) cross-sectional SEM image and EDX elemental maps of the near-surface region.

Table 3. EDX results for the locations marked in Fig. 3(b, d)

Location	Elements composition (at%)					Type of carbides
	Ni	W	C	Cr	Mo	
1	30.26	27.65	35.42	3.00	3.67	M ₆ C
2	29.61	27.65	35.58	3.11	4.06	M ₆ C
3	24.73	24.57	44.28	2.57	3.85	M ₆ C
4	12.29	4.34	45.16	38.21	0	M ₂₃ C ₆
5	45.25	4.57	24.81	25.30	0.07	M ₂₃ C ₆
6	15.38	5.30	35.89	43.29	0.14	M ₂₃ C ₆

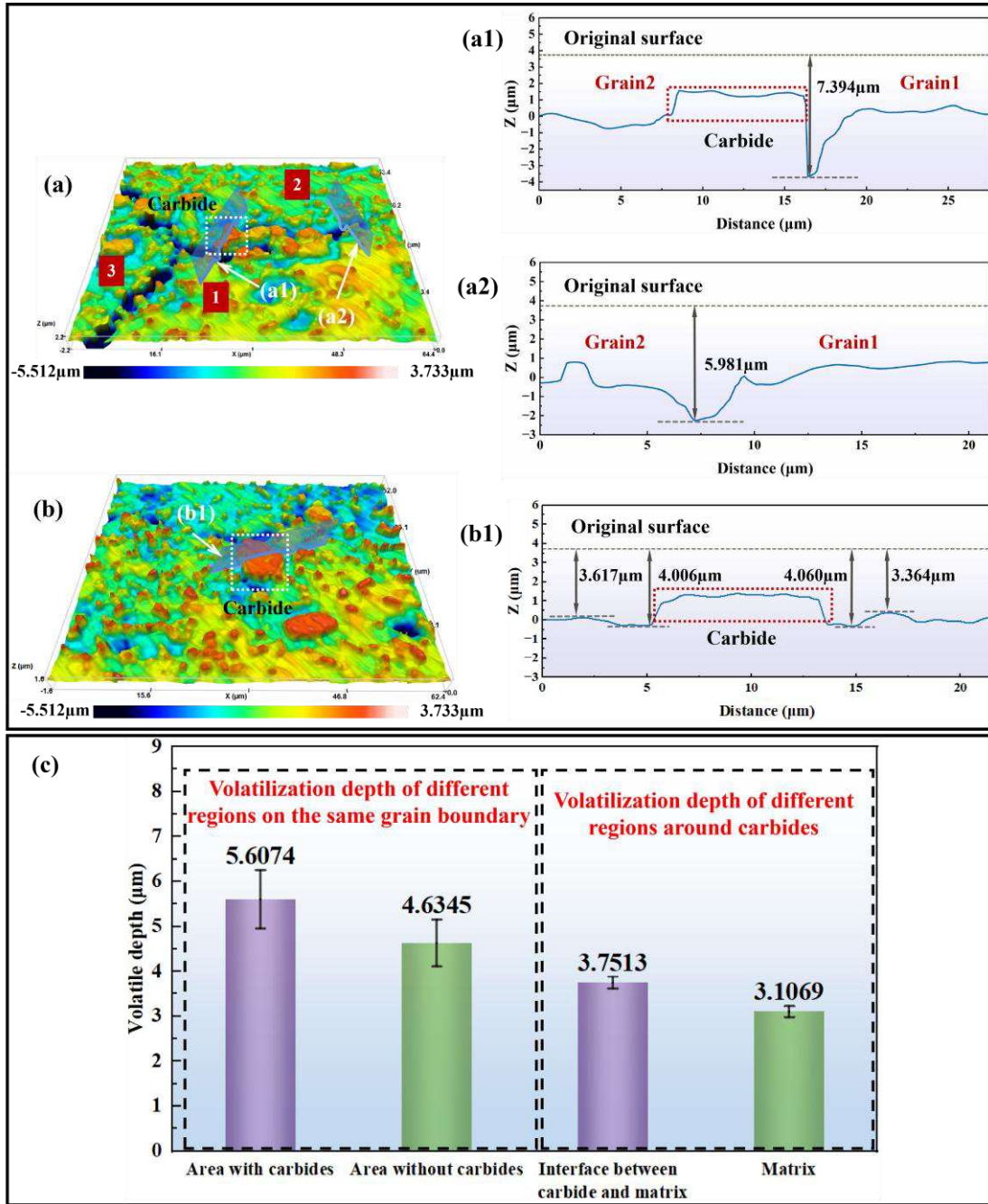


Fig. 4. (a,b) Laser confocal 3D reconstructions of selected regions of the VT material (color bars indicate height in μm). Profiles (a1) and (a2) correspond to two sections across the grain boundary in (a), with (a1) intersecting a carbide and (a2) not intersecting a carbide. Profile (b1) corresponds to a section across an intragranular carbide in (b). (c) Statistical comparison of recession depths at grain boundaries, carbide/matrix interfaces, and within grains.

3.2 Changes in tensile properties after high-temperature, ultra-high-vacuum exposure

The tensile stress–strain curves of the NVT and VT materials are shown in Fig. 5(a), and the corresponding strengths and elongations are summarized in Fig. 5(b). Table 4 lists the yield strength (YS), ultimate tensile strength (UTS), and elongation (EI) for both conditions at room temperature and 900 °C. Relative to the NVT material, the VT material shows decreases

in YS, UTS, and EI at both test temperatures. At room temperature, YS decreases from 404 to 347 MPa (14%), UTS from 861 to 837 MPa (3%), and EI from 49% to 41% (16%). At 900 °C, the deterioration is more pronounced: YS, UTS, and EI decrease by 31%, 24%, and 22%, respectively, relative to the corresponding NVT values. Thus, prior volatilization causes substantial degradation of the high-temperature tensile properties.

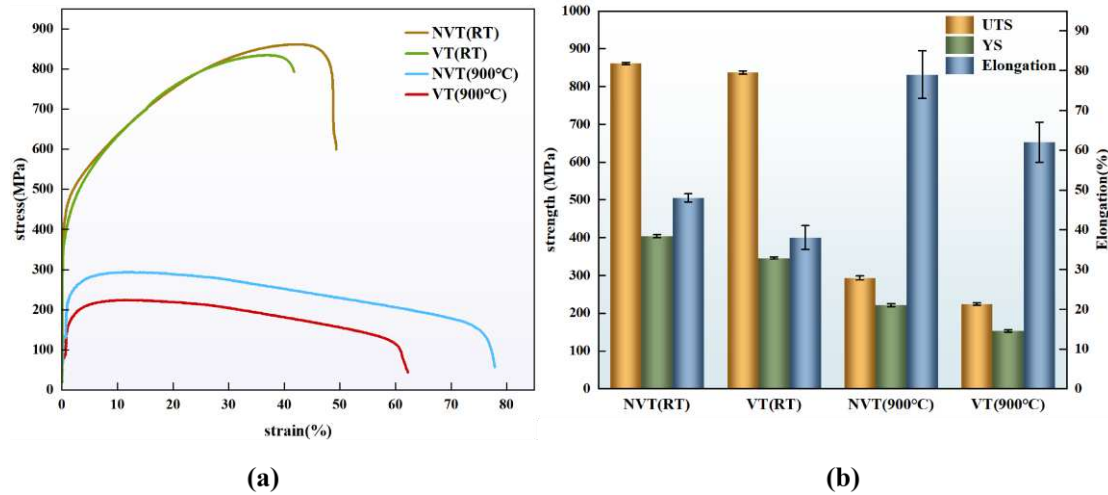


Fig. 5. (a) Tensile stress–strain curves and (b) yield strength, ultimate tensile strength, and elongation of the NVT and VT materials at room temperature and 900 °C.

Table 4. Mechanical properties of the NVT and VT materials at room temperature and 900 °C.

T(°C)	Sample	YS(MPa)	UTS(MPa)	EI(%)
RT	NVT	404±4	861±3	49±1
	VT	347±3	837±4	38±3
900°C	NVT	221±4	293±5	79±6
	VT	153±3	224±3	62±5

3.3 Surface morphology of the tensile gauge sections

Figure 6 shows SEM images of the gauge-section surfaces of the NVT and VT specimens after room-temperature tensile testing. Both specimen types exhibit pronounced necking, and the regions adjacent to the fracture surfaces show typical planar slip features. Numerous cracks are present on both surfaces. In the VT material, the surface microcracks are primarily associated with two damage modes: fracture of brittle carbides and interfacial debonding between the carbides and matrix.

Figure 7 shows SEM images of the gauge-section surfaces after tensile testing at 900 °C. In the NVT material, surface cracks are concentrated mainly within the necked region (Fig. 7(a)). They are short and serrated and propagate at approximately 45° to the tensile axis. By contrast, cracks are distributed throughout the gauge section of the VT specimens (Fig. 7(b)). These cracks can be classified broadly as deep intergranular cracks along grain boundaries or shallow, strip-like transgranular cracks within grains. The number and total area of cracks wider than 10 μm were quantified in three regions: region 1 near the grip, region 2 at the center of the fractured specimen, and region 3 near the fracture surface (Fig. 7(a, b)). Crack width was defined as the maximum width of each crack, and the statistical results are presented in Fig. 10(a, c, d). The surface crack-area fraction is substantially higher for the VT

specimens than for the NVT specimens. Numerous intergranular cracks are also present near the grip of the VT specimens. The VT specimens contain a larger proportion of wide cracks: in region 3, their widths are concentrated mainly in the ranges of 30–40 μm and $> 40 \mu\text{m}$, whereas those in the NVT specimens are predominantly 10–20 μm . The difference is even more pronounced in regions 1 and 2. In the NVT specimens, cracks in region 2 occur only in the 10–20 and 20–30 μm ranges, and no cracks wider than 10 μm are detected in region 1.

Figure 8 presents macroscopic images and laser-confocal three-dimensional (3D) reconstructions of the NVT and VT specimens tested at room temperature. The NVT specimen (Fig. 8(a)) exhibits gradual variations in surface height and a continuous, regular shear slope at the fracture edge. Its limited height variation, low roughness, and uniformly distributed slip traces indicate homogeneous plastic flow during tensile deformation. By contrast, the VT specimen (Fig. 8(b)) exhibits a nonuniform height distribution, with pronounced local depressions and steep shear offsets near the fracture surface. Its overall surface-height variation is also substantially greater. Irregular micropits in some regions suggest that volatilization-induced changes in surface structure or composition promoted localized plastic deformation during tensile loading. Nevertheless, the overall ductile fracture mode remained unchanged. Figure 9 presents macroscopic images and laser-confocal 3D reconstructions of the NVT and VT specimens tested at 900 °C. The reconstructions and profiles across the cracks show that the NVT surface near the fracture is relatively flat, with uniformly distributed contour variations (Fig. 9(a)). By contrast, the intergranular cracks in the VT specimen are substantially deeper and have wider openings (Fig. 9(b)). High-temperature volatilization under ultrahigh-vacuum therefore intensified surface damage and promoted deeper crack propagation during high-temperature tensile deformation. Crack depths were quantified in six surface regions of both specimen types (Fig. 9(a, b)); for Regions 5 and 6 of the VT specimen, the measured depth corresponds to grain-boundary sinking. As shown in Fig. 10(b), intergranular cracks are substantially deeper in the VT specimen than in the NVT specimen, and their depth increases progressively toward the fracture surface.

Together, the crack-area fraction, width, and depth measurements indicate that surface grain boundaries in the VT specimens are preferential sites for crack initiation and constitute the principal weak links during tensile deformation.

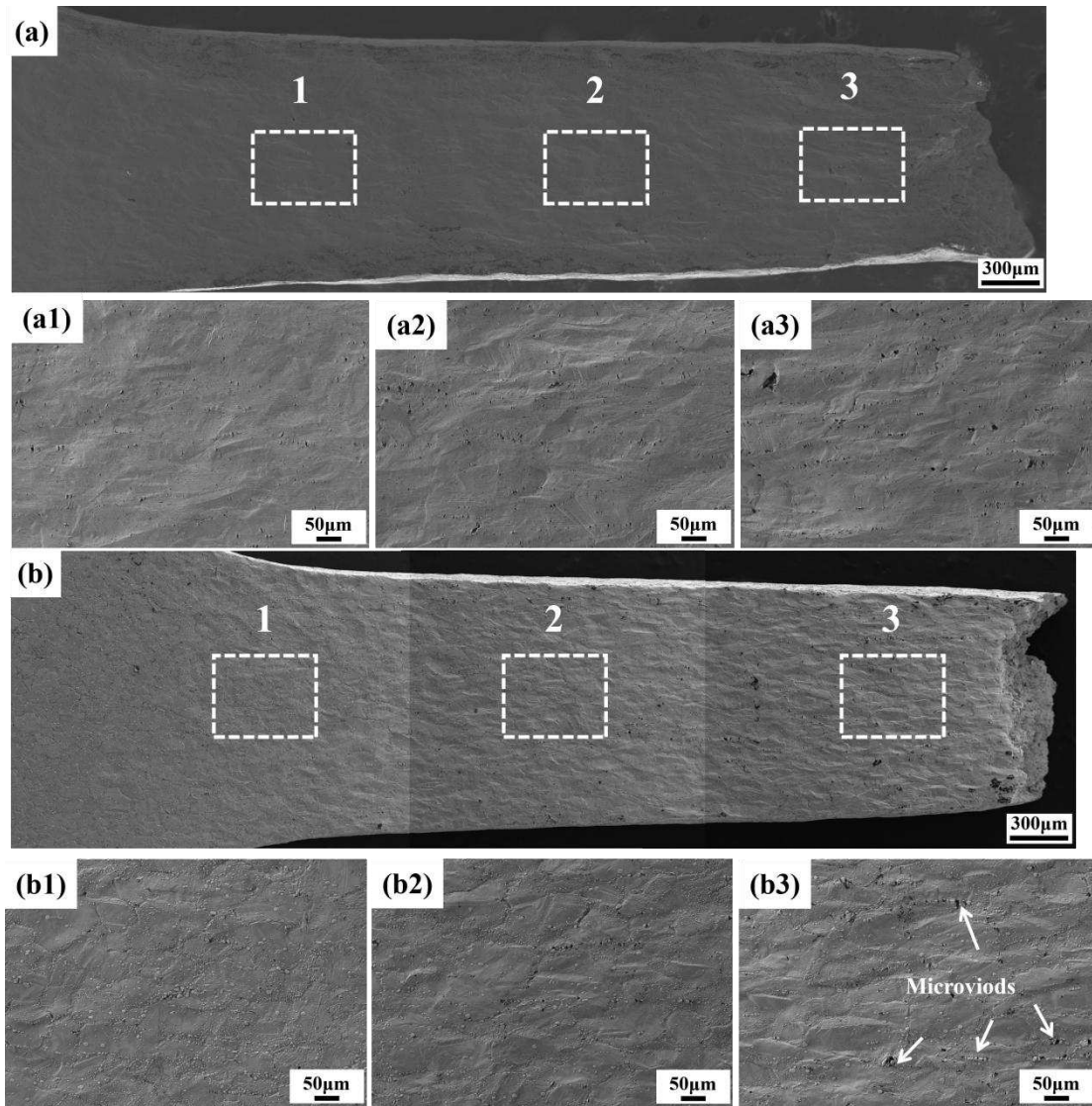


Fig. 6. SEM micrographs of the gauge section surface after room-temperature tensile testing: (a) NVT specimen, with (a1, a2, a3) showing Regions 1, 2, and 3 indicated in (a), respectively; (b) VT specimen, with (b1, b2, b3) showing Regions 1, 2, and 3 indicated in (b), respectively.

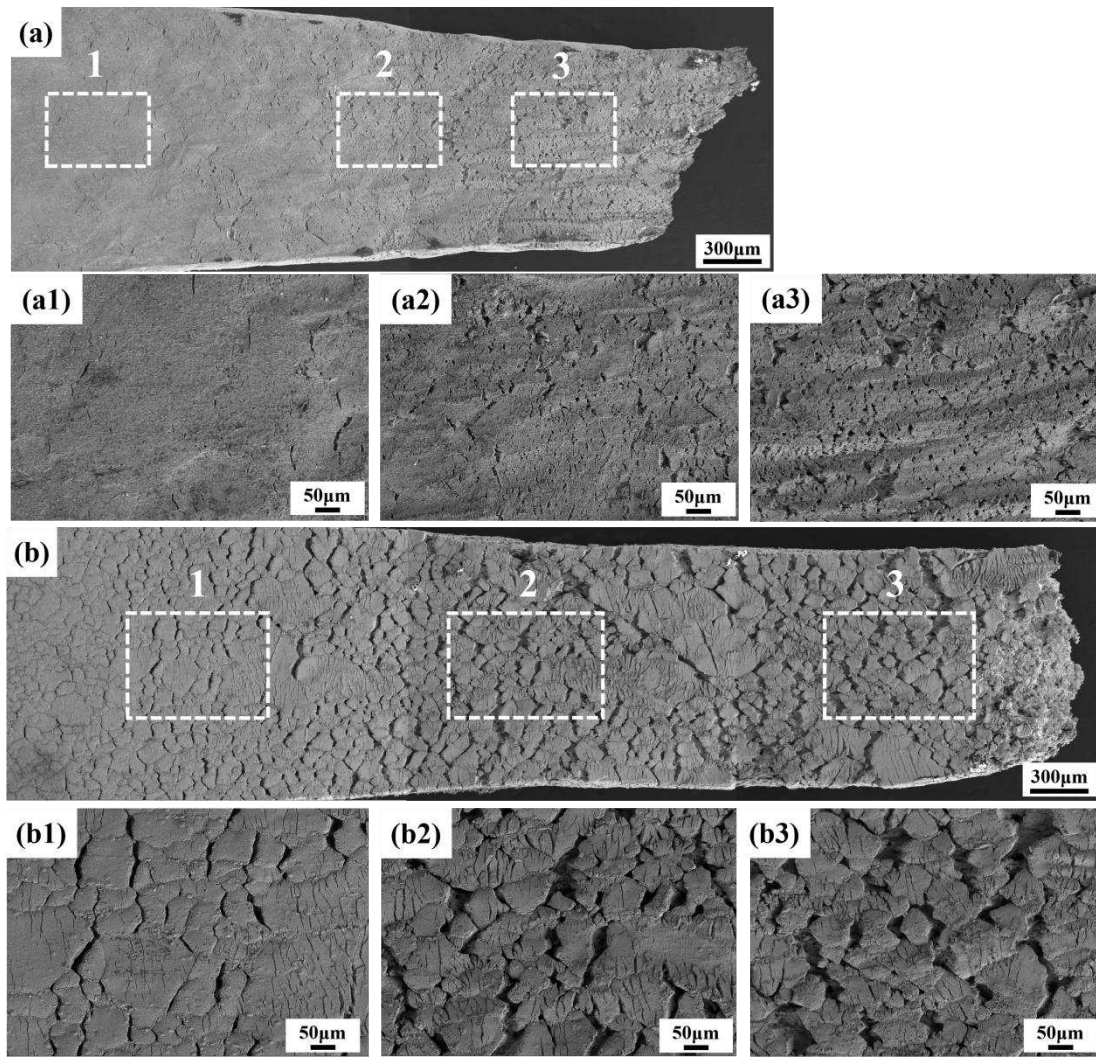


Fig. 7.

SEM micrographs of the gauge section surface after tensile testing at 900 °C: (a) NVT specimen, with (a1, a2, a3) showing Regions 1, 2, and 3 indicated in (a), respectively; (b) VT specimen, with (b1, b2, b3) showing Regions 1, 2, and 3 indicated in (b), respectively.

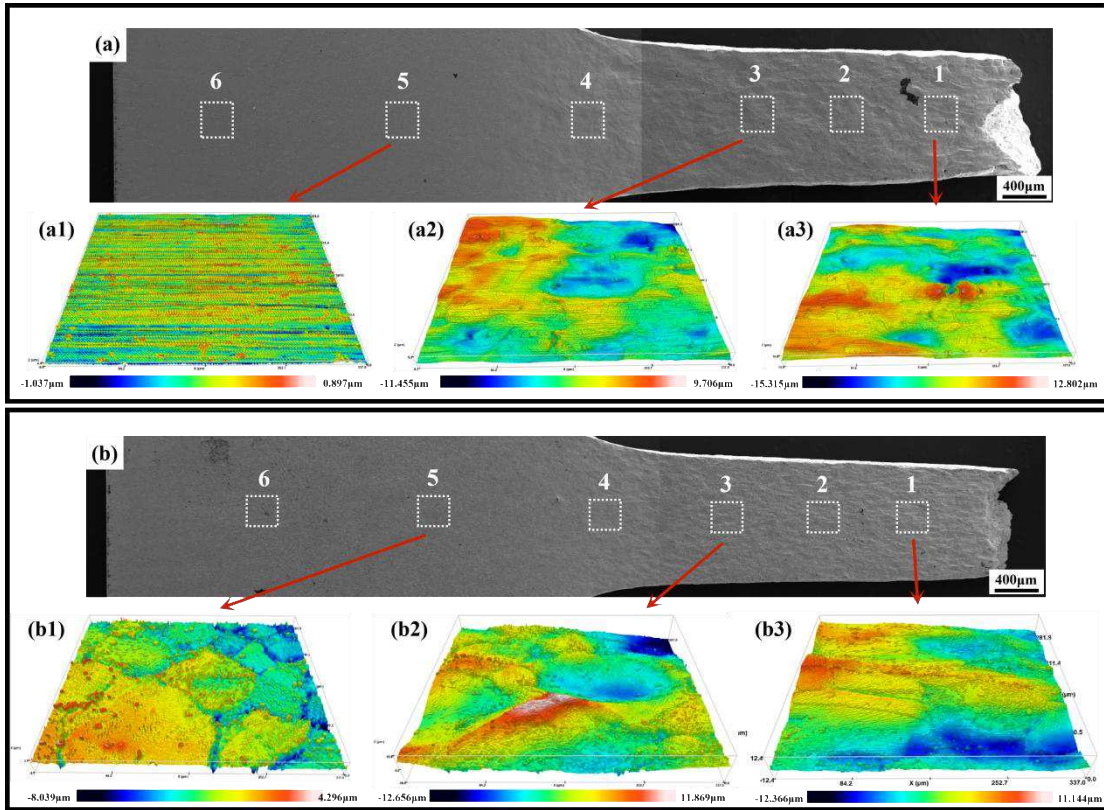


Fig. 8.

Macroscopic surface morphologies of (a) NVT and (b) VT specimens after room-temperature tensile testing.

White boxes denote the regions selected for crack depth statistics. (a1, a2, a3) Laser confocal 3D reconstructions of Regions 5, 3, and 1 in (a), respectively (color bars represent height in μm); (b1, b2, b3) Laser confocal 3D reconstructions of Regions 5, 3, and 1 in (b), respectively (color bars represent height in μm).

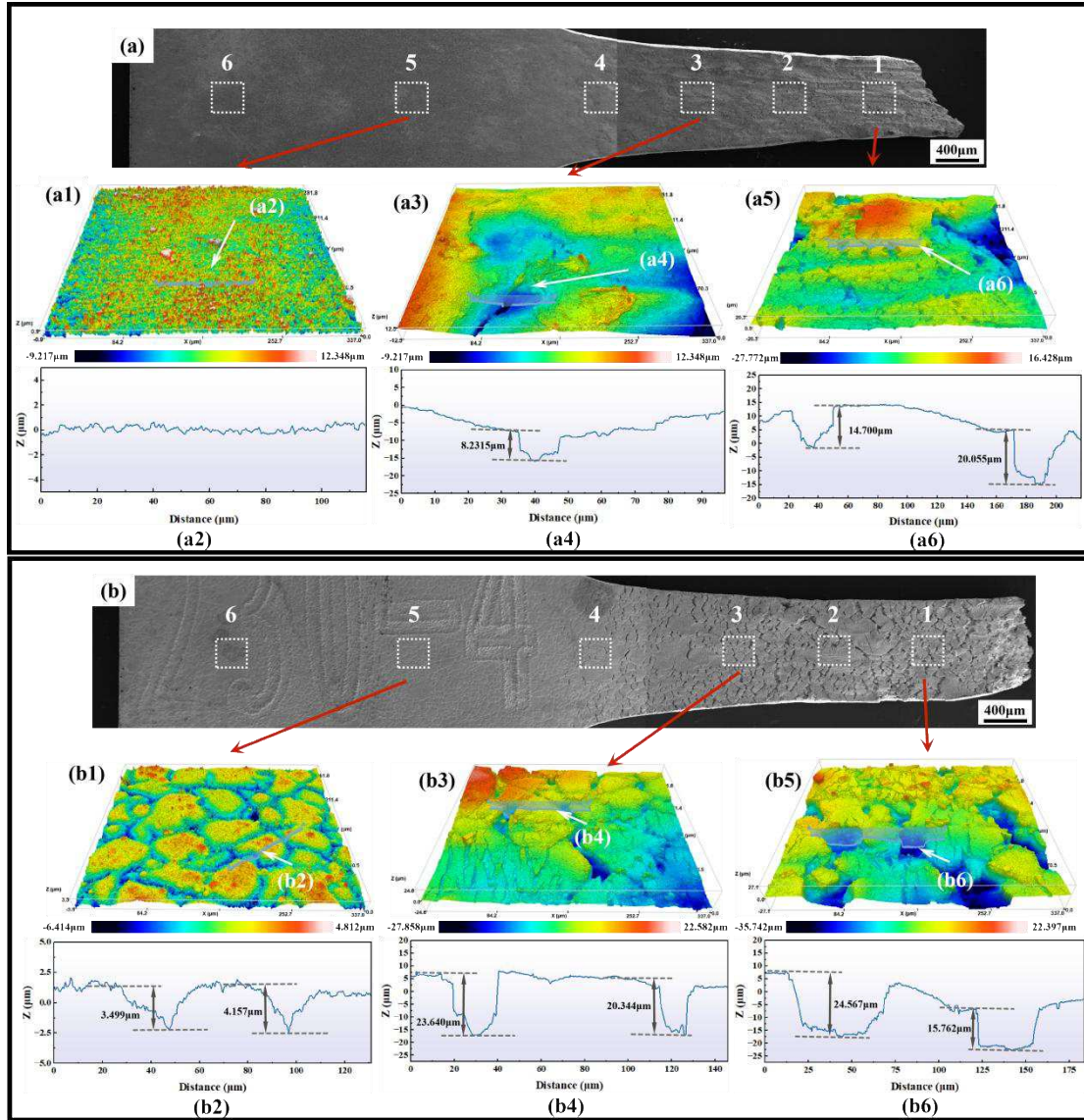


Fig. 9 Macroscopic surface morphologies of (a) NVT and (b) VT specimens after tensile testing at 900 °C.

The white boxes indicate the regions selected for crack depth statistics. (a1, a3, a5) Laser confocal 3D reconstructions of Regions 5, 3, and 1 in (a), respectively (color bars represent height in μm). (a2, a4, a6) Cross-sectional profile waveforms along lines traversing the cracks in the corresponding regions. (b1, b3, b5) Laser confocal 3D reconstructions of Regions 5, 3, and 1 in (b), respectively (color bars represent height in μm). (b2, b4, b6) Cross-sectional profile waveforms along lines traversing the cracks in the corresponding regions.

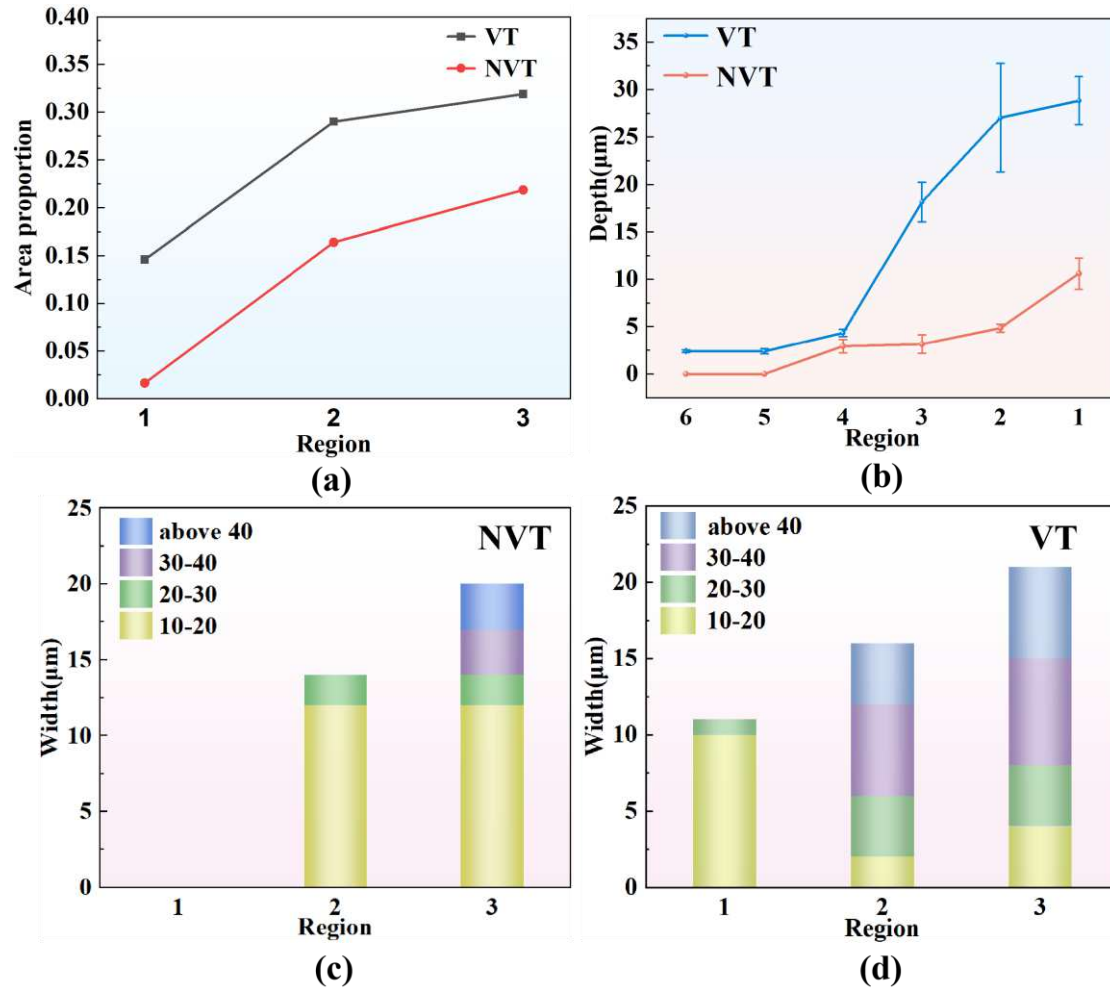


Fig. 10. (a) Surface crack-area fraction and (c, d) crack-width distributions in the three regions marked in Fig. 7 after tensile testing at 900 °C; (b) average surface crack depth in the six regions marked in Fig. 9.

3.4 Fracture-surface characterization

Figure 11 shows the room-temperature tensile fracture surfaces of the NVT and VT materials. Both contain numerous equiaxed circular or elliptical dimples of various sizes (Fig. 11(b, e)). Carbide particles are present within the dimples, and EDX analysis (Fig. 11(c)) identifies them as M_6C carbides. These particles evidently fractured during tensile deformation. Both fracture surfaces display transgranular, dimpled features characteristic of predominantly ductile fracture. Unlike the NVT material, however, the VT material exhibits elongated strip-like cracks that are morphologically distinct from the surrounding dimples. EDX analysis (Fig. 11(f)) shows that these cracks are surrounded by Cr-rich $M_{23}C_6$ carbides.

Figure 12 shows the fracture surfaces of the NVT and VT materials tested at 900 °C. Both exhibit necking, consistent with an overall ductile fracture mode. The NVT material displays well-defined fibrous zones and shear lips, suggesting that cracks initiated near the specimen center and propagated outward to form the fibrous zone, followed by shear instability near the surface. Its large, deep dimples (Fig. 12(b)) indicate substantial local plastic deformation before fracture. The VT material also exhibits distinct fibrous zones and shear lips, although the shear lips are asymmetric (Fig. 12(c)). This asymmetry suggests that cracking initiated at the end with the less-developed shear lip. Local cleavage facets (Fig.

12(e)) and limited intergranular features (blue circles in Fig. 12(c)) occur at this end, and fan-shaped markings on the facets extend inward from the surface. These observations further support surface crack initiation at the less-developed shear lip. Intergranular features are also evident at the nearby fracture front (Fig. 12(f)), indicating predominantly brittle crack initiation with minimal plastic deformation. As the crack propagated inward, the fracture mode gradually changed from brittle cleavage to ductile fracture, as indicated by the appearance of dimples. However, the dimples in the VT material are smaller than those in the NVT material, suggesting that microvoid coalescence occurred before the voids had fully grown. Final fracture occurred at the more-developed shear lip, indicating that the remaining cross-section sustained a high shear stress and underwent substantial localized plastic flow before final instability. Overall, fracture of the VT material progressed from brittle initiation through mixed-mode propagation to ductile instability.

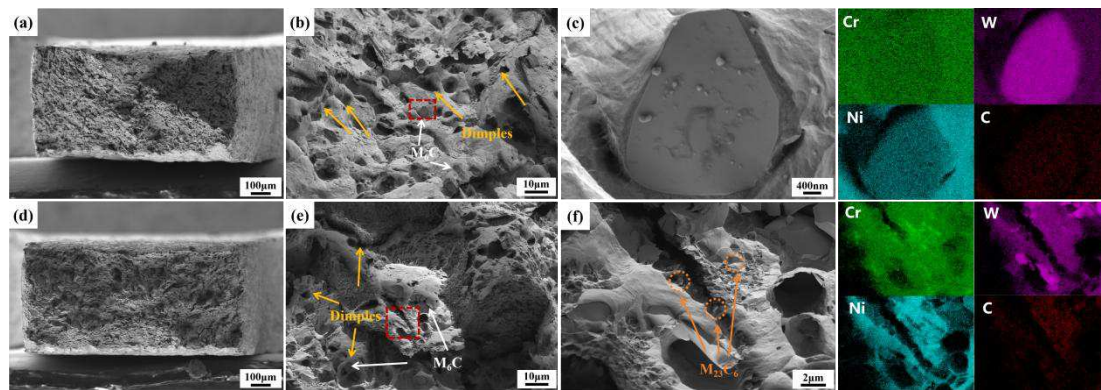


Fig. 11. SEM micrographs and EDX analyses of room-temperature tensile fracture surfaces at different magnifications: (a–c) NVT specimen and (d–f) VT specimen. (b, e) Higher-magnification views showing ductile dimples on the fracture surfaces; (c, f) Enlarged views and corresponding EDX spectra of the red-boxed regions in (b) and (e), respectively. The dimples in the NVT fracture surface (b) contain M_6C particles, whereas cracks on the VT fracture surface (f) are associated with $M_{23}C_6$ particles.

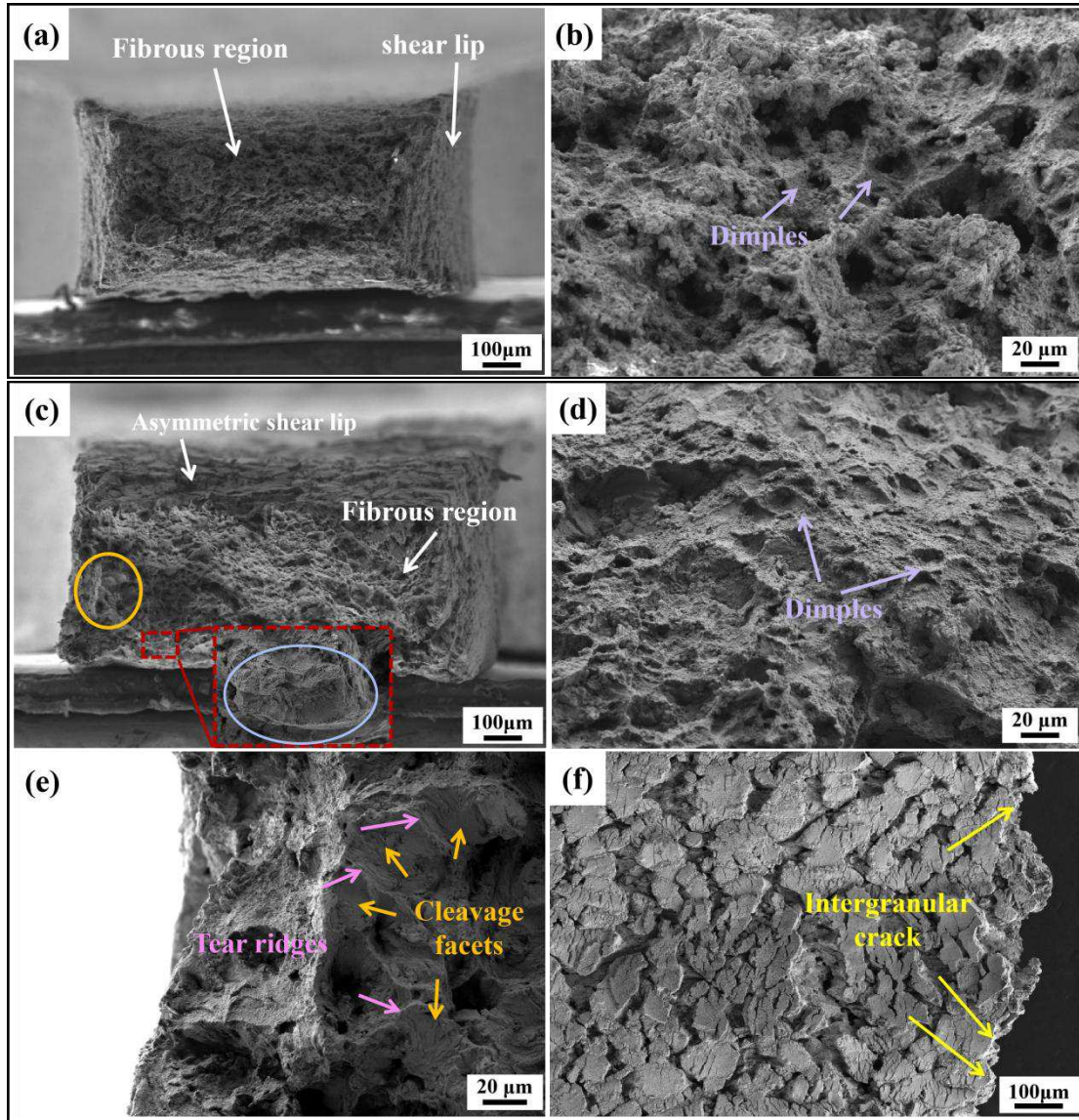


Fig. 12. SEM micrographs at different magnifications of the fracture surfaces after tensile testing at 900 °C: (a–b) NVT specimen and (c–f) VT specimen. (b) Ductile dimples on the NVT fracture surface, which are larger and deeper than those observed on the VT fracture surface (d). (e) Cleavage facets in the yellow-circled region in (c). (f) Fracture front of the VT specimen.

4 Discussion

4.1 Formation of surface defects in Haynes 230 during high-temperature volatilization under ultrahigh-vacuum

As shown in Fig. 3, prolonged exposure of Haynes 230 to a high-temperature, ultra-high-vacuum environment causes substantial microstructural changes in the surface region, including grain-boundary sinking, increased surface-carbide precipitation, deep pores around carbide particles, and a near-surface carbide-free zone. Under these conditions, Ni and Cr volatilize preferentially because of their higher saturated vapor pressures. By contrast, W has a substantially lower volatilization rate and is largely retained in the matrix. The volatilization rates of metallic elements in a high-temperature vacuum can be described by the

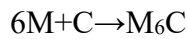
following relationships [29-34] :

$$\lg P = A + B/T + C \lg T + 10^{-3}DT \quad (2)$$

$$W_m = (P\sqrt{m}) / \sqrt{2\pi kT} \quad (3)$$

Where W_m is the mass volatilized per unit area per unit time ($\text{g cm}^{-2} \text{s}^{-1}$), m is the mass of one atom (kg), A , B , C , and D are element-specific parameters, and k is the Boltzmann constant. The saturated vapor pressures, P , of Ni, Cr, and W at $T = 1173 \text{ K}$ (900°C) were substituted into Eq. (2) to calculate their volatilization rates. The relevant parameters and calculated values are summarized in Table 5. At 900°C , the volatilization rates of Ni and Cr are many orders of magnitude higher than that of W.

Grain boundaries provide short-circuit pathways for atomic transport; consequently, volatile elements, particularly Ni and Cr, migrate to the surface much more rapidly along grain boundaries than through the grain interiors. The lower binding energy of atoms at grain boundaries also facilitates their detachment from the solid and transfer into the gas phase. Meanwhile, continuous pumping under ultrahigh-vacuum removes the volatilized atoms and prevents gas-phase re-equilibration. Elemental loss therefore occurs preferentially at grain boundaries, producing grain-boundary sinking. As volatilization proceeds, Ni and Cr are depleted continuously, whereas less-volatile elements such as W become relatively enriched at surface grain boundaries. This enrichment promotes precipitation of W-rich M_6C carbides at surface grain boundaries according to the following proposed reaction:



M_{23}C_6 is a Cr-rich carbide that normally precipitates at grain boundaries. The substantial loss of Ni and Cr during volatilization, together with preferential grain-boundary volatilization, disrupts the thermodynamic equilibrium of the near-surface region. Consequently, M_{23}C_6 does not form in this region, resulting in a narrow carbide-free zone. Selective volatilization of Ni and Cr also establishes steep concentration gradients from the interior toward the surface. Because Ni and Cr volatilize much more rapidly than refractory elements such as W, the resulting imbalance in diffusional flux causes vacancies to accumulate near the surface. Once supersaturated, these vacancies aggregate preferentially at low-barrier nucleation sites, particularly grain boundaries and carbide/matrix interfaces. Their continued aggregation and coalescence ultimately produce observable microscopic voids.

Table 5. Parameters for Ni, Cr, and W and their calculated volatilization rates at 900°C

Element	A	B	C	D	$W_m/\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$	$W_m/\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$
Ni	10.557	-22606	-0.8717	0	4.03536E-11	1.45273E-7
Cr	6.800	-20733	0.4391	-0.4094	9.17008E-10	3.30123E-6
W	2.945	-44094	1.3677	0	6.25076E-30	2.25315E-26

4.2 Effects of microstructural evolution on the mechanical properties of Haynes 230

At room temperature, fracture is governed primarily by M_6C carbides. Microvoids nucleate and grow through debonding at M_6C /matrix interfaces and subsequently coalesce through microshear-band formation. During low-temperature tensile deformation, dislocations cannot shear the M_6C particles; instead, they bypass or climb over them and accumulate at the carbide/matrix interfaces. The resulting dislocation pile-ups produce local stress concentrations and ultimately fracture the M_6C particles under tensile loading [35]. The

susceptibility of carbide particles to cracking increases with particle size. As shown in Fig. 3, numerous coarse M_6C particles are distributed at surface grain boundaries and within grains in the VT material and therefore influence its room-temperature mechanical properties. Numerous grain-boundary microcracks are also present. The EDX maps in Fig. 13(d) show Cr-rich $M_{23}C_6$ carbides in these cracked regions, while the fracture surface in Fig. 11 contains large cracks at interfaces between the Cr-rich carbides and matrix. During tensile loading, continuous grain-boundary $M_{23}C_6$ carbides promote micropore formation and crack propagation [36], thereby reducing both the tensile ductility and strength of Haynes 230.

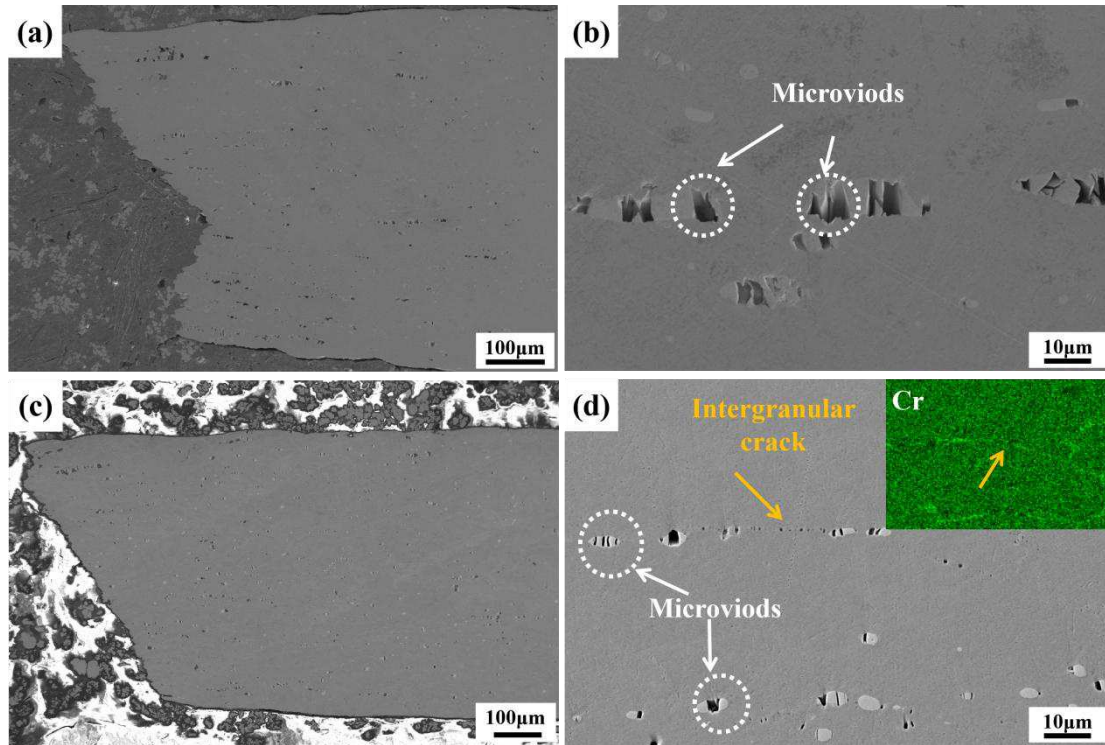


Fig. 13. Axial sections of specimens after room-temperature tensile testing: (a) NVT specimen and (b) enlarged view of (a); (c) VT specimen and (d) enlarged view of (c).

The cracks on the gauge-section surface of the NVT specimens tested at 900 °C are short, serrated shear cracks, indicating ductile fracture. The abundant dimples on the fracture surface further demonstrate extensive plastic deformation and microvoid coalescence, consistent with the stress–strain curves. At 900 °C, the deformation mechanism changes and grain-boundary strength decreases markedly. Under high-temperature tensile conditions, cracks are concentrated predominantly at the specimen surface (Fig. 15). In the VT specimens, surface grain-boundary sinking produces local stress concentrations during loading. The intergranular cracks propagate approximately perpendicular to the tensile axis and are substantially deeper than the strip-like intragranular cracks (Fig. 9(b6)). Thus, the recessed surface grain boundaries act as preferential sites for stress concentration and crack initiation, reducing both elongation and tensile strength.

Oxygen has a pronounced detrimental effect on the high-temperature mechanical properties of Ni-based alloys. Proposed oxidation-induced damage mechanisms include the formation of brittle external and internal oxides, vacancy injection [37], CO or CO₂ bubble formation [38], and the release of embrittling alloying elements at grain boundaries [39, 40].

At 900 °C, substantial brittle oxides form on the specimen surfaces, as confirmed by the EDX point analyses in Fig. 14 and Table 6. The oxide scale on the VT material exhibits a more pronounced spinel structure. Oxidized Haynes 230 typically develops an outer spinel Cr_2MnO_4 layer and an inner dense Cr_2O_3 layer [41, 42], with Cr_2O_3 providing the principal protection. The XRD patterns in Fig. 14(c) show both Cr_2O_3 and Cr_2MnO_4 on the VT surface, whereas neither phase is detected on the NVT surface, possibly because the oxide content is below the XRD detection limit. Oxide-scale thicknesses were quantified from the EDX line scans in Fig. 15. For the NVT material, the surface and fracture-surface scales (Fig. 15(c, d)) are 0.8198 and 0.6017 μm thick, respectively. Their difference indicates that approximately 0.2181 μm of oxide formed during heating. For the VT material, the corresponding thicknesses (Fig. 15(g, h)) are 3.4142 and 2.0578 μm , giving a difference of 1.3564 μm . The scale on the VT material is therefore substantially thicker. It also has a distinct layered structure, comprising a loose upper spinel layer and a lower layer that is less strongly bonded to the matrix than that in the NVT material. Such a loose scale can severely degrade tensile properties [43]. During heating before tensile testing, the NVT material rapidly forms a dense Cr_2O_3 scale that suppresses inward oxygen diffusion. Prior volatilization, however, substantially depletes Cr from the VT surface, preventing rapid formation of a dense scale and allowing continued oxygen ingress. Re-establishing a protective Cr_2O_3 scale requires accelerated outward diffusion of Cr from the matrix. This redistribution, coupled with rapid oxidation, produces the much thicker scale observed in Fig. 15(f). During tensile deformation, the metallic matrix deforms plastically, whereas the brittle oxide scale has a much lower fracture strain. The scale therefore cracks at low strain, producing microcracks that penetrate the underlying matrix and act as initiation sites for macroscopic cracks. Grain boundaries also provide rapid oxygen-diffusion pathways. In the VT material, recessed grain boundaries are directly exposed to the atmosphere, accelerating oxygen ingress and oxidation. The combined effects of grain-boundary stress concentration and preferential oxidation promote intergranular crack initiation and propagation, thereby severely degrading high-temperature mechanical performance. Figure 16 schematically summarizes the microstructural evolution and corresponding changes in the mechanical properties of Haynes 230.

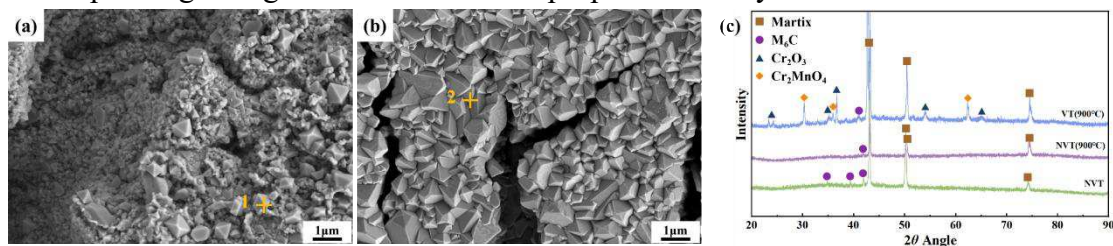


Fig. 14. Surface morphologies of the (a) NVT and (b) VT materials after tensile testing at 900 °C.

Table 6. Surface EDX point analyses of the NVT and VT materials after tensile testing at 900 °C, corresponding to Fig. 14.

Location	Elements composition (at%)					
	O	Cr	Ni	Mn	W	Mo
1	34.33	40.14	23.75	1.04	0.38	0.35
2	25.26	2.23	71.52	0.16	0.74	0.14

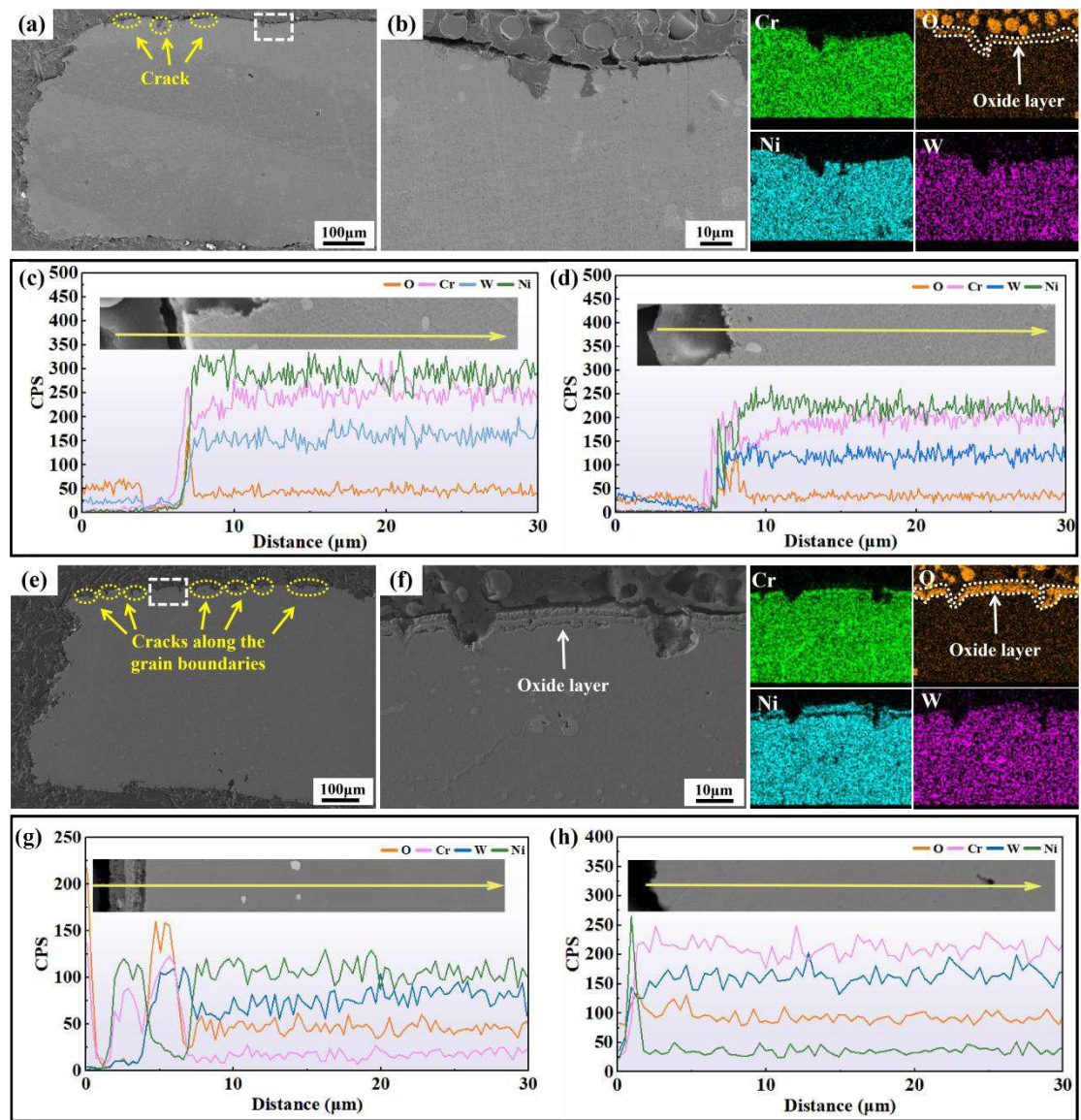


Fig. 15. NVT material: (a) axial-section micrograph after tensile testing at 900 °C; (b) enlarged view and EDX elemental map of the region in (a); and (c,d) EDX line scans across the specimen surface and fracture surface, respectively. VT material: (e) axial-section micrograph after tensile testing at 900 °C; (f) enlarged view and EDX elemental map of the region in (e); and (g,h) EDX line scans across the specimen surface and fracture surface, respectively.

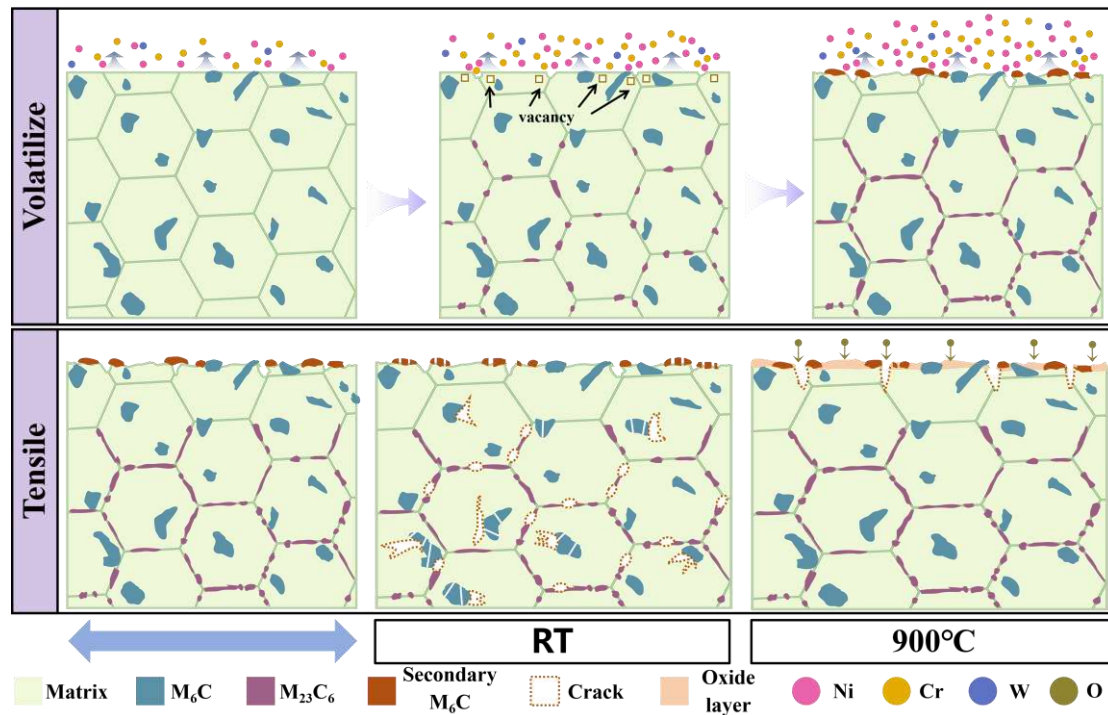


Fig. 16. Schematic illustration of the microstructural evolution and changes in mechanical properties. The arrows indicate the tensile direction.

5 Conclusions

- (1) At 900 °C under ultrahigh-vacuum, rapid grain-boundary diffusion and the relatively high volatility of Ni and Cr, together with continuous pumping, cause preferential elemental loss. The resulting grain-boundary sinking and vacancy accumulation ultimately lead to pore formation.
- (2) Volatilization-induced depletion of Ni and Cr causes relative W enrichment near the surface and promotes M₆C carbide precipitation at grain boundaries. Meanwhile, suppression of near-surface M₂₃C₆ precipitation produces a carbide-free zone, further modifying the surface microstructure.
- (3) At room temperature, the VT material exhibits decreases of 14% in yield strength and 16% in elongation relative to the NVT material. Continuous M₂₃C₆ carbides along grain boundaries facilitate microcrack propagation during tensile deformation and contribute to this degradation.
- (4) At 900 °C, the VT material exhibits decreases of 31%, 24%, and 22% in yield strength, ultimate tensile strength, and elongation, respectively. Prior Cr depletion prevents the rapid formation of a dense protective oxide scale and permits oxygen ingress along grain boundaries, while grain-boundary sinking produces local stress concentrations. Together, these effects make the weakened grain boundaries preferential sites for intergranular cracking under tensile loading.

CRedit authorship contribution statement

Shuting Yuan: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Wanhuan Yang:** Writing – review & editing, Conceptualization, Supervision, Project administration, Funding acquisition. **Jichun Zou:** Writing – review & editing. **Jiandong Kang:** Writing – review & editing. **Binlin Hua:** Writing – review & editing. **Yurui Chen:** Writing – review & editing. **Shen Li:** Writing – review & editing, Conceptualization, Supervision. **Weihua Zhong:** Writing – review & editing, Conceptualization, Supervision, Project administration, Funding acquisition. **Wen Yang:** Conceptualization, Supervision, Writing – review & editing.

Data availability

All relevant data that support this study cannot be shared at this time as the data also forms part of an ongoing study. Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the financial support of the CNNC Science Fund for Talented Young Scholars (Grant No. FY020270624941), the CIAE Science Fund for Talented Young Scholars (Grant No. YC020260424195), the National Defense Basic Research Program (JCKY2024201C005), Young Elite Scientists Sponsorship Program of the Beijing High Innovation Plan (Grant NO. 20251048).

References

- [1] H.M. Tawancy, High temperature creep behaviour of an Ni-Cr-W-B alloy, *Journal of Materials Science*, 27 (1992) 6481–6489.
- [2] T. Zhou, H. Ding, X. Ma, W. Feng, H. Zhao, A. Li, Y. Meng, H. Zhang, Effect of precipitates on high-temperature tensile strength of a high W-content cast Ni-based superalloy, *Journal of Alloys and Compounds*, 797 (2019) 486–496.
- [3] T.D. McLouth, D.B. Witkin, J.R. Lohser, S.D. Sitzman, P.M. Adams, Z.R. Lingley, G.E. Bean, J.-M. Yang, R.J. Zaldivar, Temperature and strain-rate dependence of the elevated temperature ductility of Inconel 718 prepared by selective laser melting, *Materials Science and Engineering: A*, 824 (2021) 141814.
- [4] S. Zhang, L. Wang, X. Lin, H. Yang, W. Huang, The formation and dissolution mechanisms of Laves phase in Inconel 718 fabricated by selective laser melting compared to directed energy deposition and cast, *Composites Part B: Engineering*, 239 (2022) 109994.
- [5] J.-R. Zhao, F.-Y. Hung, T.-S. Lui, Microstructure and tensile fracture behavior of three-stage heat treated inconel 718 alloy produced via laser powder bed fusion process, *Journal of Materials Research and Technology*, 9 (2020) 3357–3367.
- [6] W.R. Martin, J.R. Weir, Effect of Elevated-Temperature Irradiation on Hastelloy N, *Nuclear Applications*, 1 (1965) 160–167.
- [7] S. Chomette, J.M. Gentzittel, B. Viguier, Creep behaviour of as received, aged and cold worked INCONEL 617 at 850°C and 950°C, *Journal of Nuclear Materials*, 399 (2010) 266–274.
- [8] H. Jiang, J. Dong, M. Zhang, Phase transformation of alloy 617B during 10000 h aging: An element redistribution-related process, *Journal of Alloys and Compounds*, 765 (2018) 586–594.

- [9] W. Yang, J. Zou, S. Li, D. Gao, X. Zhao, Y. Chen, S. Yuan, J. Kang, B. Hua, Z. Shen, W. Zhong, Microstructure-dependent volatilization of haynes 230 alloy in ultrahigh vacuum at high temperatures, *Corrosion Science*, 265 (2026) 113821.
- [10] H. Wang, N. D'Souza, S. Zhao, D. Welton, N. Warnken, R.C. Reed, Effects of elemental vaporization and condensation during heat treatment of single crystal superalloys, *Scripta Materialia*, 78-79 (2014) 45–48.
- [11] J.D. Whittenberger, Effect of Long-Term 1093 K Exposure to Air or Vacuum on the Structure of Several Wrought Superalloys, *Journal of Materials Engineering and Performance*, 2 (1993) 745–758.
- [12] X. Meng, S. Lyu, X. Xie, C. Tang, W. Yu, W. Hou, C. Wang, J. Qu, J. Du, Hot Corrosion Behavior and Damage Mechanism on Yield Property of Nickel-Based Superalloy, in: *Materials*, 2025, pp. 1749.
- [13] B. Sun, T. Zhang, L. Song, L. Zhang, Oxidation behavior in static air and its effect on tensile properties of a powder metallurgy EP962NP nickel-based superalloy, *Journal of Alloys and Compounds*, 934 (2023) 167795.
- [14] H.J. Lee, H. Kim, D. Kim, C. Jang, Microstructure evolution of a Ni–Cr–W superalloy during long-term aging at high temperatures, *Materials Characterization*, 106 (2015) 283–291.
- [15] D. Kim, I. Sah, C. Jang, Effects of high temperature aging in an impure helium environment on low temperature embrittlement of Alloy 617 and Haynes 230, *Journal of Nuclear Materials*, 405 (2010) 9–16.
- [16] D. Kim, I. Sah, C. Jang, Effects of aging in high temperature helium environments on room temperature tensile properties of nickel-base superalloys, *Materials Science and Engineering: A*, 528 (2011) 1713–1720.
- [17] R. Luo, Q. Liu, P. Gao, T. Liu, H. Ding, D. Zhang, Y. Cao, X. Cheng, Effect of microstructural evolution and mechanical properties of Haynes 230 superalloy during long-term aging at 700 °C, *Journal of Alloys and Compounds*, 947 (2023) 169495.
- [18] J.D. Whittenberger, 77 to 1200 K tensile properties of several wrought superalloys after long-term 1093 K heat treatment in air and vacuum, *Journal of Materials Engineering and Performance*, 3 (1994) 91–103.
- [19] J.D. Whittenberger, Tensile properties of haynes alloy 230 and inconel 617 after long exposures to LiF-22CaF₂ and vacuum at 1093 K, *Journal of Materials Engineering and Performance*, 3 (1994) 763–774.
- [20] J.D. Whittenberger, Tensile Properties and Structure of Several Superalloys after Long- Term Exposure to LiF and Vacuum at 1173 K, *Journal of Materials Engineering and Performance*, 4 (1995) 657–673.
- [21] S. Niu, K. Yin, Q. You, X. You, Y. Wang, Y. Tan, The alloying elements dispersion and its mechanisms in a Ni-based superalloy during electron beam remelting, *Vacuum*, 166 (2019) 107–113.
- [22] X. You, S. Shi, Y. Tan, L. Zhao, J. Zheng, X. Zhuang, Y. Li, Q. You, P. Li, W. Long, The evaporation behavior of alloy elements during electron beam smelting of Inconel 718 alloy, *Vacuum*, 169 (2019) 108920.
- [23] A. Stupnik, P. Frank, M. Leisch, Atom probe, AFM, and STM studies on vacuum-fired stainless steels, *Ultramicroscopy*, 109 (2009) 563–567.
- [24] D.T. Bourgette, Evaporation of Iron-, Nickel-, and Cobalt-Base Alloys at 760 to 980°C in High Vacuums, Oak Ridge National Laboratory, (1964).
- [25] T. Yao, M. Wang, X. Xi, Z. Nie, High-temperature oxidation behavior of self-passivating W-xCr-Al alloys with different Cr contents, *Journal of Alloys and Compounds*, 1051 (2026) 185994.
- [26] K. Esleben, B. Gorr, H.J. Christ, D. Mukherji, J. Rösler, Effect of Different Cr and Ni Additions on Oxidation Behavior of Co-Re-Based Alloys, *JOM*, 72 (2020) 393–402.
- [27] J. Zou, S. Chen, Z. Shen, X. Zhao, J. Gao, Z. Wang, M. Wang, K. Cai, S. Li, W. Yang, W. Zhong, W. Yang, Intragranular corrosion behavior of 310S austenitic stainless steel in supercritical carbon dioxide environments, *Journal of Materials Research and Technology*, 36 (2025) 3227–3239.
- [28] Y. Han, X. Xue, T. Zhang, R. Hu, J. Li, Grain boundary character correlated carbide precipitation and mechanical properties of Ni-20Cr-18W-1Mo superalloy, *Materials Science and Engineering: A*, 667 (2016) 391–401.

- [29] I. Langmuir, The Vapor Pressure of Metallic Tungsten, *Physical Review*, 2 (1913) 329–342.
- [30] Y. Li, X. Wang, F. Wang, Y. Tian, B. Yang, Volatilization behavior of impurities in molybdenum concentrate through vacuum distillation, *Vacuum*, 199 (2022) 110926.
- [31] A.M. Mikhailov, K.A. Zubarev, G.I. Kotel'nikov, A.E. Semin, K.V. Grigorovich, Vaporization of the components of nickel alloys in a vacuum induction furnace, *Steel in Translation*, 46 (2016) 26–28.
- [32] N. Xiong, Y. Tian, B. Yang, B.-Q. Xu, D.-C. Liu, Y.-N. Dai, Volatilization and condensation behaviours of Mg under vacuum, *Vacuum*, 156 (2018) 463–468.
- [33] Q. You, S. Shi, X. You, Y. Tan, Y. Wang, J. Li, Evaporation behavior of Ni, Cr and Fe in Inconel 718 superalloy during electron beam smelting, *Vacuum*, 135 (2017) 135–141.
- [34] C.B. Alcock, *Thermochemical Processes, Biorefineries*, 2001.
- [35] G. Bai, J. Li, R. Hu, Z. Tang, X. Xue, H. Fu, Effect of temperature on tensile behavior of Ni–Cr–W based superalloy, *Materials Science and Engineering: A*, 528 (2011) 1974–1978.
- [36] X. Li, M. Ou, X. Yu, X. Hao, Y. Ma, Effect of C Content on the Microstructure and Stress Rupture Properties of Nickel-Based Superalloy K4750, *Journal of Materials Engineering and Performance*, 32 (2023) 7322–7336.
- [37] M.C. Pandey, P. Rama, On the Less Known Effects of Environment and Specimen Geometry on Creep Fracture of Nickel Alloys, *Defence Journal*, 40 (2013).
- [38] R.P. Oleksak, C.S. Carney, G.R. Holcomb, Ö.N. Doğan, Structural Evolution of a Ni Alloy Surface During High-Temperature Oxidation, *Oxidation of Metals*, 90 (2018) 27–42.
- [39] K.L. Auth, J. Brouzoulis, M. Ekh, A fully coupled chemo-mechanical cohesive zone model for oxygen embrittlement of nickel-based superalloys, *Journal of the Mechanics and Physics of Solids*, 164 (2022) 104880.
- [40] C.T. Liu, C.L. White, Dynamic embrittlement of boron-doped Ni₃Al alloys at 600°C, *Acta Metallurgica*, 35 (1987) 643–649.
- [41] L. Jian, P. Jian, H. Bing, G. Xie, Oxidation kinetics of Haynes 230 alloy in air at temperatures between 650 and 850°C, *Journal of Power Sources*, 159 (2006) 641–645.
- [42] H.-M. Tung, J.F. Stubbins, Incipient oxidation kinetics and residual stress of the oxide scale grown on Haynes 230 at high temperatures, *Materials Science and Engineering: A*, 538 (2012) 1–6.
- [43] B. Du, H. Li, W. Zheng, X. He, T. Ma, H. Yin, Study of oxidation behavior and tensile properties of candidate superalloys in the air ingress simulation scenario, *Nuclear Engineering and Technology*, 55 (2023) 71–79.