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The Story of High Entropy Alloys: From the Immiscible to the Miscible States in Alloys—The Entropy versus the Enthalpy Alloys

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Abstract

The role of entropy and enthalpy plays an essential key for the formation of an alloy. This paper illustrates how an alloy is to form and what and why the properties of the alloy are going to have by the entropy and enthalpy effects via a designed enthalpy-entropy plane (EE-plane) based on the Gibbs free energy equation and the introducing a charactering pseudo-unitary lattice (PUL) for entropy alloys. Based on the PUL scheme, the so-called four effects in high entropy alloys are simply nothing but the entropy effect with the other three accompanying effects: the distortion, slow diffusion and cocktail effects.

Keywords

EE-Plane, Pseudo-Unitary Lattice (PUL), High Entropy Alloy Four Effects, Entropy Alloys, Enthalpy Alloys, Solubility, Solid Solution

1. Introducing Enthalpy vs. Entropy Plane (Called EE-Plane) Based on the Gibbs Free Energy Equation [1] and [2]

It is well-known that two or more elements make an alloy to be in one of immiscible (segregation), miscible (solid solution), and overmiscible (intermetallic compound) states by the fundamental principles of solid thermodynamics and physical metallurgy. When the contained elements in an alloy are mixed by melting them in a refractory crucible, whether the miscibility state of this alloy will be, depends closely on the cohesive force between two atoms of the two different institutional elements. If the cohesive forces make the resultant enthalpy (ΔH) of this mix system positive (expel for different elemental atoms), null, or negative (attract for different elemental atoms for a spontaneous mixing process), then the alloy will be in the state of segregation, solid solution or even intermetallic. This consideration above clearly only touches on the chemical enthalpy of the system. One knows that obtaining solid solution (showing good elongation and toughness of alloys and metals) is the design basis of all metals. The most difficult for improvement to get the solid solution state is how to raise the solubility of solute in a solvent. Historically this difficult aspect of increasing solubility limits the design ability of producing a good and useful alloy.

Looking at the Gibbs free energy (ΔG) one can have an equation of $\Delta G = \Delta H - T\Delta S$, where T is the system temperature and ΔS is the entropy change after the mixing reaction of the system. $T\Delta S$ is actually a physical entropy energy change of the system. This suggests one to think about the entropy effect on mixing or designing an alloy. For the most convenient way for the entropy effect to involve in the mixing process of an alloy, it is to raise the number n of the component elements since one is easily able to increase the ΔS of an equal molar system by $R\ln(n)$, where R is the gas constant of 8.314 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $\ln(n)$ is the nature logarithm of n. The second law of thermodynamics points out that for any spontaneous process, the entropy change of the system plus the entropy change of the surrounding environment is always non negative. Therefore, ΔS can be positive or negative, but the sum of the spontaneous processes $\Delta S \geq 0$, thus ΔG is lower than or equal to ΔH by an amount of non negative $T\Delta S$. The Gibbs free energy is the total energy change for any process such as in mixing components of an alloy. The thinking route for making an alloy to be whether immiscible or miscible, now rises by a degree of freedom via introducing this physical entropy energy in the system. If we introduce a new plane by a horizontal ΔH abscissa axis and a semi-vertical $T\Delta S$ ordinate axis (since $T\Delta S \geq 0$), then we have three regions of immiscibility, solid-solution miscibility, and intermetallic miscibility in this $\Delta H - T\Delta S$ plane by two lines of $|\Delta H| = T\Delta S$, *i.e.*, lines $|\Delta H| = T\Delta S$ and $-\Delta H = T\Delta S$ in the 1st quadrant and the 2nd quadrant, respectively. Now the plane is divided into three regions, that is to say, two regions in which $|\Delta H| < T\Delta S$ and one region of $|\Delta H| > T\Delta S$. The region surrounded by $\Delta H = T\Delta S$ and the positive ΔH abscissa is an immiscibility region (called Region I), A region which is surrounded by $-\Delta H = T\Delta S$ and the negative ΔH abscissa is an intermetallic region (called Region III) and that surrounded by the two lines of $|\Delta H| = T\Delta S$ is a solid solution state region called Region II. Thus one can easily draw the three regions in the enthalpy-entropy plane accordingly.

2. Introduction to Pseudo-Unitary Lattice (PUL) [2] [3] in a Multi-Principal Elemental System: Enthalpy Alloys and Entropy Alloys

In a multi-principal elemental alloy system which has given the alloy solid-solutionized is called a high entropy alloy in that the solid-solutionized alloy comes from the high entropy effect in this multi-principal elemental system. For an equal molar alloy, as the number of institutional elements in this alloy increases the entropy change increases according to $R\ln(n)$ just described in the above section of this paper. Since the fraction of the member elements decreases when the number of the members increases, therefore there exists an optimum in entropy in a multi principal member alloy system, *i.e.*, there exists optimum numbers in multi principal numbers in alloy system, e.g., 5 to 13 principal members for alloys with optimum entropy. We know that as $\Delta G = 0$ the system is said to be reversible. The regions where $\Delta G < 0$ are Regions II and III which are called in miscible states, while on the other hand, that of $\Delta G > 0$ is Region I which is called in immiscible state. One also knows that as $\Delta H \ll 0$, the alloys tend to form intermetallic compounds or intermetallics, we call these alloys as "enthalpy alloys". As alloy systems where $|\Delta H| = -\Delta H \ll T\Delta S$, which is in the left hand side portion of Region II, the entropy part overrides the enthalpy part of the system, the alloys are in the solid solution state. Alloy systems satisfied $|\Delta H| = \Delta H \ll T\Delta S$, which is in the right hand side portion of Region II, are also in the solid solution state. To reach this important point is under the assumption that there exists a symmetrical effect for the entropy effect against the enthalpy effect. This seems reasonable for both positive and negative enthalpy systems. Under this assumption of equal effect of entropy against enthalpy, one has the vertical V-shape of Region II where the alloys are in the solid solution state, and the width of the V-region (Region II) is equal to $2\ T\Delta S$, that is to say, for alloy systems satisfied the formation of solid solution states, the width in Region II enlarges as $T\Delta S$ increases, and the range in system enthalpy for the solid solution to form enlarges to the range of $2\ T\Delta S$. We call this as entropy on the effect of the improved solid solutionization of alloys, that is to say, the solubility of alloys arises by the entropy effect. According to experimental results, this is verified. By the entropy effect we mean that the solubility of the alloy increases. Experiments also find the structure of the entropy alloys tends to form simple crystal structures such as fcc, bcc, and hcp, although there are so many kinds of member elements which range from 5 to 13 kinds of member elements and sometimes existing order structures in fcc, bcc, and hcp. [4] We call these lattice structures as "pseudo-unitary lattice" (PUL) which shows like a lattice structure of a pure element, but actually containing several elemental atoms of multi-principal member elements in that lattice. The PUL is the DNA of the entropy alloys. It manifests the main effect of entropy on the entropy alloys. Once the entropy effect prevails the format PUL keeps no matter what the entropy alloy is under working processes such as annealing and solution treatment, therefore we have a slow or sluggish effect of atom diffusion. Since the PUL has several elements in itself, the size of member elemental atoms is not equal the lattice is likely distorted once the PUL formed, and the properties of the alloy readily possess the so-called "cocktail" effect. One sees at this moment that the latter three effects in entropy alloys are obviously three accompanying effects of the entropy effect.

3. The Existence Experiment and the Nature of Entropy Alloys

The existence experiment of entropy alloys by Chen at Hsinchu National Tsing Hua University at Chen's alloy laboratory [5] was demonstrated in 1995. The study that the alloys remain in their nature of metal state was first shown in literature [6].

4. Examples for Enthalpy Alloys and Entropy Alloys at Temperatures above and below the Melting Temperatures of Member Elements in Alloys during Alloy Metallurgical Processing

Enthalpy alloys are found with high difference in electronegativity between member elements which form chemical bonds and tend to produce compounds that can be found in textbooks. Entropy alloys, on the other hand, are found with small difference in electronegativity between member elements that lay in the same or neighbor column(s) in the Periodic Table with small difference in $|\Delta H|$. Entropy alloys are also able to find at high temperatures above their individual melting temperatures since enthalpy depends closely on temperature and usually decreases with temperature, and entropy energy ($T\Delta S$) does too. Mischmetals of lanthanum elements are good examples in nature for entropy alloys. The enthalpy-entropy plane thus can use in discussion of phase change during metallurgical processes at different working temperatures [2].

5. Conclusion

We have shown the EE plane to illustrate the solubility rise in entropy alloys and this principle gives the entropy effect on the alloys. Under the entropy effect, the entropy alloys tend to possess a pseudo-unitary lattice (PUL) after their formation, e.g., melting or mechanical alloying. The PUL is the DNA of the entropy alloys, which gives other three accompanying effects, the distortion, the slow diffusivity of atoms, and the cocktail effects in their solid solution states of the alloys.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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