Computational Materials Science 148 (2018) 69–75

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Melting temperature of CoCrFeNiMn high-entropy alloys

M.A. Gutierrez [a], G.D. Rodriguez [a], G. Bozzolo [d], H.O. Mosca [a,b,c,*]

[a] GRUCAMM, UTN Gral. Pacheco, H. Yrigoyen 288, B1617FRP General Pacheco, Buenos Aires, Argentina
[b] Gerencia de Investigación y Aplicaciones, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, B1650KNA San Martín, Buenos Aires, Argentina
[c] Instituto Sabato, Universidad Nacional de San Martín (UNSAM) – Comisión Nacional de Energía Atómica (CNEA), San Martín, Buenos Aires, Argentina
[d] Loyola University Maryland, 4501 N. Charles St, Baltimore, MD 21210, USA

ARTICLE INFO

Article history:
Received 18 May 2017
Received in revised form 8 February 2018
Accepted 11 February 2018

Keywords:
High entropy alloys
Alloy design
Melting temperature
BFS method
Atomistic modeling

ABSTRACT

Atomistic modeling of CoCrFeNiMn ($0 < x_{Mn} < 25$ at.%) high entropy alloys shows that the melting temperature as a function of Mn concentration does not follow the behavior consistent with a homogeneous solid solution, exhibiting a maximum value for 8.7 at.% Mn. Using the concepts of the BFS method for alloys, a description of the phenomenon is provided, showing that sluggish diffusion generates changes in the atomic distribution that lead to this anomalous behavior. This theoretical analysis is meant to provide a template for studying complex compositions and fine effects in high entropy alloys, which would be hard to detect experimentally but that could have an impact on potential applications of these complex materials.

1. Introduction

The CoCrFeNi and CoCrFeNiMn high-entropy alloys (HEA) have been the subject of numerous recent studies [1–28]. Partly due to their specific properties but also to the abundance of experimental [1–15,20–25] and theoretical [16–19] work performed on them, they have quickly become standards within the emerging field of HEAs. These two equiatomic alloys have enough elements to be considered high-entropy alloys, as they both form (for the most part [2,10,14,26–28]) homogeneous fcc solid solutions, and they both have remarkable mechanical and thermal properties [2,3,5–7]. In addition, the limited number of elements also makes them easier to investigate with standard theoretical or modeling tools [16–19].

Overall, these model systems provide excellent testing grounds for new approaches, capitalizing on the extended body of experimental work that already exists. In terms of alloy design, however, one obstacle still remains. Alloys, usually based on an original binary structure, become more complex as minority elements are added in order to induce desired changes in their properties. This process, however, increases the risk of losing the essential features that characterize their basic formulation. With the extensive knowledge on binary and, in some cases, ternary combinations, it is a sometimes a lengthy but generally successful approach to determine the final composition that meets desired criteria. However, uncertainties multiply as the number of elements increases, because of the intensive and expensive experimental work needed to validate any new choice or change in composition. At the same time, theoretical background becomes also more difficult to obtain. In this sense, HEAs present a distinctive challenge, testing the limitations of any current approach to alloy design. With HEAs, the starting point is already widely different from that of a more typical binary mix: in a multi-dimensional phase diagram, all that is known is that in the vicinity of its center (i.e., equiatomic composition), the system has a high probability of forming a (mostly) single-phase disordered alloy due to the maximum high configurational entropy, although this feature does not, by itself, guarantee such outcome [4]. As recent research shows, several other factors come into play [20], which could have a major impact on the resulting phase structure. Beyond that point, either changing the concentration of each element or adding/removing others in order to change the properties, becomes a much more complex task, as there is practically no information available, starting with the simple fact that it is not known what the range of concentrations for which the original single-phase structure exists [4], and whether substituting just a single element could lead to a different phase structure [20]. As such, the experimental work needed in order to gain more insight or fine tune properties is nearly prohibitive, while it is also true that the number of options and the

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[*] Corresponding author at: Gcia.Investigación y Aplicaciones, CNEA, Av. Gral Paz 1499, (B1650KNA), San Martín, Argentina.

E-mail address: hmosca@cnea.gov.ar (H.O. Mosca).

https://doi.org/10.1016/j.commatsci.2018.02.032
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paths to be pursued are substantially less restrictive than in the case of binary or ternary based alloys.

One additional feature is prevalent in HEAs. While it is true that many of the compositions studied tend to exhibit the expected main and dominant feature (a continuous solid solution), it is also true that the formation of small intermetallic precipitates is mostly unavoidable, even if their presence does not preclude the alloy from having strong HEA characteristics [2,10,14]. It is also possible that the mix of so many elements could lead to subtle changes in the apparently uniform solid solution matrix (i.e., subtle differences in the concentration of all elements within the alloy), without altering too much its naturally homogenous distribution of the different atomic species. For HEAs, such fine effects, enhanced or diminished by the varied diffusion rates within such complex environment, could be as relevant in determining their final properties, in a way similar to how the inclusion of small amounts of a given minority addition could have in a two-element based alloy. One of the many questions that arise is then how to predict, visualize, or model such relatively minor changes, that could have rather significant consequences on the final properties of the HEA, and thus minimize the necessarily extensive experimental work.

The purpose of this communication is to shed some light on that question. To answer it, a quantum approximate method which, due to its formulation, provides an efficient framework for dealing with multicomponent systems, is applied to the study of CoCrFeNi and its derivative system CoCrFeNiMn, in order to determine changes in properties due to the addition of Mn. Covering the range between 0 and 25 at.% Mn, modeling of these systems shows that there is a peculiar behavior of the melting temperature as a function of Mn concentration, which exhibits a maximum value for a relatively low Mn concentration (8.7 at.%), somewhat away from the equimolar case but still within the range of the fcc solid solution (which, as modeling shows, is conserved for all values of Mn concentration). This feature has not been determined experimentally, as studies are limited to only two cases: $x_{Mn} = 0$ and 20 at.% [15,26,27]. Other than the serendipitous finding while examining this 5-element system theoretically, there is no reason why any experimental work should or could be intended to find such unexpected anomaly. The fact that it is predicted by the calculations, suggests that as the concentration of Mn increases, processes are set in motion that manifest themselves via one very important macroscopic property of the HEA. The modeling shows that this can be explained with subtle changes in the atomic distribution within the solid solution. As such, and somewhat regardless of whether this feature is desired or not for any specific application, this test case constitutes an example of how simple atomistic modeling could help the alloy design process by minimizing the costly and lengthy experimental work. This test system, CoCrFeNiMn, besides the reasons listed above, is particularly suited for this study, as several previous studies provide an experimental basis for validation of the parameterization of the modeling tool. It is also interesting to see that while changes on the concentration of the variable element (in this case, Mn) may lead to rather noticeable changes in the melting temperature, these are not reflected in other properties. This could be a point of interest in the process of HEA design, as it provides a path to follow in the otherwise blind search for additions that will not alter the basic phase structure of the alloy but focus on desired changes in specific properties. Regarding the modeling tool used in this work, the Bozzolo-Ferrante-Smith (BFS) method for alloys [29,30] (using parameters determined via first principles calculations [31]), this analysis may prove it to be a versatile tool for dealing with such complex systems, as it has been shown that it is equally accurate for simple binary systems as well as for multicomponent alloys. As a proof of concept, the BFS method has been applied to ternary, quaternary, and quinary alloys [33,37–40], and it has been also used to predict complex phenomena such as lanthanide migration in nuclear fuels, involving as many as 15 elements [41].

2. The BFS method for alloys

The BFS method is a quantum approximate method suitable for applications to multicomponent systems [29,30]. The method is based on the notion that the energy of formation of a given atomic configuration (with unrestricted number and type of elements) can be defined as the superposition of the individual atomic contributions, $\Delta H = \sum \varepsilon_{i.}$ Each individual contribution ε_i consists of a strain energy term,ε_i^S, which accounts for the change in geometry relative to a single monoatomic crystal of the reference atom *i*, and a chemical energy term, ε_i^C, where every neighbor of the reference atom *i* is in an equilibrium lattice site of a crystal of species *i*, but retaining their chemical identity. To completely separate the effect of changes in geometry (strain energy) from changes in chemical composition (chemical energy), a reference term, $\varepsilon_i^{C_0}$, is added in the calculation of the chemical energy, computed in the same way as ε_i^C, but where the neighbors of the reference atom have the same identity as the reference atom. A coupling function, g_i, ensures the correct volume dependence of the chemical energy contribution (i.e., the chemical energy vanishes at large interatomic distances). The net contribution ε_i to the total energy of formation is then

$$\varepsilon_i = \varepsilon_i^S + g_i(\varepsilon_i^C - \varepsilon_i^{C_0}) \quad (1)$$

The parameters needed for the calculation of the different contributions are easily determined using the Linearized Augmented Plane Wave method [31]. The single element parameters are obtained from the zero temperature equation of state of the pure fcc solids, while the interaction parameters needed for the calculation of the chemical energy are obtained from the energy of formation as a function of volume curves for each and every one of the fcc-based binary combinations of all the elements. A full description of the steps needed to compute the different terms in Eq. (1), as well as the parameters, can be found in Ref. [29]. The bulk modulus can be computed from the energy of formation as a function of volume. Using the expression for the universal binding energy relationship (UBER) [32], the scaling length *l*, which describes the curvature of the curve at equilibrium, can be computed and related to the bulk modulus as

$$l = \sqrt{\frac{E_a}{12\pi B_0 r_{WSE}}} \quad (2)$$

where E_a is the cohesive energy per atom, B_0 is the bulk modulus, and r_{WSE} is the equilibrium Wigner-Seitz radius. E_a, r_{WSE} and *l* can be obtained by fitting the energy of formation as a function of volume to the universal expression. Finally, temperature effects are obtained from large scale Monte Carlo simulations, described in detail in Ref. [33]. For the coefficient of thermal expansion (CTE), we implemented the approach described and illustrated in [34]. We refer the reader to Ref. [34], as a full description of the methodology and the operational equations proves to be too lengthy for this paper. The heat capacity, C_v, was computed using the expression in Ref. [35].

$$C_v = \frac{\alpha B_0 V}{\gamma} \quad (3)$$

where α is the CTE, B_0 is the bulk modulus, V is the atomic volume, and γ is Grunesein's constant. This can be written in terms of previously computed quantities [36], leading to

$$C_v = \frac{E_a \alpha V}{4.56\pi\, r_{WSE}^2 l} \quad (4)$$