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Functional limits of chemical short-range order for hydrogen-resistant alloy design

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Abstract

Chemical short-range order (CSRO) is increasingly invoked as an alloy-design lever for tailoring properties in complex concentrated alloys, yet the conditions under which it influences materials performance remain poorly defined. Establishing this boundary is challenging because processing routes used to modify CSRO often introduce concurrent changes in composition and microstructure. Hydrogen degradation provides a particularly stringent test of the CSRO paradigm because hydrogen transport and embrittlement are intrinsically sensitive to local atomic environments and transport kinetics. Here, by isolating the effect of CSRO in two chemically distinct face-centered cubic (FCC) alloy systems, equiatomic CoCrNi and commercial Inconel 625, while maintaining composition and microstructural features unchanged, we show that near-saturated experimentally accessible CSRO states leave apparent hydrogen diffusivity and embrittlement susceptibility unchanged. The reproducibility of these observations across both systems demonstrates that structurally detectable CSRO can remain functionally silent with respect to hydrogen degradation. More broadly, these findings define the functional limit of CSRO-based alloy design, demonstrating that the sub-nanometric energetic perturbations typical of CSRO in FCC alloys are insufficient to serve as an effective design lever against hydrogen-assisted degradation.

Chemical short-range order (CSRO) has emerged as a central concept in alloy design for complex concentrated alloys (CCAs). By modifying local atomic environments, CSRO has been proposed as a potential route to tailor mechanical behavior^{1–3}, corrosion resistance^{4–11} and radiation tolerance^{12–16}. Yet the growing prominence of this paradigm has outpaced experimental evidence establishing when CSRO exerts a measurable influence on materials performance. Owing to its intrinsically sub-nanometric scale and subtle structural signature, CSRO remains difficult to capture and quantify experimentally^{17–24}, and much of the current understanding of its effects therefore derives from atomistic and computational studies^{25–33}. Moreover, processing routes used to manipulate CSRO frequently modify composition, grain size, texture, and phase content simultaneously^{1,4–10}, obscuring its intrinsic contribution to materials performance. As a result, the field would greatly benefit from experimentally grounded criteria for when CSRO should be expected to influence materials performance and when it should remain functionally silent.

Hydrogen degradation provides a particularly stringent test of this question because hydrogen transport and embrittlement are inherently sensitive to local atomic environments, trapping energetics and defect-mediated transport pathways. Atomistic simulations have predicted that CSRO substantially alters hydrogen diffusivity in CoCrFeMnNi CCA, suggesting a route to improved hydrogen embrittlement (HE) resistance³⁴. More recently, atomistic simulations in CoNiV CCA further indicated that CSRO redistributes hydrogen solution energetics and preferred interstitial environments, potentially reducing hydrogen uptake³⁵. However, these predictions remain experimentally unvalidated. Existing experimental evidence in CoNiV CCA³⁶ is similarly inconclusive owing to the lack of direct diffusivity measurements and rigorous quantification of CSRO states. The clearest experimental demonstration comes from body-centered cubic (BCC) TiV alloys³⁷, where large interstitial site-energy contrasts (~ 20 kJ mol⁻¹) produce measurable changes in hydrogen transport following atomic redistribution by CSRO. Whether analogous effects exist in face-centered cubic (FCC) CCAs, where the corresponding energetic contrasts are expected to be substantially smaller, remains experimentally unresolved. More broadly, hydrogen degradation is an especially informative benchmark for assessing the design relevance of CSRO: if CSRO cannot measurably influence hydrogen transport and embrittlement, despite

their strong sensitivity to local energetic perturbations, then the assumption that CSRO could serve as a potential alloy-design parameter must be reconsidered.

Here, we test whether CSRO constitutes an effective strategy for hydrogen-resistant alloy design by isolating its effects in two chemically distinct FCC alloy systems: equiatomic CoCrNi, the best-characterized single-phase model system for experimental and computational investigations of CSRO^{1,21,25,30,38–42}; and commercial Inconel 625, selected to examine whether the observed phenomena extend to industrially relevant multicomponent superalloys. By combining large-scale molecular dynamics simulations using a purpose-built deep-learning interatomic potential with direct measurements of hydrogen transport and embrittlement, we show that near-saturated experimentally accessible CSRO states produce negligible changes in apparent hydrogen diffusivity, embrittlement susceptibility and the associated damage evolution. These findings establish that CSRO can remain functionally silent with respect to hydrogen degradation and, more broadly, define an experimentally grounded functional limit for the use of CSRO as an alloy-design parameter.

To isolate the effect of CSRO, we first establish that thermal aging alters chemical order without measurable microstructural evolution. Electron backscatter diffraction (EBSD), high-energy synchrotron X-ray diffraction (HE-SXRD), transmission electron microscopy (TEM) and scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS) reveal statistically equivalent grain size ($d \approx 24 \mu\text{m}$), crystallite size ($c \approx 18 \mu\text{m}$), average number of twin boundaries per grain ($n \approx 0.3$), crystallographic texture ($\leq 2.5 \text{ mrd}$), phase constitution, and chemical homogeneity in the recrystallized and aged CoCrNi conditions (**Fig. 1a–l**). Both conditions retain a single FCC phase without evidence of precipitation, secondary phase formation or elemental segregation, indicating that aging does not measurably alter conventional microstructural descriptors. We further perform atom probe tomography (APT), which reveals spatially homogeneous elemental distributions with only subtle deviations from ideal binomial statistics (**Fig. 1m–o**). Although the APT results alone cannot unambiguously establish the presence of CSRO^{21,43}, they exclude chemical heterogeneity as possible origins of the observed behavior.

To validate CSRO formation during aging in the CoCrNi, we performed differential scanning calorimetry (DSC) by measuring the temperature-dependent specific heat

capacity, $C_p(T)$, during two independent heating cycles (**Fig. 1p, q**). The first heating cycle of the recrystallized condition exhibits an exothermic response, $\Delta H = -5.68 \text{ J g}^{-1}$ ($-0.32 \text{ kJ mol}^{-1}$), consistent with CSRO formation upon heating, whereas the aged condition exhibits an endothermic signal, $\Delta H = 7.64 \text{ J g}^{-1}$ (0.43 kJ mol^{-1}), associated with the dissolution of pre-existing CSRO^{23,38,39}. Together, these responses correspond to a total enthalpy difference of 13.32 J g^{-1} (0.75 kJ mol^{-1}) between the two initial states. This enthalpy difference arises from reversible CSRO evolution, reflecting the glass-transition-like kinetic arrest behavior previously reported for CoCrNi³⁸. The same behavior is observed when applying the same experimental strategy to commercial Inconel 625 (**Supplementary Fig. 1**). Furthermore, the aging conditions employed here correspond to near-saturated experimentally accessible CSRO states previously established for CoCrNi, with longer aging treatments producing no significant increase in ordering degree³⁹. The second heating cycle exhibits a shifted baseline together with an endothermic signal consistent with the dissolution of CSRO re-established during cooling, as previously reported for CoCrNi³⁹. Collectively, the first and second heating cycles confirm the reversible nature of CSRO evolution and establish that the two thermal treatments produce markedly different degrees of CSRO while leaving the remaining microstructural variables statistically unchanged, thereby providing the experimental framework required to isolate the intrinsic role of CSRO in the subsequent hydrogen transport and embrittlement measurements.

To provide atomistic insight into the influence of CSRO on hydrogen transport, we performed Monte Carlo (MC) simulations for the model equiatomic CoCrNi alloy. Owing to the chemical complexity of Inconel 625, our computational analyses were restricted to CoCrNi. The continuous decrease in potential energy with increasing MC swaps shows that the system evolves toward energetically favorable atomic configurations (**Fig. 2a**). Consistently, we quantified CSRO degree using Warren–Cowley parameters, which reveal increasingly pronounced deviations from randomness with increasing MC evolution (**Fig. 2b**). At the saturated CSRO state (CSRO degree 3), Co–Co and Ni–Ni pairs exhibit preferential homoatomic association, whereas Cr–Cr and Co–Ni nearest-neighbor pairs are avoided. Conversely, Co–Cr and Cr–Ni interactions are preferentially favored relative to a random solid solution (RSS). These trends are reflected in the redistribution of homo- and heteroatomic bond distributions (**Fig. 2c**).

These simulations therefore capture substantial local chemical rearrangements representative of near-saturated experimentally accessible CSRO states.

Despite these substantial modifications in local atomic arrangements, hydrogen transport remains remarkably insensitive to CSRO. We quantified hydrogen mobility through mean-squared displacement (MSD) analyses, which reveal nearly identical diffusion behavior for RSS and CSRO degree 3 across all investigated temperatures (**Fig. 2d**), yielding activation energies (Q) of 0.407 and 0.415 eV (39.3 and 40.0 kJ mol⁻¹), respectively. The hydrogen diffusivities (D) in the RSS and CSRO degree 3 configurations differ by less than a factor of 1.3 over the entire temperature range examined (**Fig. 2e**). We nevertheless find that CSRO measurably alters local hydrogen partitioning, promoting preferential occupation of Ni-rich environments and reducing H–Co associations (**Fig. 2f–h**), demonstrating that H–metal interactions remain sensitive to CSRO.

The extent to which CSRO influences hydrogen transport ultimately depends on the magnitude of the energetic perturbations it introduces into the hydrogen energy landscape. The strongest experimental evidence that CSRO can alter hydrogen transport comes from BCC TiV alloys, where CSRO redistributes hydrogen among interstitial sites with solution-energy differences of ~20.0 kJ mol⁻¹, generating energetic contrasts sufficiently large to measurably reduce macroscopic hydrogen diffusivity³⁷. By comparison, atomistic simulations by Zhou *et al.*³⁴ predicted that CSRO suppresses hydrogen diffusivity in CoCrFeMnNi, corresponding to an increase in the hydrogen migration barrier of $\Delta Q = 0.19$ eV (~18.3 kJ mol⁻¹). More recently, Chen *et al.*³⁵ reported atomistic simulations on CoNiV, a system exhibiting pronounced V-centered CSRO and strong V–H interactions. Their calculations predict that CSRO raises the average hydrogen solution energy by ~0.07 eV (~6.8 kJ mol⁻¹), indicating substantial modification of the local hydrogen solution-energy landscape. Although these studies quantify different energetic descriptors governing hydrogen transport (including solution-energy differences, migration barriers, and average solution energies), they consistently indicate that the magnitude of the CSRO-induced energetic perturbation varies substantially across alloy systems. In the present CoCrNi, however, our atomistic calculations predict an increase of only 0.008 eV (~0.8 kJ mol⁻¹) (**Fig. 2e**). Thus, although CSRO alters hydrogen partitioning among local environments, the CSRO-induced energetic perturbation in CoCrNi (~0.8 kJ mol⁻¹) remains far below

those reported for TiV (~ 20.0 kJ mol⁻¹)³⁷, CoCrFeMnNi (~ 18.3 kJ mol⁻¹)³⁴, and CoNiV (~ 6.8 kJ mol⁻¹)³⁵, indicating that the CSRO-induced energetic perturbation is insufficient to measurably alter macroscopic hydrogen transport, a prediction directly examined experimentally in the following sections.

To assess the influence of CSRO on hydrogen transport, we performed gaseous hydrogen permeation measurements over a broad temperature range for both the recrystallized and aged CoCrNi conditions (**Fig. 3**). Although the permeation transients are not identical and exhibit modest differences in both breakthrough behavior and steady-state hydrogen flux (**Fig. 3a**), these features are influenced by specimen thickness. Because the apparent hydrogen diffusivity (D_{app}) was determined from the breakthrough time using equations (2) and (3), which explicitly normalize for specimen thickness, the extracted D_{app} values increase monotonically with temperature for both conditions (**Fig. 3b**). Although the aged condition exhibits slightly higher D_{app} at 773 and 823 K, both conditions remain within the same diffusivity regime (10^{-11} m² s⁻¹), and the observed differences are comparable to the experimental uncertainty. Similarly, Arrhenius analysis yields apparent activation energies (Q_{app}) of 97.5 ± 12.5 and 118.5 ± 11.6 kJ mol⁻¹ for the recrystallized and aged conditions, respectively. Given the overlap between the associated uncertainties, these values cannot be considered statistically distinct.

The permeation measurements therefore provide no evidence that CSRO produces a measurable change in either D_{app} or Q_{app} governing hydrogen transport. Instead, they experimentally confirm that only sufficiently large CSRO-induced energetic perturbations translate into measurable changes in macroscopic hydrogen diffusion. The same absence of measurable CSRO effects on hydrogen transport is reproduced in commercial Inconel 625 (**Supplementary Fig. 2**), indicating that this behavior extends beyond model CCAs. Previous studies further show that even substantial microstructural modifications, such as coherent γ' precipitation, exert only a marginal influence on hydrogen diffusivity in FCC CCAs⁴⁴, consistent with this conclusion.

We note that the temperatures employed during gaseous hydrogen permeation testing (723–823 K) lie within the regime over which CSRO evolution becomes thermodynamically accessible (**Fig. 1p, q** and **Supplementary Fig. 1**). Consequently, some bidirectional relaxation of the initial ordering states during thermal equilibration

cannot be excluded: the recrystallized condition may develop additional CSRO upon heating, whereas the aged condition may undergo partial disordering. Such *in situ* evolution would tend to reduce the initial contrast in CSRO between the two conditions. The persistence of statistically indistinguishable permeation transients despite this potential relaxation therefore provides a conservative bound on the influence of experimentally accessible CSRO on macroscopic hydrogen transport. This interpretation is independently reinforced by the room-temperature mechanical and fractographic measurements (**Figs. 4–6** and **Supplementary Figs. 3–5**), where thermally activated evolution of CSRO is kinetically negligible over the experimental timescale and the distinct initial ordering states are effectively preserved. Together, these complementary measurements demonstrate that the observed transport equivalence reflects an intrinsically weak coupling between experimentally accessible CSRO and hydrogen degradation rather than an artifact of thermal relaxation.

The absence of measurable transport changes further suggests that the CSRO-induced perturbation of local interstitial-site energetics is insufficient to measurably alter bulk hydrogen transport over the tested temperature range. This behavior contrasts with the pronounced effects reported for grain boundaries, dislocations, chemically heterogeneous interfaces, oxide films, and carbide-containing microstructures^{45–52}, all of which modify hydrogen trapping and thereby influence hydrogen tolerance. Although such features may mitigate HE by immobilizing hydrogen and interrupting damage propagation pathways, they also increase hydrogen solubility and can act as potential sources of hydrogen for HE⁵³, highlighting the delicate balance required for trapping-mediated hydrogen tolerance. Unlike these defects and mesoscale chemical heterogeneities, the sub-nanometric chemical perturbations associated with experimentally accessible CSRO states are insufficient to measurably modify hydrogen transport or local hydrogen partitioning in these FCC alloys.

Having established pronounced differences in CSRO, we evaluated whether these differences influence the mechanical response to hydrogen charging for both the recrystallized and aged CoCrNi conditions (**Fig. 4**). We observe progressively increasing HE indices (δ_{loss}) with increasing charging duration in both microstructural states, yet the measured δ_{loss} values remain statistically indistinguishable between the recrystallized and aged conditions. The δ_{loss} reaches $(8 \pm 2)\%$ and $(3 \pm 2)\%$ after 1 day of charging, increasing to $(15 \pm 1)\%$ and $(12 \pm 1)\%$ after 7 days in the recrystallized

and aged conditions, respectively (**Fig. 4a, d**). Despite substantial differences in CSRO degree, uniform elongation (ϵ_{UE}) and elongation to failure (ϵ_{EF}) remain statistically indistinguishable between the recrystallized and aged conditions across all hydrogen charging durations investigated (**Fig. 4c, f**). Although the aged condition exhibits slightly higher yield strength (σ_y), and ultimate tensile strength (σ_u) after hydrogen charging, with maximum increases of only 26 MPa (~7.5%) and 28 MPa (~3.7%), respectively (**Fig. 4b, e**), these differences do not translate into measurable changes in the hydrogen-assisted mechanical response. Notably, the absence of measurable differences in the uncharged tensile response extends previous observations that CSRO alone produces negligible strengthening effects in CoCrNi^{39–41}. Thus, CSRO exerts a limited influence not only on the intrinsic mechanical response, but also on its susceptibility to hydrogen-assisted degradation. This mechanical insensitivity mirrors the transport results presented above (**Fig. 3**), suggesting that CSRO neither substantially alters hydrogen uptake nor redistributes hydrogen sufficiently to modify crack initiation and propagation processes. The sub-nanometric perturbations introduced by CSRO therefore are insufficient to measurably influence hydrogen-assisted mechanical degradation. Similar trends emerge in Inconel 625 (**Supplementary Fig. 3**), indicating that the limited role of CSRO extends beyond model CCAs and may represent a broader characteristic of FCC alloy systems.

To gain mechanistic insight into hydrogen-assisted deformation, we examined whether the substantial differences in CSRO influence the defect evolution associated with hydrogen-assisted deformation. Using post-mortem high-energy synchrotron X-ray diffraction (HE-SXRD) line-scan analyses along fractured tensile specimens (**Fig. 5a**), we obtained spatially resolved measurements of dislocation density (ρ), providing mechanistic insight into the deformation processes governing hydrogen-assisted failure in CoCrNi. The ρ profiles exhibit three distinct regions: a high-dislocation-density region adjacent to the fracture surface associated with localized necking, followed by an extended plateau corresponding to homogeneous plastic deformation along the gauge section, and finally a gradual decrease toward the grip region, where deformation is minimal (**Fig. 5b, c**). This spatial evolution is consistent with progressive strain localization preceding final fracture in FCC alloys. Despite their substantially different degrees of CSRO, both the magnitude and spatial evolution of ρ remain virtually identical between the recrystallized and aged conditions. The maximum near-

fracture ρ decreases from $\sim 4.09\text{--}4.53 \times 10^{15} \text{ m}^{-2}$ in the uncharged state to $\sim 3.04\text{--}3.26 \times 10^{15} \text{ m}^{-2}$ after 7 days of hydrogen charging, while preserving nearly identical spatial evolution in both conditions (**Fig. 5b1–b3, c1–c3**). Similar behavior is observed in Inconel 625 (**Supplementary Fig. 4**), indicating that the limited influence of CSRO on ρ evolution extends beyond model CCAs.

The lower near-fracture ρ measured after hydrogen charging suggests that hydrogen promotes earlier strain localization and premature fracture, thereby limiting the total plastic deformation accumulated prior to failure^{46,54}, consistent with the progressive increase in δ_{loss} (**Fig. 4** and **Supplementary Fig. 3**). Critically, however, we detect no discernible effect of CSRO on ρ evolution at any position along the gauge length. This observation is consistent with recent *in situ* HE-SXRD work demonstrating that varying degrees of CSRO in CoCrNi do not alter the evolution of ρ during tensile deformation³⁹.

Although hydrogen has been predicted to reduce the stacking-fault energy (SFE) of FCC alloys and thereby promote deformation mechanisms involving planar defects and phase transformation^{55,56}, we further note that all HE-SXRD patterns of CoCrNi and Inconel 625 remain fully indexed to the FCC phase irrespective of hydrogen charging condition (**Fig. 5d–i** and **Supplementary Fig. 4**), revealing no hydrogen-induced phase transformation. These observations show that any hydrogen-induced modification of the fault-energy landscape is insufficient to measurably alter the operative deformation pathways under the present conditions. We further note that recent studies^{42,57,58} have shown that CSRO increases the SFE in CoCrNi, thereby enhancing FCC phase stability. Therefore, if hydrogen is unable to trigger any detectable phase transformation in the recrystallized condition, such transformations would be even less likely in the aged state containing a higher degree of CSRO. These observations show that the defect-mediated deformation pathways remain invariant despite substantial differences in CSRO degree in these alloys, providing a mechanistic explanation for the statistically equivalent hydrogen embrittlement susceptibility observed in **Fig. 4** and **Supplementary Fig. 3**.

We next examined whether the substantial differences in CSRO influence the fracture mechanisms associated with hydrogen-assisted damage. For the CoCrNi, fractographic analyses reveal that the operative fracture modes remain unchanged despite the pronounced differences in CSRO (**Fig. 6**). In the uncharged condition, we

observe fully ductile fracture surfaces in both recrystallized and aged specimens (**Fig. 6a, a1, a2, d, d1, d2**), characterized by homogeneous microvoid coalescence, confirming the intrinsic mechanical equivalence of the two microstructural states. Following hydrogen charging, both conditions develop an identical three-zone fracture morphology consisting of (I) a near-surface intergranular fracture layer, (II) a transition region and (III) an interior ductile region dominated by dimples. We find that the depth of the intergranular fracture layer, which provides a microstructural signature of the hydrogen-affected region, remains statistically indistinguishable between the recrystallized and aged conditions, reaching $24 \pm 4 \mu\text{m}$ and $21 \pm 5 \mu\text{m}$ after 1 day of charging (**Fig. 6b, b1, b2, e, e1, e2**), and $65 \pm 6 \mu\text{m}$ and $61 \pm 8 \mu\text{m}$ after 7 days (**Fig. 6c, c1, c2, f, f1, f2**), respectively. We observe the same behavior in Inconel 625 (**Supplementary Fig. 5**), further demonstrating that the insensitivity of fracture behavior to CSRO extends beyond model CCAs.

This systematic transition from intergranular fracture near the hydrogen-charged surface to ductile microvoid coalescence within the specimen interior is consistent with the concentration-dependent activation of hydrogen-assisted fracture mechanisms involving grain-boundary weakening and decohesion^{59,60}. Nevertheless, hydrogen-enhanced decohesion (HEDE) and hydrogen-enhanced localized plasticity (HELP) are frequently considered synergistic rather than mutually exclusive mechanisms^{53,61–63}. Regardless of the relative contributions of HEDE and HELP, we detect no measurable influence of CSRO on either the extent or the morphology of the hydrogen-affected fracture regions. The fractographic observations directly mirror the transport measurements. The equivalent intergranular fracture depths are consistent with the identical hydrogen diffusivities, indicating that CSRO does not modify either hydrogen transport or the subsequent development of hydrogen-assisted damage. Together, these observations complete a consistent picture across all experimental observables.

In summary, we demonstrate that experimentally accessible near-saturated CSRO states in both the model CoCrNi alloy and the commercial Inconel 625 alloy do not alter hydrogen transport or embrittlement behavior. These findings demonstrate that, at least in the alloys studied here, structurally detectable CSRO does not translate into functional control of hydrogen degradation when the local energetic perturbations introduced by CSRO remain too small to measurably influence hydrogen transport and the mechanisms governing hydrogen-assisted failure. More broadly, our results define

a functional limit for CSRO-based alloy design. CSRO should not be assumed to be a generally effective alloy-design parameter unless the target property is directly coupled to the local chemical and energetic landscape that CSRO modifies. For hydrogen-resistant FCC alloy design, this shifts the focus toward microstructural features that operate on the structural scales governing hydrogen-assisted damage evolution.

Methods

Alloy production and thermomechanical processing

The equiatomic CoCrNi alloy was produced by arc melting high-purity elements (>99.99 wt.%) under an argon atmosphere. The ingots were remelted five times to ensure chemical homogeneity, homogenized at 1473 K for 4 h, water quenched, and subsequently hot rolled at 1423 K to a thickness of 2 mm, followed by water-quenching. The material was then cold rolled to a thickness reduction of ~50% and annealed at 1273 K for 1 h followed by water quenching, producing a fully recrystallized FCC microstructure with equiaxed grains. To obtain CSRO-aged specimens, the heat treatment was conducted at 748 K for 100 h, followed by water-quenching. Prolonged aging times at this temperature do not significantly increase the CSRO content³⁹.

To evaluate the broader relevance of our conclusions, the commercial Inconel 625 superalloy was selected owing to its widespread industrial relevance and to determine whether the role of CSRO identified in CoCrNi extends beyond model CCAs. Inconel 625 was subjected to homogenization at 1473 K for 4 h, water quenching, and subsequent aging at 748 K for 100 h, following the same experimental strategy adopted for CoCrNi. Note that the aging temperature of 748 K remains below the precipitation range of the strengthening γ' and γ'' phases, consistent with the experimentally confirmed absence of secondary phases (**Supplementary Fig. 1**). Direct comparisons between CoCrNi and Inconel 625 are intended to evaluate the qualitative influence of CSRO on hydrogen transport and embrittlement rather than to establish direct quantitative relationships between the two alloy systems.

Microstructural characterization

A scanning electron microscope (Scios 2 DualBeam) equipped with energy-dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD) detectors was used

to characterize the microstructures and determine the chemical compositions. The measured composition of the equiatomic CoCrNi is Co_{33.5}Cr_{33.8}Ni_{32.7} (at.%), consistent with the nominal composition. The corresponding composition of the Inconel 625 is Ni-21.0Cr-7.4Mo-2.6Nb-1.5Fe-0.7Ta (wt.%). EBSD maps were acquired at 25 kV using step sizes between 0.8 and 3.3 μm and analyzed using ATEX software⁶⁴. Grain size (d) measurements were determined considering high-angle grain boundaries (HAGBs) with misorientations ($\theta \geq 15^\circ$) excluding annealing twin boundaries (ATBs), whereas crystallite size (c) measurements included ATBs. In addition to d and c , the average number of ATBs per grain (n) was calculated according to equation (1)⁶⁵:

$$n = \left(\frac{d}{c} \right) - 1 \quad (1)$$

where the term -1 accounts for the inclusion of grain boundaries in the crystallite size calculation. EBSD specimens were prepared by mechanical polishing using diamond suspensions followed by electropolishing in a solution containing 5 vol.% perchloric acid and 95 vol.% ethanol at 273 K.

Transmission electron microscopy (TEM) was conducted using a FEI Talos F200X (cold field-emission gun) operated at 200 kV. TEM foils were prepared by mechanical grinding followed by ion milling using a Gatan PIPS II.

High-energy synchrotron X-ray diffraction

High-energy synchrotron X-ray diffraction (HE-SXRD) single-shot measurements were performed to identify the phase structure of the recrystallized and aged specimens. The HE-SXRD were performed at the P07 High Energy Materials Science beamline of PETRA III, operated and coordinated by Helmholtz-Zentrum Hereon⁶⁶. An incident beam energy of 87.1 keV ($\lambda = 0.14235 \text{ \AA}$) and beam size of $500 \times 100 \mu\text{m}^2$ were employed. Diffraction patterns were collected using a two-dimensional Perkin-Elmer fast detector (2048×2048 pixels). A LaB₆ powder standard was used to calibrate the distance between the specimen and the detector (1.324 m). The diffraction patterns were subsequently integrated into one-dimensional diffraction profiles for analysis.

Atom probe tomography

Atom probe tomography (APT) specimens were prepared using a Ga focused ion beam instrument (FEI Helios FIB) equipped with a Ga-ion source. Analyses were

performed using a local electrode atom probe (LEAP 5000 XR™, Cameca Instruments Inc.) operated in voltage mode with a pulse fraction of 20% at a specimen temperature of 60 K. Three-dimensional reconstruction and compositional analysis were carried out using Cameca AP Suite 6.3 software.

Differential scanning calorimetry

The specific heat capacity (C_p) at constant pressure was measured by differential scanning calorimetry (Netzsch DSC 404C) under flowing argon. Specimens (~40 mg) were analyzed between 373 and 973 K using a heating rate of 10 K min⁻¹ and a cooling rate of 40 K min⁻¹, with two cycles of heating and cooling. Only heating segments were considered for C_p analysis. Sapphire was used as the calibration standard and an empty platinum crucible as the reference baseline, following ASTM E1269-18⁶⁷. C_p values were calculated using Proteus® software. The energies associated with exothermic and endothermic reactions were determined by numerical integration of the corresponding peak areas. Measurement uncertainty was assessed using K₂CrO₄ standard and estimated to be ~4.3%. The DSC protocol and data analysis procedures followed the methodology established in our previous work³⁹.

Hydrogen permeation

The hydrogen diffusion coefficient (D_{app}) was determined by hydrogen gas permeation using disk-shaped specimens (12 mm in diameter and ~250 μm thick). Both surfaces were mechanically polished, and the hydrogen-entry side was coated with a 50 nm Pd layer to facilitate hydrogen dissociation and prevent oxidation. Measurements were conducted at 723, 773, and 823 K under a hydrogen pressure of 2 MPa using a custom-built gas permeation apparatus. The selected temperature range represents a practical compromise between experimental sensitivity and measurement reliability. At lower temperatures, the breakthrough times for the present specimen thickness would become prohibitively long, substantially reducing experimental throughput and increasing baseline drift. Conversely, reducing the specimen thickness to compensate for slower diffusion would require more aggressive mechanical preparation, increasing the likelihood of introducing deformation that alters the dislocation density and the thermally established CSRO state. In addition, excessively thin specimens are more susceptible to surface and oxide-related boundary effects, which may dominate the permeation response rather than the intrinsic bulk hydrogen diffusion targeted in this

study. The hydrogen flux emerging from the detection side was monitored using a Pfeiffer Prisma QMS 200 mass spectrometer and recorded as a function of time. At least two independent specimens were tested for each condition. Experimental procedures and data analysis followed the methodology established in our previous work⁴⁴. D_{app} was obtained from the permeation transients using the breakthrough time method derived from Fick's second law⁶⁸, as defined in equation (2):

$$D_{app} = 0.5 \frac{L^2}{\pi^2 t_b} \quad (2)$$

where t_b is the breakthrough time, determined from the intersection between the tangent drawn at the inflection point of the permeation transient and the time axis, and L is the specimen thickness. The temperature dependence of D_{app} can be described by Arrhenius equation (3):

$$D_{app} = D_0 \exp\left(\frac{-Q_{app}}{RT}\right) \quad (3)$$

where D_0 is the pre-exponential factor, Q_{app} is the apparent activation energy for diffusion, R is the gas constant, and T is the temperature.

Hydrogen embrittlement testing

Hydrogen embrittlement susceptibility was evaluated by slow strain-rate tensile testing using flat dog-bone specimens (gauge length: 14.4 mm; width: 2.7 mm; thickness: 1 mm) machined along the rolling direction by electrical discharge machining. Prior to hydrogen charging, specimens were ground to 2000 grit and the specimen surfaces, except for the gauge section, were coated with liquid electrical insulating tape to restrict hydrogen ingress to the gauge region. Electrochemical hydrogen charging was performed at 298 K in an aqueous solution consisting of 0.5 M H_2SO_4 + 2 g L^{-1} $\text{CH}_4\text{N}_2\text{S}$ at a current density of 20 mA cm^{-2} for 1 and 7 days. A platinum mesh served as the counter electrode. Immediately after charging, specimens were stored in liquid nitrogen (LN_2 , ~77 K) to minimize hydrogen loss and were tested within 5 min after removal. Tensile tests were conducted at 298 K using an Instron 5500R universal testing machine at an initial strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. Three independent specimens were tested for each condition.

Hydrogen embrittlement index (δ_{loss}) was calculated according to equation (4):

$$\delta_{loss} = \left(\frac{\varepsilon_{EF(H-u)} - \varepsilon_{EF(H-c)}}{\varepsilon_{EF(H-u)}} \right) \times 100\% \quad (4)$$

where $\varepsilon_{EF(H-u)}$ and $\varepsilon_{EF(H-c)}$ correspond to the elongation to failure of uncharged and hydrogen-charged specimens, respectively.

Fracture specimens were cleaned with acetone and stored under vacuum prior to fractographic analysis.

Post-mortem characterization

Post-mortem HE-SXRD line-scan measurements were performed on fractured tensile specimens to determine the spatial evolution of the local dislocation density (ρ) from the fracture surface towards the grip section. The same HE-SXRD experimental setup described above was used. A schematic illustration of the line-scan geometry is shown in **Fig. 5a**. Starting from the fracture surface (x_0), specimens were scanned towards the grip section (x_n) along the tensile axis using a step size of 100 μm . Raw diffraction patterns were calibrated and subsequently azimuthally integrated over the full 360° range using pyFAI-based tools (pyFAI-calib2 and pyFAI-integrate⁶⁹) combined with in-house developed Python routines. Dislocation densities were quantified using the modified Williamson–Hall (WH) method^{70,71}. Using a pseudo-Voigt function, the eight FCC reflections (111), (200), (220), (311), (222), (400), (331) and (420) were fitted. Moreover, instrumental broadening was corrected using a LaB₆ pattern. The modified WH method requires the use of the elastic stiffness constants (C_{11} , C_{12} , and C_{44}). For CoCrNi⁷², $C_{11} = 193$ GPa, $C_{12} = 116$ GPa, and $C_{44} = 128$ GPa were used, whereas for Inconel 625⁷³, $C_{11} = 243$ GPa, $C_{12} = 157$ GPa, and $C_{44} = 118$ GPa were adopted. All modified WH fits yielded residual errors of $R_{wp} < 3.7\%$. Further details regarding the dislocation density calculations are provided in our previous works^{65,74}.

Fractographic analyses were performed using a Helios 5 DualBeam scanning electron microscope operated in secondary electron (SE) mode at 20 kV to identify fracture features. The thickness of the intergranular fracture layer was quantified from measurements performed perpendicular to the fracture surface at multiple locations along the entire intergranular fracture layer. For each specimen, at least 50 measurements were obtained from images acquired at different magnifications to ensure statistical reliability. Image analysis was performed using ImageJ software⁷⁵.

Atomistic simulations

The deep potential (DP) model for equimolar CoCrFeMnNi–H systems originates from our previous work³⁴, which was trained using extensive spin-polarized density functional theory (DFT) datasets covering multi-component alloys and interstitial hydrogen configurations. To improve the predictive accuracy for the target CoCrNi–H system investigated here, we supplemented the original training database with massive additional DFT calculation data of ternary CoCrNi–H configurations, including random solid solution (RSS), CSRO aggregates, interstitial hydrogen at octahedral/tetrahedral sites, vacancy defects and stacking fault structures containing Co, Cr, Ni, and H. The augmented dataset was then used to retrain and tune the DP model to form an updated CoCrNi–H deep potential.

Subsequent comparisons were carried out between the original baseline potential and the newly tuned CoCrNi–H potential. Predictions of CSRO thermodynamics and hydrogen diffusion (D) remained highly consistent between the two potentials, indicating that the original potential already possesses sufficient transferability to describe CoCrNi–H. Monte Carlo (MC) and molecular dynamics (MD) analyses in this paper adopt the tuned DP potential with supplementary CoCrNi–H DFT training points.

Large 12,800 atoms supercells were constructed to capture the full spatial distribution of CSRO structures. To drive the formation and evolution of CSRO, MC atomic swap operations were coupled with MD relaxation, with elemental swap cycles executed every 0.02 ps and the MC scaling temperature maintained at 500 K. Simulation snapshots were extracted at four representative MC swap stages (0, 200×10^3 , 500×10^3 , 1000×10^3 swap steps) corresponding to fully RSS, low CSRO (CSRO degree 1), medium CSRO (CSRO degree 2), and saturated CSRO (CSRO degree 3) equilibrium states, respectively.

The average Warren–Cowley (CSRO) parameter $\left(\alpha_{AB}^{(n)}\right)^{76,77}$ was calculated as defined in equation (5):

$$\alpha_{AB}^{(n)} = 1 - \frac{P^{(n)}(A|B)}{x_B} \quad (5)$$

where $P^{(n)}(A|B)$ is the conditional probability of finding a B atom in the n^{th} coordination shell around an A atom, and x_B is the global atomic fraction of B in the alloy. In a fully

RSS, $P^{(n)}(A|B) = x_B$, yielding $\alpha_{AB}^{(n)} = 0$. These parameters were calculated from equilibrated structures extracted after different MC steps mentioned above, after the system had reached equilibrium.

Additionally, Warren–Cowley parameters describing H–metal pair correlations ($\alpha_{Hj}^{(n)}$), were calculated according to equation (6):

$$\alpha_{Hj}^{(n)} = 1 - \frac{P^{(n)}(j|H)}{x_j} \quad (6)$$

In a fully RSS, $P^{(n)}(j|H) = x_j$, yielding $\alpha_{Hj}^{(n)} = 0$. Negative values of $\alpha_{Hj}^{(n)}$ indicate preferential association between hydrogen and element j , whereas positive values indicate avoidance relative to a random distribution. The $\alpha_{Hj}^{(n)}$ were calculated from equilibrated simulation snapshots corresponding to both the RSS and CSRO degree 3 states and averaged over all hydrogen atoms.

For visualization of metal-metal and metal-hydrogen bonding networks the Open Visualization Tool (OVITO) was used to post-process all equilibrium atomic structures. Interatomic bonding networks were rendered using the OVITO ‘Create bonds’ modifier. Metal atom pairs separated by distances of 4.0 Å were connected to visualize the overall spatial distribution of CSRO; metal-hydrogen bonding with interatomic distances of 2.5 Å were linked to characterize the preferential bonding between metal and hydrogen atoms.

All hydrogen diffusion MD simulations were performed on the identical 12,800-atom large supercell systems pre-equilibrated to RSS and CSRO degree 3 states. The pre-equilibrated chemical configurations remained unchanged throughout the MD diffusion simulations. No further atomic swap operations were performed, ensuring that hydrogen diffusion was evaluated for fixed CSRO states. Prior to dynamic diffusion runs, interstitial hydrogen atoms were randomly inserted into the octahedral interstitial sites of the FCC matrix at a fixed concentration of 3 at.%. This concentration was selected to ensure statistically robust sampling of local hydrogen environments while remaining within the dilute interstitial regime, and matches that employed in our previous work on CoCrFeMnNi³⁴, ensuring that differences in hydrogen transport behavior between the two alloy systems reflect differences in alloy chemistry and CSRO character rather than simulation methodology. The MD time step was set to

0.001 ps for all simulations, with a total simulation duration of 0.4 ns to ensure sufficient hydrogen hopping events for reliable diffusion statistics. Simulations were performed over a series of temperatures to determine Arrhenius diffusion activation energy (Q) curves for both RSS and CSRO degree 3 models.

The hydrogen mean-squared displacement (MSD) was calculated, according to the following equation (7)³⁴:

$$MSD(t) = \frac{1}{N} \sum_i^N [(x_i(t) - x_i(0))^2 + (y_i(t) - y_i(0))^2 + (z_i(t) - z_i(0))^2] \quad (7)$$

where x_i , y_i , and z_i are the coordinates of the i th hydrogen atom at time t , and N is the total number of hydrogen atoms. Atomic positions at $t = 0$ were used as reference configuration. MSD-time curves were then fitted to derive hydrogen diffusion coefficients for RSS and CSRO degree 3 structures.

Data availability

All relevant data generated or analyzed during this study are available in the source data file provided in the additional information.

Code availability

The deep-learning interatomic potential, atomistic simulation data, and any in-house Python code are available from the corresponding authors upon reasonable request.

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Author contributions statement

D.D.S.S. and F.G.C. conceived the study and formulated the central hypothesis. D.D.S.S. designed the overall research workflow. X.Z. conducted the atomistic simulations. D.D.S.S. carried out alloy production and processing and performed the hydrogen charging and tensile testing experiments. G.Y.K. provided the facilities and resources for the hydrogen charging experiments. S.C.M. and D.S.S. performed the hydrogen gas permeation tests. C.L.G.P.M. and V.P.B. conducted the thermal and microscopy analyses. E.M.M. performed the APT characterization. G.G.R. and N.S. conducted the HE-SXRD experiments at PETRA III/DESY, and G.B. analyzed the diffraction data and quantified the dislocation density evolution. D.D.S.S. integrated and interpreted the computational and experimental results and led the writing of the manuscript. A.F.A., and P.H.F.O. provided critical feedback during manuscript preparation. F.G.C. supervised the project. F.G.C., D.M. and A.J.K. secured funding and contributed to manuscript development. All authors contributed to manuscript revision, reviewed the final version and approved the submitted manuscript.

Competing interests statement

The authors declare no competing interests.

Additional Information

Supplementary Information and **Source Data** are available in the online version.

Correspondence and requests for materials should be addressed to David D. S. Silva or Xiaoye Zhou.

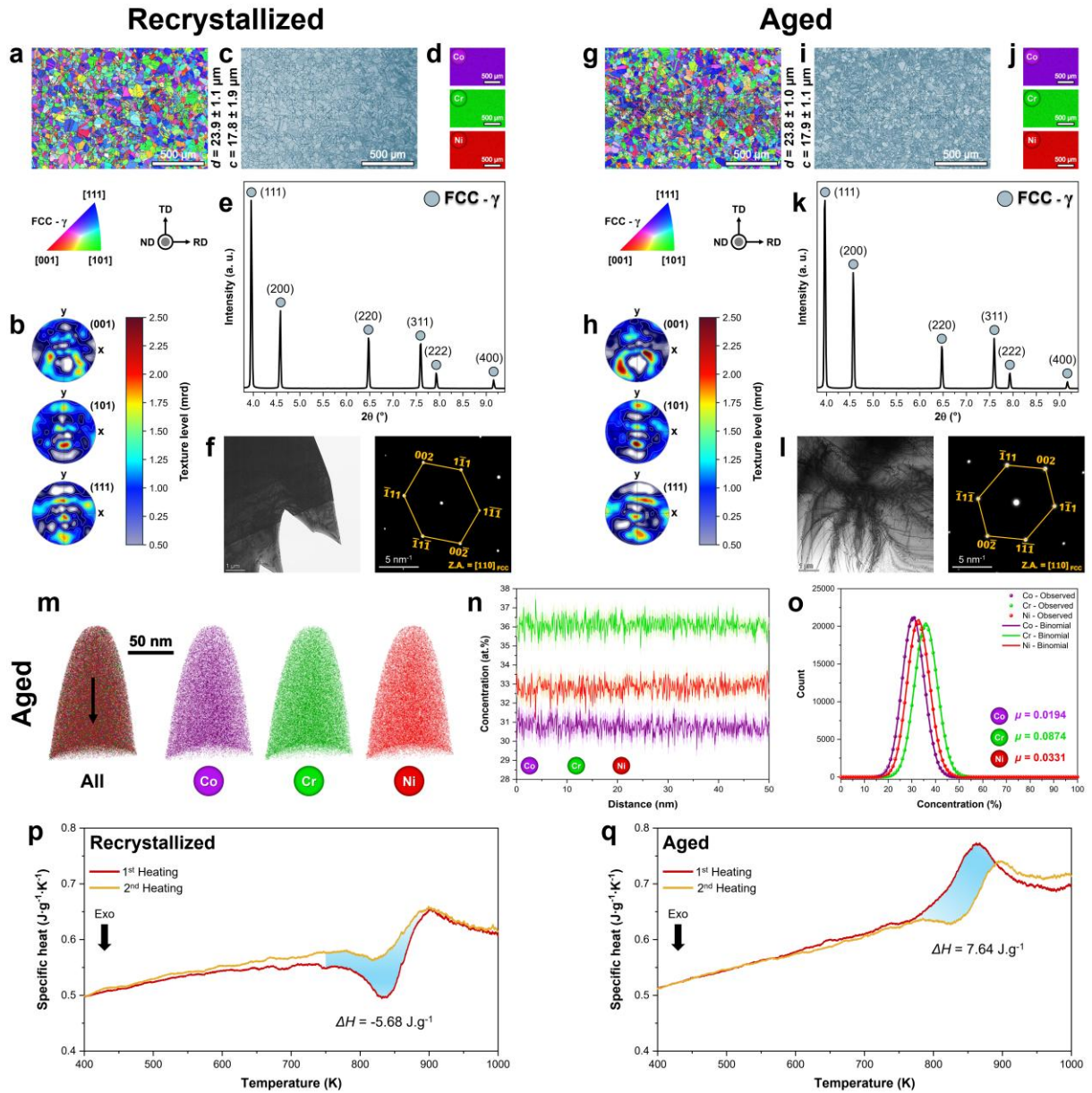


Fig. 1 | Multi-scale structural, microstructural, and thermal characterization of the CoCrNi alloy in the recrystallized and aged conditions. **a–f, g–l** EBSD analysis, SEM-EDS maps, HE-SXRD patterns, and TEM analysis, of the recrystallized and aged conditions, respectively. **m–o** APT analysis in the aged condition, **m** 3D atom map reconstruction showing the overall distribution of elements, along with individual elemental maps for Co (purple), Cr (green), and Ni (red). The arrow indicates the analysis direction; scale bar: 50 nm. **n** One-dimensional compositional profiles along the analysis direction, and **o** Frequency distribution of atomic concentrations compared with binomial distributions. The μ values quantify the deviation from randomness for each element. **p, q** Specific heat as a function of temperature curves obtained during DSC testing (heating cycles), of the recrystallized and aged conditions, respectively. Red lines are for the first heating cycle, and orange lines correspond to the second heating. The exothermic (Exo) direction is marked by an arrow. The exothermic and endothermic responses are associated with CSRO formation and dissolution, respectively.

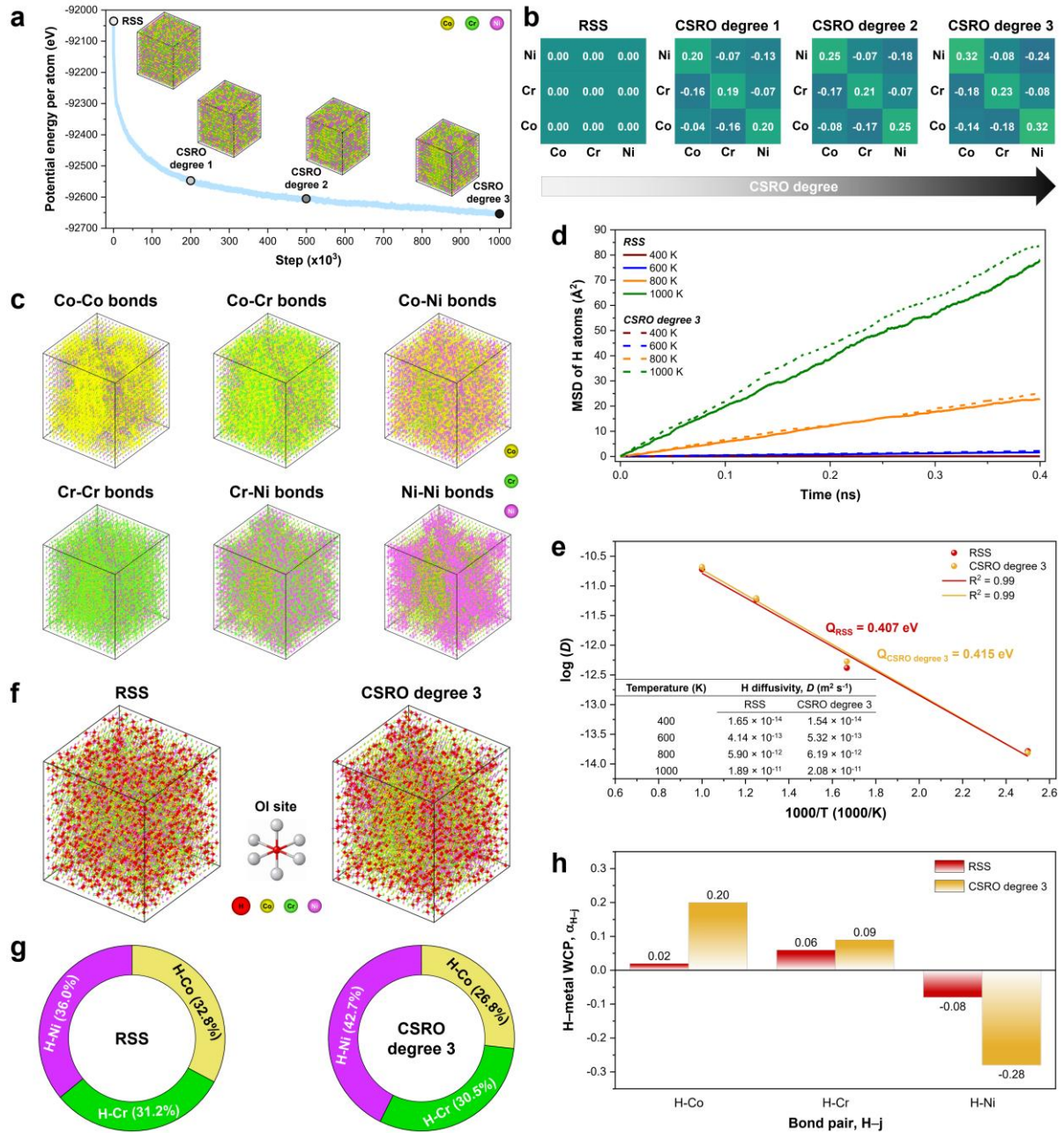


Fig. 2 | Atomistic simulations of the effect of CSRO on local atomic configurations and hydrogen transport in CoCrNi alloy. **a** Evolution of the potential energy during MC simulations used to generate RSS and increasing degrees of CSRO. **b** Corresponding WCPs, showing the progressive development of CSRO. **c** Distribution of homoatomic and heteroatomic bond pairs in the CSRO degree 3 structure. **d** Hydrogen MSD in the RSS and the CSRO degree 3 structures at different temperatures. **e** Arrhenius plot of the hydrogen diffusivity (D) for the RSS and CSRO degree 3 structures. Solid lines represent linear fits to the Arrhenius equation used to determine the activation energies (Q). The inset in panel **e** shows the D values for each condition. **f** Spatial distribution of hydrogen atoms in the RSS and CSRO degree 3 structures, illustrating hydrogen occupation of octahedral interstitial (OI) sites. **g** Relative fractions of H-metal local environments in the RSS and CSRO degree 3 structures. **h** WCPs describing H-metal pair correlations in the RSS and CSRO degree 3 structures.

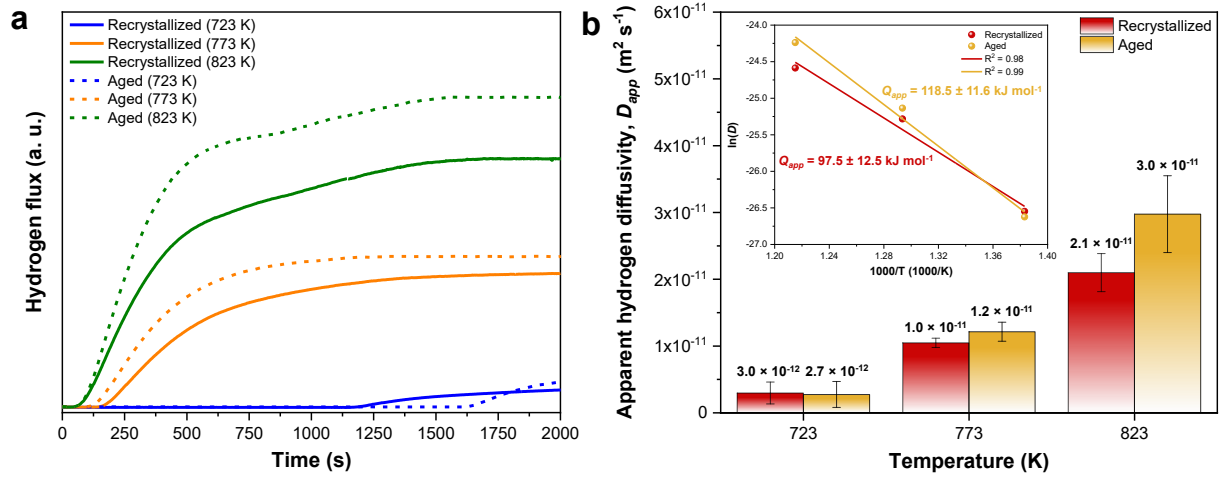


Fig. 3 | Experimental hydrogen transport behavior in recrystallized and aged CoCrNi alloy.

a Representative gaseous hydrogen permeation curves measured at different temperatures. Solid and dashed lines correspond to the recrystallized and aged conditions, respectively. **b** Apparent hydrogen diffusivity (D_{app}) values calculated from the permeation measurements for the recrystallized and aged conditions as a function of temperature. Error bars represent the standard deviation of independent measurements. The inset in panel **b** shows Arrhenius plots of D_{app} . Solid lines represent linear fits to the Arrhenius equation used to determine the apparent activation energies (Q_{app}).

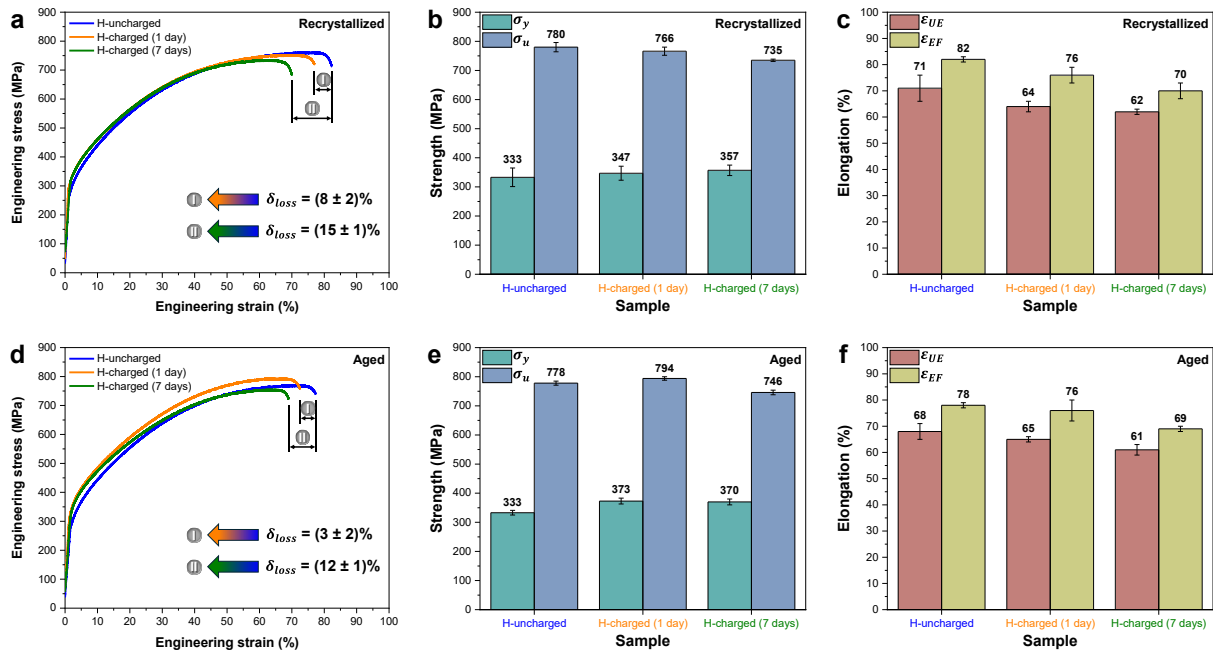


Fig. 4 | Tensile response of CoCrNi alloy in the recrystallized and aged conditions before and after hydrogen charging. a, d Representative engineering stress–strain curves of the recrystallized and aged conditions, respectively, tested at room temperature (298 K) in the uncharged state and after hydrogen charging for 1 and 7 days. The corresponding hydrogen embrittlement index (δ_{loss}) is indicated. **b, e** 0.2% offset yield strength (σ_y) and ultimate tensile strength (σ_u) of the recrystallized and aged conditions, respectively, before and after hydrogen charging. **c, f** Uniform elongation (ϵ_{UE}) and elongation to failure (ϵ_{EF}) of the recrystallized and aged conditions, respectively, before and after hydrogen charging. Reported error values represent the standard deviation of all measurements.

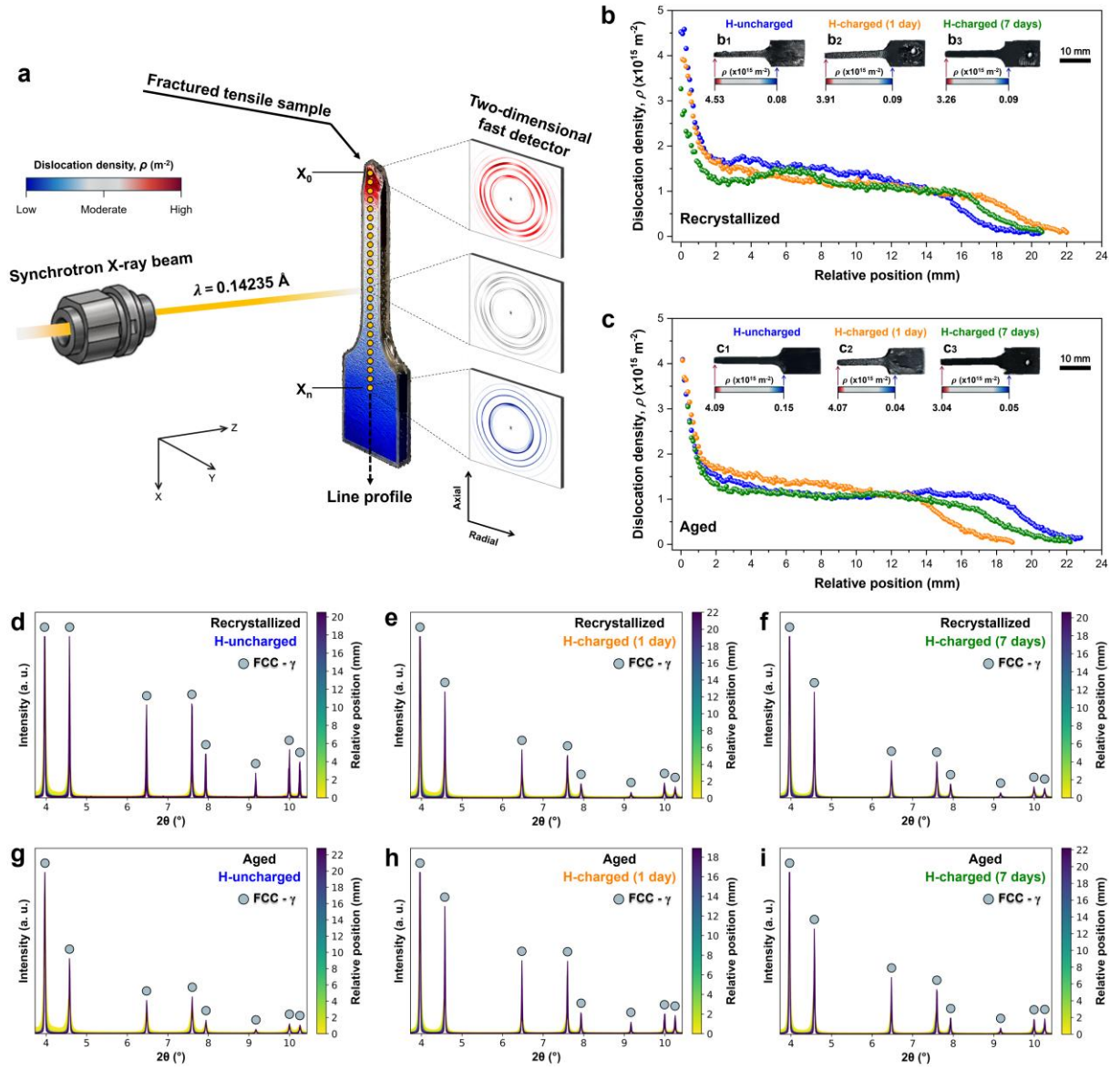


Fig. 5 | *Post-mortem* high-energy synchrotron X-ray diffraction analysis in CoCrNi tensile specimens tested before and after hydrogen charging. **a** Schematic illustration of the *post-mortem* HE-SXRD line-scan experiment used to quantify spatial variations in dislocation density along fractured tensile specimens. Representative diffraction rings broadening associated with high, intermediate and low dislocation density regions are shown. **b**, **c** Spatial distributions of dislocation density (ρ) along fractured tensile specimens in the recrystallized and aged conditions, respectively, tested in the uncharged state and after hydrogen charging for 1 and 7 days. The insets (**b**₁–**b**₃, **c**₁–**c**₃) in panels **b**, **c** show representative fractured specimens and the corresponding dislocation density maps. **d**–**f**, **g**–**i** HE-SXRD patterns acquired at different positions along fractured tensile specimens in the recrystallized and aged conditions, respectively, before and after hydrogen charging. The changing peak broadening reflects the spatial evolution of the dislocation density, as quantified in panels **b**, **c**.

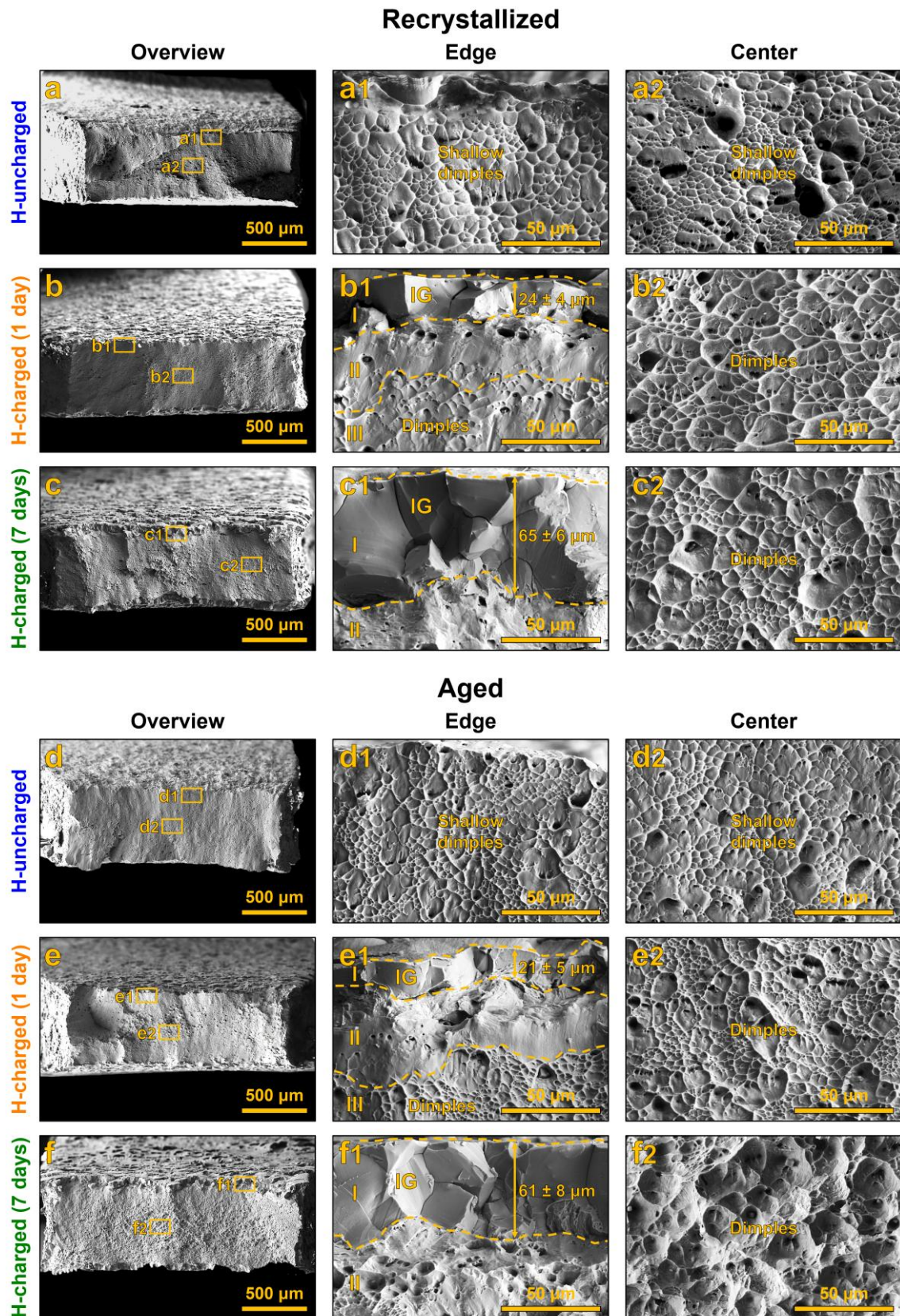


Fig. 6 | Fractographic analysis of CoCrNi alloy tensile specimens in the recrystallized and aged conditions before and after hydrogen charging. a–c, d–f Low-magnification overview fractographs and corresponding high-magnification SEM images acquired at the edge (**a1–c1, d1–f1**) and center

(**a2–c2, d2–f2**) regions of fractured tensile specimens in the recrystallized and aged conditions tested in the uncharged state and after hydrogen charging for 1 and 7 days, respectively. The insets in panels **a–c, d–f** show the orange boxes which indicate the position where the magnified images (**a1–f1, a2–f2**) were taken. In the uncharged state (**a, d**), fracture surfaces are dominated by ductile microvoid coalescence, characterized by uniformly distributed shallow dimples across both edge and center regions. Following hydrogen charging (**b, c, e, f**), a near-surface intergranular (IG) fracture layer develops near the specimen surface, whereas the specimen interior remains predominantly ductile and characterized by dimpled fracture. The hydrogen-charged specimens exhibit three distinct fracture regions: (I) a near-surface intergranular fracture layer, (II) a transition region, and (III) an interior ductile region characterized by dimples, as indicated in panels **b1, c1, e1, f1**.

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