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Elemental segregation in solid-solution high-entropy alloys: Experiments and modeling

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ABSTRACT

Recent experiments showed that elemental segregation occurs in some high entropy alloys (HEAs) although their X-ray diffraction patterns exhibit a nominal single-phase solid solution structure. Based on the 3-D atom probe tomography (APT) results obtained from the FeNiCoCrCu HEA, here we propose a simple thermodynamics model based on the notion that elemental segregation facilitates stabilizing the solid solution phase with a minimized Gibbs free energy. Our model enables distinguishing nominal single-phased solid-solution HEAs with and without elemental segregation. The predictions of our model are found in good agreement with the experimental data reported hitherto in the literature.

1. Introduction

Exploration of novel alloy design strategies is a long-standing but crucial topic in materials science, which is driven by the urge from many pillar industries [1–9]. To signify the nontraditional alloy design paradigm, the term of "high entropy alloy" (HEA) was recently proposed, which refer to the alloys with typically five or more elements mixed at an equal or nearly equal molar fraction [10]. Due to the advent of HEAs, the alloy design space has been greatly expanded compared to that of conventional alloys, the latter of which is mainly based on one or two principal elements [1,11]. It was once thought that intermetallic compounds are likely to form in a multi-component alloy, therefore leading to embrittlement and harmful to the alloy's structural applications [12]. However, although comprising multi-principal elements, HEAs can form random solid solutions as opposed to intermetallic compounds [1–3,9,10,13]. To understand the underlying mechanisms, different criteria and models have been proposed or developed [5–7,11,14–18]. Nevertheless, the issue of phase stability in HEAs still remains heavily debated till today [9].

In theory, the high-entropy effect in a multi-component alloy manifests itself as the formation of a single-phased random solid solution [1,2,8,9,13], which, according to the prior works including experiments and simulations [2,6,7,9,11,16–22], is affected by many factors, such as mixing configurational entropy, atomic size misfit, mixing enthalpy and many others. In practice, people often used the X-ray diffraction (XRD) results to judge whether a HEA can form single-phased random solid solution or not. These results were widely used in the literature as the references for theoretical modeling and numerical simulations [5–7,9,11,12,14,16–26]. However, recent experiments clearly showed that elemental segregation can take place in some HEAs even though their XRD patterns display a nominal single-phase solid solution structure [27–30]. To explain this phenomenon, a simple argument is that a few particular constituent elements, such as Cu and Fe, in a HEA have positive mixing enthalpy, hence leading to elemental segregation in order to minimize the total Gibb's free energy. This argument is reasonable but inadequate to fully explain the phenomenon of elemental segregation in HEAs, in which the mixing enthalpy of different constituent elements could be either positive or negative. Conceptually, the argument based on the mixing enthalpy alone does not take into account the possible high-entropy effect, the latter of which is supposed to stabilize the random solid solution phase regardless of the mixing enthalpy. As an example, it was recently reported that the deposited FeCoNiCrCu HEA film is single-phased solid solution [27] whereas the as-cast bulk FeCoNiCrCu

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HEA shows significant elemental segregation [27,29]. Again, this indicates that elemental segregation in HEAs has to be studied with the consideration of both entropy and enthalpy of mixing. However, due to the multi-component nature, a simple but robust thermodynamic criterion that can be used to predict elemental segregation in different kinds of HEAs is still lacking. In this work, we intend to elucidate the physical mechanisms of elemental segregation in HEAs and provide a simple thermodynamic model that takes into account the combined effect of mixing entropy and mixing enthalpy in order to guide the design of single-phased HEAs.

2. Experimental methods

The alloy ingot with an equiatomic composition of FeCoNiCrCu was synthesized by arc-melting a mixture of pure metals (>99.99 wt%), in a high-purity argon atmosphere. To achieve a good chemical homogeneity, the molten was melted repeatedly for 5 times, which was subsequently drop-cast into a Cu mold with a shape of 1 mm thick sheet. To investigate the annealing effect, one sample was annealed at 1000 °C for 1 h. The phase constitution of the obtained samples was identified through an X-ray diffractometer (XRD), and the microstructures of the alloys were characterized through a scanning electron microscope (SEM). To reveal the local elemental distribution, an X-ray energy-dispersive spectrometry (EDS) was employed on the tens-of-microns scale. To further reveal details of the elemental distributions at the atomic scale, a LEAPTM tomography was carried out at a specimen temperature of 50 K under ultrahigh vacuum (UHV) conditions of 1×10^{-8} Pa. The pulse rate was 2×10^{5} Hz and the pulse-voltage to standing- DC voltage ratio (pulse fraction) was 15–20%. The APT tip with a radius <50 nm were prepared from the as-cast samples using standard techniques.

3. Theory and analysis

In line with the reported experimental results [27–30], we first postulate that elemental segregation in the solid-solution HEAs only causes the chemical inhomogeneity but does not change the lattice structure, thereby resulting in a nominal XRD pattern of single-phased random solid solution, as shown by many previous experiments [27–30]. From the viewpoint of equilibrium thermodynamics, elemental segregation comes about to minimize the mixing Gibb's free energy of a solid-solution HEA, which can be expressed as

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

where ΔH_{mix} and ΔS_{mix} denote the enthalpy and entropy of mixing, respectively. For a solid solution without a significant atomic size effect [6,7,31,32] as well as magnetic and electronic effects [5,6,9,33], ΔS_{mix} can be approximated as

$$\Delta S_{mix} = -k_B \sum_{i=1}^{n} c_i \ln c_i \quad (2)$$

where k_B is the Boltzmann's constant and c_i the atomic fraction of the ith element for a total number of n elements [10]. To estimate the mixing enthalpy, people were used to employ the Miedema model which gives

$$\Delta H_{mix} = \sum_{i \neq j} \Omega_{ij} c_i c_j \quad (3)$$

where $\Omega_{ij} = 4\Delta H_{ij}$, in which ΔH_{ij} is the mixing enthalpy of a binary liquid [2,18]. However, the above formulation does not take into account the effects from the high-order atomic interactions and is usually not used directly for the prediction of equilibrium phases [34]. As a remedy, we propose a simple modification to the Miedema model by assuming

$$\Delta H_{mix} = \beta \sum_{i \neq j} \Omega_{ij} c_i c_j \quad (4)$$

where β is an empirical parameter regulating the effect of the mixing enthalpy to that of the mixing entropy, the value of which can be determined by comparing the experimental data to our

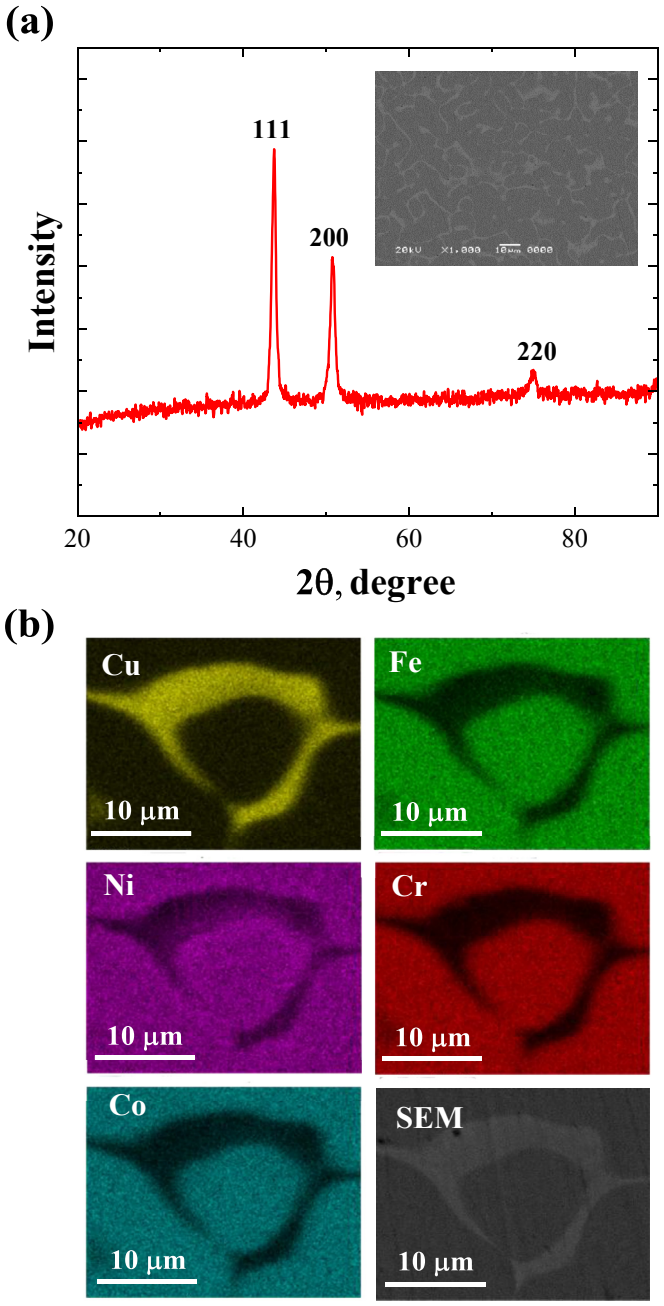

Fig. 1. (a) X-ray diffraction pattern of the as-cast FeCoNiCrCu alloy, the inset shows the corresponding SEM micrograph, and (b) elemental distributions determined by EDX for local areas with the scale bar of 10 μm. Note that the black color indicates a low concentration of the corresponding element.