

Research

Formation of Complex Patterns in Refractory High-Entropy Alloys

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Abstract:

High-entropy alloys (HEAs) composed of multiple principal elements exhibit a remarkable diversity of microstructures, especially when refractory metals and magnetic $3d$ transition elements are combined. Despite extensive experimental work, the fundamental mechanisms governing the formation of such complex patterns remain insufficiently understood. In this study, we investigate microstructural evolution in tin-containing refractory HEAs and propose a minimal theoretical model capable of reproducing the observed configurational richness. Experimentally, scanning electron microscopy reveals drastic microstructural changes induced by Sn and by the addition of Fe, Ni, Cu, or Nb. Theoretically, of our interest are different patterns that appear in those high entropy alloys. They consist of multiple constituents and by varying their relative concentration rich diversity of quantitatively and qualitatively different configurations could emerge. Theoretical explanation of these patterns generic mechanism is still lacking. In this contribution we present a minimal model that illustrates possible mechanisms yielding such configurational diversity. For this purpose, we use 2D Ising lattice model consisting of classical spins in an external transversal field Ω at temperature zero. In this approach we mimic key properties of high-entropy patterns by interaction matrix J . Our simple model exhibits symmetry breaking structural transitions on varying Ω . The emergent spin configurations are seeded by J eigenvectors. Therefore, different structures of J yield different patterns. Furthermore, even for a fixed system configuration one could nucleate diverse patterns on varying histories of samples where mode-coupling interactions play significant roles.

Keywords: High-entropy alloys; Refractory metals; Microstructure; Pattern formation; Ising model; SEM-BSE

1. Introduction

High-entropy alloys (HEAs) represent a paradigm shift in alloy design, where multiple principal elements are combined in near-equiatomic ratios to stabilize simple solid-solution phases through high configurational entropy. Since their introduction (Yeh et al., 2004), HEAs have attracted significant interest due to their exceptional mechanical, thermal, and chemical properties.

Refractory HEAs, containing elements such as Hf, Ti, Zr, Nb, Ta, or W, are particularly promising for high-temperature applications because of their high melting points and excellent mechanical stability (Tietz & Wilson, 1965). In this work, we focus on Hf-Ti-Zr-based alloys modified with Sn and 3d transition metals (Fe, Ni, Cu, Nb). Sn is commonly used in conventional alloys and strongly influences phase stability and segregation behavior. The addition of magnetic 3d elements introduces further complexity, enabling potential applications in electronic and magnetic devices.

Previous studies (Gačnik et al., 2021) have shown that Sn-containing refractory HEAs exhibit superconductivity and complex multiphase microstructures. However, the mechanisms behind the emergence of these patterns remain unclear. Here, we combine experimental characterization with a minimal theoretical model to elucidate the origin of microstructural diversity.

2. Material and Methods

2.1. Alloy Preparation

All alloys were synthesized by arc melting under an Ar atmosphere. First, a ternary HfTiZr alloy (HTZ) was prepared as a reference. Sn was then added to form the quaternary HfTiZrSn alloy (HTZS). Finally, Fe, Ni, Cu, or Nb were added individually to obtain five-component alloys:

- HfTiZr (HTZ)
- HfTiZrSn (HTZS)
- HfTiZrSnFe (HTZS-Fe)
- HfTiZrSnNi (HTZS-Ni)
- HfTiZrSnCu (HTZS-Cu)
- HfTiZrSnNb (HTZS-Nb)

Each ingot was re-melted several times to ensure homogeneity.

2.2. SEM-BSE Imaging

Microstructures, exhibiting complex patterns, and chemical composition was determined by Scanning Electron Microscopes (SEM) JEOL JSM-7600F Schottky FE SEM equipped with INCA Oxford 350 EDS SDD, ThermoFisher Quanta 650 ESEM equipped with EDS Oxford Instruments AZtec Live, Ultim Max SDD 40 mm², and Karl Zeiss Supra 35 VP SEM with EDS analysis. The samples' surfaces were prepared by the FIB Helios NanoLab NL650 FEI dual-beam system.

The surface of HEAs was imaged by Backscattered Electrons (BSE), technique available in all described SEMs. Backscattered electron (BSE) imaging was used to visualize compositional contrast: brighter regions correspond to heavier elements (Hf, Sn), while darker regions indicate lighter elements (Ti, Fe, Ni, Cu).

2.3. EDS Analysis

Chemical compositions of individual phases were determined by SEM-EDS (Energy Dispersive Spectroscopy). Some very small or very dark inclusions could not be reliably quantified due to detector limitations.

2.4. Theoretical Modelling

We present a simple toy model to illustrate conditions for which a rich diversity of competing configurations could appear in systems of our interest. Our focus is to identify inherent properties and frustrations needed enabling rich diversity of diverse patterns observed in our magnetic systems.

For this purpose, we use classical Ising spin lattice-type model of N spins in a transverse field (Jelen et al., 2024). The local spin orientation at the i -th site is determined by the unit vector $\hat{\mathbf{s}}_i$. We express the system in the Cartesian system (x, y, z) , which is defined by the unit vector triad $(\hat{\mathbf{e}}_x, \hat{\mathbf{e}}_y, \hat{\mathbf{e}}_z)$. Mutual interactions of spins are described by interaction matrix J . The matrix component J_{ij} describes the interaction between the z -axis components of i -th and j -th spin placed at locations $\vec{\mathbf{r}}_i$ and $\vec{\mathbf{r}}_j$, respectively. For sake of simplicity use the XY-type model, where the orientation of spins is confined to the Cartesian (x, z) plane. We parametrize spin orientations in terms of angles θ_i :

$$\hat{\mathbf{s}}_i = \cos\theta_i \hat{\mathbf{e}}_x + \sin\theta_i \hat{\mathbf{e}}_z. \quad (1)$$

To increase complexity of different states we introduce presence of a homogeneous external field which favors homogeneous alignment along the x -axis. Hence, introduce a simple competition within a system and analyses under what conditions one could obtain diversity of competing configurations. The resulting dimensionless interaction energy of N -interacting spins is expressed as (Jelen et al., 2024).

$$W = -\frac{1}{2} \sum_i \sum_j J_{ij} s_i^z s_j^z - \Omega \sum_i s_i^x. \quad (2)$$

The sums run over all the spin sites of the system. Direct inter-spin interactions could impose parallel ($J_{ij} > 0$) or antiparallel ($J_{ij} < 0$) mutual alignment of interacting spins. Different probability distributions of J_{ij} values in our model mimics different constituents and spatial inhomogeneities of magnetic systems studied. The transverse field Ω introduces anisotropy into the system. To increase diversity of potential configurations we set $\vec{\Omega} = \Omega \hat{\mathbf{e}}_x$. This setting imposes frustrations: i.e., J_{ij} imposes alignment among the z -axis and Ω in the orthogonal direction. In the limit $\Omega \rightarrow \infty$ and finite values of J_{ij} this ordering field tends to align the spins homogeneously along $\hat{\mathbf{e}}_x$. In our approximate treatment we neglect thermal fluctuations.

3. Results

In the following we present typical experimentally measured patterns in our samples. Afterwards we discuss possible pattern generating mechanisms.

3.1. Microstructures

In **Figure 1** we present backscattered-electron SEM images of all six alloys in the HfTiZrSnM (M=Fe, Ni, Cu, Nb) system. The images highlight how adding Sn and different transition metals (Cu, Fe, Ni, Nb) drastically changes the microstructure. Figure 1 shows six SEM backscattered-electron (BSE) images, each corresponding to one alloy in the HfTiZrSnM system (M = Fe, Ni, Cu, Nb). BSE contrast correlates with average atomic number: brighter are heavier elements (Hf, Sn), darker are lighter elements (Ti, Fe, Ni, Cu). The figure visually demonstrates how adding Sn and different transition metals drastically changes the microstructure. Baseline alloy HfTiZr (HTZ) is presented in **Figure 1a**). It contains microstructure of μm -sized grains with dark edges. Grain interior is brighter (Hf-rich) and edges are darker (Ti-rich). It has no inclusions or secondary phases. This alloy is the only single-phase system in the series. The Ti segregation to grain boundaries is driven by lattice-strain minimization. Master Sn-containing alloy HfTiZrSn (HTZS) is shown in **Figure 1b**). It exhibits large, several 10 μm faceted grains with straight edges, which are slightly darker than interiors. Matrix is light grey and contains many small inclusions,

some very dark that can not be determined by SEM-EDS. Sn addition produces four-phase microstructure with $\text{Hf}_{20}\text{Ti}_{12}\text{Zr}_{32}\text{Sn}_{37}$ grains, rewritten as $(\text{Hf}, \text{Ti}, \text{Zr})_5\text{Sn}_3$ and $\text{Hf}_{19}\text{Ti}_{17}\text{Zr}_{32}\text{Sn}_{32}$ grain edges, appearing darker than the grain interior. This is the first appearance of the characteristic $(\text{Hf}, \text{Ti}, \text{Zr})_5\text{Sn}_3$ grains that dominate all Sn-containing alloys. **Figure 1c)** shows the master Sn-containing alloy with added Fe. Adding iron produces very large faceted grains (10-100 μm). Matrix is darker and contains many small inclusions, mostly light gray, some very dark. The darker the inclusion appear, the lighter elements it contains. Next alloy contains Ni and is presented in **Figure 1d)**. It is similar to HTZ and HTZ-Fe regarding large light-grey grains. Matrix contains many bright inclusions and some very dark inclusions. This alloy has four distinct Ni-containing phases giving strong contrast variations. **Figure 1e)** shows HfTiZrSnCu alloy with distinctive “bean-shaped” grains, unlike all other alloys. Grains contain many freckles (small contrast variations). Matrix shows variable grey levels, indicating strong compositional fluctuations. In addition, it shows some small black inclusions. HfTiZrSnNb alloy, presented in **Figure 1f)** has much simpler microstructure than Fe, Ni or Cu alloys. The large light $(\text{Hf}, \text{Ti}, \text{Zr})_5\text{Sn}_3$ grains are embedded in a HfTiNb -rich darker-grey matrix.

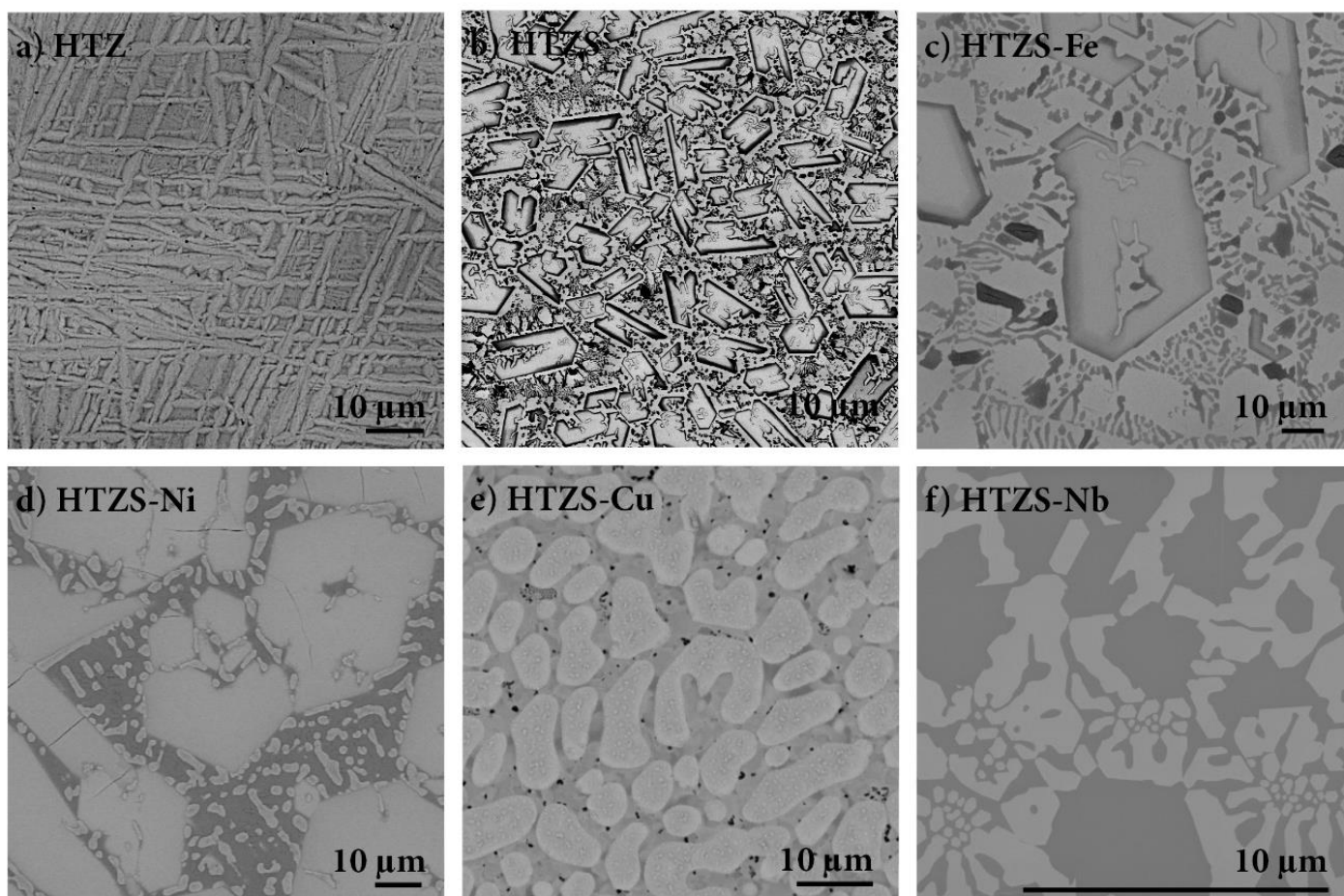


Figure 1. SEM BSE images of **a)** HfTiZr master alloy (HTZ), **b)** HfTiZrSn (HTZS), **c)** HfTiZrSn-Fe (HTZS-Fe), **d)** HfTiZrSnNi (HTZS-Ni), **e)** HfTiZrSnCu (HTZS-Cu), **f)** HfTiZrSnNb (HTZS-Nb).

In addition to imaging, chemical composition of individual phases (different grey shades on the BSE images) was determined by Energy Dispersive Spectroscopy (EDS) in SEM. The results are presented in **Table 1**.

Table 1. SEM-EDS chemical composition of investigated alloys. The column “Appearance of the phases” describes morphologic appearance of the phase in the SEM-determined microstructure.

Alloy	Appearance of the phases	Composition
HfTiZr	grains interior	Hf38Ti34Zr28
	grains' dark edges	Hf32Ti41Zr27
HfTiZrSn	large grains interior	Hf20Ti12Zr32Sn37
	large grains edges	Hf19Ti17Zr32Sn32
	matrix	Hf30Ti36Zr20Sn14
	dark inclusions	Can not be determined by SEM EDS
HfTiZrSnFe	large grains	Hf19Ti10Zr33Sn36Fe2
	small bright inclusions	similar to large grains, less Sn, more Ti
	matrix	Hf25Ti25Zr4Sn2Fe44
	dark inclusions	Can not be determined by SEM EDS
HfTiZrSnNi	large grains	Hf16Ti11Zr32Sn35Ni6
	small bright inclusions	Hf30Ti17Zr3Ni50
	matrix	Hf22Ti38Zr6Sn2Ni32
	dark inclusions	Can not be determined by SEM EDS
HfTiZrSnCu	grains (beans), freckles on beans	Hf18Ti11Zr29Sn32Cu10
	matrix-dark	Hf20Ti25Zr10Sn3Cu42
	matrix-bright	Hf25Ti33Zr7Sn2Cu33
	dark inclusions	~Hf18Ti48Zr7Sn3Cu24
HfTiZrSnNb	grains	Hf19Ti11Zr30Sn36Nb4
	matrix	Hf25Ti24Zr13Sn14Nb24

3.2. Theoretical Analysis

We introduce scalars $u_i = \sin\theta_i$, where $u_i \rightarrow 0$ in the limit $\Omega \rightarrow \infty$. Thus, it holds

$$\hat{s}_i = \sqrt{1 - u_i^2} \hat{e}_x + u_i \hat{e}_z. \quad (3)$$

Our interest is to show how diverse patterns of spin configurations could emerge from known statistical properties of J_{ij} on decreasing Ω where we originate from initially spatially homogeneous patten aligned along $\hat{e}_x$. The latter conditions is realized in the limit $\Omega \rightarrow \infty$ (i.e., $\Omega \gg J_{ij}$). For this aim we expand W in terms of small values of u_i up to the 4th power:

$$W \sim -\frac{1}{2} \sum_i \sum_j J_{ij} u_i u_j - \Omega \sum_i \left(1 - \frac{u_i^2}{2} - \frac{u_i^4}{8}\right) = W_h + \frac{\Omega}{8} \sum_i u_i^4. \quad (4)$$

Here W_h stands for harmonic contribution. Minimization of W_h yields the equilibrium equations $\sum_j J_{ij} u_j = \Omega u_i$. We express them in the matrix notation as

$$\underline{J} \hat{\mathbf{u}} = \Omega \hat{\mathbf{u}}, \quad (5)$$

$\underline{J} = \{J_{ij}\}$ stands for the interaction matrix. N -dimensional vectors $\hat{\mathbf{u}} = (u_1, u_2, u_3, \dots, u_N)$ describe configuration of spins that are slightly misaligned from the $\hat{e}_x$ direction. Solution of Equation (5) determines eigenvector (modes) $\hat{\mathbf{u}}^{(m)}$ of $\underline{J}$:

$$\underline{J} \hat{\mathbf{u}}^{(m)} = \Omega_m \hat{\mathbf{u}}^{(m)} \quad (6)$$

where Ω_m stands for eigenvalues. The eigenvectors are normalized and orthogonal, i.e.,

$$\sum_i u_i^{(m)} u_i^{(n)} = \delta_{mn}, \quad (7)$$

and δ_{mn} stands for the Kronecker symbol.

For relatively large values of Ω , where the harmonic approximation works well, one express $\hat{\mathbf{u}}$ as the superposition of eigenmodes

$$\hat{\mathbf{u}} = \sum_m A_m \hat{\mathbf{u}}^{(m)}, \quad (8)$$

where A_m are amplitudes of modes. Considering the expansion Eq.(8) and orto-normal condition Eq. (7), one obtains

$$W = -N\Omega + \frac{1}{2} \sum_m A_m^2 (\Omega - \Omega_m) + \frac{1}{4} \sum_m \sum_n \sum_k \sum_l \sigma_{mnkl} A_m A_n A_k A_l, \quad (9)$$

$$\sigma_{mnkl} = \frac{\Omega}{2} \sum_i u_i^{(m)} u_i^{(n)} u_i^{(k)} u_i^{(l)}. \quad (10)$$

In the following, we study configurational evolution on decreasing Ω . We first neglect the interaction among competing modes. Afterward, we consider cases where modes are coupled. In the approximation of decoupled modes it follows

$$W \sim -N\Omega + \sum_m \left(\frac{1}{2} A_m^2 (\Omega - \Omega_m) + \frac{1}{4} A_m^4 \sigma_m \right), \quad (11)$$

where we introduced

$$\sigma_m = \frac{\Omega}{2} F_4^{(m)}, \quad (12)$$

$$F_n^{(m)} = \sum_i u_i^{(m)n}, \quad (13)$$

where $n \in \{1, 2, 4\}$. Note that $F_2^{(m)} = 1$ because the/ modes are normalized. Minimization of W yields

$$A_m = \sqrt{(\Omega_m - \Omega)/\sigma_m} \quad (14)$$

for $\Omega_m < \Omega$ and $A_m = 0$ for $\Omega_m \geq \Omega$. Thus, the modes open via 2nd order phase transition on decreasing Ω below the corresponding eigenvalue Ω_m . The total response of the system is given by Eq.(8).

However, in general, the modes could be coupled where the coupling terms appear as fourth-order terms in Eq.(9). For illustration purposes, we focus to cases when only two modes are coupled. In this case

$$W = -N\Omega + \frac{1}{2} \sum_m A_m^2 (\Omega - \Omega_m) + \frac{1}{4} \sum_m (\sigma_m A_m^4 + \sum_{l \neq m} (4\mu_{ml} A_m A_l^3 + 3\gamma_{ml} A_m^2 A_l^2)), \quad (15)$$

$$\text{where } \mu_{ml} = \frac{\Omega}{2} \sum_i u_i^{(m)} u_i^{(l)3}, \quad \gamma_{ml} = \frac{\Omega}{2} \sum_i u_i^{(m)2} u_i^{(l)2}.$$

Note that contributions weighted by μ_{ml} are sensitive to relative orientation (i.e., the sign of amplitudes) of modes. An equilibrium (meta)stable configuration, in which two (i.e., m -th and l -th) modes are opened, is determined by equations

$$\frac{\partial W}{\partial A_m} = \frac{\partial W}{\partial A_l} = 0, \quad \frac{\partial^2 W}{\partial A_m^2} = \frac{\partial^2 W}{\partial A_l^2} > 0, \quad \frac{\partial^2 W}{\partial A_m^2} \frac{\partial^2 W}{\partial A_l^2} - \left(\frac{\partial^2 W}{\partial A_m \partial A_l} \right)^2 > 0. \quad (16)$$

The condition, where such a configuration becomes unstable, is determined by

$$\left(\frac{\partial^2 W}{\partial A_m \partial A_l} \right)^2 - \frac{\partial^2 W}{\partial A_m^2} \frac{\partial^2 W}{\partial A_l^2} = 0. \quad (17)$$

4. Discussion

The experimental results demonstrate that small compositional changes—particularly the addition of Sn and magnetic 3d elements—lead to qualitatively different microstructures. One obtains diversity of different patterns via relatively small changes in relative concentration of systems ingredients.

Furthermore, we present a simple toy model which pinpoints possible pattern generating mechanisms and key quantitative parameters from which one could predict emergent qualitative structure observed macroscopically. For this purpose, we assumed that key properties of different compositions could be mimicked by the interaction matrix $\underline{J}$. This matrix consists of direct interaction J_{ij} between i -th and j -th sample constituent. In our rough modelling we assumed Ising model-like inter-spin interactions. We assume that essential properties of different compositions and relative concentrations of ingredients are well fingerprinted by $\underline{J}$. For example, for a reference Sample A let us assume that all the spins are the same (i.e., we have a homogeneous sample consisting of a single element) placed on a simple square lattice. If they would exhibit short range ferromagnetic interaction, where $J_{ij} = J > 0$ has a constant positive value among 1st neighbours and is zero otherwise, $\underline{J}$ would possess in 3D six lines parallel to the diagonal where $J_{ij} = J$. As a contrast state we chose spin glass systems (Sample B) [5] where distribution of J_{ij} values is essentially random and $\langle J_{ij} \rangle = 0$ ($\langle \dots \rangle$ stands for the ensemble average). In these case random values of J_{ij} appear along the 6 parallel lines of $\underline{J}$. Furthermore, one needs in the model a parameter which could drive a structural phase transition. For this purpose we introduced in our model an external ordering field $\vec{\Omega}$, where $\underline{J}$ and $\vec{\Omega}$ have competing ordering tendencies. This allowed us to study structural transformation at zero temperature, which simplifies required mathematics of the problem. Key results are as follows. We focused on the regime on decreasing Ω where the spatially homogenous structure of classical spins initially aligned along $\vec{\Omega}$ becomes influenced by $\underline{J}$. Our analysis reveals that the formed pattern can be expressed as a superposition of modes which represent $\underline{J}$ eigenvectors. Furthermore, on decreasing Ω the 1st mode opened corresponds to the largest eigenvalue $\Omega_{\max}$ of $\underline{J}$. For instance, such a mode would be “extended” (i.e., nonlocal) and “localised” (spatial variations appear locally) (Sherington and Kirkpatrick, 1975) in Sample A and Sample B, respectively. In the case of extended modes due to the mode coupling terms (see Eq.(15)) the growth of lower modes could be suppressed on further decreasing Ω . Therefore, there would be only one mode contribution (corresponding to $\Omega_{\max}$) in overall system response, see Eq.(8). However, if $\underline{J}$ exhibits “localised” states mode blocking is essentially less significant. Consequently, the system might exhibit a pattern where several modes are superimposed. Note that coupling between modes increases on increasing the spatial overlap of the modes. In case that overlapping is important then one could by appropriate initial perturbation excite a particular $\underline{J}$ mode preferred by system, which could then persist if it is protected by suppressing mode overlapping interactions. Our analysis reveals that one could make quantitative predictions about possible states by constructing appropriate interaction matrix $\underline{J}$ of the system. Furthermore, to have a variety of different states one needs some inherent anisotropy in the system.

5. Conclusions

We considered diversity of patterns in high-entropy metallic alloys. Our microscopic analysis reveals that one could realise a rich pallet of different configurations by varying relative concentration of key constituents. We constructed a simple toy model to identify possible reasons for such diversity. We supposed that patterns are dominantly influenced by magnetic interactions among constituents which we mimicked by the interaction matrix $\underline{J}$. We believe that different ingredients in the sample are fingerprinted in rather complex

structure of $\underline{J}$ and consequently rich complexity of possible emergent patterns. For this purpose, one needs frustration within the system and competition among diverse configurations. Note that our model represents a first step towards theoretical understanding of observed pattern complexity in high-entropy metallic alloys. Namely, in the minimal model we neglected thermal fluctuations and enforced phase transition by a tuneable external field. Our future goal is to develop a more realistic model with tuning parameters reflecting real samples.

Conflicts of Interest: The authors declare no conflict of interest.

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