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Machine Learning-Enabled Tomographic Imaging of Chemical Short-Range Atomic Ordering

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In solids, chemical short-range order (CSRO) refers to the self-organization of atoms of certain species occupying specific crystal sites. CSRO is increasingly being envisaged as a lever to tailor the mechanical and functional properties of materials. Yet quantitative relationships between properties and the morphology, number density, and atomic configurations of CSRO domains remain elusive. Herein, it is showcased how machine learning-enhanced atom probe tomography (APT) can mine the near-atomically resolved APT data and jointly exploit the technique's high elemental sensitivity to provide a 3D quantitative analysis of CSRO in a CoCrNi medium-entropy alloy. Multiple CSRO configurations are revealed, with their formation supported by state-ofthe-art Monte-Carlo simulations. Quantitative analysis of these CSROs allows establishing relationships between processing parameters and physical properties. The unambiguous characterization of CSRO will help refine strategies for designing advanced materials by manipulating atomic-scale architectures.

compositions, structures, and imperfections from the macro- to microscale and even atomic scale. Alloy making traditionally involves the introduction of small quantities of one or more species, solutes, into a matrix of a solvent element. During processing, one or more (meta)stable phases form that modify the response to physical or mechanical stimulation.^[1] In the past decade, so-called high/mediumentropy alloys (H/MEAs) have been introduced, whereby multiple elements are mixed in equal, or close to equal quantity. Although initially assumed to be chemically disordered,^[2] i.e., atoms from these principal elements randomly occupy sites of the crystalline lattice, recent studies have suggested that atomicscale, chemical short-range order (CSRO) is far more prevalent in H/MEAs than

1. Introduction

Over time, strategies were developed to tailor the properties of materials to societal needs, by manipulating their initially assumed, offering a potential lever to tailor their properties.^[2b,3] A representative H/MEA is CoCrNi, in which the presence and

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nature of CSRO are currently debated.^[2b,3b,d-g,4] Transmission Y. Wei Ecole Polytechnique Fédérale de Lausanne School of Engineering

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electron microscopy (TEM)-based approaches are most prevalently used to resolve CSRO,^[2b,3b,d,g,5] but reports on the presence and configuration of CSRO have been thus far contradictory, even for samples synthesized in the same conditions (Table S1; Supplementary Text, Supporting Information). Due to the intrinsic limit of two-dimensional projection imaging, it has been pointed out that the observed electron reflections may originate from factors other than CSROs, e.g., planar defects and higherorder Laue zones.^[5,6] An alternative, reliable, 3D analytic perspective of CSRO is hence needed to reconcile these controversies, but also to facilitate the use of CSRO in the materials design.

Atom probe tomography (APT) has long been expected to probe CSRO in 3D, but recognizing CSRO has been hindered by its anisotropic spatial resolution and imperfect detection efficiency.^[7] Overcoming these limitations by manual analysis has proven impossible.^[8] Inspired by other machine learning (ML) methods developed to process complex microscopy and microanalysis data,^[9] and building on our previous efforts,^[7c,10] we introduce a bottom-up approach to quantify in 3D the CSRO domains in APT data from CoCrNi, termed ML-APT, that does not require any prior knowledge of the CSRO configurations, in contrast with previous work^[10] (Supporting Information). The overall flowchart is presented in Figure S1 (Supporting Information). ML-APT enables the identification of CSROs as well as the guantification of the number density of ordered domains, their configurations, elemental site occupancy, and size/morphology. Monte-Carlo simulations are then used to rationalize our analyses, facilitating an understanding of ordering reactions. We finally showcase how to establish a direct processing-CSRO-property relationship, paving the way for further material design opportunities.

2. Results and Discussion

2.1. APT Results

An equiatomic CoCrNi alloy was analyzed in two states, first following the homogenization, and, second, after the homogenization and annealing (Methods and Table S2, Supporting Information). We performed correlative scanning electron microscopy-electron backscattered diffraction (EBSD)-focused ion beam (FIB)-APT to characterize their microstructure in grains of selected orientation (Figure 1a), i.e., {002} and {111}. Figure 1b-e details a typical APT analysis from the annealed sample. Figure 1b is a detector hit map with a pattern corresponding to the symmetries of {002} crystallographic planes, and Figure 1c is the 3D atom map reconstructed around this pole. A close-up in Figure 1d shows resolved {002} atomic planes. The reconstruction was calibrated to the reported interplanar spacing of face-centred-cubic (fcc) CoCrNi.^[11] Spatial distribution maps^[12] are calculated along the depth (z-SDMs) to exploit these most highly resolved signals and to evaluate the CSRO. The z-SDM indicates the characteristic period of each elemental pair along a specific direction, which is similar to a split pair correlation function used in, e.g., TEM.^[3c] The z-SDMs of different elemental pairs obtained in a 2-nm voxel are plotted in Figure 1e. The peakto-peak distance for each elemental pair is the same, suggesting a homogenous solid solution. Typical clustering algorithms in the APT community^[8c,13] have been tested but cannot identify CSROs (Figure 1f,g and Supporting Information). A similar analysis along {111} planes is provided in Figure S2 (Supporting Information). The spatial resolution for {022} planes is insufficient to perform subsequent analyses.

2.2. ML-APT Framework

As detailed in Figure 2a for L12-CSRO, for the random solid solution of fcc-based CoCrNi alloys, the elemental occupation of each site is equiprobable. CSRO occurs when particular sites have a higher probability to be occupied by a specific element, e.g. the face-centered sites are more likely to be Cr/Ni while the edges are Co atoms. At higher probability, up to close to 100%, CSRO is established and can facilitate the nucleation of long-range chemical order. The corresponding Co-Co z-SDMs along the <002> from simulated APT data are shown in Figure 2b, and the peaks close to ± 0.18 nm and ± 0.54 nm are disappearing with the evolution of CSRO. Any type of CSRO can be detected, provided that its signature in the z-SDMs along a particular orientation is clear. This allows us to recognize different CSRO configurations without any prior knowledge, which is conceptually unlike the previous up-bottom strategy with prior possible ordered or CSRO structures.^[7c,10]

The ML-APT workflow to reveal CSRO in H/MEA is as follows. First, we generated artificial APT data along <002> or <111> containing either a randomly distributed fcc-matrix or CSRO (Methods). The weak CSRO was not simulated, as the signal to background ratio of the peaks at ΔZ values such as ± 0.18 nm and ± 0.54 nm is typically too low to confidently identify them experimentally. The FCC and strong CSRO, were labeled as 0 and 1, respectively. Over 10000 of corresponding z-SDMs patterns are recorded for each orientation (Table S3, Supporting Information). This synthetic data is fed into an optimized 1D convolutional neural network (CNN) to obtain an fcc-matrix/CSRO binary classification model (Figure 2c; Methods and Figure S3a, Supporting Information). Note that a random forest algorithm has been tested but its performance is not better than the applied 1DCNN.^[10] ML-APT shows excellent performance for both simulated and experimental test datasets (Methods and Figures S3b-d and S4, Supporting Information). It is further tested on a set of physically-informed large-scale CoCrNi artificial APT data with L1₂-CSRO domains with a diameter of 0.7–2.0 nm (Methods, Supporting Information), and ML-APT distinguishes these well (Figure S5 and Supporting Information). The gradient-weighted class activation mapping,^[7c,14] which uses gradients of any target concept flowing into the final convolutional layer to produce a coarse localization map highlighting the important regions in the image for predicting the concept, reveals that ML-APT performs the classification by focusing on the specific peaks of the z-SDMs that can be used to accurately classify the fcc/CSRO in both simulated and experimental data (Figure S6, Supporting Information). Finally, experimental z-SDMs were subjected to preprocessing and then input into ML-APT to obtain 3D CSRO distributions (Figure 2d; Methods, Supporting Information).

2.3. 3D Perspective of CSRO

Typical examples of 3D distributions of CSRO domains obtained from ML-APT, applied to Co–Co, Cr–Cr, and Ni–Ni, are presented

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Figure 1. Typical APT data of the equiatomic CoCrNi alloy after annealing at 1273K for 120 h and conventional data analysis to look for CSRO. a) The EBSD inverse pole figure highlights the grains used for APT experiments. b) Representative 2D detector hit map. One centric {002} crystallographic pole is labeled. c) Precise 3D APT reconstruction along the <002> orientation. d) Local close-up of a thin slice in (c) along the <002>. e) z-SDMs of different elemental pairs in a representative 2-nm voxel in (c). Its signature corresponds to the fcc structure and its unit cell is given. Two kinds of conventional APT analysis approaches: f) frequency distribution analysis of Co, Cr, and Ni atoms compared to the binomial random distributions, and g) *k*-nearest neighbor (KNN) distance analysis (k = 1 and 5) of Co-Co, Cr-Cr, and Ni-Ni elemental pairs. Exp and Ran labels correspond to the results obtained by experimental and random-labeled datasets, respectively.

in Figures 3 and S7 (Supporting Information) along <002> and <111>, respectively. Cross-species elemental pairs were not analyzed to avoid possible biases arising from differences in evaporation fields affecting the spatial resolution^[15] and this samespecies information is enough to analyze the CSRO (Supporting Information). Figure 3a shows a typical spatial distribution of these domains with a near-spherical morphology (Figure S8, Supporting Information). Its z-SDM and that of the remaining fcc matrix data are plotted in Figure S9 (Supporting Information), matching well with those from simulations as outlined in Figure 2b. Figure 3b-d shows size distributions of domains in which the Co-Co, Cr-Cr, and Ni-Ni are classified as ordered, respectively. The Pearson's correlation coefficient (PCC) and contingency coefficient $(\mu)^{[16]}$ are used to test the statistical significance of the difference between these distributions and a chemically randomized dataset, with µ found more sensitive than PCC to characterize such subtle differences. We defined a threshold to classify the (non-)randomness at 0.25. The choice of 0.25 is explained in Methods (Supporting Information). The Ni-Ni distribution is non-random, with a μ of 0.32, especially when the domain has more than 35 atoms (<1 nm)

(Figure 3e), while the distribution of the two other elements is closer to random (μ <0.25). Figure 3d,e demonstrates that these CSRO domains with sizes below 35 atoms are primarily statistically and randomly formed. Considering the average diameter of one CSRO is generally ≈ 1 nm, it is reasonable to conclude that domains with fewer than 35 atoms are mostly disordered. Figure 3f is an example of the Ni-Ni CSRO domain, and the corresponding Ni-Ni z-SDM is plotted in Figure 3g, showcasing an interplanar spacing of Ni atoms is twice as large as that in the fcc-matrix (Figure 1e) (those of Cr-Cr and Ni-Ni still keep 0.18 nm as shown in Figure S10, Supporting Information), which matches the L1₂/DO₂₂-type structure with the Ni-Ni repulsion on {100} as explained in Figure 4a. Although other crystal structures may also match this repulsion scenario, we use the most often experimentally observed L12/DO22-type structures.[5b] For comparisons, along the <111>, the three kinds of CSROs are all different from the random state with $\mu \ge 0.25$ (Figure S7b-d, Supporting Information). This suggests that there is either Co/Cr/Ni repulsion on $\{111\}$, which matches the L1₁-type structure, as detailed in Figure S7e (Supporting Information) and Figure 4b.

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Figure 2. Proposed ML-APT framework to recognize multi-type CSROs in CoCrNi alloys. a) Unit cells of random-fcc, weak, and strong $L1_2$ -CSRO. b) Typical Co-Co z-SDMs along the <002> with the evolution of CSRO after performing APT simulation. c) Schematic diagram of the optimised 1D CNN structure to obtain a random-fcc/CSRO recognition model. d) Flowchart of processing experimental data to obtain 3D CSRO distribution.

Figure 4c,d provides values of μ for the two studied material states and orientations. Along $\{002\}$ planes, the value of μ of Co-Co or Cr-Cr CSROs remains below 0.25. Non-statistical Ni-Ni CSRO rises from 0.18 to 0.27 after annealing at 1273K for 120 h, with a number density of 4.81×10^{25} m⁻³ of CSRO domains with atomic configurations matching the L1₂/DO₂₂ structures with the Ni-Ni repulsion on {100} (Figure 4a,e). Note that the probability for the L1₀ structure is much lower compared to that for the $L1_2/DO_{22}$ considering only one elemental pair has an obvious repulsive tendency. Along {111} planes, after the homogenization, values of μ for Co-Co and Ni-Ni CSRO are close to or above 0.25, suggesting the existence of L11-domains with the Co/Ni repulsion on the {111}, with a number density in the range of $2.98-3.18 \times 10^{25}$ m⁻³ (Figure 4b,e). After the annealing, the values of µ of Co-Co, Cr-Cr, and Ni-Ni pairs are above 0.25, matching with the L11-type structure with Co-Co/Cr-Cr/Ni-Ni repulsions on the {111}, with a number density of 4.73×10^{25} $m^{-3},\,4.66\times10^{25}\ m^{-3},$ and $4.73\times10^{25}\ m^{-3},$ as determined from Co-Co, Cr-Cr, and Ni-Ni pairs, respectively (Figure 4b,e). Only L1₁-domains exist after the homogenization, and their number density increases after the annealing, during which a high density of $L1_2/DO_{22}$ -domains appears (Figure 4e,f). Overall, the number density of CSRO domains is approximately three times after the annealing compared to that after the homogenization. It should be pointed out that {111} plane has four rotational variants, i.e., {111} (i.e., (111), (111), (111), or (111)), and Figure 4e is the analysis of the given population of CSRO-domains along only one variant that can be imaged in that particular APT dataset with sufficient resolution to perform the analysis. An additional dataset obtained along another {111} variant leads to comparable results (Figure S20 and Supporting Information). One can estimate the overall number densities by extrapolating the obtained number







Figure 3. 3D quantitative analysis of CSRO along <002> in the annealed CoCrNi alloy. a) 3D distribution of Ni-Ni CSROs with the mapping of elements. The front and top views of typical clusters are provided. Different colors mark different CSRO domains. b–d) Size distributions of the identified Co–Co, Cr–Cr, and Ni–Ni CSROs, respectively. The results from the chemically randomized dataset (Methods, Supporting Information) are compared with Pearson's correlation coefficient (PCC) and Pearson contingency coefficient (μ). This CSRO size refers to the APT-counted atoms and the size of 55 atoms ideally corresponds to a 1-nm cube. An upper tail occurring at 155 atoms appears, because we have added all those containing over 155 atoms into this particular bin. e) Local enlargement of the colored region in (d) which is different from the random curve. f) 3D atom map of a typical Ni-Ni CSRO domain extracted from (e). g) Its corresponding Ni-Ni z-SDM (Cr–Cr and Co–Co z-SDMs are provided in Figure S10, Supporting Information).

density on one {111} plane and multiplying it by four, enabling a more accurate quantitative relationship between CSRO and associated properties. For example, there are more than 36 additional CSRO domains within a 10³-nm³ volume after the annealing as compared to that after the homogenization, which will influence materials' properties, including for instance the electrical resistivity as discussed below. During the entire process, the CSROs almost keep the spherical shape (Figure S8, Supporting Information) with the size of 20-155 APT-counted atoms (0.7-1.5 nm in diameter) (Figure 3 and Figure S7, Supporting Information). Note that these observed domains along {002} and {111} are not the same ones. A comparison of the compositions between CSRO domains and raw data suggests that there is no obvious statistical difference between them, indicating that only the ordering changed and not the composition (A quantitative explanation is provided in Supporting Information). Moreover, we compared the results from laser and voltage pulsing modes (Supporting Information), as shown in Figure S11 (Supporting Information), which show comparable results, which can be rationalized based on previous reports of the moderate changes in the depth resolution between voltage and laser pulsing modes.^[17] Analysis of the combined elemental pairs for each individual domain is not recommended due to the nature of the CSRO, which reflects the local elemental fluctuation at a very early stage of thermally activated ordering.

2.4. Electrical Response

The occurrence of CSRO in solid solutions is often associated with the modifications of physical properties.^[8a,b,18] The influence of CSRO on the mechanical properties of CoCrNi has been studied widely,^[2b,3d,5a,11a] with inconsistent conclusions, but functional properties have only rarely been investigated. Here,



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Figure 4. 3D atomic-level details of multi-type CSROs in CoCrNi alloys under different heat treatments and arising electrical resistivity change. a) The $L1_2/DO_{22}$ -CSRO structure with the Ni–Ni repulsion on {100}. b) The $L1_1$ -CSRO structure with the A-A or B-B repulsion on {111}. Element A or B refers to sites that are enriched in Co, Cr, or Ni but cannot be the same simultaneously (an intuitive explanation is given in Figure S7e, Supporting Information). c,d) Changes of Pearson contingency coefficient (μ) under different heat treatments along <002> and <111>, respectively. The colored regions highlight the changes of μ after the annealing. Three APT datasets were analyzed to obtain the statistical results for each data point. A value of μ = 0.25 is regarded as the threshold between CSRO and random states. e) Number-density change ($\times 10^{25}$ m⁻³) of different types of CSROs under heat treatment. f) Derived CSRO structural evolution from homogenization to annealing. The corresponding CSRO configurations are plotted in (a) and (b). g) Evolutions of electrical resistivity under different heat treatments.

we measured the electrical resistivity of the two material states (Methods). The annealing-induced multiple CSROs in CoCrNi alloys resulted in a 17% rise in the room-temperature electrical resistivity (Figure 4g), higher than previous reports (+4.8%) in ref.[5a] which can be explained by the formation of a higher density of CSRO domains during the furnace cooling compared to a quench. This reveals a high sensitivity of the electrical resistivity upon changes in the CSRO state, maybe more so than the mechanical response. This remarkable increase in resistivity implies that the increasing CSRO might lead to a reduced electronic density of states at the Fermi level, consistent with the previous density functional theory calculations in the CoCrNi system.^[19]

2.5. Monte-Carlo Simulation

ML accelerated ab initio Monte-Carlo (MC) simulations (Methods, Supporting Information) were performed to predict the

temperature-dependent equilibrium CSROs and associated crystalline structures.^[20] Calculated temperature-dependent heat capacities reveal two peaks due to first-order phase transformations (Figure S12, Supporting Information). One occurs at around 900K, which is confirmed by differential scanning calorimetry (DSC), and the second occurs at around 225K which is below the detection limit of DSC due to sluggish diffusion kinetics at low temperatures. Predicted first NN Warren-Cowley parameters (Methods) suggested repulsion of Cr-Cr, Co-Ni, Co-Co and attractions of Ni-Ni, Cr-Ni, Co-Cr above the phase transformation peak, as shown in Figure S13 (Supporting Information). To identify the possibly locally appearing crystalline ordered clusters in the CSROs regime, Figure 5a,b visualize the calculated CSRO diffuse intensity map (α_q) (Methods, Supporting Information) in the (001) and (111) planes, respectively, at 1000K. For the (001), a (1, 0.5, 0) special point is revealed for Cr-Cr, suggesting, e.g., a DO₂₂ ordering.^[21] Besides, a (001) peak is also presented for the Ni–Ni and Co–Co pairs: local clusters of L1₂ or L1₀ ordering are



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Figure 5. CSROs predicted by Monte-Carlo simulations. a,b) Predicted CSRO diffuse intensity map, α_q , of Co–Co, Cr–Cr, and Ni–Ni pairs at 1000K in (001) and (111) planes, respectively. The reciprocal space vectors are given in units of $2\pi/a$, where *a* is the lattice parameter.

suggested for these two. The intensity of L1₂ or L1₀ consistent CSRO peak is strongly enhanced by magnetic effects (Supporting Information). Further peak analysis in the 3D reciprocal space found (0.5, 0.5, 0.5) maxima for Cr-Cr and Ni-Ni pairs, which are also revealed by projecting the calculated α_q in the (111) as shown in Figure 5b, which would be consistent with local L1₁ configurations (i.e., ordering along <111>). Compared with APT measurements (Figure 4), ordering along <002> for Ni-Ni, as well as ordering along <111> for Cr-Cr and Ni-Ni are confirmed by MC simulations. For Co-Co pairs, the correlations related to L1₁ are less pronounced (Figure S17, Supporting Information). Previous studies predominantly suggested the presence of L1₁ and/or L12- CSRO with Cr-Cr repulsion. Here, we conducted further investigations by studying an additional CoCrNi sample that was annealed at 1273K for 120 h followed by quenching, allowing for comparison with previous furnace cooling condition to address this discrepancy (Supporting Information).

Although the ML-APT enables tomographic imaging of CSRO in CoCrNi alloys, there are some inherent limitations at the current status, as for all experimental techniques. First, high-quality APT experimental data is needed (see Supporting Information for how to determine the quality), to maximize the spatial resolutions, to enable more accurate recognition of CSRO patterns. Enhancing data quality, and maybe even breaking the limitation for analysis of only specific sets of planes, could arise from better modeling atom probe tomography^[22] to optimize data acquisition parameters and enable the analysis of the cross-species elemental pairs, even if the compositional complexity of the material will impose limits in the achievable precision.^[7b] Moreover, voxelization (here $1 \times 1 \times 1$ nm³) lowers the accuracy and may preclude the identification of small CSRO domains. With higher data quality, the ML-APT could be used with smaller voxels. Finally, there could be ways to directly apply other 3D-based ML techniques to detect CSRO after enhancing the APT data quality.^[23]

3. Conclusion

To conclude, the proposed ML-APT approach enables us to settle previous debates on CSRO in CoCrNi alloys, and evidence atomic-scale details of CSRO beyond the state-of-the-art. It simultaneously resolves CSRO at both the individual-domain and overall (statistical) levels. In comparison to other approaches for CSRO characterization, our proposed ML-APT analysis only relies on the measured APT mass spectra and is hence independent of interatomic potentials needed to interpret CSRO from X-ray/neutron techniques.^[4] Moreover, ML-APT provides 3D elemental-specific information and is hence capable of identifying multiple types of CSRO (Figures 3 and 4). The observed CSRO configurations were rationalized herein by Monte-Carlo simulations. The electrical response could be a better indicator of CSROs than mechanical properties. The individual influence SCIENCE NEWS _____



of CSRO on the mechanical properties is seemly limited at room temperature, whereas, the co-existing CSRO and medium-range order could be a better approach to designing new H/MEAs with better (cryogenic) mechanical properties via adjusting the processing parameters (e.g., thermal history^[24] and deformation)^[25] or microalloying (e.g., adding Ti or Al).^[26] Our method can be generally used for other H/MEAs as well as for complex engineering materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Y.L., Y.G., Z.W., and B.G. designed the project. Y.L. is the lead experimental/data scientist. M.S. and B.i.G. prepared the materials and heat treatments. Y.L. performed the FIB/APT experiments and analyzed the APT data with the help of B.G. Y.L. programmed the machine learning framework with the help of Y.W. and T.C. H.Z. and Y.Y. performed the electrical resistivity measurements. Y.G. programmed and performed the MC simulations. Y.G. and S.G. performed the ab initio calculations and constructed the ML potentials. Y.L., Y.G., Z.W., and B.G. wrote the manuscript. All authors contributed to the discussion of the results and commented on the manuscript.

Data Availability Statement

The data that support the findings of this study are openly available in figshare at https://doi.org/10.6084/m9.figshare.24274780, reference number 1. The ML-APT software is available at the GitHub address https: //github.com/a356617605.

Keywords

artificial intelligence, atomic-scale characterization, high/medium-entropy alloys, local chemical ordering, tomographic imaging

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Supporting Information

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Machine Learning-Enabled Tomographic Imaging of Chemical Short-Range Atomic Ordering

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Supplementary Information for

Machine Learning-Enabled Tomographic Imaging of Chemical Short-Range Atomic Ordering

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Including:

Methods Supplementary Figure S1-S22 Supplementary Table S1-S4 Supplementary Text References

Methods

Materials preparations

The equiatomic CoCrNi was argon-arc melted from pieces of raw metals with high purity (>99.9 wt.%) in a water-chilled copper crucible. Then, the as-cast samples were divided into two pieces and sealed into Ar-atmosphere quartz capsules to avoid oxidation. One was homogenised at 1473K for 48h followed by water quenching, and the other was homogenised at 1473K for 48h and then annealed at 1273K for 120h followed by furnace cooling to room temperature.

Atom probe tomography (APT) experiments

The site-specific preparation procedure used for APT needle-like specimens was performed via the correlative electron backscattered diffraction (EBSD) and FEI Helios focused ion beam (FIB) with a Xenon plasma ion source. The APT measurements were performed on a CAMECA Inc. LEAP 5000XR in the laser pulsing mode at 50-60K, 0.7% detection rate, 20pJ laser energy, and 200 kHz pulse rate. Three APT datasets were collected to obtain statistical results for each state. To survey the effect of running parameters, we made four additional APT datasets in the voltage pulsing mode at 70K, 0.5% detection rate, 20% pulse fraction, and 200 kHz pulse rate. APT reconstruction and initial analysis were performed using AP Suite 6.1 and reconstructions were calibrated using the procedure described in Refs. ^[1]. The mass spectrum of typical APT data is shown in Figure S14. The average composition of specimens measured by APT is close to equiatomic $Co_{31}Cr_{31}Ni_{31}$ with minor impurities (Table S2). Note that there is no clustering of these impurities, especially O, C, and H atoms. The potential effect of hydrogen-containing molecular ions in the CoCrNi system was excluded due to their limited amounts (Supplementary Text). Due to the descending quality of z-SDMs along the radial direction, a 10-nm radius clipping around a specific pole is applied for all APT datasets.

ML-APT workflow

Different from our previous work with prior possible ordered or CSRO structures ^[2], due to the prior-unknown CSRO configuration in CoCrNi, we generated simulated CSRO z-SDM patterns along different directions to infer CSRO motifs. The periodicity or peak distance of z-SDMs are changed, respectively, when CSRO occurs or different analysis directions are applied (Figure S15).

As shown in Figure 2b, for generating simulated matrix and CSRO patterns along $\langle 100 \rangle$, two supercells with the size of $1 \times 1 \times 1$ nm³ (the lattice parameter is 0.36nm) are firstly generated, around fcc and L1₂. Note that the change in the composition of each fcc cell has a minor effect on the simulated z-SDMs. There is limited compositional fluctuation in the experimental data and the domains with concentrations below 5 at.% account for 1–2% only, as shown in Figure S19, and even then the SDMs retain sufficient information. Then, atoms are shifted from their theoretical sites in x, y, and z directions according to Gaussian functions to simulate the anisotropic spatial resolutions met in APT, followed by randomly discarding certain fractions of atoms to mimic the imperfect detection efficiency. Finally, the corresponding 1D z-SDMs along (100) are generated, as exampled in Figure S15. The peak positions of the experimental z-SDMs are not always at theoretical sites due to the trajectory aberration. Hence, we augmented the dataset by adding additional 5200 synthetic data in which the peak-to-peak distance was randomly modified by ± 0.03 nm. All parameters for generating simulated z-SDMs are listed in Table S3. For the matrix and

CSRO patterns along $\langle 111 \rangle$, the same procedure is performed for the z-SDMs of fcc and L1₂ structure but with the lattice parameter of 0.41nm, and an example is presented in Figure S15. The two sets of synthetic z-SDMs banks (over 20000 curves) are used to train the following CNN to generate the corresponding CSRO recognition models.

The detailed structure of used CNN is described in Figure S3a. The uncertainty is calculated by 5 models from 5-fold cross-validation. The obtained model exhibits almost 100% training, validation, and test accuracies on the synthetic data (Figure S3b-d). The model was further tested using 88 pre-processed experimental z-SDMs for each type of CSRO. The procedure of experimental data pre-processing involves smoothing the raw z-SDMs and background reduction ^[2b]. The classification is evaluated by the area under the curve (AUC) of the receiver operating characteristic curve (ROC)^[3]. The CNN exhibits high AUC values and low uncertainties after data augmentation, i.e., 0.98±0.01, 0.94±0.01, 0.96±0.00 for Co-Co, Cr-Cr, and Ni-Ni CSRO, respectively (Figure S4). These scores suggest that the obtained CNN can successfully classify experimental data. The CNN was implemented using the Keras 2.2.4 with the TensorFlow 1.13.1 backend on Python 3.7. Note that the reported hyperparameters' values in Figure S3a are the result of a thorough tuning procedure based on the training, validation, and test results on synthetic and real datasets (like the tested convolutional layer number: 1~3; filter number: 8~64; kernel size: 5-15, neurons of full layer: 32~500; learning rate: 0.001~0.1). A dropout layer with a rate of 0.5 was used to avoid overfitting as shown in Figure S3b-d. The quick model converge performance shown in Figure S3b is mainly due to the rather simple 1D signal of z-SDMs.

We further tested ML-APT using large-scale CoCrNi APT artificial data as ground truth. This large-scale dataset can incorporate important factors related to field evaporation physics by extracting crucial features from previous physics-based simulation ^[4]. The Co(CrNi)₃-L1₂ domains, with a diameter ranging from 0.7 to 2.0 nm, are embedded into a CoCrNi-fcc matrix. The shifting distance of atoms in the lateral reconstruction direction is set as with the maximum of 5th nearest neighbour distance, while that in the depth reconstruction direction was tuned to mimic the trend in Figure S18 a. The standard deviation of the Gaussian function applied to shift atoms in the depth reconstruction direction is 0.07, which closely resembles the previous physics-based simulation ^[4]. Then 48% of atoms are discarded. The final simulated L1₂ domains are shown in Figure S5a. Different voxelization strategies (using the $2 \times 2 \times 2$, $1 \times 1 \times 1$, or $0.5 \times 0.5 \times 0.5$ m³ voxel with a 1, 0.5, or 0.25nm stride) are tested, and finally, the one using a $1 \times 1 \times 1$ nm³ voxel with a 0.5nm stride was adopted considering the good balance between recognising accuracy and computing efficiency. Even in a truly random yet concentrated solid solution, some local environments similar to CSRO randomly form, with no specific ordering driving force. Thus, a chemically-randomised dataset was built to make comparisons by fastening the raw x, y, and z sites but randomly shuffling the species of elements.

Next, APT data is voxelised into millions of 1-nm cubes with a 0.5nm stride that are further transformed into z-SDMs via a Python-based parallel program. These experimental curves are made pre-processing and then fed into the obtained CNN model to derive the 3D distribution of CSRO. A threshold of 3.75 is reasonably for separating the FCC and CSRO (see Figure S18). Note that this CNN model generally classifies messy z-SDM patterns into fcc to avoid bias from

low-quality signals. The density-based spatial clustering of applications with noise (DBSCAN) algorithm ^[5] is applied to make a clustering analysis. The same hyperparameters are applied to all experimental datasets after careful tuning. The morphology of CSRO is described following the plot of the oblateness versus aspect ratio ^[6]. The results essentially reflect the spatial distribution of CSRO domains, as in Figure S5b, yet these inevitably include some randomly-occurring small CSRO domains. These domains would appear notwithstanding the method used to characterise CSRO, and for TEM-based methods, they would combine with additional factors (planar defects, surface oxides, and higher-order Laue zones) to generate backgrounds that can make it more challenging to identify CSRO ^[7].

To understand where the CNN model is focusing, we applied the gradient-weighted class activation mapping ^[2a, 8]. Its output is a heat map for a given class label and the results are shown in Figure S6.

Determination of the threshold of 0.25 to classify (non-)randomness

First, we created multiple chemically-randomised datasets from experiments performed along different poles, using the method outlined in Stephenson et al. ^[9]. We then compared these chemically-randomised datasets from the same experimental data to obtain the μ . After analysing nine groups of randomised distributions, an average μ value of 0.22 with a standard deviation of 0.035 was obtained. We chose 0.25, the upper limit, as a baseline for these randomised distributions in experimental data. Above 0.25 suggests the occurrence of CSRO in this system.

Electrical resistivity measurement

The room-temperature electrical resistivity of each heat treatment state was obtained by the fourprobe resistance measurement using a KEITHLEY 4200-SCS device. Five specimens for each state were measured to calculate the statistical results.

Specific heat capacity measurement via differential scanning calorimetry (DSC)

We measured the constant-pressure specific heat capacity (c_p) from 313 to 1073 K using a NETZSCH 404C DSC, following the ASTM E1269 using a sapphire standard. The homogenised CoCrNi sample was heated under an argon atmosphere at a constant heating rate of 10 K/min. The sample experienced a full heating-cooling cycle before measurement to rule out the exothermic reactions due to non-equilibrium cooling during the quenching process ^[10]. Two independent experiments were performed and the error of specific heat capacity of 5% was estimated.

Monte-Carlo simulation

Density functional theory (DFT) calculations: Non-spin-polarised DFT calculations were performed using the projector augmented wave (PAW) method ^[11] as implemented in the Vienna *ab initio* Simulation Package (VASP) ^[12]. The provided PAW potentials ^[13] were employed, treating the $3p^63d^84s^1$, $3p^63d^54s^1$, and $3p^63d^94s^1$ orbitals as valence electrons for Co, Cr, and Ni, respectively. The generalised gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) ^[14] parameterisation was utilised for the exchange-correlation function. The calculations were performed using a 500eV kinetic-energy cutoff and a $6 \times 6 \times 6$ k-point mesh (corresponding to 11,232 kp·atom) according to the Monkhorst-Pack scheme ^[15]. Structural relaxations of atomic

positions at a fixed volume (at lattice parameter a = 3.61Å, corresponding to measurement at 1100K by neutron diffractions ^[10]) with total energy convergence of 2×10^{-3} meV/atom was employed. We used $3 \times 3 \times 3$ CoCrNi supercells with 108 atoms, which allows for an equiatomic composition. To analyse the impact of magnetism, spin-polarised calculations (see Supplementary Text) have been utilised with similar parameters, see also ^[16].

Machine-learning inter-atomic potential: An on-lattice machine-learning inter-atomic potential, called low-rank potential (LRP, after ^[17]) is fitted to describe the total energy for a given distribution of chemical elements on the fcc lattice. The central idea of this type of potential is to formulate the energy contributed by each atom at a specific lattice site, by its environmental atoms at neighbouring lattice sites (within a certain radius cut-off) which is parameterised by a highdimensional tensor $A \in \mathbf{R}^{M_1 \times M_2 \times \cdots \times M_{N+1}}$ (where *M* is the number of chemical components, e.g. 3) for CoCrNi; N the number of neighbours to be considered, e.g. N = 12 for first nearest neighbours (NNs) of an fcc crystal lattice); it turns out that the high-dimensional tensor can be well approximated by low-rank representations by the tensor-train decomposition following ^[17-18]. This significantly reduces the number of hyperparameters needed to describe the local atomic environment energy surface while retaining high accuracy. Detailed formulations can be found in Refs. ^[17-18]. The mathematical procedure yields significantly higher accuracy over the traditionally used cluster expansion (CE) approach when training on density functional theory (DFT) calculations of a defined alloy composition ^[17]. Atomic relaxation effects (stress relaxations) can be accounted for within the formalism. Figure S16 shows training and validation errors compared with DFT calculations (after stress relaxation) for CoCrNi equiatomic composition. Rank-8 shows the optimum accuracy with residual mean square error (RMSE) below 1meV/atom.

Monte-Carlo samplings: Coupled with trained LRP potentials, we performed Metropolis Monte-Carlo (MC) simulations in the canonical ensemble (NVT). The fcc supercell with a size of $12 \times 12 \times 12$ (6912 atoms) was initialised with random occupation of Co/Cr/Ni atoms. We annealed the simulations box at each target temperature, with heat capacity convergence criteria of 10^{-6} $k_{\rm B}$ /atom. After convergence, MC sampling of the same number of steps allows for statistically highly converged CSRO and prediction of heat capacity. The CSRO is described here by using the Warren-Cowley SRO parameters, α_{ii}^r , as

$$\alpha_{ij}^r = 1 - \frac{p_{ij}^r}{c_i c_i} \tag{1}$$

where *c* denotes the nominal composition; the pair probability (*p*) of chemical elements *i*, *j* at each *r*-NN shell can be directly calculated by the MC sampling. Up to 20th NNs pair correlation parameters α_{ij}^r are calculated.

Crystal structural identification of CSROs: To identify the crystal structure predicted for CSROs, calculated α_{ij}^r (for each elemental pair, at each temperature) are projected to the reciprocal space following the static concentration wave method ^[19], consistent with

$$\alpha(\mathbf{q})_{ij} = \sum_{r} \sum_{k \in r} \alpha_{ij}^{k} e^{-i\mathbf{q}\mathbf{R}_{k}}$$
(2)

where α_{ij}^k defined for each lattice site k at r-NN shell (referenced to defined lattice site) with real space position. **R**_k is Fourier transformed to the reciprocal (**q**) space. Projections are done either in 2D for visualisations, or in 3D for peak identifications where locations of each local minima/maxima of $\alpha_{\mathbf{q}}$ are analysed (see Supplementary Text for the analysis of $\alpha(\mathbf{q})_{ij}$ along high symmetry paths in the first Brillouin zone).

Statistical analysis for experimental data

Three APT datasets with the volume of $20 \times 20 \times 100 \text{ nm}^3$ at least were often analysed to obtain the statistical results for each data point in all crucial findings. The mean and standard deviation values were provided. The Pearson's correlation coefficient and contingency coefficient (μ) were used to test the statistical significance of the difference between experimental distributions and a chemically-randomised dataset, as like in Figure 3.



Figure S1 ML-APT overview. We developed a framework for deciphering the details of multitype CSROs in H/MEAs, which combines ML, APT experiments/simulations, Monte-Carlo simulations, and electrical measurements. (a) First, a series of site-specific APT experiments are performed to collect the desired data, which are voxelised into millions of 1-nm cubes that are transformed into z-SDMs. (b) Then, a CSRO recognition model is obtained by utilising the simulated CSRO pattern bank to train a neural network. Its reliability is verified by a large-scale APT simulation. (c) Third, the pre-processed experimental z-SDMs are fed into the CSRO recognition model to obtain the 3D CSRO distribution. The details of multiple-CSROs are revealed, supported by atomistic simulations. (d) Finally, the composition/processing-CSRO-electrical resistivity relationships are built.



Figure S2 APT data of a typical equiatomic CoCrNi alloy along $\langle 111 \rangle$. (a) Representative 2D detector hit map. One centric $\{111\}$ crystallographic pole is highlighted. (b) Precise 3D APT reconstruction along the $\langle 111 \rangle$ orientation. (c) Local close-up of a thin slice in (b) along $\langle 111 \rangle$. (d) z-SDMs of different elemental pairs in a representative 2-nm voxel in (b). The peak distance is about 0.2nm, matching well with the theoretical $\{111\}$ plane distance of the CoCrNi fcc structure.



Figure S3 Details of the optimised 1D CNN structure and the training, validation, and test results using the synthetic data. (a) The 1D CNN configuration. (b), (c) The evolutions of the training and validation losses and accuracies. The quick converge performance is mainly due to the simple 1D signal of z-SDMs. (d) The confusion matrix of the test results using the 10% simulated data.



Figure S4 ROC analysis of the 1D CNN obtained using 88 experimental z-SDMs for each type of CSRO. (a), (b), (c) ROC curves of Co-Co, Cr-Cr, and Ni-Ni CSROs with uncertainties, respectively, with peak shift data augmentation (Table S3); (d), (e), (f) ROC curves of Co-Co, Cr-Cr, and Ni-Ni CSROs with uncertainties, respectively, without peak shift data augmentation. For each label, we plot its ROC curve regarding each element of the label indicator matrix as a binary prediction. Five models from five-fold cross-validation provide five ROC curves for each class, and the mean value and standard deviation are plotted. The mean AUC and its standard deviation of each class are also provided. After data augmentation, the performance of the model is enhanced.



Figure S5 Test of ML-APT in large-scale APT simulation with L1₂-CSRO domains which simulates the experimental depth resolution distribution in Figure S18a. (a) Front and top views of simulated Co(CrNi)₃-L1₂ CSRO APT data with a diameter ranging from 0.7 to 2.0 nm. Matrix atoms are hidden for a better visualisation and a unit cell of Co(CrNi)₃-L1₂ is given. (b), (c) Front and top views of recognised CSRO domains in simulated data and chemically-randomised data, respectively, via the proposed recognition model using $1 \times 1 \times 1$ nm³ scanning cubes with a 0.5nm stride. The two recognised results are named " $1 \times 1 \times 1$ " and "Random data". (d), (e) Distributions of atom counts along Z and Y directions in " $1 \times 1 \times 1$ " and "Random data", respectively. The relevant Pearson's correlation coefficient (PCC) values are given. (f) Morphology maps of the simulated CSRO domains in (a) and detected ones in " $1 \times 1 \times 1$ " (b). The size and colour of one circle denote the number of atoms within one domain. (g) Number densities versus CSRO size range corresponding to simulated, " $1 \times 1 \times 1$ ", and "Random data". The size refers to the APT-counted atoms and the PCC values are listed in the inserted table. The μ used in Figure 3 cannot be adopted here due to the rather discretized size of simulated data which leads to massive zeros in the size distribution plot.



Figure S6 Visualisation of the obtained CNN model on two classes of z-SDMs via gradientweighted class activation mapping. (a) fcc and (b) CSRO from simulated (left) and experimental (right) data. The more red, the more attention. For the former, the model is looking at whether there are peaks at the zones close to the ΔZ with ± 0.18 and ± 0.54 nm. For the latter, the model focuses on the zones close to the ΔZ with 0, ± 0.36 nm.



Figure S7 Quantitative 3D analysis of CSRO along <111> in the annealing CoCrNi alloy. (a) 3D distribution of Co-Co CSRO. (b), (c), (d) Size distributions of the identified Co-Co, Cr-Cr, and Ni-Ni CSROs, respectively. The results from the chemically-randomised dataset are compared with the PCC and Pearson contingency coefficient (μ). The coloured regions highlight the size ranges different from the random curves. (e) A schematic diagram of Co-Co L1₁-type CSRO. The Co-Co plane spacing is 0.4 nm, while the Cr/Ni-Cr/Ni plane spacing can be either 0.2 or 0.4 nm depending on the concentration of Cr/Ni in the A plane. For example, when A plane consists of Co₆₀(Cr, Ni)₄₀ and B is Co₁₀(Cr, Ni)₉₀, the Co-Co spacing is approximately 0.4 nm while Cr/Ni is approximately 0.2 nm. When A plane consists of Co₉₀(Cr, Ni)₁₀ and B is Co₁₀(Cr, Ni)₉₀, all the Co-Co, Cr-Cr, and Ni-Ni spacing are 0.4 nm.



Figure S8 Morphology analysis of different CSROs along <002> in the annealing CoCrNi alloy. (a) Co-Co CSROs. (b) Cr-Cr CSROs. (c) Ni-Ni CSROs. The colour and radius of each circle denote the number of atoms within one domain.



Figure S9 Ni-Ni z-SDMs of Ni-Ni CSRO in Figure 3a and the remaining fcc matrix. A periodic peak occurrence each about 0.36 nm can be observed in the Ni-Ni CSROs.



Figure S10 Corresponding z-SDMs of Co-Co, Cr-Cr, and Ni-Ni from the same region as Figure 3g. The z-SDM of Ni-Ni has a spacing of 0.36nm, while the other two elements have a spacing of 0.18nm.



Figure S11 APT data using the voltage-pulsing mode (Methods) and its comparison with the laser-pulsing mode. (a) APT data of a typical equiatomic CoCrNi alloy along $\langle 002 \rangle$ using the voltage-pulsing mode. A local close-up of a thin slice along $\langle 002 \rangle$ is shown. (b) Changes of μ under different heat treatments and pulsing modes along $\langle 002 \rangle$.



Figure S12 Specific heat capacities (c_p) measured by DSC and predicted by MC as well as CSROs predicted by MC (without spin polarisation). (a) and (b) Ni₂Cr-type structures predicted below around 225K and 900K, respectively. (c) Predicted CSROs at 1000K suggesting combinations of L1₁, L1₂ and DO₂₂ types of local chemical orders. (d) and (e) Predicted CSRO diffuse intensity map, α_q , of Co-Co, Cr-Cr and Ni-Ni pairs at 100K and 600K (corresponding to structure (a) and (b) respectively) in (001) and (111) planes, respectively. The high intensity of several characteristic peaks at 100K and 600K suggests the tendency of long-range ordering at low temperatures. Reciprocal space vectors are given in units of $2\pi/a$. Note that no lattice vibrations or electronic excitations have been included in present simulations, which can explain the discrepancies of quantitative heat capacities between predictions and measurements. Nevertheless, the influence of phonons on predicted phase transformation temperature and CSRO structure is not significant for the CoCrNi system ^[20], if no point defect (e.g. vacancies) is considered.



Figure S13 Temperature-dependent 1st NN Warren-Cowley parameter predicted by MC simulations (without spin polarisation). The repulsion of Cr-Cr, Co-Ni, Co-Co and attractions of Ni-Ni, Cr-Ni, Co-Cr above 900K can be observed. Note that these tendencies consider all 1st NNs, i.e. 360°, not that along one specific direction.



Figure S14 Typical CoCrNi APT mass spectrum.



Figure S15 Typical z-SDMs of fcc-matrix and CSRO along different directions. (a) z-SDMs of fcc and (b) CSRO along <100> and <111>, respectively.



Figure S16 Training and validation error of LRP compared with DFT calculations (without spin polarisation). 20 independent fittings were done for each rank; the best 10 of each were selected for Monte-Carlo samplings which give the standard deviation of predicted α and c_p .



Figure S17 Influence of magnetism on predicted CSRO structure. Projection of predicted α_q along high-symmetry paths in the first Brillouin zone, (a) with and (b) without magnetic effects. The inclusion of magnetism significantly increases the CSRO with a pronounced Cr-Cr repulsion at the X-point indicating a tendency for L1₂/L1₀ instability. In both cases (a) and (b), the tendency for L1₁ CSRO (peaks at L-point) is observed for all same-species elemental pairs. A minimum at the W-point (correlated to DO₂₂ ordering) is slightly enhanced without spin-polarisation.



Figure S18 Predicted results of the Co-Co CSROs along <002> corresponding to experimental and large-scale simulated datasets (Similar trends apply to Cr-Cr and Ni-Ni). (a) Frequency distribution of predicted CSRO probabilities of the 0.5-nm voxels from experimental data in Figure 3b. A large-scale simulation was made to mimic the distribution in Figure S5. (b) The z-SDMs generated from the data corresponding to zones in (a). A threshold of 3.75 was reasonably used in this work to separate fcc and CSRO due to the obvious CSRO signatures above 3.75.





Results of LogNormal distribution fitting

	Original data (at.%)	CSRO domains (at.%)
Со	33.83±12.35	31.99±7.70
Cr	36.88±12.45	34.97±9.60
Ni	32.36±12.57	33.84±9.42

Figure S19 Compositional distributions (Co, Cr, Ni) of recognised Ni-Ni CSROs domains from Figure 3a. The distributions from original data are superimposed for comparisons. The fitting results (mean and variance) using the LogNormal distribution are listed.



Figure S20 Comparison between two groups of APT data analysis collected from two {111} grains. (a) Changes of Pearson contingency coefficient (μ) under different heat treatments on two {111}. The coloured regions highlight the changes of μ after the annealing. A value of μ =0.25 is regarded as the threshold between CSRO and random states. (b) Number-density change (×10²⁵ m⁻³) of different types of CSROs under heat treatment and different {111}.



Figure S21 Comparison of the type and degree of CSRO in different annealing samples. (a) and (b) Changes of Pearson contingency coefficient (μ) under two annealing states along <002> and <111>, respectively. The coloured regions highlight the changes of μ after the annealing followed by quenching. Three APT datasets were analysed to obtain the statistical results for each data point. A value of μ =0.25 is regarded as the threshold between CSRO and random states. The same experimental parameters are applied.



Figure S22 Estimation of in-depth resolution. (a) The annular zone around the {002} pole with the inner (R1) and outer (R2) radius are scanned to generate experimental z-SDMs. (b-f) z-SDMs corresponding to different annular zones 0-2, 2-4, 4-6, 6-8, and 8-10 nm, respectively. A Gaussian function has been fitted to the central peaks of these z-SDMs to calculate the sigma (σ) value, enabling the measurement of the resolution. (g) The result from the 10-nm radius zone.

Authors	Heat treatment	CSRO configuration	Method	
Zhang at al. ^[21]	Homogenisation at 1473K for 48h, quenching	No diffuse streak		
Zhang et al.	Annealing at 1273K for 120h, furnace cooling	Diffuse streaks	-	
Zhou et al. ^[22]	Annealing at 873K and 1273 K for 1 h, quenching	L11-like (Cr/CoNi {113})	-	
Zhang et al. ^[23]	1073-1273K for 240h, quenching	L11-like	-	
Hsiao et al ^[24]	Homogenisation at 1473K for 48h, quenching	L11-like (Cr/CoNi {111})		
	Annealing at 1273K for 120h, furnace	L11-like (Cr/CoNi {111}) and L12-	TEM-based method	
	cooling	like (Cr-Cr repulsion on {100})		
Listel ^[7a]	Homogenisation at 1473K for 168h, quenching	TEM artefacts possibly from thin		
	Annealing at 773K for 168h, quenching	nealing at 773K for 168h, quenching duenching film effects, surface steps, or planar defects, etc., rather than CSRO		
Walsh et al. ^[7b]	-	TEM artefacts possibly from planar defects, rather than CSRO	-	
Coury et al. ^[7c]	-	TEM artefacts possibly from higher- order Laue zones, rather than CSRO		
Imous et al. [25]	Homogenisation at 1373K for 24h, quenching	No CSRO	Qualitative APT	
Inoue et al. [20]	Annealing at 973K for 384h,	L12-like (Co/Ni-Co/Ni repulsion on	analysis	
	quenching	{100})		
Walsh et al. ^[26] and Zhang et al. ^[27]	-	Co–Cr and Cr-Cr repulsion	DFT	
Tamm et al. ^[28]	≥800K	Ni-Cr attraction and Cr-Cr repulsion	DFT + MC	
Ghosh et al. ^[16]	≥900K	(Co,Ni)–Cr attraction and Cr-Cr repulsion	DFT + ML-MC	
Du et al. ^[29]	≥800K	L1o-like (Cr/CoNi {100}), L11-like (Cr/CoNi {113}), and Cr/CoNi {110}	DFT-ML + MC-MD	
Zhang et al. ^[27]	As-cast	Cr-Cr repulsion	Extended X-ray absorption fine structure (EXAFS)	

Supplementary Tables Table S1 Summary of reported CSROs in CoCrNi alloys.

Hsiao et al. ^[25] and Zhang et al. ^[27]	See above	inconclusive	Neutron scattering	
	Homogenisation at 1473K for 48h,	L11-like CSROs (Co/Ni repulsion on		
	quenching	{111})		
This work	Annealing at 1273K for 120h, furnace cooling	L1 ₂ /DO ₂₂ -like (Ni repulsion on	ML-APT	
		$\{100\}$) and L1 ₁ -like (Co/Cr/Ni		
		repulsion on {111}) CSROs		

Element	Content, at.%
Со	31.47 <u>+</u> 1.16
Cr	31.27 <u>+</u> 3.00
Ni	31.02 <u>+</u> 0.66
Н	5.20 <u>±</u> 1.89
0	0.05 ± 0.03
Si	0.05 ± 0.03
Fe	0.09 ± 0.01
Ti	0.25 ± 0.12
He	0.47 ± 0.20
С	0.12 ± 0.07

 Table S2 Bulk compositions of CoCrNi APT data from three datasets.

 Fluenut
 Content at %

Note that H atoms mainly come from the chamber and their spatial distribution is uniform.

Table S3 Parameters for building the synthetic z-SDMs bank. Note that σ represents the standard deviation of the Gaussian function applied to shift atoms in x, y, z reconstruction directions to simulate the anisotropic spatial resolutions (depth resolution is better than the lateral direction). Using Larger σ_z will generate messier z-SDMs, which is meaningless for training the ML model.

Category	Number of z-SDMs	$\sigma_x=\sigma_y, nm$	σ_z, nm	Detect efficiency	Peak shift, nm
fcc	6500	0.2~0.8	0.01~0.06	0.2~0.7	-0.03~0.03
CSRO	3900	0.2~0.8	0.02~0.05	0.2~0.7	-0.03~0.03

Isotope mass number	Natural abundance (atom %)	Ni+ isotopes from experiments (atom %)
58	68.08	66.18
60	26.22	25.77
30	1.14	2.68
62	3.64	3.87
64	0.92	1.50

Table S4 Comparisons of isotope ratios of Ni+ between experimental values and natural abundance.

Supplementary Text

Comparisons between the previous report in Table S1 and our work

Our present work essentially settles previous debates on whether CSRO is present in CoCrNi alloys. First, CSROs indeed exist even after the homogenisation but with a number density of 2.46 $\times 10^{26}$ m⁻³ (6.16×10²⁵ multiplied by 4). Our specimen condition is similar to those of Zhang et al. ^[21] and Hsiao et al. ^[24]. Zhang et al. ^[21] did not find CSRO in the homogenised state by energy-filtered TEM, while Hsiao et al. ^[24] reported L1₁-ordered nanoclusters (Cr repulsion) with a diameter of approx. 6 nm via energy-filtered scanning-electron nanodiffraction. Our APT results suggest the existence of L1₁-CSROs but with Co or Ni repulsion after the homogenisation (Figure 4e). The average size of L1₁-CSROs is only approximately 1 nm (see Figure S7), which is much smaller than that from Hsiao et al. ^[24]. Moreover, previous TEM work mainly revealed the existence of L1₁-CSROs (Cr repulsion) in the annealed state ^[7a, 22-23], while we observe various kinds of L1₁ (Co or Cr or Ni repulsion) and L1₂/DO₂₂ (Ni repulsion) CSROs in the annealing sample followed by furnace cooling.

To solve this debate, we studied an additional CoCrNi sample that was annealed at 1273K for 120h followed by quenching, for comparison with the furnace cooled condition. As shown in Figure S21, we can now mainly observe the Cr-Cr repulsion along the <111> or 360° after quenching. Compared to the previous furnace cooling state, the quenching state more accurately reflects the high-temperature condition, making it more consistent with previous reports and our simulations. Additionally, this suggests that adjusting heat treatment parameters can indeed modulate the type and degree of CSRO. The weaker CSRO tendency observed in the quenching state compared to the furnace cooling state is reasonable, considering the latter involves more kinetic factors. He et al. ^[30] recently developed an approach to measure CSRO using APT in a CoCrNi sample that was annealed at 773K for 500 hours followed by quenching. This method balances the limitations of APT with the threshold values of CSRO to map the regimes where the required atomistic neighbourhood information is preserved and where it is not. However, Cr-Cr pairs were found to cluster, which have not been reported in Extended Data Table 1 or our work. These findings need to be verified using different methods in the future.

Note that these CSRO clusters should not be regarded as a stable phase in the sense of thermodynamic equilibrium, i.e., the alloy is still in a single-phase regime thermodynamically. The CSRO clusters are in fact local elemental fluctuations within a single phase. The L1₂-CSRO with the Ni repulsion is consistent with the qualitative APT analysis results from Inoue et al. ^[25].

Novelty and significance of current ML-APT work

(1) Advance of the current approach for complex concentrated alloys

First, it is important to note that the challenges posed by the complex concentrated CoCrNi alloy and other M/HEAs are inherently different from the binary Fe-Al alloy. The previously proposed method developed to analyse CSRO in Fe-Al^[2b] requires prior knowledge of the possible CSRO configurations, like D0₃ and B₂-like structures. For the CoCrNi, or other M/HEAs, the potential CSRO configurations are unknown in advance. While hypothetical estimations could be made, the possible elemental occupancy combinations can be daunting due to the high number of combinations; for instance, the L1₂ structure in the CoCrNi system alone has 8 combinations. In comparison, the newly developed method that we demonstrate on CoCrNi does not require any

prior knowledge of the CSRO configurations. Those possible CSRO configurations are deduced after obtaining all information from pairs of the same species. This allowed us to derive the multiple CSRO configurations in CoCrNi, through analyses of over 15 successful datasets, obtained along different crystallographic orientations.

Furthermore, this new approach is more versatile – it can be readily applied to the Fe-Al system, while the method developed for the Fe-Al cannot be applied to the CoCrNi due to the priorunknown CSRO configurations. Here, we also demonstrated its application to CoCrNi, as well as the VCoNi system –which compares well with the literature. Many other possible systems could be investigated in the future, including FeMnAlC (L1₂-CSRO in fcc), five- or six-component Cantor alloys (L1₂-CSRO in fcc), and semiconducting ^[31] and thermoelectric materials ^[32], amongst others. The potential ramifications of this work, spanning material design to simulations, signify its sweeping influence.

(2) Beyond methodological progress, the more important aspect lies in addressing the hotly debated CSRO in CoCrNi alloys in 3D with quantitative data.

First, with the help of the proposed approach, it is the first time that the CSRO in CoCrNi alloys has been accurately and quantitatively imaged experimentally in 3D. This work confirms previous theoretical and experimental reports, such as the existence of CSRO in CoCrNi, but goes beyond them by identifying several types of CSRO (not only L1₁-CSRO but also L1₂-CSRO with different elemental occupations), some of which have not been observed experimentally in TEM-based methods (like L1₁ (Co or Ni repulsion) and L1₂/DO₂₂ (Ni repulsion) CSROs in the annealing sample followed by furnace cooling).

Moreover, comparing the annealing samples with different cooling rates (furnace cooling or quenching), we concluded that adjusting processing parameters, such as thermal history, can be leveraged to manipulate CSRO and consequently design novel H/MEAs with enhanced properties. These quantitative results corresponding to each state have not been reported in CoCrNi alloys previously.

Last, the obtained fruitful 3D quantitative information of multiple CSROs, such as the number density of ordered domains, their configurations, elemental site occupancy, and size/morphology, is very beneficial for establishing a direct processing-CSRO-property relationship, which was not available before our work.

Typical clustering algorithms in APT to look for CSRO

The typical clustering algorithms in APT are based on the difference between experimental and random-labelled datasets through e.g. *k*-nearest neighbour distance analysis (Figure 1f) or frequency distribution analysis (Figure 1g) ^[6b, 33]. There is no clear evidence of CSRO, which is ascribed to a large number of reconstructed atoms departing from their 1st nearest neighbours after field evaporation and reconstruction ^[4]. However, the relationship of 1st nearest neighbour was still maintained along a set of {002} or {111} planes in the depth, as indicated in Figure 1e ^[4, 25], leaving a valuable opportunity to search for CSRO in CoCrNi alloys, as already achieved for long-range orders utilising ML ^[2a].

Performance of ML-APT in large-scale simulated APT data

Our ML-APT effectively distinguishes these domains from the fcc matrix in terms of spatial distributions (PCC>0.82), morphology, and size distributions (PCC=0.51) (Figure S5). This model is also applied to a randomised dataset, enabling the recognition of CSRO forming randomly. The PCC of 0.3 (Figure S5g) suggests that our model can classify reliably CSRO and random structures.

Influence of only analysis of same-species elemental pairs

Analysis of same-species elemental pairs is sufficient to extract the 3D quantitative information on multiple CSRO configurations in CoCrNi alloys. For a *n*-component system, there are n(n - 1)/2 independent correlation functions. In a binary A-B system, one would usually compute and display the A-B correlation function. However, if one had only measured the A-A correlation, it would also be sufficient, because of the additivity rule (1=A-A plus A-B). The same rule applies for ternaries and there are 3 independent correlation functions. In principle, one could deduce the A-B, A-C, B-C correlation functions from measured A-A, B-B and C-C. A detailed theoretical analysis has been made ^[34] to provide a solid support of our opinion.

For example, the Ni-Ni repulsion on {001} suggests that the Co or Cr element has a higher probability to occur on neighbouring planes. Thus, Ni-Co or Ni-Cr pairs on {001} planes can be deduced. Based on same-species elemental pairs, and the information derived for cross-species elemental pairs, we can rule out other possible structures and determine L1₂/DO₂₂-type CSRO with the Ni-Ni repulsion on {001} as shown in Figure 4a, and that is the most often experimentally observed. It is also similar along <111>. Our MC simulations in Figure S17 can confirm the tendencies for L1₂ or D0₂₂ or L1₁- CSRO only based on the same-species elemental pairs information, although cross-species elemental pairs can be well-predicted.

Structures predicted by Monte-Carlo simulations below 900K

Without spin-polarisation, the Ni₂Cr (oI6) structure, as revealed by the special point of (2/3, 2/3, 0) in the calculated CSRO diffuse intensity map (α_q , in Figure S12 d and e), is suggested to be stable below around 900K with the partitioning of Co and Ni against Cr as shown in Figure S12 ^[16]. Further partitioning of Co against Cr (i.e. -Cr-Ni-Ni-Cr-Co-Co- stacking sequence along [110] of the fcc lattice) is predicted below around 225K; this is, without spin-polarisation, also the structure of the lowest ground-state energy found in this study, as shown in Figure S12a.

Influence of magnetism on predicted CSRO structure

The influence of magnetism on predicted CSRO structure has been further studied. Considering the experimental small magnetic transition temperature of CoCrNi of a few K only ^[35], a paramagnetic approach is considered in which for each atomic configuration, the total energy is averaged over different magnetic states ^[16].

Figure S17 shows α_q projected to high-symmetry points in the first Brillouin zone at high temperatures with and without considering spin polarisation. Magnetic effects increase the overall CSRO parameters. This is attributed to the coupling of magnetic and chemical interactions. Inclusion of spin polarisation also changes the CSRO intensities qualitatively. Particularly, the W peak (characteristic for the DO₂₂ structure) disappears and the X peak (characteristic for the L1₂

structure) is significantly intensified. It is suggested that this intrinsic interaction between magnetism and CSRO is responsible for the different experimentally observed CSRO facets.

Compositions of CSRO domains

The compositional distributions (Co, Cr, and Ni) of recognised Ni-Ni CSROs domains from Figure 3a are shown in Figure S19. As compared to those from the original data, there is no significant difference between them. The calculated average composition of each element from CSRO domains is almost the same as that from the original data considering the variance, meaning that only the ordering changed and not the composition. It is similar to that along <111>.

Comparisons between different pulsing modes

We compared the results from laser and voltage pulsing modes, as shown in Figure S11. The ML-APT results based on different pulsing modes are generally consistent, e.g. Ni-Ni $L1_2/DO_{22}$ CSROs exist after the annealing. The individual value of μ appears different, which may be due to a better control of the field evaporation conditions, and more pronounced differences in the evaporation fields of the different species at lower temperature ^[36]. In any case, and as supported by the literature, the depth resolution in laser pulsing mode is sufficient ⁴¹, and was chosen as it leads to larger datasets that provide better statistics.

Comparison of APT data analysis for two {111} grains

We collected another group of APT data lifted out from a neighbour grain with an orientation close to the $(1\overline{1}1)$ planes, supposing that our first set of data was obtained near (111). The results are shown in Figure S20. First, the same types of L1₁-CSRO are found, shown in Figure S20a, and the number density of L1₁-CSRO is also similar in Figure S20b. This is reasonable because of the symmetries of the fcc system. However, it should be noted that only a single L1₁-CSRO can be imaged at a time, yet there are four <111> variants. Thus, for simplicity, we can multiply the number density obtained from one {111} plane by four to estimate the total number densities, thus establishing a quantitative relationship between CSRO and its properties.

Definition of high-quality APT data

We investigate the variation of the in-depth resolution by scanning the z-SDM around the {002} pole, as demonstrated in Figure S22. As had been done in previous study for the resolution ^[37], Gaussian functions are fitted to the central peaks of the resulting z-SDMs to ascertain the σ values, facilitating the measurement of in-depth resolution. The calculated σ increases from 0.016 to 0.084 nm as the radius varies from 0-2 to 8-10 nm. However, the average σ , based on the 10-nm radius zone, is approximately 0.037 nm, smaller than the 0.07 nm value applied in the large-scale simulation mentioned above. A lower σ value indicates higher data quality. Using a large-scale simulation with a σ value of 0.07 nm confirms that the presently collected data is of sufficient quality for CSRO analysis in CoCrNi. Here, we propose a procedure to assess the quality of APT data for CSRO analysis in CoCrNi via ML-APT.

Firstly, the pole must be observed for subsequent analysis. Secondly, the change in in-depth resolution should be determined by scanning the z-SDM around the specific pole, similar to Figure S22. The obtained σ values should ideally be less than approximately 0.08 nm in CoCrNi. The first peak near the center becomes unclear when the σ value exceeds 0.08. Thirdly, applying a

large-scale simulation that mimics the experimental conditions to validate the model's performance, as depicted in Figure S5 and Figure S18a.

This procedure can be adapted to other alloying systems, although certain crucial thresholds may need adjustment.

Effect of peak overlap of different species, hydrides, detector efficiency, and instrument on guantitative CSRO analysis

Peak overlap and hydrides: After carefully analysing the mass-to-charge curve in Figure S14, it is observed that only Cr^{2+} ions are present without any Cr hydrides or peak overlapping. Additionally, Co mainly exists as Co^{2+} , and the likelihood of peak overlapping at 29.5 Da between Co^{2+} and NiH²⁺ is very low (NiH²⁺ was never reported in the analysis of metallic systems). To evaluate the overlap at 59 Da between NiH⁺ and Co⁺, we compare the experimental isotope ratios of Ni⁺ with the natural abundances, as listed in Table S4. The minute difference observed suggests the presence of a very small fraction of NiH⁺ at 59 Da. This minimal overlap is expected to have a negligible effect on the results. Overall, there is no significant influence on the results in terms of the peak overlap and hydrides in the current work.

Detection efficiency and instrument: The large-scale simulation in Figure S5 used a 52% detection efficiency, and the ML model obtained, trained by simulated data incorporating a range of imperfect detection efficiencies (ranging from 0.2 to 0.7, as shown in Table S3), effectively resolves CSRO. Hence, the current adoption of 5000XR (with reflection) data with a detection efficiency of 52% is deemed sufficient for CSRO analysis. While the 5000XS (without reflection) data offers an efficiency of 80% and slightly better lateral resolution, there is a higher likelihood of potential peak overlapping and tailing, which could exacerbate the situation. Based on our experience, the 5000XR data is the optimal choice for CSRO analysis, given its favourable peak splitting ability and sufficient detection efficiency.

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