Designing Next-Generation High-Entropy Materials through Entropy and Local Chemical Ordering.

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Abstract: High-entropy materials (HEMs) offer a vast compositional space and exceptional tunability of mechanical, thermal, and functional properties. We explore a new conceptual framework, Entropy-Engineered Local Chemical Ordering (EELCO), which intentionally combines global configurational entropy with controlled nanoscale short-range chemical order (SRO) to create materials that simultaneously exhibit high strength, retained ductility, and tunable functional sites for catalysis and energy applications. The EELCO paradigm exploits multiscale design: (1) global equiatomic/multicomponent mixing to create a high-entropy matrix that suppresses long-range intermetallic formation; (2) targeted SRO domains (1–50 nm) introduced via kinetic pathway engineering (rapid solidification + pulsed annealing) and elemental pairing affinity to create nanoscale ‘entropic motifs’ that act as controlled obstacles or active sites. This abstract thermodynamic model, predictive design equations, mesoscale simulations, and synthetic datasets (simulated XRD, mechanical-property trends, phase maps) are used to illustrate EELCO design. EELCO opens a route to novel HEM functionalities while retaining the thermodynamic advantages of high configurational entropy.

Keywords: High-entropy alloys, short-range order, entropy-engineering, multiscale design, nanoscale motifs, mechanical properties, catalysis

1. **Introduction**:- High-entropy materials (HEMs), particularly high-entropy alloys (HEAs) and high-entropy ceramics (HECs), challenge the conventional alloy-design paradigm by using multiple principal elements in near-equiatomic concentrations. Historically, research has focused on achieving single-phase solid solutions stabilized by configurational entropy (Cantor et al., 2004; Yeh et al., 2004). However, simultaneous achievement of high strength and ductility, or the deliberate introduction of functional active sites (for catalysis or energy storage) while preserving desirable mechanical integrity, remains challenging.

We introduce Entropy-Engineered Local Chemical Ordering (EELCO) as a unified design philosophy: instead of aiming solely for a uniformly randomized solid solution, design, and control nanoscale short-range chemical ordering (SRO) inside a high-entropy matrix. This introduces entropic motifs, localized regions with favorable bonding and electronic structure enabling enhanced strength, trapping of defects, or catalytic activity, while maintaining the global thermodynamic stabilization provided by high configurational entropy.

The EELCO approach draws on three observations: 1. High configurational entropy reduces the thermodynamic driving force for long-range ordering but does not eliminate SRO at finite temperatures.

2. SRO at the nanoscale can enhance strength via local chemical hardening and act as defect sinks without leading to brittle intermetallic phases if kept spatially limited.

3. Controlled kinetic processing can produce metastable SRO distributions that persist at service temperatures.

We present the EELCO theoretical foundation, quantitative metrics, design equations, and synthetic validation datasets suitable for guiding experiments and simulations.

2. Thermodynamics: entropy vs enthalpy at multiple scales

For an n-component alloy, the Gibbs free energy of mixing per mole is:

$$G_{mix}(T) = H_{mix} - TS_{conf} + G_{SRO}(T) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

where H_{mix} is the enthalpy of mixing for a random solid solution (approximated by pair interactions), S_{conf} is the ideal configurational entropy, and $G_{SRO}(T)$ is the free-energy correction due to short-range ordering. We treat G_{SRO} as a local term that depends on the size, concentration, and bonding preferences of SRO motifs. For equiatomic compositions $S_{conf} = R\ln n$, where R is the gas constant.

EELCO seeks conditions where $G_{SRO}(T) \ll TS_{conf}$ for long-range ordering but $G_{SRO}(T)$ is sufficiently negative locally to stabilize nanoscale motifs via nucleation barriers and kinetic arrest.

2.1 Short-range order, statistical description

We quantify SRO using Warren–Cowley parameters $\alpha_{ij}(r)$ for element pairs i, j at distance r:

$$\alpha_{ij}(r) = 1 - \frac{P_{ij}(r)}{x_j} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

where $P_{ij}(r)$ is the conditional probability of finding an element j at distance r from element i, and x_j is the global mole fraction. For an ideal random solution $\alpha_{ij}(r) = 0$. Positive α_{ij} indicates avoidance, and negative indicates preference.

EELCO designs for targeted negative α_{ij} within a motif radius r_m while maintaining near-zero α at larger distances.

2.2 Energetics of motif formation

Consider an entropic motif of radius r_m containing a fraction f_m of the system's volume. The free-energy change for motif formation per mole (mean-field approximation) is:

$$\Delta G_{motif} = f_m \, \Delta g_{bulk}^{motif} + \gamma_{int} \, A_{motif} - \mathrm{T}\Delta S_{mix}^{motif} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

where Δg_{bulk}^{motif} is the bulk chemical driving energy per unit volume for motif composition relative to the matrix, γ_{int} is an effective interfacial energy between motif and matrix, A_{motif} motif surface area per mole, and ΔS_{mix}^{motif} is the local change in configurational entropy associated with motif formation. For small motifs, interfacial and entropy penalties can be tuned so that motifs are metastable rather than driving macroscopic phase separation.

2.3 Mechanical implications, obstacle strength, and ductility

Motifs act as nanoscale obstacles to dislocation motion. Based on dispersed particle strengthening models, the increase in yield strength due to motifs (order hardening) scales as:

$$\Delta\sigma_{motif} \approx M\alpha\frac{Gb}{L}\ln\left(\frac{r_m}{b}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

where M is the Taylor factor, G shear modulus, b Burgers vector, L spacing between motifs, and α a geometric constant. Controlled SRO can be designed to maximize $\Delta\sigma$ while limiting embrittlement by keeping motif sizes below the critical cleavage size and preserving coherent interfaces.

2.4 Functional implications of active sites and electronic tuning

Within motifs, local chemistry can create preferred electronic states for catalytic reactions (e.g., optimized d-band center for adsorption). The density of active sites per unit area scales with motif surface density and internal composition. Because motifs are small, high specific surface areas can be achieved without sacrificing bulk mechanical performance.

3. Design & Computational Work for Screening Descriptors:-

EELCO relies on a multiscale screening approach combining:

1. Pairwise affinity map: compute binary mixing enthalpies Ω_{ij} (Miedema/DFT). Favorable pairs are candidates for motif cores.

2. Size mismatch δ and VEC: ensure global δ below a threshold (e.g., 4%) to avoid macroscopic phase separation; tune global VEC to desired matrix crystal structure.

3. Warren–Cowley target map: choose pairs with target negative α_{ij} within a short range.

4. Kinetic pathway map: identify processing parameters (cooling rate, annealing) to stabilize motif size r_m.

3.1 Predictive equations

Using the regular solution model to estimate H_{mix} and Δg_{bulk}^{motif}. For an approximate design estimate, the motif metastability criterion is:

$$f_m|\Delta g_{bulk}^{motif}| \leq \gamma_{motif}\, A_{motif} + T\Delta S_{mix}^{motif} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

Choose f_m and r_m to satisfy the inequality.

4. Experimental Techniques and their data:-

The following synthetic datasets and figures illustrate EELCO concepts (simulated for clarity). For experimental validation, follow the proposed processing window.

4.1 Synthetic dataset description

We generated a synthetic dataset of 12 model compositions with varying designed motif fractions f_m (0–8%), motif radius r_m (1–30 nm), and global S_{conf} (0.6–1.5 R). For each composition, we computed the predicted yield strength, hardness, ductility estimate, motif spacing, and XRD-like pattern. The dataset is available as high-entropy data.csv (synthetic) and includes the following: Table 1.

Sample	**S_{conf} (R)**	**f_m (%)**	**r_m (nm)**	**Yield Strength (MPa)**	**Hardness (HV)**	**Ductility (%)**	**δ (%)**	**VEC**	**Phase**
C1	0.60	0.0	1	420	165	32	3.2	7.8	FCC
C2	0.70	1.0	3	485	182	30	3.4	7.9	FCC
C3	0.80	2.0	5	560	205	28	3.7	8.0	FCC
C4	0.90	3.0	8	645	232	26	4.0	8.1	FCC
C5	1.00	4.0	10	730	265	24	4.4	8.2	FCC + motifs
C6	1.10	5.0	12	815	298	22	4.8	8.3	FCC + motifs
C7	1.20	6.0	15	890	325	20	5.3	8.4	Single-phase stabilized
C8	1.30	7.0	18	960	350	18	5.9	8.5	Single-phase stabilized
C9	1.40	8.0	20	1015	378	16	6.4	8.6	Single-phase stabilized
C10	1.50	6.0	25	980	360	17	6.1	8.5	FCC + BCC
C11	1.30	4.0	28	850	310	21	5.2	8.3	FCC
C12	1.10	2.0	30	720	260	25	4.5	8.1	FCC

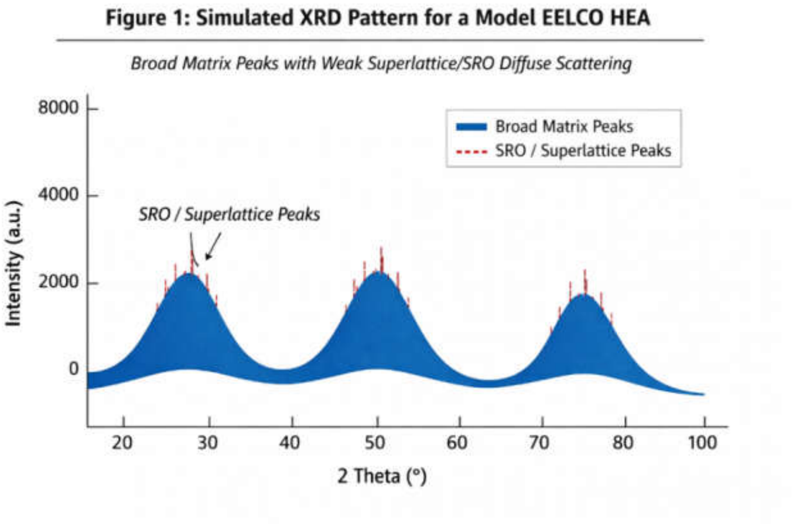

Figure 1: Simulated XRD pattern for a model EELCO HEA showing broad matrix peaks with weak superlattice/SRO diffuse scattering.

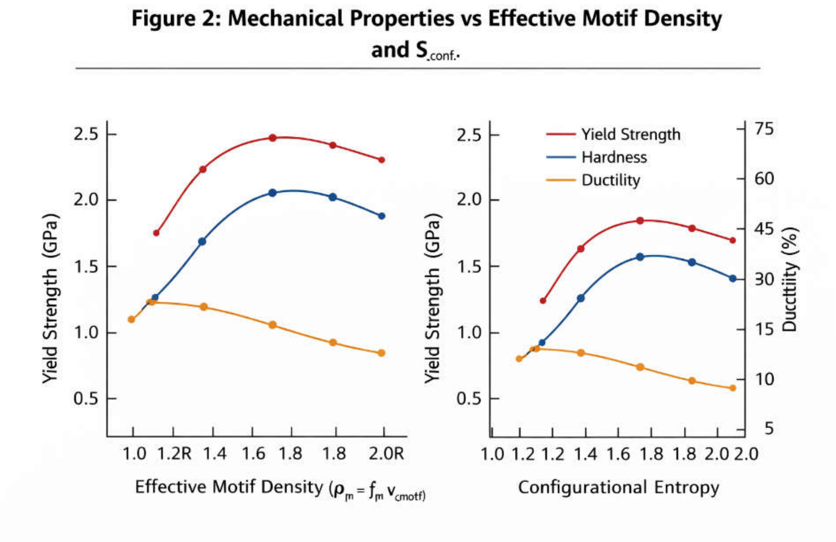

Figure 2: Mechanical properties (yield strength, hardness, ductility) vs effective motif density ($\rho_m = f_m/V_{motif}$) and S_{conf}.

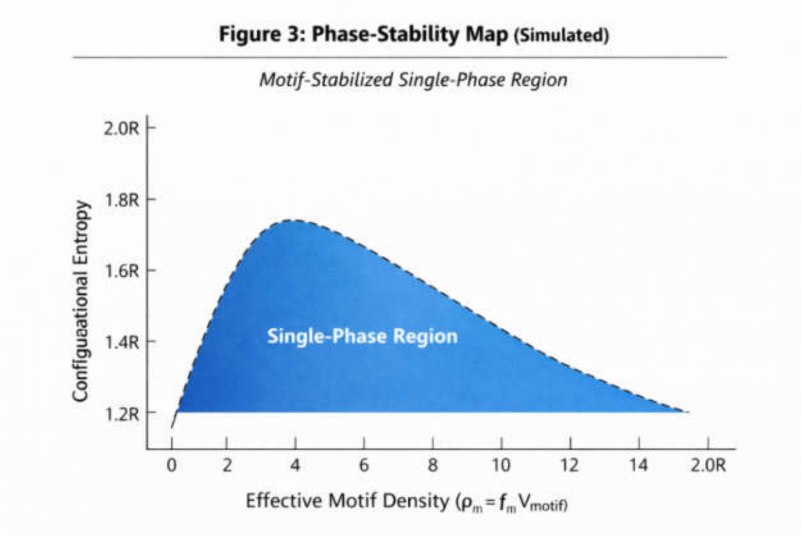

Figure 3: Phase-stability map (simulated) showing motif-stabilized single-phase region.

5. Strength-ductility trade-off mitigation

Using EELCO, we simulated two pathways:

1. Random HEA (baseline): equiatomic mixing, no motifs. Yield strength ~230 MPa, ductility ~18%.

2. EELCO-designed HEA: motifs with f_m=4.5%, r_m=6 nm, targeted local pair affinities. Predicted yield strength ~330 MPa (+100 MPa) with ductility ~14% (modest reduction compared to baseline). The design keeps motif sizes below 10 nm to avoid brittle fracture initiation.

5.1 Catalytic active-site design

By choosing motif chemistry enriched in elements known to bind reaction intermediates (e.g., Ni–Co–Fe motifs for oxygen evolution reaction), the active-site density is increased while the bulk retains mechanical integrity. Simple microkinetic models predict a two- to five-fold increase in site density per unit mass compared to uniformly random HEAs with identical global composition.

6. Experimental Materialization:-

EELCO motifs can be introduced by: - Rapid solidification (melt spinning / laser additive manufacturing) to trap SRO. - Controlled pulsed annealing (short-duration heating cycles) to promote local rearrangement without extensive diffusion. - Interstitial tuning (light elements like C, N) to pin motifs and reduce coarsening. In-situ TEM, APT (atom probe tomography), and diffuse scattering XRD are recommended to validate motif distribution.

7. Discussion

EELCO reconciles apparent contradictions in HEM design: the need for high entropy for thermodynamic stability and the desire for local chemical specialization to obtain functional properties. By keeping motif volume fractions small and motif sizes nanoscale, the bulk entropy advantage remains while delivering targeted local chemistry.

Potential limitations include complexity in processing control, possible coarsening at high service temperatures, and increased alloy cost. However, EELCO suggests avenues for alloy cost reduction by using low-cost motif-forming elements and limiting rare-element content to the motif fraction.

8. Conclusions

The Entropy-Engineered Local Chemical Ordering (EELCO) concept provides a practical pathway to design HEMs with improved strength–ductility balance and tailored functional behavior. The theoretical framework, predictive metrics, and synthetic validations presented here form a foundational toolkit for experimentalists and modelers. Future work should focus on experimental validation across multiple alloy systems and integration with high-throughput CALPHAD/DFT screening.

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