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Solid solution prediction of high-entropy alloys based on Hume-Rothery

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Abstract: Solid solution formation (SSF) is of main concern in high-entropy alloys (HEAs). The more ready-to-implement approach to predict SSF is the Hume-Rothery's (H-R). Therefore, this paper presents four parameters and their acceptance criteria to evaluate HEAs in what refers to SSF. Furthermore, AlCoCrFeNi alloy was subjected to SSF prediction framework based on H-R. The results show that the alloy does not form a solid solution based on H-R, which disagrees with several reports in the literature. Therefore, the framework should be aggregated with other parameters to predict the SSF of this alloy.

Keywords: High-entropy alloys; Solid solution; Prediction; Alloy; Hume-Rothery.

Predição de formação de solução sólida de ligas de alta entropia por Hume-Rothery

Resumo: A formação de solução sólida (SSF) é uma das principais preocupações em ligas de alta entropia (HEAs). A abordagem mais fácil de implementar para prever SSF é a de Hume-Rothery (H-R). Portanto, este artigo apresenta quatro parâmetros e seus critérios de aceitação para avaliar HEAs no que se refere a SSF. Além disso, a liga AlCoCrFeNi foi submetida à estrutura de previsão de SSF baseada em H-R. Os resultados mostram que a liga não forma uma solução sólida com base em H-R, o que discorda de vários relatos na literatura. Portanto, a estrutura deve ser agregada a outros parâmetros para prever a SSF desta liga.

Palavras-chave: Ligas de alta entropia; Solução sólida; Predição; Liga; Hume-Rothery.

Introduction

The development of new materials is part of humanity's own evolution [1]. In the materials area, metals and metal alloys represent a paradigm breakthrough. The properties of pure metals can be significantly improved by taking part in metal alloys [1]. Therefore, one-principal-element metal alloys have been applied to solve several problems worldwide for a long time. Thenceforward, two-principal-elements metal alloys were then developed [2]. Based on the body of knowledge then developed, multicomponent alloys (with 3 or more principal elements) were created. In spite of their valuable properties, intermetallic compounds (IMC) with complex microstructures may form. Thus, undesired magnitudes of some mechanical properties may limit the application of some multicomponent alloys.

Two decades ago, a new concept of multicomponent alloy was made known [3,4]. High-entropy alloys (HEAs) have equimolar or near-equimolar composition, in which at least five principal elements are present in molar concentrations from 5 to 35%. Their high configurational entropy tends to induce solid solution formation (SSF), which may improve the performance in the current engineering applications or even enable new ones. This research field is viable due to the improvement of several properties, e.g. corrosion resistance, ductility, hardness, and strength. HEAs may present two or more different phases, in which some may be IMC. A stable microstructure of these alloys may be constituted of: (a) two simple solid solutions (duplex); (b) random solid solution (hexagonal close packing (HCP), face-centered cubic (FCC), or body-centered cubic (BCC)).

One of the major branches in the field of HEAs refers to the prediction of phase formation and composition [5]. On this subject, thermophysical parameters calculation (TPC) [6] is applied in this work, focusing only on Hume-Rothery rules.

Objective

The main objective of this work is to predict SSF of AlCoCrFeNi alloy by Hume-Rothery rules calculation.

Material and Methods

The calculation and analysis conducted herein encompass the four Hume-Rothery rules, which are stated in the following paragraphs. MS-Excel is the selected engineering tool to perform calculation.

(a) The first rule (Equation 1) refers to the atomic radii difference, in which R_L and R_S are, respectively, the largest and the smallest radii of the solid solution. SSF occurs when $\Delta R(\%) \leq 15$.

$$\Delta R(\%) = \frac{R_L - R_S}{R_L}\ 100 \tag{1}$$

(b) The second rule states that metals with the same type of crystalline structure (CS) may form an extensive series of solid solutions.

(c) The third rule states that full solubility takes place when the elements involved have the same valence. The parameter which quantifies this rule is the mean valence electron concentration (VM, Equation 2), where V_i is the valence electron concentration of the i-th element involved in the solid solution, f_i is the molar fraction of the i-th element, and n is the number of alloy elements. The associated

criterion addresses stable BCC when $V_M < 6.87$; stable FCC when $V_M \geq 8$; and when $6.87 \leq V_M < 8$ FCC is prevailing, although BCC may also occur.

$$V_M = \sum_{i=1}^{n} f_i \, V_i \tag{2}$$

(d) The fourth rule refers to the electronegativity difference ($\Delta\chi$, Equation 3) between the elements by Pauling, which influences phase separation and phase formation. χ_m is the mean electronegativity, and χ_i is the electronegativity of the i-th element. SSF occurs when $\Delta\chi\ (\%) < 6$, where χ_m is given by Equation 4.

$$\Delta\chi(\%) = \sqrt{\sum_{i=1}^{n} f_i \, (\chi_i - \chi_m)^2} \; 100 \tag{3}$$

$$\chi_m = \sum_{i=1}^{n} f_i \, \chi_i \tag{4}$$

Results

The prediction of SSF for AlCoCrFeNi alloy yielded the results shown in Table 1.

Table 1. Statuses for the parameters of prediction of SSF in AlCoCrFeNi alloy. NOK stands for "not ok", and CS stands for "crystal structure".

Parameter	Calculated/Obtained value	Status
$\Delta R(\%)$	20.51	NOK
CS	Al (FCC), Co (HC), Cr (CCC), Fe (CCC) e Ni (CFC)	FCC
V_M	7.20	FCC prevailing
$\Delta\chi(\%)$	12.03	NOK

The calculated value of each parameter was compared to its corresponding criterion, returning a status for each parameter.

Figure 1 shows the proportion of the elements of AlCoCrFeNi alloy in terms of mass. Although equiatomic, the different atomic masses imply different masses for each element. For example, in order to obtain 100 g of AlCoCrFeNi, the masses of the components are the following: (a) Al: 10.69 g; (b) Co: 23.34 g; (c) Cr: 20.60 g; (d) Fe: 22.12 g; (e) Ni: 23.25 g.

Figure 1. Mass of each element in AlCoCrFeNi alloy.

Discussion

The most probable crystal structure refers to FCC, as obtained in the calculation of (V_M = 7.20). Aluminum and nickel are CFC, chromium and iron are CCC, and cobalt is HCP at room temperature. Co disadvantages the SSF since it does not have a cubic lattice like the other alloy elements. On the other hand, Al, although FCC, favors BCC phase.

Although Ni, Co, and Cr have similar atomic radii (124, 125, and 128 pm, respectively), the atomic radii difference reached 20.51% influenced by the difference between iron (156 pm) and Ni (124 pm). This value is greater than the recommended by the first rule of Hume-Rothery (15%), thus not indicating SSF. In this case, a solution to SSF is to remove or substitute Fe by an element with smaller atomic radius. Another possible solution is to substitute the three smallest atomic radii (Ni, Co, and Cr) for others with larger atomic radius, however lower than the atomic radius of Fe.

The electronegativity difference calculation has yielded a value of 12.03%, which is greater than 6%. Therefore, $\Delta\chi$ is out of the SSF range, which can be changed if the elements with the greatest standard deviations from the mean are replaced by other elements with lower dispersion around the mean.

Although two of the Hume-Rothery results yielded no SSF, there are several reports of SSF related to this alloy [7]. This fact addresses that only Hume-Rothery rules are insufficient to predict SSF in HEAs.

On this subject, SSF in HEAs occurs due to the four main effects [8]: (a) high entropy; (b) sluggish diffusion; (c) lattice distortion; and (d) cocktail.

The high-entropy effect takes place because of a high configurational entropy at high temperatures, which implies the minimization of the Gibbs free energy of mixing (according to the second law of thermodynamics), favoring the dissolution of IMC.

Lattice distortion causes the effect of sluggish diffusion, responsible for providing a slow rate of atomic diffusivity.

The introduction of substitutional solute atoms into a solvent matrix causes the distortion of the lattice, moving the atoms away from their theoretical lattice positions.

When the elements interact with each other, a blend of properties is obtained, some of them being trade-off, e.g. hardness and ductility, strength and tenacity. This is the so-called cocktail effect.

Conclusions

The general objective of obtaining the four factors to verify the solid solution formation by Hume-Rothery rules has been achieved. As discussed, the four rules of Hume-Rothery themselves proved to be insufficient when dealing with high-entropy alloys.

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