The effect of atomic radius modification on topological parameters of high-entropy alloys

Raphael Basilio Pires Nonato
University of Sorocaba (UNISO), Sorocaba – SP,
and Federal Institute of Santa Catarina (IFSC), Chapecó – SC

Thomaz Augusto Guisard Restivo
University of Sorocaba (UNISO), Sorocaba – SP

ABSTRACT
The atomic radii of the elements involved in the composition of metal alloys, especially high-entropy alloys (HEAs), change due to the specific local interaction between the atoms. This fact leads to an update in the atomic radii of the elements involved that depends on the alloy constituents. This update reflects a more realistic prediction of the alloy's behavior. In this particular, one of the most widespread approaches in terms of HEAs design is the parametric one. Therefore, in this paper we calculate topological parameters of HEAs considering two conditions: (a) atomic radii as pure metals (without atomic radii modification); (b) atomic radii in the context of the designed alloys (with atomic radii modification). Both results are compared to analyze the impact of the radii update in the HEAs designed. The former is calculated via the software DIAMOY 2.0, and the latter is obtained via DIAMOY 3.0. When comparing the conditions before and after atomic radii modification, the results show that the topological parameters increased up to 330%, which turned the statuses of the parameters inadequate to form solid solution.

Keywords: High-entropy alloys, Multicomponent alloys, Alloy design, Atomic radius.

1 INTRODUCTION

A wide variety of materials was developed by researchers all over the world aiming at providing responses to a great sort of demands. Noticeably, among the main concerns about a material, properties are here highlighted. The properties of a material directly affect its performance and are consequence of its structure, which, in turn, depends on the manufacturing processes employed in the obtainment of the referred material. In the context of metallic materials, they can be classified as pure metals or metal alloys. Although the former class may represent the solution in many practical situations, they usually present limited properties (which restricts their application) (RAZUAN *et al*., 2013). A commonly applied alternative is the traditional alloys, consisting of one or two main elements (SHUN *et al*., 2012).

The multicomponent alloys, which contains three or more main elements, expand the list of possible solutions to more complex requirements (VARGAS-OSORIO *et al*., 2023). In terms of structure, they may present intermetallic compounds associated with complex microstructures, resulting in undesired properties.

These multicomponent alloys commonly present interstitial compounds (Hagg phases). Under nonequilibrium conditions, some of these compounds form metallic glasses.

Aiming at forming solid solutions without intermetallic compounds, high-entropy alloys (HEAs) were then proposed. The design scope of HEAs covers at least 5 up to 13 main elements (with molar fraction from 5 to 35%). The residual elements have molar fraction of less than 5%. In the solidification process, HEAs present high entropic effects (which tends to induce simple solid solutions) (CARLUCCI *et al*., 2024).

The large variety of possible HEAs turn the task of obtaining all of them unfeasible (CANTOR, 2014). Therefore, four main approaches are commonly applied to design HEAs: (a) machine learning, which is a computational tool to statistically explore the design space (BUTLER *et al*., 2018) (b) calculation phase diagrams (CALPHAD) (ZHANG *et al*., 2012) (ZHANG *et al*., 2014); (c) molecular dynamics (MD) simulations (GAO; ALMAN, 2013) (XIE *et al*., 2013); (d) parametric approach, in which an ensemble of parameters and criteria are applied (TAZUDDIN *et al*., 2016) (TAZUDDIN *et al*., 2017).

The focus of this paper is on the parametric approach (ab-initio or first-principles calculations), which consists of calculating an ensemble of parameters and observing some criteria. The main objective of this approach is to predict if the resulting alloy will be a solid solution, an amorphous one, or will have intermetallic compounds. Quantum physical laws are the basis to the existing parameters and criteria. The parametric approach presents a great variety of parameters and criteria, in which some of them are selected according to the specific HEA to be designed. In view of this, there is a relative difficulty in selecting the most adequate collection of parameters and criteria to achieve the solid solution stability. This difficulty is often surpassed by selecting the most relevant and frequently reported in the literature. The referred approach does not need experimental data and has a high predictive capacity. On the other hand, it has a high computational cost because of the necessity to scan a large design space.

In the context of the parametric approach, some topological parameters include the atomic radii of the involved elements in their formulation. Commonly, the atomic radii of the involved elements are considered as the values presented in pure metals. However, in alloys, there is a change of local electronic environment, implying a modification of atomic radii. This type of modification is relevant to the formation of amorphous, crystalline, and intermetallic compounds because the radii update influences the lattice distortion (HU *et al*., 2017).

In view of this, topological parameters of HEAs are calculated in this paper observing two separate situations: (a) atomic radii of pure metals involved (without atomic radii modification); (b) atomic radii in the context of the designed alloys environment (with atomic radii modification). The results from both situations are then compared to analyze the impact of the radii modification in the designed HEAs. The former situation is calculated via the software DIAMOY 2.0 (NONATO; RESTIVO, 2023), and the latter is obtained via the updated software DIAMOY 3.0.

2 CALCULATION OF THE PARAMETERS WITHOUT MODIFICATION (AS IN PURE METALS)

This calculation is extracted from (NONATO; RESTIVO, 2023), in which the following parameters related to the radii of the elements are calculated: (a) atomic radii difference; (b) mean atomic radius; (c) polydispersion of atomic radii; and (d) topological discrepancy. The input data were typed in the software named DIAMOY 2.0 and seven output data were extracted from it for each alloy. Metal alloys 6 and 4 (RESTIVO; RESTIVO, 2021) were subjected to calculation in DIAMOY 2.0, obtaining the results found in Fig.1 and Fig. 2, respectively.

In addition to the four parameters, three statuses were also defined: (a) status of atomic radii difference; (b) status of polydisperdion of atomic radii; and (c) status of topological discrepancy. Although the screens in Fig. 1 and Fig. 2 show twenty parameters and five statuses, in this paper the focus is on the four parameters and three statuses already mentioned because only these four parameters are function of the atomic radii. For easiness of view, Tab. 1 presents only the referred information for alloy 6 and 4.

Table 1: Four parameters and three statuses for alloys 6 and 4 before radii modification (BRM).

Input data	Alloy 6, A6	Alloy 4, A4
Atomic radii difference, ARD, (%)	14.286	14.286
Status of atomic radii difference, $SARD$, (OK/NOK)	OK	OK
Mean atomic radius, MAR, (pm)	134.614	132.027
Polidispersion of atomic radius, $PDAR$	0.052	0.059
Status of polydispersion of atomic radii, $SPAR$, (OK/NOK)	OK	OK
Topological discrepancy, TD	1.179	1.181
Status of topological discrepancy, STD, (OK/NOK)	NOK	NOK

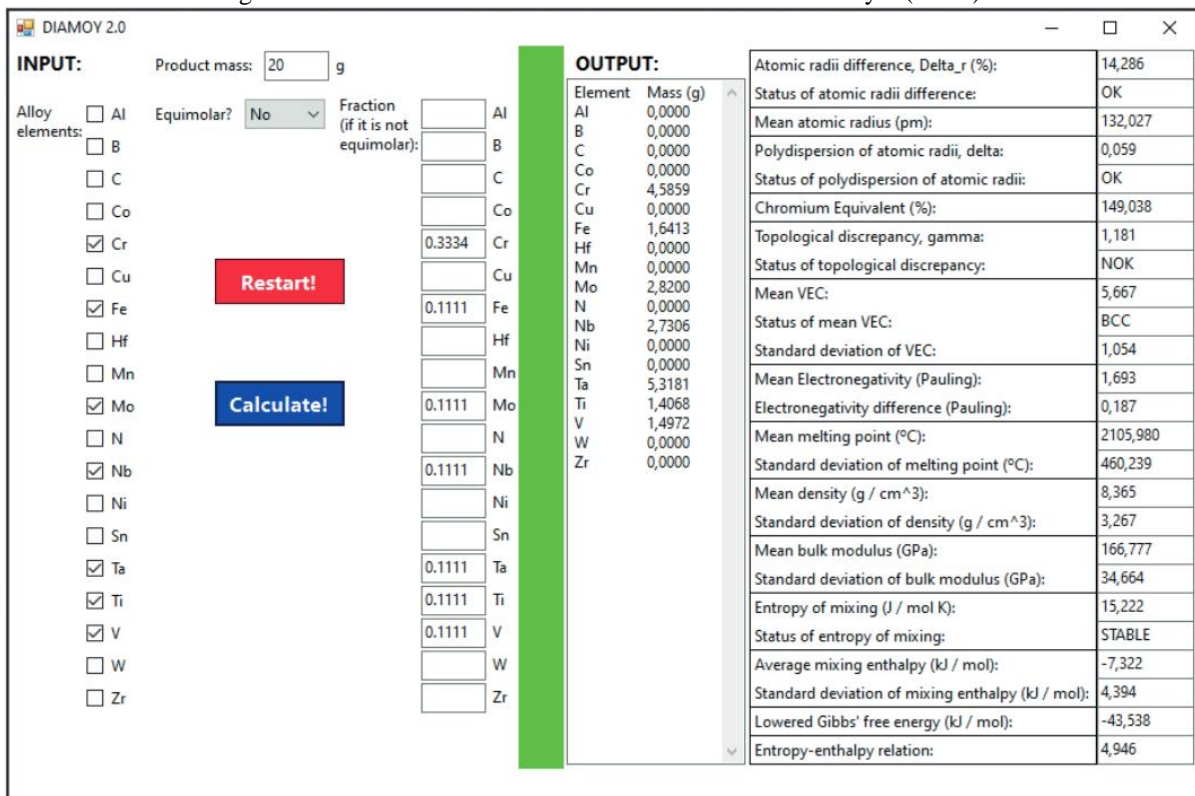**Source:** own authorship (2024).

Figure 1: DIAMOY 2.0 screen with the results for metal alloy 6 (BRM).
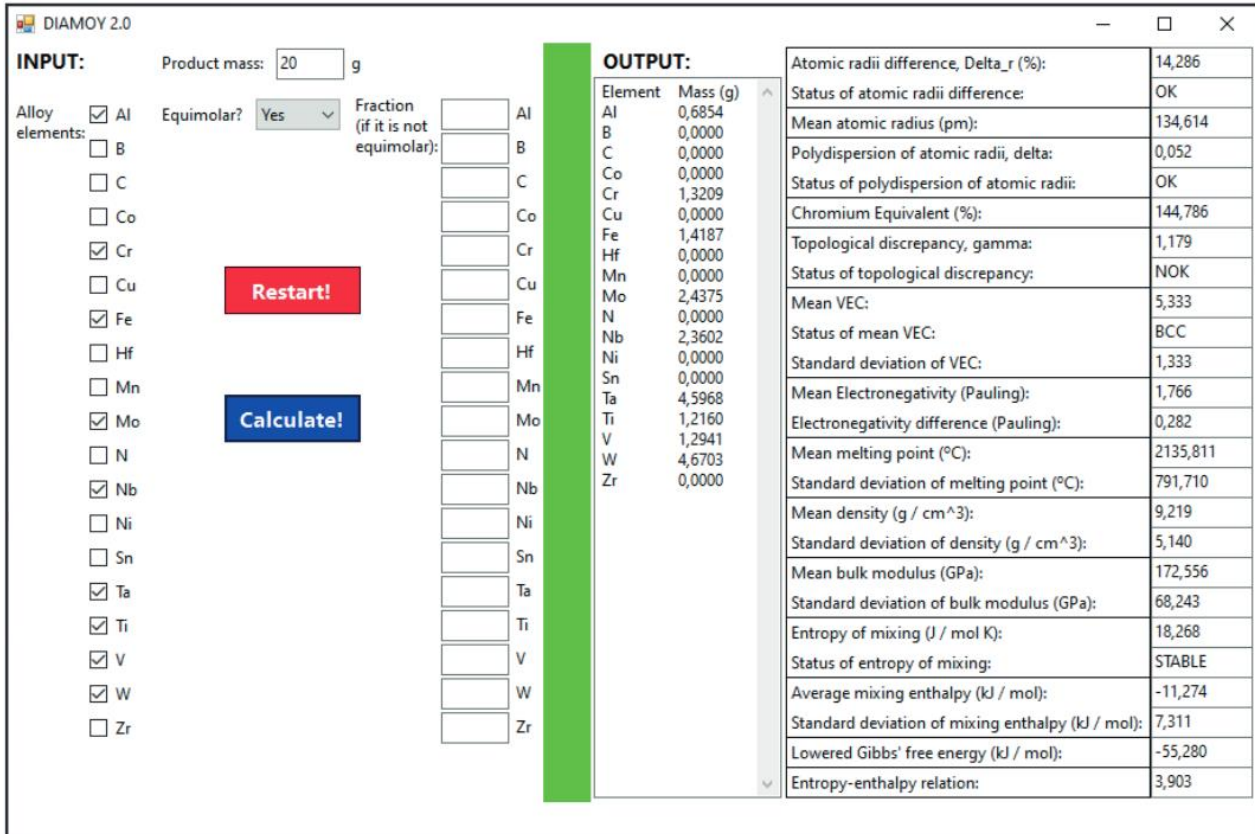
Source: NONATO; RESTIVO, 2023.

Figure 2: DIAMOY 2.0 screen with the results for metal alloy 4 (BRM).

Source: NONATO; RESTIVO, 2023.

3 CALCULATION OF THE MODIFIED PARAMETERS (IN ALLOYS)

With the implementation of radii modification, the calculation via software DIAMOY 3.0 presents the results shown in Tab. 2 for alloys 6 and 4, in what refers to the selected parameters and statuses. Fig. 3 and Fig. 4 present the screens of the software DIAMOY 3.0 for alloys 6 and 4, respectively.

Table 2: Four parameters and three statuses for alloys 6 and 4 after radii modification (ARM).

Input data	Alloy 6	Alloy 4
Atomic radii difference, *ARD*, (%)	51.720	51.720
Status of atomic radii difference, *SARD*, (OK/NOK)	*NOK*	*NOK*
Mean atomic radius, *MAR*, (pm)	135.924	133.683
Polidispersion of atomic radius, *PAR*	0.224	0.204
Status of polydispersion of atomic radii, *SPAR*, (OK/NOK)	*NOK*	*NOK*
Topological discrepancy, *TD*	2.237	2.189
Status of topological discrepancy, *STD*, (OK/NOK)	*NOK*	*NOK*

Source: own authorship (2024).

Figure 3: DIAMOY 3.0 screen with the results for metal alloy 6 (ARM).

Source: own authorship (2024).

Figure 3: DIAMOY 3.0 screen with the results for metal alloy 4 (ARM).

Source: own authorship (2024).

4 DISCUSSION

The results for alloys 6 and 4 are simultaneously shown in Tab. 3. By observing the results from DIAMOY 2.0 (before radii modification) and from DIAMOY 3.0 (after radii modification), all the parameters have increased. Consequently, now all the statuses are with the status of "NOK".

The first column refers to the parameters and statuses in their abbreviated form. The next three columns refer to alloy 6 (before radii modification, after radius modification, and the percentual relative error between "before" and "after" radii modification). The last three columns analogously refer to alloy 4.

Table 3: Comparison of the parameters and statuses for alloys 6 and 4 before (BRM) and after (ARM) radii modification.

Input data	A6 (BRM)	A6 (ARM)	A6 (%)	A4 (BRM)	A4 (ARM)	A4 (%)
ARD (%)	14.286	51.720	262.033	14.286	51.720	262.033
$SARD$ (OK/NOK)	OK	NOK	NA^*	OK	NOK	NA^*
MAR (pm)	134.614	135.924	0.973	132.027	133.683	1.254
PAR	0.052	0.224	330.769	0.059	0.204	245.763
$SPAR$ (OK/NOK)	OK	NOK	NA^*	OK	NOK	NA^*
TD	1.179	2.237	89.737	1.181	2.189	85.351
STD (OK/NOK)	NOK	NOK	NA^*	NOK	NOK	NA^*

Source: own authorship (2024). *NA stands for not applicable.

In the case of the parameter "atomic radii difference, ARD (%)", now the first rule of Hume-Rothery is violated, which leads to alloys 6 and 4 not forming a stable solid solution. The comparison between before and after the radii modification shows a considerable increase of 262.033% in this parameter.

The parameter "mean of atomic radius, MAR (pm)", presents its maximum positive variation in alloy 4 (1.254%), and its minimum positive variation in alloy 6 (0.973%). This result makes MAR higher than before, probably causing a higher lattice distortion, which may be an advantage in the design of hard alloys.

The "polydispersion of atomic radii, PAR" parameter is responsible for the highest positive variation of all the parameters. 245.763% for alloy 4, and 330.769% for the alloy 6. The solid solution tends to fbe stable in the case this parameter is within the range [1.1%, 6.6%], which it is not the case when the atomic radii is modified.

The parameter "topological discrepancy, TD," presents an increase of 85.351% in alloy 4, and 89.737% in alloy 6. In order to form a solid solution, TD has to be lower than 1.175. Although this parameter for the alloys 6 and 4 is already higher than the acceptable limit (before radii modification), TD after radii modification is even more distant from this limit, which makes more difficult to form a stable solid solution.

5 CONCLUSIONS

This paper presented the calculation of topological parameters and statuses of HEAs based on the parametric approach design before and after the atomic radii modification. The main concept relies on the change of local electronic environment in alloys. The extremely hard multicomponent alloys 6 and 4 were calculated in the software DIAMOY 2.0 (without atomic radii modification) and in the software DIAMOY 3.0 (with atomic radii modification), respectively.

In addition, the concept of HEAs was defined, differentiating HEAs from other multicomponent alloys. HEAs were also distinguished from pure metals and from the conventional alloys.

The results for the designed alloys (6 and 4) showed that the atomic radii modification moved the results away from the accepted limits and ranges to form solid solutions, i.e. it is less likely to form stable solid solutions after modification of atomic radii.

Therefore, based on this paper, the results presented for alloys 6 and 4 showed a large discrepancy between before and after radii modification. Other alloys may be subjected to this type of calculation in order to expand the list of possibilities of analysis, and consolidate the conclusions obtained in this paper.

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