Corrosion is a ubiquitous failure mode of materials. Often, the progression of localized corrosion is accompanied by the evolution of porosity in materials previously reported to be either three-dimensional or two-dimensional. However, using new tools and analysis techniques, we have realized that a more localized form of corrosion, which we call 1D wormhole corrosion, has previously been misclassified in some situations. Using electron tomography, we show multiple examples of this 1D and percolating morphology. To understand the origin of this mechanism in a Ni-Cr alloy corroded by molten salt, we combined energy-filtered four-dimensional scanning transmission electron microscopy and ab initio density functional theory calculations to develop a vacancy mapping method with nanometer-resolution, identifying a remarkably high vacancy concentration in the diffusion-induced grain boundary migration zone, up to 100 times the equilibrium value at the melting point. Deciphering the origins of 1D corrosion is an important step towards designing structural materials with enhanced corrosion resistance.

Corrosion is a notorious problem leading to early failure and increased cost to mitigate for engineering systems in aircraft, bridges, and nuclear reactors as well as functional devices such as batteries, sensors, and biomedical implants. While some classical theories predict a uniform corrosion process, corrosion is often accelerated at specific sites due to various types of material defects and distinct local environments. Accelerated localized corrosion can proceed insidiously for years as it is intrinsically more difficult to detect. Thus, localized corrosion presents a greater threat for component failure than uniform corrosion, especially when coupled with stress leading to processes such as stress-corrosion and sulfidation-induced cracking. However, the detection, prediction, and study of localized corrosion are extremely challenging, as the length-scale of incubation sites is very small, typically at the nanometer scale and below, beyond limits of non-destructive detection. Traditional high-resolution imaging techniques struggle to efficiently capture the phenomenon in its early stages due to multiple issues such as a small, non-representative field of view, the limits of imaging across timescales, the inability to recover three-dimensional (3D) information from 2D images, and the undesired modification of source materials.
from sample preparation. The lack of understanding of localized corrosion has further added to the uncertainty in engineering systems, especially in newer, less-studied corrosive environments. A prominent example of such an environment is molten salt, which has become increasingly important as a reaction medium for materials synthesis, a solvent for materials recycling, and a coolant/fuel for next-generation nuclear reactors and concentrated solar power (CSP) plants.

Molten salt systems typically operate at high temperatures (350–900 °C) and require structural materials that can withstand these extreme conditions for years to decades. Ni or Fe-based alloys are considered strong candidates for high-temperature applications and molten salt next-generation nuclear reactors. In particular, these alloys are being tested as vessel and primary circuit structural materials for both nuclear and CSP plants, critical for containing the hot molten salt, and, in the case of some reactor designs, the molten nuclear fuel. Previously, it has been shown that the corrosion of these alloys in molten fluoride/chloride salt proceeds via the preferential leaching of the most electrochemically susceptible element (usually Cr) into the salt, which appears to create voids in the metal. Early studies proposed that these voids were discrete Kirkendall voids, or remnants of precipitates that were preferentially attacked during corrosion. However, more recent research has shown strikingly that salt exists in some of these voids, and can even lead to through-material penetration, posing a critical question on how these voids form and mediate salt infiltration into the metal. The answer to this question is the key to the fundamental understanding of localized corrosion in molten salt environments, yet it still remains unclear.

Here we experimentally show and mechanistically explain the origin of a form of highly localized penetrating corrosion in a Ni-20Cr alloy attacked by molten fluoride salt, using a combination of correlated electron microscopy and atomistic simulation. We term this phenomenon 1D wormhole corrosion, named not only for its wormhole-like 1D morphology but also because it can function as a mass-flow pathway (in contrast to diffusional pathways), which we find is responsible for the extremely rapid infiltration of molten salt. This mechanism creates an extremely localized corrosion morphology (Figs. 1 and 2) that greatly increases the depth of penetration per volume of corroded metal when compared to other corrosion morphologies.

### Results

Figure 1 schematically shows this unique 1D void morphology, alongside comparisons to previously known localized corrosion processes such as pitting and intergranular corrosion. The directions for void growth in bicontinuous dealloying and intergranular corrosion incur no constraints, they can be described as 3D corrosion morphologies. Another well-known mechanism of void penetration is intergranular corrosion, which is confined to two-dimensional (2D) grain boundaries. In contrast, the concept of a 1D and percolating penetration through thickness/depth, such as the wormhole corrosion depicted in Fig. 1d-f, has not been documented in any open literature. In 1D wormhole corrosion, void tunnels with a high aspect ratio are constrained to grow along selected routes on GBs without fully covering the GB plane, establishing a “capillary-like” percolating system along GBs. We describe it as “1D” because GBs are regarded as a 2D percolating transport network, while the 1D wormhole corrosion builds a 1D percolating network constrained by the 2D GB network. The wormholes observed here reveal the routes that facilitate the ingress of the corrosive fluid to enable much more rapid and sustained corrosion.

When a cross-section of a GB with 1D corrosion is made, the voids along the GB manifest themselves as discontinuous “dots” (as shown in the boxed region in Fig. 1d, e), which may easily be mistaken as disconnected voids. By comparison, a cross-section of a GB with 2D corrosion would result in a continuous line of voids (Fig. 1c). As such, a
convenient way to differentiate 1D, 2D, and 3D corrosion is to produce a cross-section, observe the void morphology, and determine whether the externally corroding fluid exists in the voids. Figure 1e shows an example of this cross-sectional evidence from 1D corrosion in a Ni-20Cr alloy foil after exposing one side to fluoride molten salt at 650 °C. The experimental setup used is schematically illustrated in Supplementary Fig. 1. We found that while the samples appeared to be intact after 4 h of corrosion, the molten salt had already fully penetrated the 30-μm-thick Ni-20Cr foil via 1D wormhole corrosion, as evident in the scanning electron microscopy (SEM) image showing molten salt at the opposite side of the sample (Fig. 3d). To further confirm this 1D infiltration, we used argon ion-milling to prepare a cross-section (see Supplementary Fig. 1), and we performed correlated electron microscopy characterization on the surface of the cross-section. Figure 1e shows a typical SEM image (false-colored) of the cross-sectioned surface depicting several discrete voids. While the voids appear discontinuous along the GB, the voids are expected to be connected via linked voids on different planes based on our 1D model and the presence of salt within. To verify this, the corresponding region in Fig. 1e is serially sectioned with a focused ion beam (FIB) and imaged with the SEM to create a 3D reconstruction. The resulting reconstruction, shown in Fig. 1f and Supplementary Movie 1, proves the connectivity of the voids along the GB, forming a network of 1D tunnels that facilitate molten salt infiltration. Another 3D reconstruction of a much larger volume is presented in Fig. 2a, b and Supplementary Movie 2, showing the percolating network of 1D wormholes in another representative sample and the reproducibility of this experiment. A FIB sample lifted out near the center of the cross-section surface (see Supplementary Figure 1e) along the GB is characterized by scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX). The presence of potassium in the voids demonstrates the existence of salt in the crevices along the GBs, further supporting our observation that 1D percolating “wormholes” facilitate rapid salt penetration. The salt is likely wicked by capillary forces into the open voids, and must be present at the head in electrochemical systems. It should be noted that the morphology of discontinuous voids along GBs can also be found in the cross-sections of other systems with intergranular voids due to radiation damage, Kirkendall effects, or etched precipitates. However, 1D corrosion is differentiated by the fact that the voids are interlinked and form a percolating network. Filiform corrosion can also produce similar 1D and percolated channels, but these surface effects are confined to specific metal/organic-film interfaces, and therefore coupled with a thin film delamination process. The 1D-like channel formation underneath the organic coatings during filiform corrosion is not considered a bulk corrosion (i.e., depth penetration) mechanism like 1D wormhole corrosion. Also, the 1D wormhole corrosion is significantly different from other “1D” corrosion morphologies reported in previous literatures (see more discussions in the Supplementary Discussion).

Pore structure is a distinguishing feature of localized versus uniform corrosion, as it dictates enhanced, local depth-penetration in materials. The more confined the void structure, the higher the rate of penetration per unit volume corroded, and the more detrimental its effects. While “finger-like” intergranular oxide protrusions have been observed before, they are only found localized at the corrosion front (i.e., deepest part of the oxidized region) serving as the terminus of 2D corrosion instead of as a global feature. Here, the wormhole corrosion that we discovered is dominated by 1D-features, suggesting that the morphology is stable despite being extremely localized. The penetration efficiency of 1D corrosion is further amplified by the lack of passivation mechanisms, as the corrosion products, once formed, can directly dissolve into the molten salt present in the 1D wormholes. By contrast, the advancement of a corrosion front along the depth direction in aqueous environments is more sluggish because the passivation layer needs to form and break repeatedly; this a typical characteristic of stress-corrosion cracking (SCC). As such, if we define the penetration efficacy as the maximum depth of corrosion divided by the total mass-loss of metal, then 1D wormhole corrosion manifests a remarkable penetration efficacy even without an externally applied stress. Such depth-focusing penetration morphology implies the need for prohibitively thick structural components to fully encapsulate the radioactive fuel during the long-term reactor operation if the 1D form of corrosion occurs and persists. Meanwhile, these percolating voids, even before complete penetration, can readily impact the mechanical performance of structural components via...
The rapid diffusion of Cr along GBs to the metal-salt interface induces the migration of the GB from the right to the left, and the area that the GB sweeps through becomes a locally dealkoyed zone. This dealkoyed zone shares the same crystal orientation as the grain on the right, yet it displays a very different composition. This DIGM process is confirmed by our STEM-EDX and TEM selected area electron diffraction (SAED) characterizations shown in Fig. 3g. The effects of GB migration on the speed of corrosion are considered to be two-fold. First, the curved GBs increase the total length of salt infiltration pathways, slowing down the penetration. On the other hand, the DIGM process will modify the local GB inclination gradually. If there is a preferential inclination for fast penetration, such a process will steer the salt front to this fast etching route along GBs, facilitating faster penetration. Since we observe such fast penetration in our experiments, the latter (i.e., preferential GB inclinations for fast penetration) appears to be the dominant process. Further discussion is presented in the supplementary materials with a Monte Carlo simulation (Supplementary Note 1 and Supplementary Movie 4). It is hypothesized that DIGM is not necessary for the formation of wormholes, yet it can impact the kinetics of wormhole formation.

Similar to the dealkoyed zone, the 1D crevice shows asymmetry along GBs, as is evident in Figs. 2c and 3e, f. A careful inspection of TEM samples extracted from different locations reproducibly shows that these crevices always reside on the Cr-depleted side of new GB positions through the DIGM zone (see schematic in Fig. 3h), suggesting an intrinsic correlation. Since there is a reduction of more than 5 at% Cr in the dealkoyed zone, we hypothesize that these DIGM zones should be rich in vacancies and vacancy clusters, and thus can act as precursors for void formation. However, the vacancies are too small to be captured by traditional high-resolution electron microscopy techniques. To measure the vacancy supersaturation in the DIGM zone, we developed a multimodal method combining energy-filtered four-dimensional scanning transmission electron microscopy (4D-STEM) lattice parameter mapping, EDX elemental mapping, and density functional theory (DFT) modeling. By combining these techniques, it is possible to analyze the local vacancy concentration qualitatively with nanometer resolution, achieving a spatial resolution at least 10 times higher than that of conventional approaches such as positron annihilation.
In this vein, the dealloying process can be depicted in a phase map that shows the intrinsic relationship between the relaxed lattice constant (\(a_0\)), vacancy fraction \((C_v)\), and Cr fraction \((C_{Cr})\). This phase map, as shown in Fig. 4b, describes the intrinsic relationship between the relaxed lattice constant \((a_0)\), the Cr fraction \((C_{Cr})\), and the vacancy fraction \((C_v)\). Starting from pristine Ni-20Cr (upper right corner of the triangle in Fig. 4b), the dealloying process shifts the DIGM zone’s position within the triangular phase map by altering \(C_{Cr}\) and \(C_v\). The upper line of this triangle represents “100% replacement,” meaning that each Cr atom removed is substituted with a Ni atom. Similarly, the bottom boundary of the triangle represents 0% replacement, indicating that no atom will refill the lattice site when a vacancy is created. One should also note that the relaxed lattice constant \(a_0\) can be related to the actual lattice spacing \(a\) and the elastic strain \(\varepsilon^e\) by

\[
\varepsilon^e = \frac{(a - a_0)}{a_0}
\]

where \(a\) and \(C_{Cr}\) can be measured by 4D-STEM and EDX, respectively. If either \(\varepsilon^e\) or \(C_v\) can be measured, then the other can be derived. We show that by measuring the strain in the non-DIGM zone, we can estimate the average \(\varepsilon^e\) within the DIGM zone using the theory of Eshelby’s inclusion (Supplementary Note 2 and Supplementary Figs. 3–4). This enables the back-calculation of \(C_v\) in the DIGM zones.

The vacancy mapping results corresponding to regions 1i and 2i are shown in Fig. 4e, and the region-averaged vacancy fractions are plotted in Figs. 4b, 4f and Supplementary Fig. 5, indicating a higher vacancy fraction in 2i than that in 1i, which is reasonable as 2i is much closer to the salt. In Figs. 3a and 3c, the Eshelby’s inclusion is used to simulate the vacancy concentrations. The supersaturation of vacancies found in these DIGM zones is a result of the rapid leaching of Cr, which drives the system out of equilibrium. The excess vacancy concentration is consistent with our observation that the voids and DIGM zone are found on the same side of the GB, strengthening our hypothesis that the dealloyed zone is a precursor to void formation. Accordingly, the previous DIGM theory by Broeder49 is revised and
temperature of 1D wormhole corrosion in Ni-20Cr during exposure to high-temperature melt. In this study, a series of advanced electron microscopy techniques including FIB, SEM, 3D tomography, SAED, and HAADF-STEM-EDX characterization are combined to discover and explain the mechanism of 1D wormhole corrosion in Ni-20Cr during exposure to high-temperature fluoride molten salt. We also developed an approach to perform nanometer-resolution vacancy mapping by combining energy-filtered 4D-STEM lattice parameter mapping and EDX with DFT simulations, revealing a remarkably high vacancy concentration to be responsible for void nucleation and 1D growth. This, in turn, allowed us to relate the asymmetric void formation to the excess vacancies in the DIGM zone. This extreme form of localized wormhole corrosion has a remarkably high mass-specific penetration capability among different corrosion mechanisms, yet it is far too localized to easily detect, making it a critical potential threat to structural materials which must be mitigated. We have conducted tomographic imaging experiments on several other corrosion systems and found similar 1D penetrating corrosion morphologies (Fig. 5 and Supplementary Movies 5–8), suggesting that 1D-type corrosion may not just be an anomaly of the molten salt environment. It is intriguing that intergranular oxide can also form a percolated network similar to the 1D wormhole corrosion (Fig. 5c, d). However, it still requires further in situ 3D observation to validate whether these oxide networks share the same mechanism as 1D wormhole corrosion, as there exist two possibilities: (1) The oxide grows in a similar way to wormhole corrosion; (2) The oxides nucleate first and then link together (like the linkage of intergranular carbides due to sensitization). The former would be true if the principal pathway of oxygen transport were to be the metal-oxide interface or the oxide itself, while the latter would be true if the metal-metal interface were to be the dominant oxygen transport pathway. The reality could even be a mixture of both cases. In fact, we believe it is probable that 1D wormhole corrosion is a common, yet hitherto largely unrecognized, type of corrosion mechanism in both molten salt environments and high-temperature corrosion reactions such as sulfidation-oxidation or fluoride that involves mass transport through liquids. However, because of the lack of dry-polishing methods such as Ar+ milling that preserve the salt-filled holes, the absence of 3D FIB-SEM tomography to reveal the internal percolation, and the complexity arising from intergranular precipitates in commercial alloys, this phenomenon was not realized until this current study.

As a consequence of 1D corrosion, strategies must now be developed to slow, prevent, or stop wormhole-type corrosion in order to increase the longevity and safety of next-generation nuclear reactors and concentrated solar power plants. The deep infiltration of salt into metal also indicates that the corrosion front is hidden deep inside the bulk, where the local chemistry can be significantly different from that near the bulk surface. As such, modeling and experimental efforts should account for the unique local chemistry inside the wormholes in order to better understand their corrosion behavior and protect against it. Also, temperature has recently been found to play a critical role on the corrosion morphologies in molten salt. Understanding how temperature interacts with 1D wormhole corrosion, especially the temperature range where 1D wormhole dominates, would offer valuable insights into mitigating it in structural materials. Last but not least, corrosion has been recently utilized as a method to produce unique void structures, such as 1D nanotubes and 3D bi-continuous structures, for functional applications such as catalysis or sensors. While we have identified this mechanism as occurring in a molten salt environment, one might envision similar scenarios in other dissolution-driven systems with the right balance of dissolution rates and diffusivity. This type of 1D percolating morphology may have important implications for creating ordered nano-porous materials for emerging applications.

**Methods**

**Fluoride salt synthesis**

Two recipes of salt were used in the corrosion experiments for different purposes: (1) FLiNaK with 5 wt% EuF$_3$, (2) FLiNaK without EuF$_3$. (i) FLiNaK with 5 wt% EuF$_3$

This kind of salt was used for all molten salt corrosion experiments except for the one in Fig. 2a, b. The salt has a composition of 27.75 wt% LiF, 11.11 wt% NaF, 56.14 wt% KF, and 5 wt% EuF$_3$. The ratio between LiF, NaF, and KF forms a eutectic (FLiNaK), while EuF$_3$ was added to increase the redox potential of the salt. Here, EuF$_3$ served as the oxidant with a reduction product of EuF$_2$. Both EuF$_3$ and EuF$_2$ have sufficiently high solubility within FLiNaK such that neither is expected to precipitate and deposit on the
metal sample. The individual salt powders were purchased from Alfa Aesar with certified purities of 99.99%, except for EuF$_3$, which has a certified purity of 99.98%. Before mixing, the powders were baked/melted at 900–1000 °C in glassy carbon crucibles (HTW Germany) inside of an argon atmosphere-controlled glove box with oxygen and moisture continuously measured below 1 ppm. Then the salt mixture was made by weighing the corresponding powder components and melting at 700 °C for 12 h to ensure mixing. 3.5 g of salt was used in each corrosion experiment.

(2) FLiNaK
To demonstrate that the addition of EuF$_3$ is not the reason for this 1D wormhole corrosion morphology, we performed a different corrosion experiment in the FLiNaK-only molten salt environment. The corresponding results in Fig. 2a, b show that this 1D wormhole morphology still exists.

Fluoride salt purity
The FLiNaK is not actively purified with HF/H$_2$ or pure metal, but it is produced in a procedure where most of the water can be removed by melting individual components (at 900–1000 °C) first. All the melting is conducted in an argon-atmosphere glove box where oxygen and moisture content is continuously maintained and measured below 1 ppm. The individual salt components are all 99.99% pure, but could contain some metallic impurities such that the FLiNaK is more corrosive in the short run.

Oxygen can exist in the atmosphere where the melting of the salt or the conduction of the experiments occurs. If the experiment is performed inside of the glove box, then oxygen is less than 1 ppm. If the experiment is performed inside of the high vacuum chamber, the oxygen content can be even less than that in the glove box. Notice that there can exist some oxygen in the salt in the form of oxides.

Metal sample preparation
The model 80Ni-20Cr wt% alloy was produced by Sophisticated Alloys Inc. with a certified purity level of 99.95%. The Incoloy 800H was purchased from Metalmen Sales, Inc. The Ni-20Cr and Incoloy 800H were rolled into 30- and 27-µm-thick foils by the H. Cross Company, respectively. The 25-µm-thick 316 L stainless steel foil was purchased from Metalmen Sales, Inc. Disks of 22 mm in diameter were sectioned from each foil and used as the corrosion samples (Supplementary Fig. 1b). They were compressed by two sealing flanges (Supplementary Fig. 1a) in the corrosion facility, forming a liquid-tight seal to keep the molten salt inside. The sample area subjected to corrosion had a diameter of 14 mm. Aside from the sample, all the materials in contact with the molten salt were made of commercially pure nickel (Nickel 200/201) so as not to add any metal impurities to the salt.

The CrMnFeCoNi high-entropy alloy (HEA) was argon arc-melted between 150–180 µA for around 1 h. This liquid-free method is critical to preserve the salt contained within the voids, avoiding post-test alteration of visible results. A notch about 1 mm in width (Supplementary Fig. 1e) was polished under a beam current between 150 µA and 180 µA for around 1 h. This flat and well-polished cross-section was used for subsequent electron microscopy characterization.

Sample preparation and SEM characterization in a FIB-SEM dual-beam system
TEM sample preparation and SEM characterization were performed in a Thermo Fisher (previously FEI) Helios G4 dual-beam system with Ga as the ion beam. The SEM images were collected with an electron beam energy of 5 keV. The relationship between the imaging direction with respect to the sample geometry is illustrated in Supplementary Fig. 1f. The TEM samples were lifted out from the cross-section surface (See Supplementary Fig. 1e). A typical FIB lift-out process is shown in Supplementary Fig. 7. First, we used the electron beam (1.6 nA) to deposit some small patterns of Pt near the region of interest as fiducial markers (See Supplementary Fig. 7c). These markers have two roles: (1) they enhance the milling accuracy during the thinning process so that the region of interest will not be over-milled; (2) they were used to test whether there were any alignment issues during the deposition
process. After that, we deposited a Pt cap on top of the region of interest using the electron beam (5 keV, 1.6 nA). Then another Pt cap layer on top of the previous Pt cap was deposited using a Ga ion beam (30 keV, 90 pA). These Pt caps were used to protect the surface structure of the sample during the preparation process. The thin film was lifted out after making a bulk trench and U-cuts, then attached to the V-notch of the copper FIB half-grid (Omniprobe®), before being welded by Pt using ion beam (30 keV, 7 pA). The sample was then thinned by a Ga ion beam with subsequently lower energies of 30, 16, 5, 2, and 1 keV step by step on both sides, and the beam currents were changed accordingly so as only to remove the milling features from the previous step. Note that only part of the lamella was thinned such that the two edges were still thick enough to provide mechanical support, to avoid film bending during the thinning process (Supplementary Fig. 7b). The EDX mapping in Fig. 2c shows that surface was well-protected by the Pt layer after the final thinning.

The FIB-SEM 3D tomography data were collected using the FEI Auto Slice & View 4.1 software and a slice thickness of 50 nm. After data collection, the image sequence was first processed by a subroutine written in ImageJ (now renamed FIJI) to correct the drift of the sample during data collection, and then re-scaled to correct the aspect ratio considering the incident angle of the electron beam. A machine learning program utilized the Weka Package to classify the features in the images. Finally, Dragonfly software was used for the 3D reconstruction and data visualization.

**EBSD grain orientation mapping**

To verify that the rugged lines in Fig. 3b are indeed GBs, we performed electron backscatter diffraction (EBSD) scans on the region in Fig. 3b. The results are shown in Fig. 3c. A FEI Strata DB235 SEM (FEI Company, Hillsboro, OR, USA) equipped with an Orientation Imaging Microscopy (OIM) system (Ametek EDAX, Mahwah, NJ, USA) was used to collect the data with a fine step size of 0.1 μm at 20 keV.

**TEM characterization**

The FEI TitanX and ThemIS were used for STEM-EDX characterization, operating at 300 keV. Both are equipped with Bruker SuperX energy-dispersive X-ray spectroscopy (EDS) detectors that enable highly efficient EDS signal collection without the need to tilt the sample to a specific angle. Each EDX map took around half an hour to acquire.

The TEAM-1 microscope at the National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory was used for 4D-STEM data collection. This microscope is double-aberration corrected and operates at 300 keV. For 4D-STEM experiments, a nanosized electron beam (~1 nm in diameter) was rastered across the sample and a nano-beam electron diffraction (NBED) pattern was collected at each real-space position of the electron beam. The sample was tilted so that the region of interest was on one of the low-index zone axes of FCC Ni-20Cr. A Gatan K3 direct electron detector with a continuum energy filter was installed for the collection of 4D-STEM data, enabling high signal-to-noise ratio and high speed (~1000 frames/s) data collection. A special bullseye-shaped condenser-2 (C2) aperture was used to shape the electron beam to enhance the accuracy of lattice spacing measurements. The energy filter and the bullseye aperture were key to the accurate lattice spacing measurements. A demonstration of their effects is shown in Supplementary Fig. 8. The data were collected on the same region in a selected Ni-20Cr sample after corrosion, with the upper 1/3 of the map in the DIGM zone.

The 4D-STEM experiments for Fig. 4 were performed at spot 5 with a 10 μm C2 bullseye aperture. The convergence angle was 2 mrad and the camera length was 320 mm. In our experiments, the monochromator lens setting was adjusted once the bullseye aperture was inserted, and the sample region of interest (ROI) was found. We tried to maximize the probe current until the center beam gets saturated in the detector so that the higher-order Bragg peaks can be more bright and clearer. That said, we were operating closer to the 50–100 pA range. Note that for the 10 μm bullseye at 2 mrad convergence angle, the size of the probe on the specimen is rather large (~1–2 nm). Even though the probe current is similar to HRSTEM, the dose rate (e/A²/s) is ~500 times smaller due to the large size of the probe. A 15 eV slit for the energy filter was used. The scan step size was 5 nm. The total number of nano-beam electron diffraction (NBED) patterns collected for regions 1 and 2 in Fig. 4 are 39,516 and 177,020, respectively. A scan performed over vacuum was also collected and used to create a template for Bragg disk detection. The py4DSTEM package was used to analyze the 4D-STEM dataset. The bullseye-shaped beam template collected over vacuum is shown in Supplementary Fig. 8d, and a typical NBED pattern on the Ni-Cr sample is shown in Supplementary Fig. 8e. The locations of Bragg disks were detected by matching the vacuum template to the diffraction disks (Supplementary Fig. 8f) and then used to analyze the lattice spacing. The average lattice parameter was calculated in a region far away from the DIGM zone and used as a strain-free reference region for normalization of the measured lattice parameters.

Since the EDX data and 4D-STEM data were taken by different TEMs at the same sample orientation, a Python script was used to align them by a series of scaling, rotation, image shift, and cropping operations. The alignment relies on the presence of unique features on the sample as fiducial markers.

An aberration, CC-corrected ARM 200CF operated at an accelerating voltage of 200 keV was employed to collect tilt series data on the Ni-4AI sample. Data were collected utilizing an annular dark field detector using a convergence angle of 27 mrad and a collection angle of 72-294 mrad. The tilt series was calculated to tilt the FIB foil against the long axis of the GB at steps of 5° for 13 steps. Calculations were performed using nanocartography. The 3D reconstruction was performed by a MATLAB-based simple back projection algorithm with the following constraints applied: (1) The GB is a flat plane, which seems to be a quite accurate assumption for our dataset; (2) All oxide nano-branches have the same thickness in the direction perpendicular to the GB. Tomviz was used for data visualization.

**Modeling of the phase map for the dealloying process**

The decrease in lattice spacing within a DIGM zone can be interpreted as a type of phase transformation induced by the changes in Cr and vacancy fractions while the crystallographic symmetry is maintained. In this vein, the whole dealloying process can be pictured in a phase map that can be calculated by DFT simulations.

For the density functional theory (DFT) simulations, the initial structure of a Ni-Cr alloy with 19.4% Cr atomic fraction was generated in a cell with 72 atoms. Cr atoms were removed from the cell to introduce vacancies. The equilibrium volumes of the cell with different Cr and vacancy fractions were calculated through conjugate-gradient minimization of the energy with respect to ionic positions, cell volume, and cell shape. Energy and force calculations during relaxation were performed using the Projector Augmented Wave (PAW) method with spin-polarization considered, as implemented in the Vienna Ab-Initio Simulation Package (VASP). A plane wave cut-off energy of 400 eV was employed, and the Brillouin zone integrations were performed using Monkhorst–Pack meshes with a 4 × 4 × 4 grid. Atomic positions were relaxed with a convergence criterion for the forces of 0.02 eV/Å. Use was made of the Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA) for the exchange-correlation function. Five different cells with increasing vacancy fractions were created by removing the Cr atoms one by one. After relaxation in VASP, the vacancy formation volume was calculated through linear fitting of the equilibrium volumes of cells. The lattice constant change due to vacancies without any replacement of Ni can thus be calculated based on the vacancy formation volume, as shown by the blue line in Supplementary Fig. 9. For the case where Cr fraction change involved replacement of Cr with Ni atoms, without any vacancy formation, the
lattice parameter was fit using experimental data as shown in Supplementary Fig. 10. From these experimental data we can thus obtain the eigen-volume associated with a Cr atom being replaced by a Ni atom.

With the DFT-calculated vacancy formation volume and the fitted eigen-volume for replacement of Cr by Ni derived from Supplementary Fig. 10, we can compute the relationship between lattice parameter and Cr fraction at any fixed replacement fraction as shown in Supplementary Fig. 9 through linear interpolation. Based on Supplementary Fig. 9, by incorporating the vacancy fraction contour, we can further obtain a detailed phase map as shown in Fig. 4b, which describes the intrinsic relationship between the relaxed lattice parameter $a_0$, the Cr fraction $C_C$, and the vacancy fraction $C_v$ in the relaxed state.

Monte Carlo simulations of grain boundary migration
A 2D Monte Carlo simulation code was written in MATLAB to visualize the effects of grain boundary migration on the salt penetration speed. This code was based on the following assumptions:

1. The initial GB is perpendicular to the bulk-metal/salt interface. The salt on the left is etching the GB and trying to penetrate to the other side of the metal. (Supplementary Fig. 2).
2. When DIGM is enabled, a limited range (called the “dynamical DIGM region”) ahead of the corrosion front will undergo grain boundary migration. A random force field will be applied to the dynamical DIGM region to deform the GBs.
3. The GBs, once filled with salt, will turn from blue to red. The migration of the red GBs is prohibited. Note that the GBs may still migrate when they are filled with salt, but we do not consider this effect in our model.

Data availability
The data that supports the findings of this study are available from the corresponding author upon request.

Code availability
py4DSTEM is an open-source package available on GitHub: https://github.com/py4DSTEM/py4DSTEM.

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Author contributions
Y.Y. and W.Z. conceived the project. A.M.M., J.L., M.P.S., M.A., and R.O.R. provided critical guidance on the project. Y.Y. performed all FIB-SEM-based experiments, TEM sample preparation and electron microscopy characterization, and carried the Monte Carlo simulation. J.C. provided guidance on the energy-filtered 4D-STEM experiments. W.Z. designed the molten salt corrosion cell, carried the corrosion experiment, and prepared the cross-sections by Ar⁺ ion milling. Y.Y., A.M.M., and S.Y. conceived the vacancy mapping method. S.Y. performed the DFT simulations. Y.Y. and S.Y.W. performed the 4D-STEM data analysis with the help of S.E.Z. Y.Y. performed the analysis of the FIB-SEM 3D tomography result with the help of Y.Z. and M.C.S. Q.Y. performed the EBSD analysis. M.L., M.J., and J.R.S. provided important feedback that facilitated a systematic data analysis. Y.Y. performed the HEA oxidation experiment. M.J.O. performed the NiAl TEM characterization. Y.Y., S.Y.W., W.Z., A.M.M., J.L., M.P.S., and D.K.S. wrote the manuscript. Y.Y., S.Y.W., and W.Z. plotted the figures. All authors contributed to the discussion of the results.

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Supplementary Materials for

One Dimensional Wormhole Corrosion in Metals

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This file includes:

- Supplementary Notes 1 to 3
- Supplementary Discussion
- Supplementary Figures. 1 to 10
- Supplementary Reference
Supplementary Note 1. The effect of grain boundary migration on the salt penetration speed

It is important to discuss the effect of grain boundary migration on the salt penetration speed. The understanding of this question could potentially inspire methods to slow the penetration of salt in metals.

Grain boundary migration can have two effects on the salt penetration:

• (1) The curved GBs elongate the total length of salt infiltration pathways, potentially slowing down corrosion. If the penetration speed $v$, defined as the distance along the grain boundary (GB) that salt etches per second, is a constant, then this effect will slow the penetration.

• (2) The diffusion-induced grain boundary migration (DIGM) process will gradually change local GB inclinations. If the penetration speed $v$ is inclination-dependent, then DIGM will better focus the salt front to find a faster etching route along GBs. This in turn will facilitate salt penetration. Here, the penetration speed $v$ is no longer a constant. Instead, it is dependent on the local GB misorientation and inclination.

A 2D Monte Carlo simulation (see Materials and Methods section) is provided to visualize the above two effects. The results are shown in Supplementary Figure 2 and Supplementary Movie 4. We compare the salt penetration in three different cases: (i) without DIGM and $v = 1$; (ii) with DIGM and $v = 1$; (iii) With DIGM and $v = 1 + 2 \cdot \tan|\theta|$, where $\theta$ is the GB inclination angle (the angle between the tangent line of GB and the horizontal axis, as illustrated in Supplementary Figure 2d). This equation is chosen such that $v$ is higher when the inclination is closer to $\pm 90^\circ$.

There is not any specific physical model underlying this equation, but the angular dependence is included to demonstrate qualitatively the effect that changes in inclination can have on the penetration rate, if those inclinations lead to higher transport along the grain boundary.

From Supplementary Figure 2 and Supplementary Movie 4, it is shown that the penetration efficiency of (ii) is significantly lower than (i), while (iii) is the fastest case. This simulation result agrees with our experiments in which we do observe fast penetration of salt in metal. Therefore, we believe that the effect (2) is more significant than (1), and thus DIGM has an overall deleterious effect on the corrosion process. If the GB migration can be mitigated or stopped by means of GB engineering, one may be able to slow the salt penetration.
Supplementary Note 2. Vacancy mapping

Note: A small portion of the discussion from the paper is reproduced here for continuity of the discussion. The portion from the paper is expanded upon in this Supplementary Note.

This decrease in the lattice spacing within the DIGM zones can be interpreted as a type of phase transformation induced by the changes in Cr and vacancy fractions while the crystallographic symmetry is maintained. In this vein, the whole dealloying process can be pictured in a phase map that can be calculated by DFT simulations. This phase map, as shown in Fig. 4b, describes the intrinsic relationship between the relaxed lattice constant $a_0$, the Cr fraction $C_{Cr}$, and the vacancy fraction $C_v$. Starting from pristine Ni-20Cr (upper right corner of the triangle in Fig. 4b), the dealloying process shifts the position of the DIGM zone within the triangle map by altering $C_{Cr}$ and $C_v$. The upper line of this triangle represents “100% replacement” meaning that for each Cr atom removed from the lattice, a Ni atom will replace it. Similarly, the bottom boundary of the triangle represents 0% replacement, indicating that no atom will refill the lattice site when a vacancy is created. One should also note that the relaxed lattice constant $a_0$ can be related to the actual lattice spacing $a$ and the elastic strain $\varepsilon^e$ by:

$$\varepsilon^e = (a - a_0)/a_0$$

where $a$ and $C_{Cr}$ can be measured by 4D-STEM and EDX, respectively. If either the elastic strain $\varepsilon^e$ in the dealloyed zones or $C_v$ can be obtained, then the other can be derived. For the non-DIGM zones (1ii and 2ii), we will assume that the vacancy fraction is the same as that before corrosion. Thus, we can deduce the elastic strain in these regions directly from analyzing Fig. 4. The strain in 1ii and 2ii are shown in Supplementary Figure 3d. For the DIGM zone (1i and 2i), however, the accurate measurement of elastic strain is nontrivial as $\varepsilon^e$ and $C_v$ are coupled. Here, we apply the theory of Eshelby’s inclusion\(^1\) to estimate of the elastic strain inside the DIGM zones.

A schematic drawing in Supplementary Figure 4 shows Eshelby’s thought experiment for an inclusion problem, which assumes that the dealloying process is a kind of phase transformation with negative eigenstrain. When we take the dealloyed zone out and allow it to relax, the reduced lattice parameter from the dealloying process causes the zone to shrink (Supplementary Figure 4a). Next, when we return this dealloyed zone to the matrix, the region around the interface inside the matrix will have to be under tensile stress in order to accommodate the deformation in the dealloyed zone. Such tensile stress is indeed captured and verified by our strain mapping results shown in Supplementary Figure 3d. According to Eshelby’s inclusion theory, we assume the dealloying process will lead to an eigenstrain of $\varepsilon^e$ in the dealloyed region, and the corresponding elastic strain is equal to $\varepsilon^e = S\varepsilon^e - \varepsilon^*$, where $S$ is the Eshelby tensor. Outside the dealloyed region, there is a strain jump $\Delta \varepsilon$ between the inclusion and matrix at interface, which can also be expressed analytically for certain shapes of the inclusions\(^2\)-\(^4\). From the analytical solutions of the Eshelby tensors for various shapes, we learned that the elastic strain in the inclusion ($\varepsilon^e$) is of the same order of magnitude as the strain at the interface in the matrix ($S\varepsilon^e + \Delta \varepsilon$). Therefore, based on the solution for a spherical Eshelby inclusion, we used the measured maximum strain near the interface in the matrix to calculate the $\varepsilon^e$ in the inclusion, as an estimate of the elastic strain inside the DIGM zones. The estimated hydrostatic elastic strain for 1i and 2i in Fig. 4 is 0.178% and 0.277%, respectively. The averaged Cr fractions in 1i and 2i are 14.9 at. % and 13.9 at. %, respectively. The averaged lattice constant for 1i and 2i can then be calculated to be 0.3538 nm and 0.3533 nm under the estimated elastic strain, respectively. The averaged vacancy fractions in
1i and 2i are approximately $1.5 \times 10^{-3}$ and $8.9 \times 10^{-3}$, respectively. The standard deviation of Cr fractions, lattice constant and vacancy fractions are plotted in Supplementary Figure 5 as error bars. These vacancy fractions are further compared with those in other systems in Fig. 4f. We found that the vacancy fractions in the DIGM zones are up to 10-100 times higher than those found in pure metals at the equilibrium melting point, and up to 1,000 to 10,000 times of that found in their equilibrium counterparts at 650°C.

Since $C_v$ and $\varepsilon^e$ are coupled in the DIGM zones, a precise measurement of elastic strain $\varepsilon^e$ in these dealloyed regions would be difficult. However, using the two dashed lines in Fig. 4b to represent limits for the relaxed lattice constant, along with the measured lattice parameters, we can obtain the upper and lower limit of the strain maps for 1i and 2i, as shown in Supplementary Figure 3e and 3f. The elastic strain in these DIGM regions obtained in this manner is tensile and the local strain maximum ranges from 0.3% to 3%.

The major uncertainties of this vacancy calculation are from two parts:

1) Accuracy of the elastic strain in the DIGM zone. We used the Eshlby’s inclusion theory to estimate the strain field in the DIGM zone. We assumed that the DIGM had a uniform and small elastic strain field, because the material was heated at a high temperature (650°C).

2) Accuracy of the lattice parameters. We considered the average lattice spacing far away from the corrosion region and with uniform strain as the reference lattice spacing for the pristine sample. This approximation will lead to uncertainty due to the influence of the defects such as dislocations. However, the error resulted from this term is considered small as averaging was performed over a large and relatively uniform volume.
Supplementary Note 3. Mechanism of DIGM in the molten salt environment

The excess vacancy fraction found in the DIGM zones is proposed to be the precursor of intergranular voids during corrosion in a molten salt environment. Therefore, we present the atomic mechanism of DIGM in molten salt by modifying the previous DIGM theory by Broeder. The atomic process of DIGM is schematically illustrated in Supplementary Figure 6.

I. Cr and Ni atoms from grain 1 and 2 will “jump” into the GB because the GB contains free volumes (vacancies) (Supplementary Figure 6a).

II. Cr at the GB leaches out and rapidly diffuses to the metal/salt interface, leaving vacancies behind in the lattice (Supplementary Figure 6b).

III. The vacancies at the GB from the leached Cr will be filled by Cr and Ni atoms in grain 1 and grain 2, creating vacancies inside the nearest planes to the GB within grain 1 and 2 (Supplementary Figure 6c).

IV. As long as molten salt is present, Cr continues to leach out at GBs. Therefore, I – III continue progressing (Supplementary Figure 6d).

V. The vacancies accumulate along the GB, causing it to broaden. However, this broadening will increase the interfacial energy. After a certain threshold, the broadening of the GB is no longer energetically favorable. Instead, the random atoms along the GB will self-organize and deposit on one side of GB (i.e., on top of a specific grain). As a result, the GB has migrated by an atomic layer. As shown in Supplementary Figure 6e, this additional layer is grown on the grain 2 epitaxially, yet it possesses a lower Cr fraction and contains excess vacancies.

VI. By repeating the process of I – V, the GB will continue migrating, and the dealloyed (DIGM) zone will grow increasingly thicker. A vacancy gradient is formed in the DIGM zone such that the atomic layer closer to the GB tends to have a higher vacancy fraction, as shown in Supplementary Figure 6f.

VII. The high concentration of vacancies in the top layer of the DIGM zone within grain 2 can easily form a void once it is in contact with the salt, leading to salt infiltration (Supplementary Figure 6g).

VIII. Once the void is formed, the atoms in grain 1 and 2 may still “jump” into the crevice, re-organize, and deposit on one of the grains. (Supplementary Figure 6h).

IX. Therefore, the crevice may meander like a river and change its location during the corrosion process (Supplementary Figure 6i).
Supplementary Discussion

Our naming of 1D does not specify ideal 1D, as characterized by a very high feature aspect ratio, neither “near atomic size” nor the tunneling into aluminum or porous silicon\textsuperscript{6–8}. We took the top-down approach by realizing that GBs are 2D defects, while 1D wormholes partially cover GBs in high aspect ratio pathways. As 2D defects, GBs require five parameters to define. We use similar language to describe wires, ropes, and cables with diameters across scales. Therefore, we think that 1D does not necessarily need to be near-atomic size, as long as the diameters do not vary significantly along the path, and the aspect ratio is quite high. We believe our features exhibit this far higher aspect ratio, as opposed to corrosion pits which have been deemed “1D” in some prior studies, yet have a small aspect ratio of depth to diameter. Finally, “1D wormhole” together refers to the observed microstructure.

Here, we would like to illustrate the difference between our work and previous corrosion studies that directly/indirectly mentioned the “1D” concept. We show that the “1D wormhole corrosion” we reported in our manuscript is significantly different from previous studies.

1. Comparison between our work and previous work that mentioned “1D” and is indeed 1D according to our definition in the manuscript.

Previous observations of 1D rod-like microstructures, for example, in the etching of aluminum, silicon, titanium with \textit{strong acids}\textsuperscript{6–8}, are not directly from selective dissolution. In most cases, a single element system is used, and the microstructure is created by fast interfacial reactions without the participation of solid-phase diffusion or the pre-distribution of elements in an alloy. More importantly, the so-called “1D” holes in previous studies do not form a percolating network, and it does not involve the discussion of GBs.

In terms of corrosion of alloys in molten salt, our observation and confirmation of the 1D wormholes laying on the 2D grain boundaries is the first recorded instance that we could find. The shape of wormholes is not as ideal (or simple) as the 1D rod-like microstructures mentioned above, as previous studies consisted of delicate experiments to intentionally create the 1D rod-like microstructure. Our wormholes appear on their own, and are robust to changes in experimental conditions, resulting in a more generalizable phenomenon. We believe that the 1D wormholes are common microstructures in molten salt corrosion (or in high-temperature liquid lead corrosion), which are previously not correctly recognized as continuous or percolating structures. Currently, the most popular interpretation of these holes in the molten salt corrosion field is that these “voids” on the cross-sections are “Kirkendall voids\textsuperscript{9},” which implies that the voids are discontinuous initially or partially discontinuous. For the corrosion of structural materials in high-temperature molten salts, we believe recognizing the 1D wormholes is important as it can
be a critical stage before 2D intergranular corrosion or other types of transgranular corrosion that initiate from GBs.

In short, we believe that 1D wormhole corrosion is a new dimensionality (1D + percolating pipelines along GBs) of corrosion in structural alloys, which must be minimized in engineering systems such as next generation nuclear power plants or concentrated solar power plants. By contrast, previous observations of 1D rod-like microstructures show a very different and non-percolating (non-capillary) morphology, and involve the use of strong acids and/or a non-structural material to create microstructures, which is more relevant in functional materials applications rather than structural materials applications.

2. Comparison between our work and previous work that mentioned “1D” and is in fact 2D according to our definition in the manuscript.

Ghaznavi et al. recently shown that “1D corrosion” can occur in Fe$_{52}$Ni$_{48}$ alloy after corrosion in a molten KCl mixture at 600˚C. The “1D” corrosion they observed is a kind of “2D” corrosion based on the definition used in our manuscript. For the 1D wormhole corrosion in our paper, the void will be discontinuous (just like isolated dots) along GBs in a cross-sectional view, as shown in Fig. 1 in this paper. In the paper by Ghaznavi et al., the voids look like long and continuous lines in the cross-sectional view, which is significantly different from our work. We assume that the 3D morphology of this slot-like voids in Ghaznavi et al.’s paper will look like platelet rather than 1D tunnels. Thus, according to our definition, the corrosion morphology in their paper may be a kind of “2D” corrosion. In addition, the 1D wormholes are along GBs, while those shown in Ghaznavi et al.’s paper are mostly intragranular voids.

3. Comparison between our work and previous work that mentioned “1D” and is in fact 3D according to our definition in the manuscript.

Previously, Pickering and Swann *et al.* mentioned “1D” in their dealloying papers. We found the corrosion morphology they found is “3D”-like rather than “1D”. The morphology of corrosion they referred to is the well-known morphology of dealloying, which is 3D based on our definition (See Fig.1 in the manuscript).

For Pickering’s dealloying experiments, it was mainly ambient temperature aqueous dealloying. They explained the phenomenon by **volume diffusion** (originally by single vacancies, then changed to by divacancies). Later, researchers such as J. Erlebacher and K. Sieradzki have provided strong evidence that ambient temperature aqueous dealloying is via a percolation dealloying mechanism (with significant contribution from **surface**
diffusion) with a resulting bicontinuous structure\textsuperscript{13}. The electron microscopy images from Pickering’s papers seem to show bicontinuous structures. Also, the experimental conditions described in the papers agree with the conditions of dealloying experiments showing a bicontinuous structure. In addition, their experiments of vaporization of Cu\textsubscript{86}Zn and Cu\textsubscript{65}Zn at elevated temperature produced either Kirkendall voids or a bicontinuous microstructure\textsuperscript{14}, the latter of which is also called vapor phase dealloying\textsuperscript{15}. While the phase transformation of CuZn alloys during the dealloying makes the interpretation of the results challenging, none of Pickering’s experiments is similar to our 1D wormholes. In their research of dealloying of Co-Pt alloys at elevated temperature in HCl vapor\textsuperscript{16}, the fraction of the less-noble element (Co) is between 70-90 at\%, but the microstructure in their work looks like a bicontinuous structure or an extreme case of liquid metal dealloying even when the less noble element concentration is significantly high\textsuperscript{17}.

For Peter Swann’s work on “corrosion tunneling,” similar to Pickering’s experiments, the Cu\textsubscript{3}Au and Cu\textsubscript{3.5}Au are dealloyed at ambient temperature in ferric chloride solutions. While they call them “tunnels,” the microstructure from their experiments is actually bicontinuous from a dealloying point of view. The tunnel seems to be the early stage of the formation of a bicontinuous structure. Although these corrosion tunnels may seem to suitably describe our 1D wormholes, the corrosion tunnels in Swann’s work and our work show significantly different features. First, the concept of tunnel by Swann et al. is further explored by A. J. Forty and G. Rowlands, who theoretically predicted the tunneling results when the alloy has a low concentration of noble metal\textsuperscript{18} (c < \textfrac{1}{2}). Now with the high-density percolation dealloying theory, we know that this \textfrac{1}{2} is close to the parting limit of ambient temperature dealloying. So, the corrosion tunneling they refer to is very likely to be the bicontinuous structure. As we mentioned in our previous discussion, bicontinuous structures are 3D, while wormholes in this paper are regarded as 1D. Second, the tunnel observed in Swann’s work show no intermediate range of lattice parameters in a diffusion zone and no elastic strain field near the tunnel\textsuperscript{12}, while our 4D-STEM experiments clearly indicated remarkable heterogeneity of lattice parameters in the diffusion-induced migration zone (Fig. 4 in main text).

In addition, while Swann et al mentioned “one-dimensional” in several of their other papers, we found that these are not used to describe the morphology of holes. Instead, the word “one-dimensional” is used to describe their simplified theoretical 1D diffusion model in which they assumed that the diffusion is normal to the surface (1967)\textsuperscript{19}, or an island of infinite width (1980)\textsuperscript{18}.

Based on the discussions above, we think the 1D wormholes reported in our manuscript are new and significantly different from previous work. However, we also found that a part of the theory of the “corrosion tunnel” by Swann\textsuperscript{12} may be used to explain some of the features found in
1D wormholes. Swann proposed that “Lateral dissolution ceases when the tunnel walls become covered with gold (the more noble element). Possibly corrosion occurs more rapidly at the hemispherical base of the tunnel because the ratio of surface area to volume dissolved is greater there and the surface is not as well covered by gold.” 12 This seems to be helpful for explaining the “focusing” mechanism in our 1D wormhole, which exhibits a very high aspect ratio. However, further in-depth studies are required to validate this theory.
Supplementary Figures

Supplementary Figure 1.
Illustration of the experimental setup, sample preparation, and imaging directions. 

a Schematic drawing of the molten salt corrosion cell, which is similar to a permeation test device. 
b - e Schematic drawing of the sample preparation process. 
f Schematic drawing illustrating the relation between SEM imaging direction and sample geometry.
Supplementary Figure 2.
Monte Carlo simulation comparing the penetration speed of salt under three different conditions: (i) without DIGM and \( \nu = 1 \); (ii) with DIGM and \( \nu = 1 \); (iii) with DIGM and \( \nu = 1 + 2 \cdot \tan |\theta| \). a - c correspond to \( t = 0 \), \( t = 228.35 \), and \( t = 589.38 \), respectively. d Definition of the GB local inclination angle \( \theta \).
Supplementary Figure 3.
Additional data for the vacancy mapping method. a–c Same as Fig. 4. d Hydrostatic strain in the non-DIGM zones (1ii and 2ii). e–f Upper bound and lower bound of the hydrostatic strain in the DIGM zones (1i and 2i). All scale bars are 200 nm.
Supplementary Figure 4.
a-b Step-by-step schematic drawing of the Eshelby’s inclusion diagram for the dealloying case assuming an infinitely large matrix.
Supplementary Figure 5.

a-c Comparison of the averaged Cr fraction, averaged relaxed lattice constant, and averaged vacancy fraction in region 1i and 2i, respectively. The error bars show the standard deviation of the data.
Supplementary Figure 6.

a-i Step-by-step schematic drawing of the DIGM process in molten salt with the consideration of vacancy supersaturation in the DIGM zone. The multicolored circles represent an atom-sized volume of sample with the same composition as the Ni-20Cr alloy.
Supplementary Figure 7.
A typical FIB lift-out process in our experiment. **a** Overview of the sample before lift-out. We first identified the GBs and then select a region (boxed) in the middle that contains a GB. **b** An enlarged view of the boxed region in **a.** **c** Deposition of fiducial markers and Pt caps to protect the sample surface. **d** Milling the bulk trench. **e** U-cuts to free the lamella from the trench. **f** Lifting-out the lamella using the Easy-lift needle. **g** Attached the lamella on a V-notch of the FIB half-grid. **h** Thinning of the lamella from both sides. **i** SEM image showing the thickness of the lamella after thinning.
Evidence showing that the bullseye aperture and the energy filter is critical for enhancing the accuracy of lattice parameter mapping. A comparison of lattice parameter maps on the same region of the same sample by different 4D-STEM experimental setups is presented: a with a traditional circular aperture, b with a bullseye aperture, and c with a bullseye aperture and an energy filter. Note that b and c look very similar because the range of the color-bar is selected to cover the whole range of values on the map. However, the tiny differences between b and c are still important for the accuracy of lattice parameter mapping. $\varepsilon_{xx}$, $\varepsilon_{yy}$, and $\varepsilon_{xy}$ are three key components in the 2D strain tensor, representing the strain in $xx$, $yy$, and $xy$ (shear) direction, respectively. $\theta$ is the local lattice rotation. d-f Illustration of the lattice parameter mapping process by 4D-STEM using a bullseye aperture. d A NBED pattern on vacuum (i.e., the electron beam does not go through any samples), which is used as a template for Bragg disk identification; e A NBED pattern on the Ni-20Cr sample, where all Bragg disks are in bullseye shape because of the bullseye aperture; f A typical Bragg disk detection result analyzed by the py4DSTEM package. The higher order Bragg disks are very dim in brightness, but their centers can still be accurately detected due to the use of the unique bullseye C2 aperture.
Supplementary Figure 9.
DFT modeling of the evolution of lattice constant during the dealloying process when the replacement fraction of depleted Cr with Ni is fixed at a constant. 0.0 replacement fraction corresponds to each depleted Cr becoming a vacancy site.
Supplementary Figure 10.
Experimental data from Ref\textsuperscript{20} and linear fit showing the effect of Cr fraction on the lattice parameter in a Ni-Cr alloy when the vacancy fraction is negligible, corresponding to the 100% replacement case.
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