



LUND UNIVERSITY

Mechanical stability and fracture behavior of the WOs sigma phase effects of composition and lattice-site occupancy

Vesti, Anders; Music, Denis; Forti, Mariano; Palumbo, Mauro; Hammerschmidt, Thomas; Olsson, Pär A.T.

Published in:
Computational Materials Science

DOI:
[10.1016/j.commatsci.2026.114699](https://doi.org/10.1016/j.commatsci.2026.114699)

2026

Document Version:
Publisher's PDF, also known as Version of record

[Link to publication](#)

Citation for published version (APA):
Vesti, A., Music, D., Forti, M., Palumbo, M., Hammerschmidt, T., & Olsson, P. A. T. (2026). Mechanical stability and fracture behavior of the WOs sigma phase: effects of composition and lattice-site occupancy. *Computational Materials Science*, 269, Article 114699. <https://doi.org/10.1016/j.commatsci.2026.114699>

Total number of authors:
6

Creative Commons License:
CC BY

General rights

Unless other specific re-use rights are stated the following general rights apply:
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

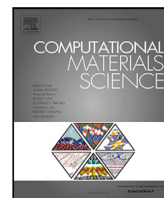
Read more about Creative commons licenses: <https://creativecommons.org/licenses/>

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00



Full length article

Mechanical stability and fracture behavior of the WOs sigma phase: Effects of composition and lattice-site occupancy

Anders Vesti ^{a,*,} Denis Music ^{b,c,} Mariano Forti ^{d,} Mauro Palumbo ^{e,}
Thomas Hammerschmidt ^{d,} Pär A.T. Olsson ^{a,b,}

^a Division of Mechanics, Materials & Component Design, Lund University, Box 118, SE 221 00, Lund, Sweden

^b Department of Materials Science and Applied Mathematics, Malmö University, SE 205 06, Malmö, Sweden

^c Biofilms Research Center for Biointerfaces, Malmö University, SE 205 06, Malmö, Sweden

^d Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-Universität Bochum, 44801, Germany

^e Department of Chemistry and NIS-INSTM, University of Turin, V. P. Giuria 7, 10125 Turin, Italy

ARTICLE INFO

Dataset link: https://github.com/AndVesti/Vesti_2025_WOs_sigma_phase

Keywords:

Tungsten

Osmium

Sigma phase

DFT

Mechanical properties

Elastic properties

ABSTRACT

Precipitates of the topologically close-packed (TCP) phases can significantly impact a material's mechanical and fracture properties. This theoretical study uses *ab initio* modeling to investigate the σ phase of WOs, focusing on composition-dependent mechanical and fracture-related properties. We find the effect of Os on WOs σ to be stronger than that of Re in WRe σ phase, with the WOs phase exhibiting peak hardness at the ideal concentration. This difference is attributed to variations in *d*-orbital filling, causing Os to favor low-coordination sites more strongly than Re. While ductility may improve at high Os contents, brittle fracture of the phase is still predicted. For Os concentrations above 78 at.%, the σ phase becomes mechanically unstable. These results indicate that subtle changes in *d*-orbital filling between Os and Re significantly affect the stability and mechanical properties of the σ phase and may apply to similar TCP phases.

1. Introduction

Intermetallic precipitates of topologically close-packed (TCP) phases, are known to have significant detrimental effects on the mechanical properties of structural materials. The σ phase, in particular, is a well-documented embrittling TCP phase, that can form in a variety of alloy systems, often with transition metals as alloy components. Examples include stainless steels, where Cr is added to improve corrosion resistance [1–3], but the formation of unwanted FeCr and FeCrNi σ phase precipitates results in increased hardness, reduced ductility and diminished corrosion resistance [2–4]. Another example is Ni-based superalloys, which are valued for their high strength at elevated temperatures [5], but the formation of σ and other TCP precipitates at elevated temperatures degrade the strength of the material and may also serve as crack nucleation sites [6–8].

The σ phase has also been observed in tungsten (W) and W-based alloys subjected to high-flux neutron irradiation [9,10]. These materials are prime candidates for plasma-facing components (PFCs) in fusion reactors due to the high thermal conductivity of W (~150 W/mK at room temperature), extremely high melting point (3680 K), and low sputtering yield [11–16]. Under neutron irradiation, W undergoes transmutation, producing the elements rhenium (Re) and osmium (Os)

that congregate and form σ phase precipitates [17–19]. The presence of these σ precipitates has been linked to the hardening and the increased brittle-to-ductile transition temperature observed in neutron-irradiated W-samples [10,20–22], which can degrade the performance of W-based PFCs. Classical atomistic simulations have shown that incoherent WRe σ precipitates act as strong obstacles for dislocation motion, thereby causing an increase in the hardness [23–25]. Investigating the formation mechanisms and intrinsic properties of these precipitates is essential for developing radiation-tolerant materials for fusion energy applications. For this, simulations based on density functional theory (DFT) can provide several valuable insights and are often the method of choice for theoretical studies of TCP phases. For the WRe σ phase, DFT has been used to estimate the thermodynamic, elastic, and fracture-related properties [26–28] and to explore the formation and preferential site occupation [29–32]. Studies on WOs precipitates, however, are largely missing in the literature. This is despite Os being the second-most common transmutation product in W [33], and indications that the irradiation-induced σ precipitates may contain Os in significant amounts [18]. Studies of the WOs phase are therefore needed to obtain a deeper understanding of the σ type precipitates in W-based PFCs.

In the present work, DFT is used to investigate the effect of varying stoichiometry and lattice site distribution on the mechanical and

* Corresponding author.

E-mail address: anders.vesti@lth.lu.se (A. Vesti).

<https://doi.org/10.1016/j.commsci.2026.114699>

Received 13 December 2025; Received in revised form 20 March 2026; Accepted 4 April 2026

Available online 7 April 2026

0927-0256/© 2026 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

fracture-related properties of the WOs σ phase. The aim is to clarify the thermodynamically preferential lattice sites and to quantify the extent to which Os reduces the overall ductility of the phase. Throughout the paper, comparison is made with the WRe phase. It is discovered that the mechanical properties of the WOs σ phase depend significantly on the Os concentration as compared to the WRe phase. We theorize that the divergent behavior of the otherwise similar phases is due to differences in the d -orbital occupancy, which results in a highly ordered WOs σ phase for concentrations near the ideal composition even at high temperatures of 1500 K. Although this study focuses on the WOs system, we anticipate that similar occupational dependencies can be observed in other TCP phases in multi-component systems, particularly transition metal alloys, where the d -electrons primarily determine bonding and stability.

2. Methods

2.1. Elastic properties and intrinsic hardness

The six independent elastic constants: C_{11} , C_{12} , C_{13} , C_{44} , C_{66} , and C_{66} of the σ phase were determined by performing finite distortions of the unit cell, while allowing full relaxation of the atomic coordinates. The elastic constants were then derived from the stress-strain relationship [34]. The Born stability criteria for the σ phase are [35]

$$\begin{aligned} C_{11} > |C_{12}|, \quad C_{44} > 0, \quad C_{66} > 0, \\ 2C_{13}^2 < C_{33}(C_{11} + C_{12}) \end{aligned} \quad (1)$$

The bulk, K_V , and shear, G_V , moduli indicate the resistance against compression and shearing of the unit cell, respectively. In polycrystalline materials, the Voigt averages determine the upper boundaries for K_V and G_V [36]. In the σ phase, these averages were calculated as

$$K_V = \frac{1}{9}(2C_{11} + 2C_{12} + C_{33} + 4C_{13}), \quad (2)$$

$$\begin{aligned} G_V = \frac{1}{15}[2C_{11} + C_{33} - (C_{12} + 2C_{13}) \\ + 3(2C_{44} + C_{66})]. \end{aligned} \quad (3)$$

Poisson's ratio, ν , and Young's modulus, E_V , were estimated from the elastic moduli [36],

$$\nu = \frac{3K_V - 2G_V}{6K_V + 2G_V}, \quad (4)$$

and [37,38]

$$E_V = \frac{9K_V G_V}{3K_V + G_V}. \quad (5)$$

The Vickers hardness was also estimated from the moduli by adopting the following empirical relation for polycrystalline materials [39]

$$H_V = 2 \left(\frac{G_V^3}{K_V^2} \right)^{0.585} - 3, \quad (6)$$

The exponent in the above relation originates from fitting a database of experimental values of H_V to those of G_V and K_V in units of GPa [39]. It should be noted that the relation is heuristic as it does not explicitly consider the microstructure, and that it is expected to have limited applicability for highly ductile metals with very low Pugh's ratios (G_V/K_V), as these can locally accumulate plastic deformations before fracture [39].

2.2. Energy release rate

The close-packed planes are relevant for fracture studies since they tend to act as either crack or slip planes. In our previous paper, we found the {004} and {330} planes to be the relevant close-packed planes of the WRe σ phase [26]. The brittle energy release rate, G_I , corresponds to the energy required to cleave the bulk crystal, thereby creating two new surfaces. In the absence of plastic deformation, G_I is

$G_I = \gamma_s + \gamma'_s$ [40], where γ_s and γ'_s are the surface energies of the created surfaces. In TCP phases γ_s and γ'_s are typically not equal.

The value of G_I was calculated for the {004} and {330} planes using a supercell with a vacuum layer of 10 Å. A convergence test with a 15 Å of vacuum yielded a difference in G_I less than 0.01 J/m², proving that 10 Å of vacuum is sufficient to prevent interaction between the free surfaces. The orientation of the crystal was chosen so that the relevant surfaces were exposed. Convergence tests were carried out using supercells containing material slabs with heights of two, three, and four unit cells. A minimum material slab height of 13.8 Å was found to be sufficient to obtain well-converged results, with the difference in G_I of the higher supercell being less than 0.01 J/m². The atoms underwent full relaxation in all three coordinate directions with a force convergence criterion of 0.01 eV/Å.

2.3. Unstable stacking fault energy

The unstable stacking fault energies, γ_{us} , were determined by creating a periodic supercell with one of the periodic boundaries coinciding with the plane of interest. A shearing interface between the neighboring periodic cells was created by imposing an in-plane displacement on the supercell vector perpendicular to the slip plane. During ionic relaxation, atoms were allowed to relax only in the direction of the slip plane normal and a force convergence criterion of 0.01 eV/Å was imposed. Convergence tests were carried out using supercells with heights of two, three, and four unit cells. It was determined that a supercell height of minimum 15.4 Å gave converged results, with the difference in γ_{us} between the two largest supercells being less than 0.07 J/m². Based on our previous theoretical work on the WRe σ phase [26], the following possible slip systems were identified: {330}<001> and {004}<100>. A recent experimental study on the FeCr σ phase [3], determined the slip systems {110}<001>, {100}<001>, {100}<010> and {111}<011> to be operative at room temperature during micropillar compression. The first two systems involved an atomic shuffling mechanism on the surfaces and are therefore excluded from this study, as such mechanisms require modeling techniques beyond the scope of the current work. In the σ phase, non-equivalent surfaces can be created by translations in the direction of the slip plane normals. In this study, the slip system surfaces indicated in Fig. 1(a) were used, as these were found to give the lowest stacking-fault energies [3,26]. The unstable stacking fault energy associated with the {004}<100> system, γ_{us}^{004} , was determined using an in-plane displacement of $\frac{1}{2}$ [100]. For γ_{us}^{330} , an in-plane displacement of $\frac{1}{2}$ [001] was used. While for γ_{us}^{100} and γ_{us}^{111} in-plane displacements of $\frac{1}{4}$ [010] and $\frac{1}{5}$ [011] were applied, respectively.

2.4. Rice's ductility parameter

According to Rice [40], under pure mode I loading, where the tensile stress acts normal to the crack plane, crack tip blunting by dislocation nucleation occurs before cleavage when the following criterion is met:

$$D \equiv \frac{G_I}{2\gamma_{us}} > 4 \frac{1 + (1 - \nu) \tan^2 \phi}{(1 + \cos \theta) \sin^2 \theta}, \quad (7)$$

where the angles θ and ϕ originate from the geometry, see Fig. 1(b), and were determined from the pure W σ phase using VESTA [41]. We note that, for the tetragonal σ phase, the angle θ depends on the lattice-parameter ratio $\frac{a}{c}$ between the [100] and [001] directions, which only varies marginally with Os content. This variation is sufficiently small for the effect on the ductility criterion to be negligible. For example, $\frac{a}{c}$ is 1.906 for the pure W σ phase and 1.909 for the pure Os phase, corresponding to a difference in θ of only 0.1°.

The close-packed {004} and {330} planes were assumed to operate as the crack planes. When {004} acts as the crack plane and dislocations nucleate on the {330}<001> slip system ($\theta = 90^\circ$ and $\phi = 0^\circ$), the Rice's criterion becomes

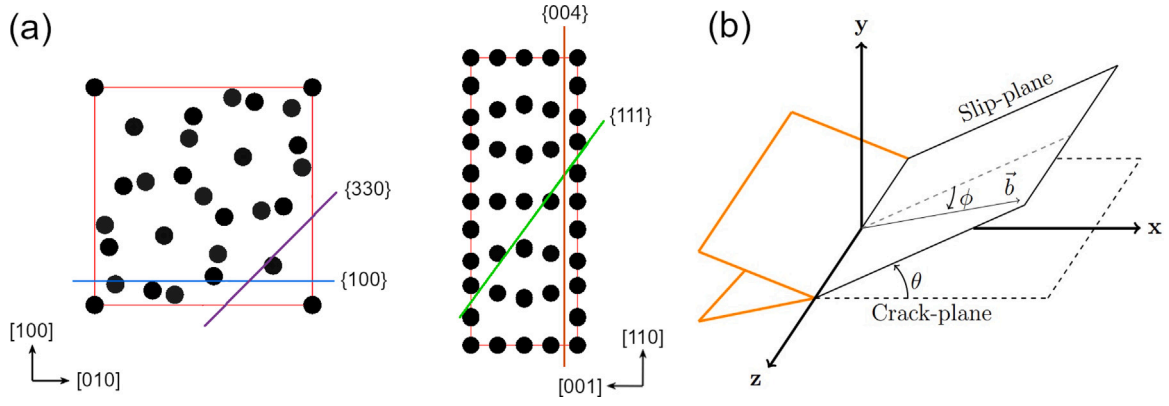


Fig. 1. (a) A model of a crack plane and slip system with slip direction $\vec{b}$ defined by angles θ and ϕ . (b) A schematic drawing of the slip planes investigated in this study.

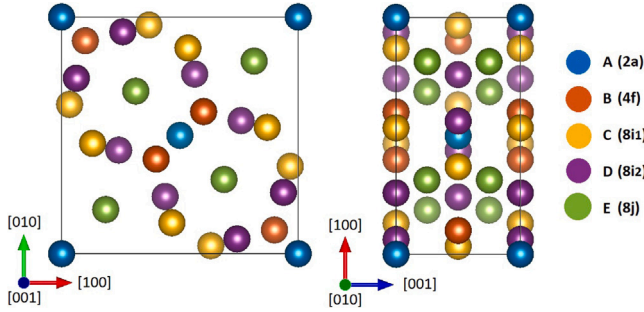


Fig. 2. Unit cell of the σ phase with the five Wyckoff sites marked with different colors (created using VESTA [41]).

$$D_{(330)[001]}^{004} \equiv \frac{G_I^{004}}{2 \cdot \gamma_{us}^{330}} > 4, \quad (8)$$

where $D_{(330)[001]}^{004}$ is the ductility parameter for the system.

For dislocations nucleating on the $\{111\}\langle 0\bar{1}1 \rangle$ slip system ($\theta = 36.58^\circ$ and $\phi = 45^\circ$), the criterion becomes:

$$D_{(111)[0\bar{1}1]}^{004} \equiv \frac{G_I^{004}}{2 \cdot \gamma_{us}^{111}} > 6.25 \cdot (2 - \nu), \quad (9)$$

while for the $\{100\}\langle 010 \rangle$ slip system ($\theta = 90^\circ$ and $\phi = 90^\circ$), dislocation emission becomes impossible as $\tan 90^\circ \rightarrow \infty$.

In the case of a $\{330\}$ crack plane, nucleation may occur on the $\{004\}\langle 100 \rangle$ slip system ($\theta = 90^\circ$ and $\phi = 45^\circ$), resulting in a Rice criterion of

$$D_{(004)[100]}^{330} \equiv \frac{G_I^{330}}{2 \cdot \gamma_{us}^{004}} > 4 \cdot (2 - \nu). \quad (10)$$

For dislocation nucleation on the $\{100\}\langle 010 \rangle$ system ($\theta = 45^\circ$ and $\phi = 0^\circ$), the criterion is

$$D_{(100)[010]}^{330} \equiv \frac{G_I^{330}}{2 \cdot \gamma_{us}^{100}} > 4.69 \quad (11)$$

and for the $\{111\}\langle 0\bar{1}1 \rangle$ system ($\theta = 53.47^\circ$ and $\phi = 45^\circ$), the criterion of ductile fracture is:

$$D_{(111)[0\bar{1}1]}^{330} \equiv \frac{G_I^{330}}{2 \cdot \gamma_{us}^{111}} > 3.88 \cdot (2 - \nu). \quad (12)$$

2.5. The sublattice model

The σ phase belongs to the group of TCP phases known as Frank-Kasper phases. Its tetragonal unit cell of the space group $P4_2/mnm$ [42]

contains 30 atoms located at the following five Wyckoff sites: 2a (12), 4f (15), 8i₁ (14), 8i₂ (12), and 8j (14), where the coordination number of the sites is written in parentheses. For easy reference, we label the sites with the letters A – E, as shown in Fig. 2. The composition that results in the lowest formation enthalpy at 0 K is referred to as the ideal composition. However, the σ phase is known to crystallize in a wide range of compositions at elevated temperatures [42]. For example, at temperatures above 1000 °C, the WOs σ phase is thermodynamically stable in the concentration range 20–35 at.% Os [43,44]. It is, therefore, essential to consider the dependence on the chemical composition regarding the material properties of the σ phase.

The σ phase is known to be non-stoichiometric, though complete atomic disorder is not observed either [45]. Instead, the preferred lattice sites of W and Os can be determined by utilizing the sublattice method, also known as the compound energy formalism [30,46–48]. The principle behind the method is to treat each Wyckoff site in the unit cell as a sublattice. The Gibbs free energy can thereby, under the assumption of ideal mixing on the sublattice sites, be written as:

$$G(x_{Os}, T) = G^{ref} - T \cdot S^{mix} \quad (13)$$

where x_{Os} is the osmium concentration and T is the temperature [48]. The reference term, G^{ref} , is assumed to be a weighted sum of the formation enthalpies at 0 K of the 32 possible sublattice configurations [49].

$$G^{ref} = \sum_{k,l,m,n,o=W,Os} (y_k^A y_l^B y_m^C y_n^D y_o^E) H_f^{klmno} \quad (14)$$

where H_f^{klmno} is formation enthalpy at 0 K of the sublattice configuration $klmno$ and y_c^s are the atomic fractions of element c on Wyckoff site s , which depend on both temperature and Os concentration. The H_f^{klmno} were calculated by subtracting the energies of pure W and pure Os in their reference states, i.e., BCC W and HCP Os, from the total energy per atom of the σ phase configuration $klmno$:

$$H_f^{klmno} = E^{klmno} - x_W \cdot E_W^{BCC} - x_{Os} \cdot E_{Os}^{HCP}, \quad (15)$$

where x_c is the concentration of element c in the $klmno$ configuration and the reference state energies are $E_W^{BCC} = -12.95$ eV/atom and $E_{Os}^{HCP} = -11.23$ eV/atom.

The configurational entropy of ideal mixing on the sublattices is:

$$S^{mix} = -\frac{k_B}{N_{cell}} \sum_s m_s \left[\sum_{c=W,Os} y_c^s \ln y_c^s \right]. \quad (16)$$

where k_B is Boltzmann's constant, N_{cell} number of atoms in the σ unit cell and m_s is the multiplicity of Wyckoff site s . By minimizing Eq. (13) at a fixed temperature with respect to y_{Os}^s , the preferential site occupancies y_{Os}^s were determined as a function of x_{Os} . The temperature of 1500 K was chosen since it has been shown to give well-matching results with experiments for the WRe phase [29]. Similarly, the Os

concentration can be kept constant, and temperature-dependent y_c^s 's are obtained.

The sublattice model is commonly applied without including vibrational contributions to the free energy, as in Eq. (13). Despite this, calculated site occupancies with the sublattice model have been shown to agree with experimental data for the MoRe σ and χ phases, the WRe σ phase [48], and in a number of ternary systems [50,51]. However, when the mass difference between the constituent elements is large, and the temperature approaches the melting temperature, vibrational contributions to the free energy can alter the shape of the convex hull and the relative stability of sublattice configurations, which may have a significant impact on disordering, as demonstrated for the CrRe σ phase [52]. In our recent study [31], we computed vibrational contributions for the WOs and WRe σ phase for temperatures up to 1500 K using the harmonic approximation. Only minor changes in the shape of the convex hull and the relative stability of the configurations were observed, which implies that vibrational contributions scale reasonably uniformly across configurations for WOs and WRe for temperatures below 1500 K. We attribute this to the similar masses of W, Re, and Os (respectively, 184, 186, and 190 a.u.) and the high melting temperatures of the WRe and WOs σ phases (roughly ~ 3000 K). This may explain why the sublattice model can predict accurate Wyckoff site occupancies for the WRe σ phase despite neglecting phonon effects [28, 48].

Following the work of Bonny et al. [28], several concentration-dependent material properties of the σ phase were expressed using the sublattice model, similar to Eq. (14). By adopting this approach, the Os-dependent values of a disordered σ phase can be estimated from the sublattice configurations. For example, the Os-dependent elastic constants C_{ij} were computed from the values of the configurations, C_{ij}^{klmno} , by using the Os content-dependent y_c^s as weights:

$$C_{ij}(x_{Os}) = \sum_{k,l,m,n,o=W,Os} (y_k^A y_l^B y_m^C y_n^D y_o^E) C_{ij}^{klmno}. \quad (17)$$

The same approach was adopted for calculating the Os content-dependent values of K_V , G_V , H_V , E_V , ν , G_I , and γ_{us} .

2.6. Numerical details

For the DFT calculations, the Vienna *Ab initio* Simulation Package (VASP 5.4) was used [53,54]. Projector augmented wave (PAW) potentials [55,56] within the generalized gradient approximation based on the Perdew–Burke–Ernzerhof (PBE) exchange–correlation [57] were used with expanded valence configurations of $5s^2 5p^6 6s^1 5d^5$ for W and $5p^6 6s^1 5d^7$ for Os, while we adopted the recommended valence configuration of $6s 5d^6$ for Re. The Methfessel–Paxton method [58] for smearing with a width of 0.1 eV was applied. An energy cut-off of 650 eV and a Γ -centered k -point grid of $7 \times 7 \times 13$ for the σ unit cell were sufficient for converging total energies to less than 0.1 meV/atom. For the electron density of states (DOS) calculations, the density of the k -point grid was doubled in each direction and the tetrahedron method with Blöchl corrections without smearing was applied [59]. For the Crystal Orbital Hamilton Population (COHP) calculations [60], the LOBSTER software [61,62] was utilized. When treating supercells, the k -point grid was adjusted to maintain the k -point density in reciprocal space. A quasi-Newton algorithm [63] was used for ionic relaxation of the unit cells with a force convergence criterion of 0.1 meV/Å and an energy convergence criterion of 1×10^{-6} eV for the self-consistency loop.

3. Results

3.1. Wyckoff site occupation of WOs

Table 1 lists the occupancy of the Wyckoff sites, the Os concentration, x_{Os} , the zero-Kelvin formation enthalpy, H_f , and the ground

Table 1

The sublattice configurations number, No., the elements of the Wyckoff sites $ABCDE$, the Os concentration x_{Os} , the formation enthalpy H_f in units of eV/atom, and the unit cell volume per atom in units Å³/atom at 0 K.

No.	$ABCDE$	x_{Os}	H_f	V_0
1	WWWWW	0.00	0.17	16.46
2	OsWWWW	0.07	0.14	16.31
3	WOsWWW	0.13	0.24	16.22
4	OsOsWWW	0.20	0.21	16.08
5	WWWWOs	0.27	0.24	15.96
6	WWWOsW	0.27	0.03	15.87
7	WWOsWW	0.27	0.15	15.99
8	OsWWWOs	0.33	0.21	15.84
9	OsWWOsW	0.33	0.01	15.71
10	OsWOsWW	0.33	0.13	15.85
11	WOsWWOs	0.40	0.27	15.76
12	WOsWOsW	0.40	0.08	15.65
13	WOsOsWW	0.40	0.27	15.75
14	OsOsWWOs	0.47	0.27	15.66
15	OsOsWOsW	0.47	0.07	15.52
16	OsOsOsWW	0.47	0.24	15.62
17	WWWOsOs	0.53	0.15	15.45
18	WWOsWOs	0.53	0.22	15.57
19	WWOsOsW	0.53	0.15	15.45
20	OsWWOsOs	0.60	0.17	15.34
21	OsWOsWOs	0.60	0.20	15.46
22	OsWOsOsW	0.60	0.14	15.31
23	WOsWOsOs	0.67	0.20	15.27
24	WOsOsWOs	0.67	0.34	15.39
25	WOsOsOsW	0.67	0.24	15.24
26	OsOsWOsOs	0.73	0.23	15.17
27	OsOsOsWOs	0.73	0.33	15.27
28	OsOsOsOsW	0.73	0.24	15.12
29	WWOsOsOs	0.80	0.33	15.11
30	OsWOsOsOs	0.87	0.34	14.97
31	WOsOsOsOs	0.93	0.44	14.93
32	OsOsOsOsOs	1.00	0.48	14.82

state volume, V_0 , of the 32 possible sublattice configurations. To easily identify the configurations, they are numbered by increasing Os content. In the following, we will refer to specific configurations using this numbering. The No. 9 configuration with Os occupying the smaller A and D sites is the most stable and occurs at the ideal composition of the σ phase, where the ratio of W to Os (or Re) is 2:1 [42]. It can be seen that V_0 reduces as the Os content increases. This is somewhat intuitive since the atomic radius of Os is smaller than that of W (1.85 Å versus 1.93 Å for W [64]). The experimentally measured volume of W_2Os is 15.41 Å³/atom [43]. The calculated volumes of the configurations with the same composition (Nos. 8–10) are just two to three percent larger, demonstrating close agreement with experiment. The cause of the overestimation is likely due to the employment of the PBE exchange correlation functional, which tends to underbind and therefore overestimates lattice constants by up to a few percent [65].

In Fig. 3(a), the H_f at 0 K of the sublattice configurations of the WOs and WRe σ phases are plotted versus the transmutation product content using triangles and squares, respectively. The results of the WRe σ phase are adopted from our previous study [26]. Some of the configurations are identified with the numbering used in Table 1, and the convex hulls of the phases are constructed using the common tangent method. Although none of the configurations exhibit negative values of H_f at 0 K, several configurations on or near the convex hull become thermodynamically stable at elevated temperatures due to phonon contributions to the free energy, as demonstrated in our recent study on the stability of the WOs and WRe σ phases [31].

The difference in the behavior of H_f between the WOs and WRe σ phase is significant in two ways. First, at high Os concentrations, the values of H_f for WOs are significantly higher than those of WRe, giving a distinct “V” shape to the convex hull of WOs compared to the relatively flatter convex hull of WRe. This may help rationalize why the WOs σ phase is reported to be thermodynamically stable

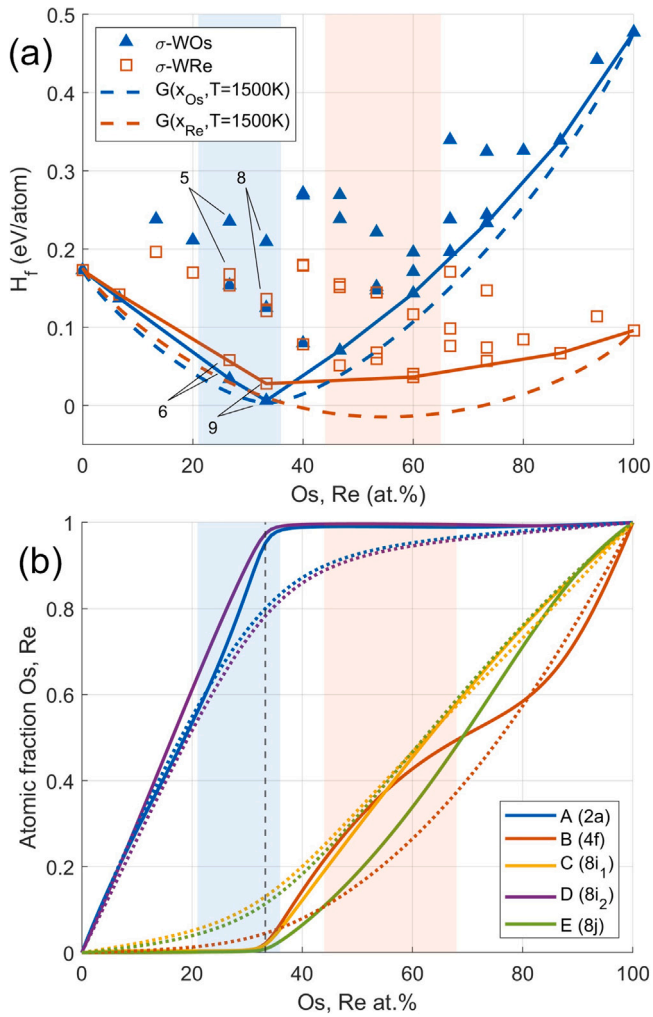


Fig. 3. In (a), the H_f at 0 K for the 32 sublattice configurations of WOs (blue triangles) and WRe (orange squares). Some configurations have been identified according to the numbering in Table 1. The convex hulls are drawn with solid lines and the free energy curves, according to Eq. (13), are drawn with dashed lines. In (b), the preferred atomic fraction of Os (solid lines) and Re (dotted lines) of the five Wyckoff sites at $T = 1500$ K. The blue and orange backgrounds indicate thermodynamically stable Os/Re concentrations of, respectively, the WOs and WRe phases at 1500 K [44].

over a narrower concentration range, closer to the ideal composition than the WRe phase [44], as indicated by the blue and orange shaded backgrounds in Fig. 3. The free energy curves of the disordered σ phases, given by Eq. (13), are shown with dashed lines in Fig. 3(a). Although this expression neglects contributions such as phonon effects, it illustrates the role of configurational entropy in stabilizing the phases. The minima of the curves fall within the experimentally reported stability regions, which for the WRe σ phase is well above the ideal stoichiometry. Second, at a given stoichiometry, the variation of H_f between the configurations is larger for WOs than for WRe. For example, at the ideal composition of 33 at.% Os/Re the difference in H_f between the No. 8 and No. 9 configurations is 0.20 eV/atom for WOs and 0.11 eV/atom for WRe [26]. This implies that the σ phase should be more ordered for WOs than WRe, since the substitution of atoms between sublattices is more energetically expensive than for WRe.

In Fig. 3(b), the atomic fractions of Os on the five Wyckoff sites that minimize the free energy at 1500 K are plotted against the total Os concentration using solid lines. The fractions of Re at the sites for the WRe phase at the same temperature have been drawn with dotted lines for comparison [26]. To our knowledge, no experimental data

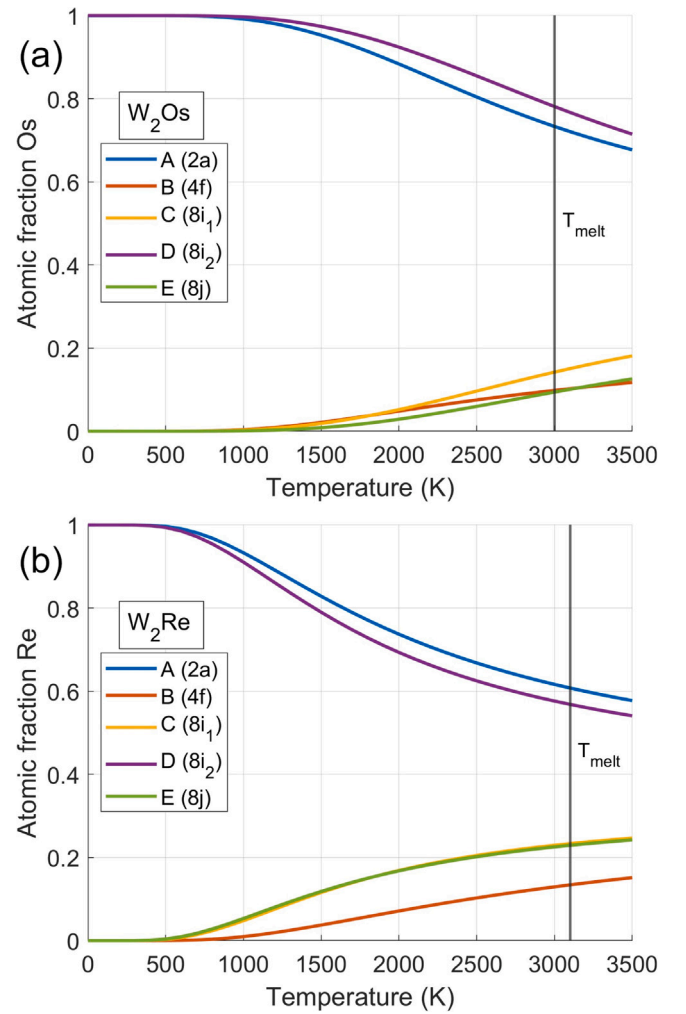


Fig. 4. Atomic fractions on the Wyckoff sites for the (a) WOs and (b) WRe σ phases at the ideal composition as a function of temperature. Their approximate melting temperatures, T_{melt} , according to their phase diagrams [44] have been marked with a vertical line.

on site occupancy of the WOs phase exist; however, experimental data confirm that the disorder of the WRe phase can be well described by a sublattice model [28,29]. It can be seen from the figure that W prefers to occupy the B, C, and E sites, while Os and Re prefer the A and D sites, with Os exhibiting a stronger preference for the sites than Re. For example, at the ideal concentration, marked with a vertical gray dashed line in Fig. 3(b), the WOs phase is almost completely ordered with the fractions of Os on the A and D sites being 0.95 and 0.97, respectively. Only when the Os concentration exceeds 33 at.%, the excess of atoms forces Os to start occupying the B, C, and E sites notably. By comparison, the WRe phase contains a higher level of disorder at the ideal concentration, with the fraction of Re on the A and D sites being 0.78 and 0.80, respectively. The blue and orange shaded backgrounds in Fig. 3 indicate the thermodynamically stable concentrations for WOs and WRe, respectively, at 1500 K [44]. At these concentrations, the Os atoms are predominantly located on the A and D sites, while for the stable range of the WRe, the fraction of Re atoms occupying the B, C, and E sites is substantial. This implies that precipitates of WOs σ phase are expected to have lower levels of substitutional disorder than their WRe counterparts. The WOs σ phase at the ideal composition remains highly ordered even at high temperatures. This can be seen in Fig. 4, which shows the temperature-dependent Wyckoff site occupancies for (a) W_2Os and (b) W_2Re . At temperatures below 1000 K, the No. 9 configuration is almost completely ordered, and only

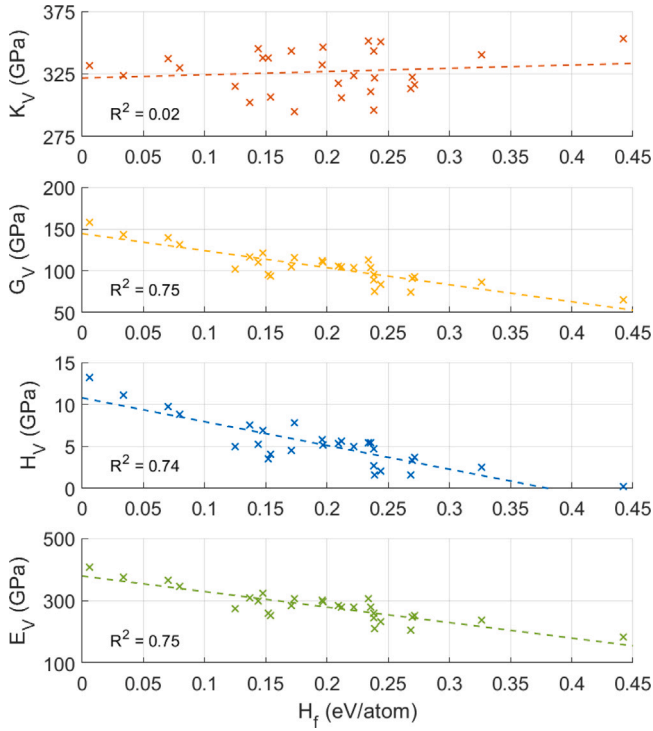


Fig. 5. Mechanical properties at 0 K of the stable sublattice configurations versus the formation enthalpy. Dashed lines indicate fits of linear regression.

at temperatures well above 1500 K does substitutional disorder on the Wyckoff sites become significant. On the contrary, for the W_2Re phase, notable substitutional disorder occurs at much lower temperatures, approximately 750 K.

3.2. Mechanical and fracture-related properties

Table 2 lists the six independent elastic constants in Voigt notation, C_{ij} ; the Voigt averages of the bulk, K_V , and shear, G_V , modulus; the Young's modulus, E_V ; Vickers hardness, H_V ; and Poisson's ratio, ν . Furthermore, the table includes the brittle energy release rate of the close-packed planes, G_I^{004} and G_I^{330} , as well as the unstable stacking-fault energies, γ_{us} , associated with several slip systems. Four configurations, marked with “+”, did not satisfy the Born criteria for mechanical stability: The configurations No. 27, 30, and 32 have negative values of C_{44} , while configuration No. 24 does not fulfill the requirement of $C_{11} > |C_{12}|$. The lack of stability for these configurations is the underlying reason for the negative values of H_V .

Configurations near the bottom of the convex hull tend to exhibit higher values of C_{44} , C_{66} , G_V , E_V , and H_V relative to the other configurations of the same stoichiometry. For example, the most stable configuration, No. 9, exhibits a G_V of 157 GPa, whereas configuration No. 8, which has the same stoichiometry, shows a significantly lower value of 105 GPa. In Fig. 5, the elastic moduli and the Vickers hardness of the stable sublattice configurations are plotted against H_f . Linear regression fits to the data are shown as dashed lines and the R^2 values are included in the graphs. From the figure it can be seen that, while there are no clear correlation between K_V and H_f ($R^2 = 0.02$), configurations of low H_f tend to exhibit high values of G_V , H_V , and E_V , though with some scatter around the regression line ($R^2 \approx 0.75$). These parameters are related to the bond strength of the structure: high values of G_V suggest a greater resistance to distortions of bond angles, while the higher E_V reflects increased stiffness of the bonds under elastic deformation. Similarly, the higher H_V indicates a greater resistance to localized plastic deformation, which can involve bond breaking or sliding of atomic planes. The above analysis suggests a

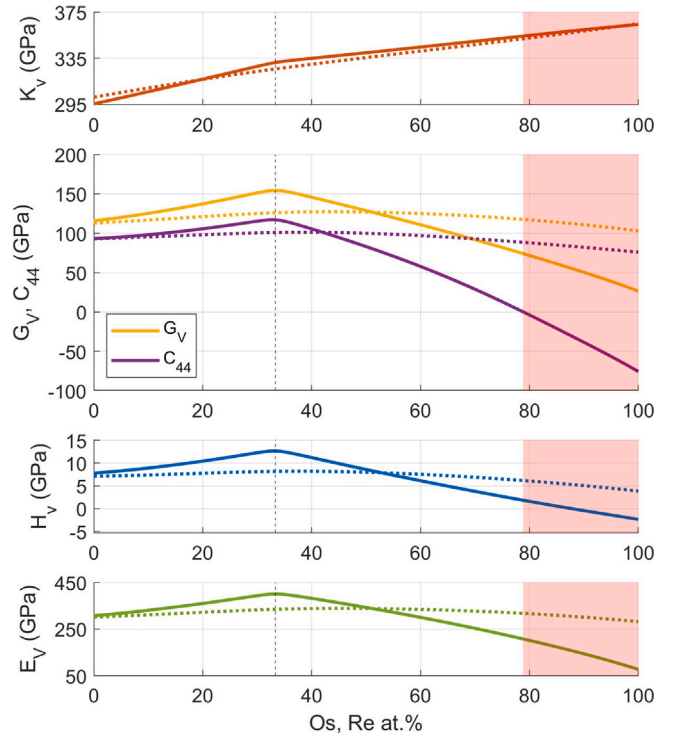


Fig. 6. Concentration-dependent mechanical properties at 0 K of the WOs phase drawn with in solid lines, while dotted lines indicate results for the WRe phase adopted from [28]. The vertical gray dashed line indicates the ideal composition and the red background indicates where the phase is unstable according to Born's criteria.

relationship between H_f and the bond strength of the WOs σ phase. However, as H_f is influenced by additional factors such as strain, electronic structure, and reference state energies, its relationship with bond strength is inherently complex and cannot be used as a direct measure of bond strength.

Using the concentration-dependent Wyckoff site occupancies as weights, concentration-dependent values of K_V , G_V , C_{44} , H_V , and E_V for the disordered WOs σ phase are estimated and drawn with solid lines in Fig. 6. For reference, the properties for the WRe σ phase, adopted from [28], are included as dotted lines. The ideal concentration has been marked with a vertical gray dashed line. It can be seen that the WOs σ phase is mechanically unstable according to the Born criterion of $C_{44} > 0$ for Os concentrations above 78%, which has been marked with a red background. The value of K_V monotonically increases with the Os content by 23% from 295 GPa at 0 at.% to 364 GPa at 100 at.% Os. The behavior of K_V is similar for the WOs and WRe σ phases. In contrast, the remaining mechanical properties display two distinct deviations between the phases: (i) the WOs σ phase exhibits a pronounced peak at the ideal composition, and (ii) the mechanical properties of the pure Os σ phase are markedly lower than the pure Re σ phase. For example, the value of G_V reaches a maximum of 154 GPa at 33 at.% Os and decreases to 27 GPa at 100 at.% Os, substantially lower than the 103 GPa observed for the pure Re σ phase. In the concentration range of 20–35 at.% Os, where the WOs σ phase is thermodynamically stable according to its phase diagram [43,44], the mean value of G_V is 148 GPa. When compared with the DFT-predicted shear modulus of 159 GPa for body-centered cubic (BCC) W [26], the mismatch in shear modulus between the precipitate and the W matrix is relatively small. At the ideal composition, the phase exhibit peak hardness, with values in H_V of 12.7 GPa and E_V of 401 GPa. In the stable concentration range, the mean values of H_V and E_V are 11.7 GPa and 384 GPa, respectively.

Table 2

The sublattice configurations number, No., the elastic constants, moduli, and Vickers hardness are given in GPa, and Poisson's ratio is dimensionless. The brittle energy release rates and unstable stacking fault energies are given in units of J/m². All parameters are calculated at 0 K. Configurations marked with “†” are mechanically unstable.

No.	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	K _V	G _V	E _V	H _V	ν	G _I ⁰⁰⁴	G _I ³³⁰	γ _{us} ⁰⁰⁴	γ _{us} ³³⁰	γ _{us} ¹⁰⁰	γ _{us} ¹¹¹
1	463	251	169	551	93	96	295	116	307	7.8	0.33	6.12	6.19	3.48	2.23	3.31	4.10
2	480	253	175	553	92	95	302	116	309	7.6	0.33	6.09	6.35	3.47	2.28	3.34	4.08
3	434	259	192	513	81	72	296	96	260	4.7	0.35	5.57	5.99	3.05	2.04	2.81	3.59
4	467	274	185	534	86	74	306	104	281	5.6	0.35	5.52	6.20	2.98	2.11	2.88	3.56
5	484	242	215	484	91	79	311	104	281	5.4	0.35	5.78	5.91	2.78	1.92	2.74	3.70
6	549	226	191	597	108	141	323	144	375	11	0.31	6.08	6.26	3.46	2.53	3.39	4.11
7	498	216	217	462	39	119	306	93	254	4.1	0.36	5.58	5.54	3.31	1.11	3.31	3.59
8	493	236	226	496	81	79	318	105	284	5.4	0.35	5.69	6.14	2.79	2.04	2.77	3.69
9	571	233	184	644	121	152	332	157	408	13	0.30	6.15	6.43	3.53	2.75	3.51	4.21
10	523	218	221	471	49	128	315	102	277	5.0	0.35	5.58	5.73	3.30	1.18	3.37	3.54
11	486	262	212	504	62	75	316	93	253	3.7	0.37	5.41	5.82	2.54	1.64	2.52	3.41
12	525	264	199	596	104	120	330	131	348	8.8	0.33	5.73	6.10	3.34	2.44	2.98	3.79
13	460	239	246	441	47	66	313	74	206	1.6	0.39	4.85	5.60	2.69	1.15	2.68	3.15
14	475	260	234	497	76	62	323	91	249	3.4	0.37	5.16	6.02	2.42	1.74	2.62	3.32
15	554	262	193	630	107	119	337	139	367	9.8	0.32	5.76	6.31	3.37	2.52	3.06	3.87
16	467	263	238	482	38	77	322	76	211	1.6	0.39	4.96	5.84	2.76	1.26	2.87	3.16
17	515	248	246	530	63	77	338	95	261	3.5	0.37	5.45	5.78	2.80	2.42	2.72	3.71
18	534	251	199	546	64	70	323	104	281	5.0	0.36	5.61	5.38	2.75	0.82	2.78	3.40
19	585	254	200	561	56	134	337	121	324	7.0	0.34	5.69	5.43	2.88	1.26	3.36	3.56
20	532	254	237	571	65	91	343	105	285	4.6	0.36	5.20	5.92	2.77	2.47	2.68	3.64
21	534	281	204	542	72	110	332	112	302	5.9	0.35	5.60	5.53	2.88	1.02	2.87	3.36
22	581	258	213	578	43	115	345	111	300	5.3	0.36	5.62	5.56	2.89	1.28	3.32	3.50
23	517	289	239	547	100	78	346	110	298	5.2	0.36	4.90	5.63	2.66	2.10	2.55	3.49
24†	274	478	234	516	10	5	328	13	37	−2.8	0.48	4.84	5.43	2.22	0.80	2.43	2.99
25	520	322	209	573	34	86	343	89	246	2.7	0.38	5.20	5.60	2.73	1.34	2.90	3.32
26	518	298	238	578	101	85	351	113	307	5.5	0.36	5.07	5.81	2.60	2.22	2.53	3.47
27†	427	316	248	540	−21	31	335	36	105	−1.8	0.45	4.77	5.64	2.39	1.00	2.59	3.04
28	550	307	212	598	24	50	351	84	233	2.0	0.39	5.07	5.64	2.65	1.31	2.94	3.22
29	511	300	220	559	42	68	340	87	240	2.5	0.38	4.98	4.99	2.45	0.96	2.63	3.31
30†	544	321	223	622	−47	72	360	58	166	−0.4	0.42	4.92	5.23	2.45	1.04	2.71	3.28
31	531	281	235	611	4	10	353	65	184	0.2	0.41	4.18	4.95	2.11	0.85	2.25	3.06
32†	511	340	236	633	−76	3	364	27	78	−2.4	0.47	4.20	5.14	2.09	0.90	2.39	3.01

The concentration-dependent, fracture-related properties of the σ phase are shown in Fig. 7. The parameters of the WOs σ phase are drawn in solid lines, while values of the WRe phase, adopted from our previous work [26], are included with dotted lines. Below 33 at.% Os, the values of G_I^{004} and G_I^{330} are fairly independent of Os content, with G_I^{330} showing a slight increase of a few percent, see Fig. 7(a). Beyond 33 at.%, both G_I^{004} and G_I^{330} exhibit a decreasing trend with increasing Os content. This decrease is significant compared to the WRe phase. For example, at 100 at.% Os, G_I^{004} and G_I^{330} are 30% and 19% lower, respectively, than at 33 at.% Os, whereas in the WRe phase the corresponding differences are only 7% and 4%.

The unstable stacking fault energies, γ_{us} , for selected slip systems are plotted in Fig. 7(b). We note that atomic shuffling on some slip planes has been reported in the FeCr σ phase [3,66]. Since shuffling mechanisms have not been considered in this study, the γ_{us} herein can be regarded as upper bounds. For 0–33 at.% Os, the value of γ_{us}^{004} and γ_{us}^{100} are nearly constant while γ_{us}^{330} and γ_{us}^{111} increase with increasing Os content. Beyond 33 at.%, the γ_{us} 's of all slip systems decrease with increasing Os content. The {330}⟨001⟩ slip system has the lowest values of γ_{us} , indicating that the {330} planes are preferred for ductile mechanisms such as slip and twinning. While the low values of γ_{us} at high Os content may improve the ductility, the effect is counteracted by a similar reduction in G_I , which lowers the barrier for brittle fracture mechanism [67].

To estimate the competition between ductile and brittle mechanisms, the ductility parameters for the crack systems are plotted in Fig. 7(c) for {004} crack planes and in Fig. 7(d) for {330} crack planes. Brittle fracture behavior is predicted for both the WOs and WRe phases, as Rice's criterion for ductile fracture, see Eqs. (8)–(10), is not fulfilled for any of the crack systems tested. The ductility parameters of the crack systems remain largely unaffected by Os concentration, except for $D_{(330)[001]}^{004}$, which exhibits peak brittleness at the ideal composition and indications of enhanced ductility at high Os contents.

4. Discussion

4.1. Wyckoff site ordering of WOs and WRe σ phase

From Fig. 3(b), it can be observed that the WOs σ phase exhibits a high degree of ordering on the Wyckoff sites corresponding to the No. 9 sublattice configuration near the ideal composition. As shown in Fig. 4(a), this ordering persists even at high temperatures. In contrast, the WRe σ phase displays a higher level of disorder than the WOs phase, even at moderate temperatures. In the following, we discuss some established theories for the ordering of the σ phase to shed light on this difference.

The stability and site occupancy of transition metal TCP phases, such as the σ phase, are guided by electronic and geometric factors [30, 68,69]. As for electronic factors, the near-icosahedral symmetry of the A and D sites in the σ phase causes a high degeneracy of the d -orbitals [30]. This means that elements with half-filled d -orbitals would have a higher DOS when occupying these sites and therefore prefer to occupy the B , C , and E sites [30]. Conversely, elements with empty, filled, or nearly filled d -orbitals, which typically have a lower number of states near the Fermi level, prefer the A and D sites [29,45]. Our results follow this description as W (valence occupancy of $6s^1 5d^5$) prefers to occupy the B , C , and E sites, while Os ($6s^1 5d^7$) and Re ($6s^1 5d^6$) show a clear preference for the A and D sites. Notably, Os, which has a more filled d -orbital than Re, shows a stronger preference for the A and D sites than Re, as shown in Fig. 3(b).

Regarding geometric factors, reducing the size mismatch between atoms and their occupied sites has also been suggested as a governing factor for site occupation in the σ phase [42,69,70]. This is known as the Frank–Kasper rule [71,72]. The mismatch is minimized when the smaller element occupies the less spacious A and D sites, and the larger element occupies the more spacious B , C , and E sites [73]. The herein-produced results also agree with this description as the larger W

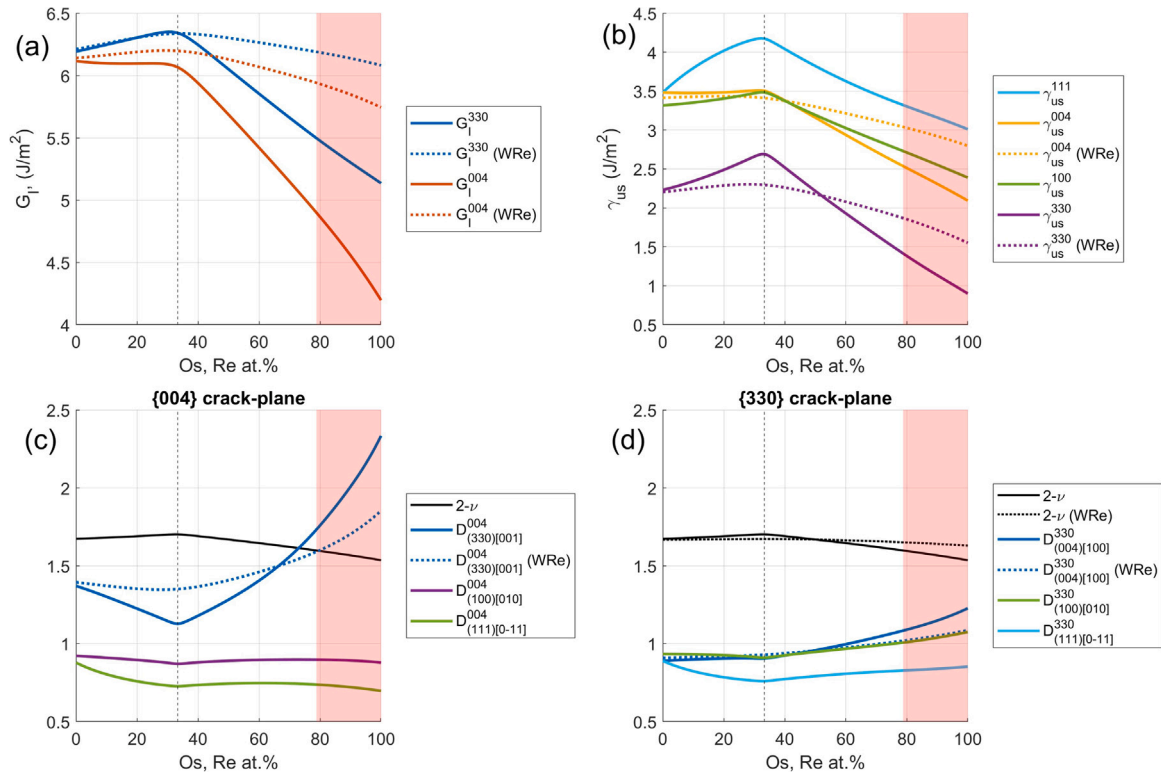


Fig. 7. Multiple concentration-dependent parameters at 0 K of the WOs phase (solid lines) and results of the WRe phase adopted from [26] have been included for reference (dotted lines). In (a), the G_s of the close-packed planes are shown, while (b) contains the γ_{us} for several slip systems. In (c) and (d), the Rice ductility parameters of, respectively, the {004} and {330} crack planes are plotted. The gray vertical dashed line indicates the ideal composition. The red background indicates concentrations for which the WOs phase is mechanically unstable.

atoms show a preference for the spacious sites and the smaller Os and Re atoms prefer to occupy the *A* and *D* sites. However, we note that the difference in size between the elements is merely a few percent, with the atomic radii of W, Re, and Os being 1.93, 1.88, and 1.85 Å, respectively [64]. Furthermore, during the relaxation of the unit cells, we observed only small changes in the internal coordinates between the WOs and WRe phase. A recent study examining a large number of σ phases suggested that electronic factors play a more dominant role in determining the H_f than atomic size differences [74]. It is therefore uncertain how significant the size mismatch effect is compared to electronic structure effects in the case of the WRe and WOs σ phases.

In order to clarify the electronic effects of element and Wyckoff site occupation, the projected DOS (pDOS) per atom projected onto the Wyckoff sites is shown Fig. 8 for three cases. The vast majority of the pDOS is dominated by contributions from the *d*-orbitals with minor contributions from the *s*- and *p*-orbitals [31]. In Fig. 8(a), configuration No. 6 is shown, where Os occupies the preferred *D* site. Here, the pDOS near the Fermi level is relatively flat for all Wyckoff sites. In Fig. 8(b), configuration No. 5 is shown, which has the same stoichiometry as No. 6 but with Os now occupying the less favorable *E* sites. When Os occupies the *E* sites, a pronounced pDOS peak from these sites appears near the Fermi level. This configuration has a high value of H_f , and has been found to be dynamically unstable [31]. Fig. 8(c) shows the corresponding No. 5 configuration for WRe. Replacing Os with Re, which has a less filled *d*-orbital, significantly reduces the peak near the Fermi level associated with the *E* sites. It has previously been shown that occupation of the *E* sites dictates the dynamic stability of the WOs σ phase, while this is not the case for the WRe σ phase [31]. These examples illustrate that the shape of the DOS is highly sensitive to Os occupying unfavorable Wyckoff sites (such as the *E* site), but much less so for Re.

To elucidate the intricate relationship between the DOS and the bond character, COHP analysis of the filling of bonding and antibond-

ing states was performed for two σ and compared with BCC-W for reference, as shown in Fig. 9. The electron DOS of BCC-W shown in Fig. 9(a) is consistent with literature results, e.g., [75]. As shown in Fig. 9(d), the Fermi level lies between bonding states (positive values of $-\text{COHP}$) and antibonding states (negative values of $-\text{COHP}$), indicating that the antibonding states are largely unoccupied, which stabilizes BCC-W. Fig. 9(b) and (c) show the DOS of the most stable σ configuration (No. 9) and the unstable configuration No. 32, respectively. A common feature of the σ configurations, also observed in the WRe σ phase [31], is the presence of two prominent low-energy peaks. The COHP analysis in Fig. 9(e) and (f) shows that these peaks correspond to bonding states that stabilize the structure. The COHP analysis shows partially occupied antibonding states near the Fermi level for both σ configurations. For configuration No. 9, the antibonding contributions at the Fermi level remain moderate, whereas for No. 32 they are significantly larger, indicating that a considerable fraction of the occupied states has antibonding character. The average integrated COHP (ICOHP) for nearest-neighbor bonds, integrated over the occupied energy range up to the Fermi level, provides a measure of the overall bonding strength, with more negative values indicating stronger bonds [60]. From the ICOHP values in Fig. 9, it can be seen that the occupation of the antibonding states weakens the overall bonding network of configuration No. 32, consistent with the mechanical instability of this configuration.

An additional feature of the DOS of the No. 9 configuration that may contribute to the stability is the pronounced decrease in the DOS near the Fermi level, highlighted by the arrow in Fig. 9(b). The inset, showing a zoom-in near E_f , indicates that the width of the decrease is about 0.2 eV, which exceeds the thermal energy at room temperature ($k_B T \approx 25$ meV). Reductions in the DOS near the Fermi level are sometimes referred to as “pseudo gaps” and may indicate more covalent-like metallic bonding [73]. This implies stronger directional bonding, which is consistent with the high value of G_s exhibited by this configuration. Conversely, the No. 32 configuration exhibits a higher

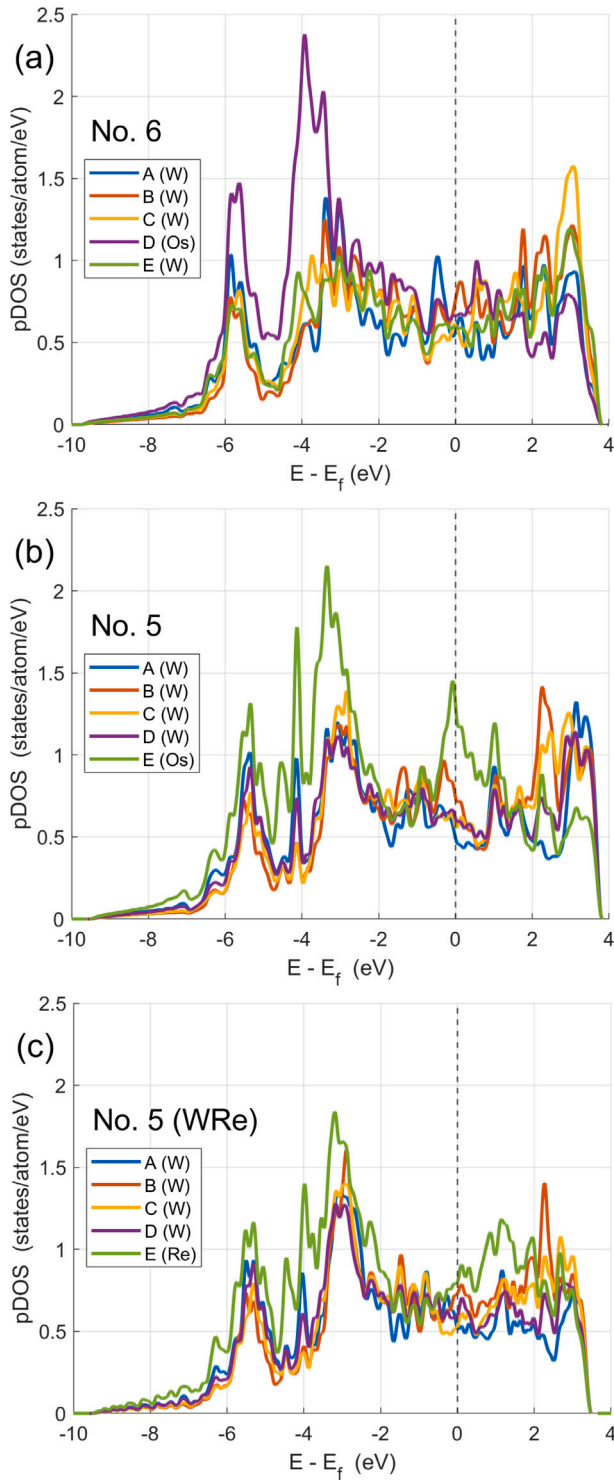


Fig. 8. Projected DOS per atom near the Fermi level projected on the Wyckoff sites, labeled A–E, for WOs configuration (a) No. 6 and (b) No. 5, and (c) WRe configurations No. 5. The data is adapted from [31]. The energy is relative to the Fermi level.

DOS at the Fermi level, indicating that E_f lies in a region of high electronic degeneracy rather than near a pseudo gap. Such an electronic configuration may be less stable, as small structural distortions can lower the energy by reducing the occupation of antibonding states. In our previous work [31], we identified an orthorhombic distortion that stabilized a dynamically unstable WOs σ configuration and reduced the

DOS at the Fermi level. Further studies into the charge distribution densities and bond-order analysis would provide more information on the electronic structure and bond network of the σ phase, but are beyond the scope of this paper.

4.2. Effect of ordering on the mechanical and fracture-related properties

As a consequence of the factors described in Section 4.1, the WOs phase exhibits a higher level of order near the ideal composition as compared to the WRe phase. Recent studies have examined the relationship between phase disorder and the resulting stability and bond strength of the σ phase. A study on the WRe σ phase found that introducing disorder, in the form of substitution on the sublattices, reduces the stability of the phase [76]. Analysis of the bonding charge density indicated stronger interactions among valence electrons in the ordered σ phases, which enhance the bond strength and stability [76]. There are also indications that the amount of disorder in the σ changes the character of the electron bonds: a study on several binary σ phases showed that in ordered structures, the bonding, while still predominately metallic, becomes more covalent in character [73]. In contrast, the bonding retains its metallic character for disordered phases, which typically have chemical compositions different from the ideal [73]. As covalent bonds are stronger than metallic bonds, this also suggests that disorder in the σ phase reduces bonding strength and stability.

The above-mentioned studies on how the bond strength and character are affected by the order/disorder of the σ phase, offer a qualitative explanation to the behavior of the mechanical and fracture-related properties of the WOs and WRe σ phases observed in this study. At the ideal composition, where the WOs phase is highly ordered, the phase exhibits peak hardness, as indicated by the maxima in the G_V , H_V , and E_V curves shown in Fig. 6, indicating increased bond strength and stiffness. Materials with covalent bonds typically exhibit high values of G_V , as their directional and localized bonds provide greater resistance to shear deformation. In contrast, materials with metallic bonds, which are delocalized, are more easily sheared. The peak in G_V at 33 at.% Os therefore aligns with the theory of the electron bonds of ordered phases being more covalent in character. Regarding resistance against uniform compression, the behavior of K_V of the WOs phase is comparable to that of the WRe phase. This may be because the difference in directionality between metallic and covalent-like bonds mainly affects shear response, whereas the resistance to uniform volumetric deformation is similar. The shear modulus is a more direct indicator of bond strength than K_V , since volume is nearly conserved during shear deformation [28]. Osmium concentrations far from the ideal composition, where the disorder in the WOs σ phase increases, result in decreasing G_V , H_V , and E_V , indicating weaker bond strength and a softening of the σ phase. When bond strength becomes weaker, the resistance of brittle separation of the close-packed planes is reduced, as indicated by the drop in G_V^{004} and G_V^{330} at high Os contents seen in Fig. 7(a). Likewise, a reduction in γ_{us} is observed, indicating a reduced resistance to dislocation emission on the slip planes. The increase in $D_{(330)(001)}^{(004)}$, at high Os contents, may indicate increased ductility; however, we emphasize that the criterion of ductile fracture is never fulfilled. The ductility parameters of the other crack and slip systems are largely unaffected by the Os content. Therefore, in a polycrystalline material, where several crack and slip systems can be active, it seems reasonable to expect that the ductility is unaffected by the Os content. The brittle fracture behavior of the precipitates implies that they could initiate points of cracking and reduce grain boundary strength when located e.g. at a grain boundary [9].

In contrast, the WRe σ phase, which exhibits a higher level of disorder at the ideal concentration, does not exhibit notable peaks in the mechanical and fracture-related parameters at this concentration. The higher degree of disorder in the WRe phase at the ideal concentration implies no covalent-like character of the metallic bonds [73] and, consequently, lower bond strength than the WOs phase at this

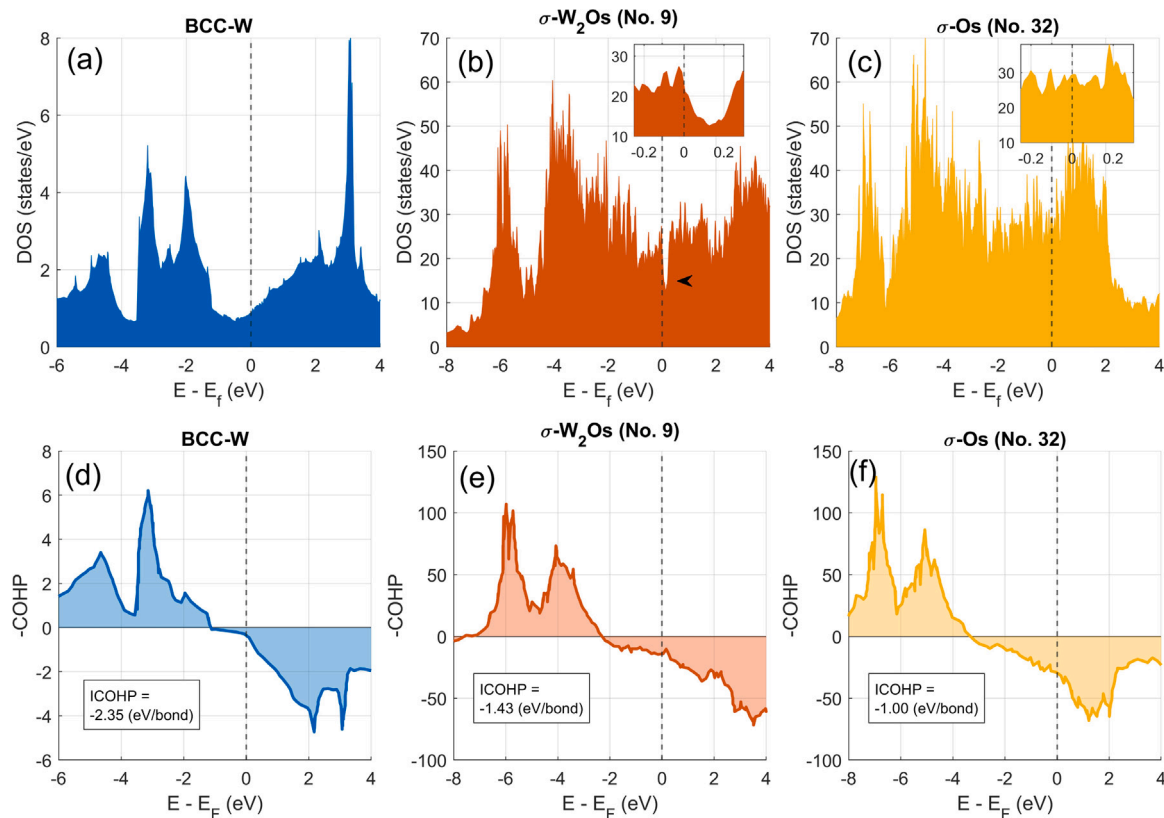


Fig. 9. Top row: DOS of (a) BCC-W, (b) the No. 9 configuration, and (c) the unstable No. 32 configuration of the σ phase, plotted relative to the Fermi level. The insets in (b) and (c) show the DOS in the vicinity of the Fermi level. Bottom row: summed -COHP of the nearest-neighbor pairs for the same structures. The insets show the average ICOHP of the nearest-neighbor bonds integrated up to the Fermi level, which is indicated by vertical dashed lines.

concentration. The WRe phase also exhibits a weaker preference for Re on the *A* and *D* sites. As a result, the stability and mechanical properties of the WRe phase are less sensitive to the composition than for the WOs phase. This is likely the reason why the influence of site occupations on the mechanical properties was not clearly distinguished in the previous studies of the WRe phase [26,28]. Another major difference between the WOs and the WRe phases is the lack of mechanical stability at high Os concentrations for the WOs phase. We note that this happens for concentrations well into the regime where the HCP phase is thermodynamically stable. This indicates that mechanical instability, in addition to the difference in the free energy, could govern the transformation from the σ phase to the HCP phase. However, further studies, which are beyond the scope of this paper, are needed to confirm this.

We note that precipitation hardening in the form of modulus hardening seems unlikely to be the cause of the experimentally observed hardening of neutron-irradiated W samples, as the shear modulus mismatch between a WOs σ precipitate in its stable concentration range and the W matrix is only a few percent. Modulus hardening is also relatively weak compared with other mechanisms of precipitation strengthening [77]. Instead, it seems more likely that the observed hardening could be due to the WOs precipitates acting as impenetrable obstacles with strong pinning of the dislocation motion. This mechanism of precipitation hardening has been documented for the WRe σ precipitates through MD simulations [23,24], although we note that equivalent studies on the WOs phase are not yet available. The main reason for this is the lack of reliable interatomic potentials for the WOs system. However, with the recently published WOs bond-order potential [32], future MD investigations on the effects of the WOs σ precipitates in W may now be possible.

The present study indicates how subtle changes in the *d*-orbital filling of Re and Os greatly influence the amount of disorder near the ideal composition, which causes different behavior of the mechanical

stability and the concentration-dependent mechanical and fracture-related properties of the WOs and WRe σ phases. These insights may also apply to σ in other systems as well as other transition metal TCP phases. For example, a study on multiple σ and χ phases showed that large differences in atomic radii and average valence electron number between the constituting elements improves the stability and atomic ordering of the phases [30]. Although that study did not examine mechanical or fracture-related properties, its findings, combined with our results, suggest that TCP phases with large difference in *d*-orbital filling between the constituting elements may exhibit peak hardness and minimum ductility at their ideal composition due to high atomic ordering, as demonstrated in the WOs σ phase.

5. Conclusions

The mechanical properties of TCP phases are critical in many structural systems. This study focuses on the WOs σ phase, which emerges from transmutation processes in W-based components used in fusion reactors. We find that both the overall Os concentration and the occupation of the Wyckoff sites affect the mechanical properties of the WOs phase to a higher degree than what has been reported for the WRe σ phase. This is likely due to the difference in *d*-orbital filling, resulting in a stronger preference for Os occupying certain Wyckoff sites, making the WOs phase highly ordered at Os concentrations near the ideal composition: W₂Os. At this composition, the WOs σ phase exhibits peaks in several mechanical properties, such as Young's modulus and Vickers hardness. For Os concentrations above the ideal concentration, the Os atoms start to occupy the energetically unfavorable lattice sites, the formation enthalpy rises sharply, and the disorder of the phase increases. This causes the hardness and resistance to shearing to diminish, and the stability of the phase is also affected, since when the Os content exceeds 78 at.%, the WOs phase no longer fulfills the Born

criteria of stability due to negative values of the C_{44} elastic constant. The fracture-related properties, i.e. the brittle energy release rates and unstable stacking fault energies also decrease for Os concentrations above the ideal. However, the Rice ductility parameter exhibited only little dependency on the Os concentrations for the crack-slip systems investigated, except for one system which indicated an improvement in ductility at high Os concentrations. Nevertheless, the Rice criterion for ductile fracture were never fulfilled for any of the crack-slip systems tested.

In contrast to the WOs σ phase, the mechanical properties of the WRe σ phase, which exhibits a higher degree of disorder, show a much weaker dependence on Re content. Recent theoretical studies on the σ phase, linking highly ordered σ phases to increased bond strength and covalent-like bond character, may offer a qualitative explanation for the deviant behavior of the mechanical properties of WOs and WRe. The results of the present study indicates that subtle differences in d -orbital filling can profoundly affect the mechanical properties of the σ phase and may be highly relevant for other transition metal TCP phases, where stability and atomic ordering are governed by similar electronic factors.

CRedit authorship contribution statement

Anders Vesti: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Denis Music:** Writing – review & editing, Methodology. **Mariano Forti:** Writing – review & editing, Methodology. **Mauro Palumbo:** Writing – review & editing, Methodology. **Thomas Hammerschmidt:** Writing – review & editing, Methodology. **Pär A.T. Olsson:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used AI-based language tools: Grammarly and ChatGPT (OpenAI) in order to improve the wording and grammar. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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.

Acknowledgments

The authors gratefully acknowledge funding from the Swedish Research Council, Sweden (grant agreements No. 2016-04162, No. 2018-04348, and No. 2022-04497). The computations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) at the National Supercomputer Centre (NSC), Linköping University, and at the PDC Center for High Performance Computing, KTH Royal Institute of Technology.

Data availability

All data and code required to reproduce the findings of this study are available at: https://github.com/AndVesti/Vesti_2025_WOs_sigma_phase. Large raw datasets are available upon reasonable request.

References

- [1] A. Brooks, C. Clayton, K. Doss, Y. Lu, On the role of Cr in the passivity of stainless steel, *J. Electrochem. Soc.* 133 (12) (1986) 2459.
- [2] A. Babakr, A. Al-Ahmari, K. Al-Jumayyah, F. Habiby, Sigma phase formation and embrittlement of cast iron-chromium-nickel (Fe-Cr-Ni) alloys, *J. Miner. Mater. Charact. Eng.* 7 (2) (2008) 127–145.
- [3] K. Kishida, M. Okutani, H. Suzuki, H. Inui, M. Heilmaier, D. Raabe, Room-temperature deformation of single crystals of the sigma-phase compound FeCr with the tetragonal D8b structure investigated by micropillar compression, *Acta Mater.* 249 (2023) 118829.
- [4] H.M. Ezuber, A. El-Houd, F. El-Shawesh, Effects of sigma phase precipitation on seawater pitting of duplex stainless steel, *Desalination* 207 (1–3) (2007) 268–275.
- [5] M. Shahwaz, P. Nath, I. Sen, A critical review on the microstructure and mechanical properties correlation of additively manufactured nickel-based superalloys, *J. Alloys Compd.* 907 (2022) 164530.
- [6] T. Hammerschmidt, J. Koßmann, C.H. Zenk, S. Neumeier, M. Göken, I. Lopez-Galilea, L.M. Roncery, S. Huth, A. Kostka, W. Theisen, et al., The role of local chemical composition for TCP phase precipitation in Ni-base and Co-base superalloys, *Superalloys 2016* (2016) 89–96.
- [7] R. Reed, M. Jackson, Y. Na, Characterization and modeling of the precipitation of the sigma phase in UDIMET 720 and UDIMET 720LI, *Met. Mater. Trans. A* 30 (1999) 521–533.
- [8] M. Hardy, M. Detrois, E. McDevitt, C. Argyrakakis, V. Saraf, P. Jablonski, J. Hawk, R. Buckingham, H. Kitaguchi, S. Tin, Solving recent challenges for wrought Ni-base superalloys, *Met. Mater. Trans. A* 51 (2020) 2626–2650.
- [9] Y. Nemoto, A. Hasegawa, M. Satou, K. Abe, Microstructural development of neutron irradiated W-Re alloys, *JNuclMater* 283–287 (2000) 1144–1147.
- [10] A. Wazeer, T. McElroy, B.T. Stegman, A. Shang, Y. Zhang, V. Singh, H. Li, Z. Shang, H. Wang, Y. Xue, et al., A brief review of the impact of neutron irradiation damage in tungsten and its alloys, *Metals* 14 (12) (2024) 1374.
- [11] H. Bolt, V. Barabash, W. Krauss, J. Linke, R. Neu, S. Suzuki, N. Yoshida, A.U. Team, Materials for the plasma-facing components of fusion reactors, *JNuclMater* 329 (2004) 66–73.
- [12] J. Linke, J. Du, T. Loewenhoff, G. Pintsuk, B. Spilker, I. Steudel, M. Wirtz, Challenges for plasma-facing components in nuclear fusion, *Matter Radiat. Extrem.* 4 (2019) 056201.
- [13] T. Marchhart, C. Hargrove, A. Marin, H. Schamis, A. Saefan, E. Lang, X. Wang, J.P. Allain, Discovering tungsten-based composites as plasma facing materials for future high-duty cycle nuclear fusion reactors, *Sci. Rep.* 14 (1) (2024) 13864.
- [14] V. Philipps, Tungsten as material for plasma-facing components in fusion devices, *J. Nucl. Mater.* 415 (1) (2011) S2–S9.
- [15] R.G. Abernethy, Predicting the performance of tungsten in a fusion environment: a literature review, *Mater. Sci. Technol.* 33 (2017) 388–399.
- [16] J. Peng, Y. Qian, D. Cereceda, A first-principles study of the structural and thermo-mechanical properties of tungsten-based plasma-facing materials, *Metals* 14 (10) (2024) 1197.
- [17] M. Fukuda, K. Yabuuchi, S. Nogami, A. Hasegawa, T. Tanaka, Microstructural development of tungsten and tungsten–rhenium alloys due to neutron irradiation in HFIR, *J. Nucl. Mater.* 455 (1–3) (2014) 460–463.
- [18] M. Dürrschnabel, M. Klimenkov, U. Jäntschi, M. Rieth, H.C. Schneider, D. Terentyev, New insights into microstructure of neutron-irradiated tungsten, *Sci. Rep.* 11 (7572) (2021).
- [19] M. Klimenkov, M. Dürrschnabel, U. Jäntschi, P. Lied, M. Rieth, H. Schneider, D. Terentyev, W. Van Renterghem, Microstructural analysis of W irradiated at different temperatures, *J. Nucl. Mater.* 572 (2022) 154018.
- [20] T. Tanno, M. Fukuda, S. Nogami, A. Hasegawa, Microstructure development in neutron irradiated tungsten alloys, *Mater. Trans.* 52 (2011) 1447–1451.
- [21] M. Fukuda, T. Tanno, S. Nogami, A. Hasegawa, Effects of Re content and fabrication process on microstructural changes and hardening in neutron irradiated tungsten, *Mater. Trans.* 53 (2012) 2145–2150.
- [22] R.G. Abernethy, J.S.K.L. Gibson, A. Giannattasio, J.D. Murphy, O. Wouters, S. Bradnam, P.L. W., M.R. Gilbert, M. Klimenkov, M. Rieth, H.C. Schneider, C.D. Hardie, S.G. Roberts, D.E.J. Armstrong, Effects of neutron irradiation on the brittle to ductile transition in single crystal tungsten, *JNuclMater* 527 (2019) 151799.
- [23] Y.R. Sharapova, A.M. Kazakov, E.A. Korznikova, A. Zinovev, D. Terentyev, S.V. Dmitriev, Effect of temperature and rhenium content in precipitates on dispersion hardening of tungsten, *Karbala Int. J. Mod. Sci.* 11 (1) (2024) 3.
- [24] G. Bonny, A. Bakaev, D. Terentyev, Assessment of hardening due to non-coherent precipitates in tungsten–rhenium alloys at the atomic scale, *Sci. Rep.* 9 (2019) 2045–2322.
- [25] Z. Wang, R. Wu, X. Wu, H. Li, Effect of Re, temperature and σ phase on mechanical behaviors of W-Re alloys: A molecular dynamics study, *Phys. Lett. A* (2025) 130829.
- [26] A. Vesti, P. Hiremath, S. Melin, P.A.T. Olsson, Ab-initio investigation of mechanical and fracture-related properties of W-Re σ and χ precipitates, *J. Nucl. Mater.* (2023) 154261.

- [27] A. Vesti, D. Music, P.A.T. Olsson, First-principles study on thermal expansion of W-Re sigma and chi phases, *Nucl. Mater. Energy* (2024) 101684.
- [28] G. Bonny, A. Bakaev, D. Terentyev, Y.A. Mastrikov, Elastic properties of the sigma W-Re phase: A first principles investigation, *Scr. Mater.* 128 (2017) 45–48.
- [29] C. Berne, M. Sluiter, Y. Kawazoe, T. Hansen, A. Pasturel, Site occupancy in the Re-W sigma phase, *Phys. Rev. B* 64 (2001) 144103.
- [30] J.-C. Crivello, A. Breidi, J.-M. Joubert, χ and σ phases in binary rhenium-transition metal systems: a systematic first-principles investigation, *Inorg. Chem.* 52 (7) (2013) 3674–3686.
- [31] A. Vesti, D. Music, T. Hammerschmidt, M. Palumbo, P.A.T. Olsson, First-principles study of dynamic instability and phase transformation in the WRe and WOs sigma phase, *Phys. Rev. Mater.* 9 (6) (2025) 063602.
- [32] A.P.A. Subramanyam, Atomistic Modelling of Defects in Transition Metal Alloys (Ph.D. thesis), Ruhr-Universität Bochum, Universitätsbibliothek, 2023.
- [33] M. Gilbert, J.-C. Sublet, Neutron-induced transmutation effects in W and W-alloys in a fusion environment, *Nucl. Fusion* 51 (4) (2011) 043005.
- [34] Y. Le Page, P. Saxe, Symmetry-general least-squares extraction of elastic data for strained materials from ab initio calculations of stress, *Phys. Rev. B* 65 (10) (2002) 104104.
- [35] F. Mouhat, F.-X. Coudert, Necessary and sufficient elastic stability conditions in various crystal systems, *Phys. Rev. B* 90 (22) (2014) 224104.
- [36] R. Hill, The elastic behaviour of a crystalline aggregate, *Proc. Phys. Soc. Sect. A* 65 (5) (1952) 349–354.
- [37] G.E. Dieter, D. Bacon, *Mechanical Metallurgy*, vol. 3, McGraw-hill New York, 1976.
- [38] B. Mayer, H. Anton, E. Bott, M. Methfessel, J. Sticht, J. Harris, P. Schmidt, Ab-initio calculation of the elastic constants and thermal expansion coefficients of Laves phases, *Intermetallics* 11 (1) (2003) 23–32.
- [39] X.-Q. Chen, H. Niu, D. Li, Y. Li, Modeling hardness of polycrystalline materials and bulk metallic glasses, *Intermetallics* 19 (9) (2011) 1275–1281.
- [40] J.R. Rice, Dislocation nucleation from a crack tip: an analysis based on the Peierls concept, *J. Mech. Phys. Solids* 40 (2) (1992) 239–271.
- [41] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.* 44 (6) (2011) 1272–1276.
- [42] J.-M. Joubert, J.-C. Crivello, Non-stoichiometry and Calphad modeling of Frank-Kasper phases, *Appl. Sci.* 2 (3) (2012) 669–681.
- [43] A. Taylor, B. Kagle, N. Doyle, The constitution diagram of the tungsten-osmium binary system, *J. Less Common Met.* 3 (4) (1961) 333–347.
- [44] T.B. Massalski, H. Okamoto, P. Subramanian, L. Kacprzak, W.W. Scott, Binary alloy phase diagrams, vol. 1, American society for metals Metals Park, OH, 1986.
- [45] C. Berne, A. Pasturel, M. Sluiter, B. Vinet, Ab initio study of metastability in refractory metal based systems, *Phys. Rev. Lett.* 83 (8) (1999) 1621.
- [46] S.G. Fries, B. Sundman, Using Re-W σ -phase first-principles results in the Bragg-Williams approximation to calculate finite-temperature thermodynamic properties, *Phys. Rev. B* 66 (1) (2002) 012203.
- [47] J.-M. Joubert, M. Phejar, Crystal chemistry and Calphad modelling of the χ phase, *Prog. Mater. Sci.* 54 (7) (2009) 945–980.
- [48] J.C. Crivello, J.M. Joubert, First principles calculations of the σ and χ phases in the Mo-Re and W-Re systems, *J. Phys.: Condens. Matter.* 22 (2009) 035402.
- [49] N. Dupin, S.G. Fries, J.-M. Joubert, B. Sundman, M. Sluiter, Y. Kawazoe, A. Pasturel, Using first-principles results to calculate finite-temperature thermodynamic properties of the Nb–Ni μ phase in the Bragg–Williams approximation, *Phil. Mag.* 86 (12) (2006) 1631–1641.
- [50] M. Palumbo, T. Abe, S.G. Fries, A. Pasturel, First-principles approach to phase stability for a ternary σ phase: Application to Cr–Ni–Re, *Phys. Rev. B—Condens. Matter Mater. Phys.* 83 (14) (2011) 144109.
- [51] J.-C. Crivello, M. Palumbo, T. Abe, J.-M. Joubert, Ab initio ternary σ -phase diagram: The Cr–Mo–Re system, *Calphad* 34 (4) (2010) 487–494.
- [52] M. Palumbo, S.G. Fries, A. Pasturel, D. Alfè, Anharmonicity, mechanical instability, and thermodynamic properties of the Cr-Re σ -phase, *J. Chem. Phys.* 140 (14) (2014).
- [53] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B* 47 (1) (1993) 558.
- [54] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* 6 (1) (1996) 15–50.
- [55] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59 (1999) 1758–1775.
- [56] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (1994) 17953–17979.
- [57] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868.
- [58] M. Methfessel, A. Paxton, High-precision sampling for Brillouin-zone integration in metals, *Phys. Rev. B* 40 (6) (1989) 3616.
- [59] P.E. Blöchl, O. Jepsen, O.K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, *Phys. Rev. B* 49 (23) (1994) 16223.
- [60] R. Dronskowski, P.E. Bloechl, Crystal orbital hamilton populations (COHP): energy-resolved visualization of chemical bonding in solids based on density-functional calculations, *J. Phys. Chem.* 97 (33) (1993) 8617–8624.
- [61] V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, Crystal orbital hamilton population (COHP) analysis as projected from plane-wave basis sets, *J. Phys. Chem. A* 115 (21) (2011) 5461–5466.
- [62] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, Analytic projection from plane-wave and PAW wavefunctions and application to chemical-bonding analysis in solids, *J. Comput. Chem.* 34 (29) (2013) 2557–2567.
- [63] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (16) (1996) 11169.
- [64] E. Clementi, D. Raimondi, W.P. Reinhardt, Atomic screening constants from SCF functions. II. atoms with 37 to 86 electrons, *J. Chem. Phys.* 47 (4) (1967) 1300–1307.
- [65] P. Haas, F. Tran, P. Blaha, Calculation of the lattice constant of solids with semilocal functionals, *Phys. Rev. B Condens. Matter Mater. Phys.* 79 (8) (2009) 085104.
- [66] K. Kishida, M. Okutani, H. Inui, Direct observation of zonal dislocation in complex materials by atomic-resolution scanning transmission electron microscopy, *Acta Mater.* 228 (2022) 117756.
- [67] A.A. Griffith, VI. The phenomena of rupture and flow in solids, *Philos. Trans. R. Soc. Lond.. Series A* 221 (582–593) (1921) 163–198.
- [68] B. Seiser, T. Hammerschmidt, A. Kolmogorov, R. Drautz, D. Pettifor, Theory of structural trends within 4d and 5d transition metal topologically close-packed phases, *Phys. Rev. B Condens. Matter Mater. Phys.* 83 (22) (2011) 224116.
- [69] M.H. Sluiter, A. Pasturel, Site occupation in the Cr–Ru and Cr–Os σ phases, *Phys. Rev. B* 80 (13) (2009) 134122.
- [70] W. Liu, X.-G. Lu, P. Boulet, M.-C. Record, Influencing factors of atomic order in the binary sigma phase, *Intermetallics* 93 (2018) 6–19.
- [71] J. Kasper, R. Waterstrat, Ordering of atoms in the σ phase, *Acta Crystallogr.* 9 (3) (1956) 289–295.
- [72] J. Kasper, Atomic and magnetic ordering in transition metal structures, *Theory Alloy. Phases* 48 (1956) 264–278.
- [73] W. Liu, X.-G. Lu, Q.-M. Hu, H. Wang, Y. Liu, P. Boulet, M.-C. Record, Atomic bonding and electronic stability of the binary sigma phase, *J. Alloys Compd.* 811 (2019) 152053.
- [74] W. Zhang, M. Forti, R. Xie, C. Barreateau, A. Taichi, J.-M. Joubert, T. Hammerschmidt, J.-C. Crivello, Prediction and characterization of chemically complex σ -phase intermetallics with graph neural network, *Acta Mater.* (2025) 121427.
- [75] M. Mrovec, R. Gröger, A.G. Bailey, D. Nguyen-Manh, C. Elsässer, V. Vitek, Bond-order potential for simulations of extended defects in tungsten, *Phys. Rev. B—Condens. Matter Mater. Phys.* 75 (10) (2007) 104119.
- [76] Z.-P. Zhu, D. Jia, W.Y. Wang, J.-L. Yin, X.-Y. Gao, S.-F. Yang, H.-F. Song, J.-S. Li, Effect of order-disorder transition on thermodynamic and electronic properties of σ and χ phases in W–Re alloy: the first-principles calculation, *Tungsten* (2024) 1–19.
- [77] E. Nembach, Precipitation hardening caused by a difference in shear modulus between particle and matrix, *Phys. Status Solidi (A)* 78 (2) (1983) 571–581.