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Modeling of high entropy alloys of refractory elements

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ABSTRACT

Reverting the traditional process of developing new alloys based on one or two single elements with minority additions, the study of high entropy alloys (HEA) (equimolar combinations of many elements) has become a relevant and interesting new field of research due to their tendency to form solid solutions with particular properties in the absence of intermetallic phases. Theoretical or modeling studies at the atomic level on specific HEA, describing the formation, structure, and properties of these alloys are limited due to the large number of constituents involved. In this work we focus on HEA with refractory elements showing atomistic modeling results for W–Nb–Mo–Ta and W–Nb–Mo–Ta–V HEA, for which experimental background exists. An atomistic modeling approach is applied for the determination of the role of each element and identification of the interactions and features responsible for the transition to the high entropy regime. Results for equimolar alloys of 4 and 5 refractory elements, for which experimental results exist, are shown. A straightforward algorithm is introduced to interpret the transition to the high entropy regime.

Development and analysis of high entropy alloys (HEA), alloys with several elements in equimolar concentrations, have become a growing field of research due to their unusual properties. Their high entropy of mixing (especially for combinations of five or more elements) tends to stabilize solid solution phases instead of intermetallic phases. Most of the research in this area has focused on mixing late transition metals leading to fcc (or bcc) solid solutions [1–16], but the recent work of Senkov et al. [17] pioneered the search for HEA with refractory elements. Their work on W–Nb–Ta–Mo and W–Nb–Ta–Mo–V remains so far the only experimental report on such HEA, with a complete description of their unusual properties. With the exception of the Ta–V system, which forms a TaV_2 ordered phase at low temperatures, all the other binary combinations form continuous solid solutions so, in a way, it is not surprising that the 4- and 5-element alloys also stabilize in a rather featureless solid solution. Because of that, these alloys might not be the best example to demonstrate and quantify the high entropy effect but, as it will be seen below, they are, as they facilitate the investigation of those properties that ultimately lead to the typical HEA outcome. One fundamental question that could and needs to be answered is when does a multicomponent system transition to the high entropy regime, as opposed to characteristic outcomes more appropriate of lower dimensional systems, where majority constituents lead to the formation of complex intermetallic compounds. Should such transition be understood, it would facilitate further research on other HEA and, from a practical standpoint, help modify their composition in order to achieve the desired effects. In this work, therefore, we apply an atomistic modeling approach to determine, from modeling data, the order parameters that govern these alloys and gain insight on the qualitative and quantitative features that lead to the characteristic high entropy effect. The approach is based on the application of the Bozzolo–Ferrante–Smith (BFS) method for alloys [18], which is ideally suited for the study of multicomponent systems, as shown in previous applications to rather complex systems [19–22]. We refer the necessary details of the method, the parameterization needed to perform the simulations, details on the standard Monte Carlo – Metropolis algorithms, and operational equations of the method to previous applications to multicomponent systems [19–22].

Simulated annealing, from high to room temperature, was performed to determine the phase structure of the same alloys studied by Senkov et al. [17], namely, $W_{27.3}Nb_{22.7}Mo_{25.6}Ta_{24.4}$ and $W_{21.1}Nb_{20.6}Mo_{21.7}Ta_{15.6}V_{21}$. Keeping in mind that these simulations do not properly address atom mobility, the results should only be taken as an indication of the underlying trends towards the formation of ordered domains or precipitates, which might not necessarily be observed under diverse experimental conditions.

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The simulation of the quaternary alloy shows three regimes. The high temperature regime ($T > 2000$ K) is characterized by a continuous solid solution with no distinguishable features regarding order or the formation of precipitates. For intermediate temperatures ($T \sim 1000$ K), Ta interactions with other atoms are activated, leading to the formation of Ta-rich domains within the computational cell. At low temperatures ($T < 400$ K), Mo shows signs of inducing short range order, although not strong enough so as to lead to the formation of clearly ordered second phases. This behavior can be illustrated with the evolution of the short-range order matrix ρ_{AB} (the probability that an atom A has an atom B as a nearest-neighbor, on average, throughout the whole computational cell). Fig. 1 shows the evolution with temperature of ρ_{WX}, ρ_{NbX}, ρ_{MoX}, and ρ_{TaX}, where X represents, in each case, either one of the other three elements. The solid solution manifests itself in the similarity of all curves (at higher temperatures), close to the nominal concentration of each element. The intermediate temperature regime is observed in the drastic change in ρ_{XTa}, indicating the formation of Ta-rich domains. Further activity by Mo is also seen in the changes in ρ_{MoX} in the remaining cases (at much lower temperature). It can be concluded that Ta is the element that has the most significant effect threatening the stability of the solid solution. This is even more striking in the 5-element alloy, due to the expected Ta–V interactions which lead to the formation of TaV_2 in the binary system below $T=1500$ K. Comparison of the evolution of the ρ matrix elements shows the effect of V to be more profound, leading to the breakdown of the solid solution at higher temperatures than those observed in the quaternary case. This, however, does not change the fact that Ta interactions with other elements, including V, are dominant, ultimately leading to a low temperature atomic structure similar to that of the quaternary alloy but with the significant presence of Ta–V ordering. Fig. 2 illustrates the differences between the 4- and 5-element alloys, showing the evolution of ρ_{TaX} with temperature.

Other (minor) changes leading to order are seen at very low temperatures, but they can be attributed to the nearly infinite diffusion characteristic of this type of simulations, not bound to be seen experimentally. Based on the behavior described above, it is then expected that Ta will play a significant role in the evolution of these alloys enhanced, in the 5-element case, by the presence of V.

Significant ordering trends (characteristic of the low temperature regime) compete with the underlying principle of HEA, where equal amounts of each element favor the formation of a continuous solid solution. This suggests that the transition to a high entropy regime could be better understood by analyzing alloys with varying V concentration (keeping the remaining four elements in equimolar amounts). To this effect, simulations of $(WNbMoTa)V_n$ alloys, referred to as C_n with n ranging from 0 to 25 at.%, were performed, and quantities such as the equilibrium lattice parameter, cohesive energy, and bulk modulus as a function of temperature were determined in each case. As an example, Fig. 3 shows the evolution of the lattice parameter for C_n alloys. All curves $a_n(T)$ in Fig. 3 can be easily fitted to an analytical function with four independent parameters which depend on the concentration of V:

$$a_n(T) = A_2 + \frac{A_1 - A_2}{1 + (T/T_0)^p} \tag{1}$$

where the parameter T_0 is related to the inflexion point located at the 'critical temperature' T_C, given by

$$T_C = T_0 \left(\frac{p-1}{p+1}\right)^{1/p} \tag{2}$$

When T_C is plotted as a function of V concentration, as seen in Fig. 4, it is clear that there is a maximum value of T_C at $x_V = 9.38$ at.%. For smaller values of x_V, there is a steady increase in T_C with increasing V concentration, but this is reversed beyond this critical value, suggesting that this is a critical concentration

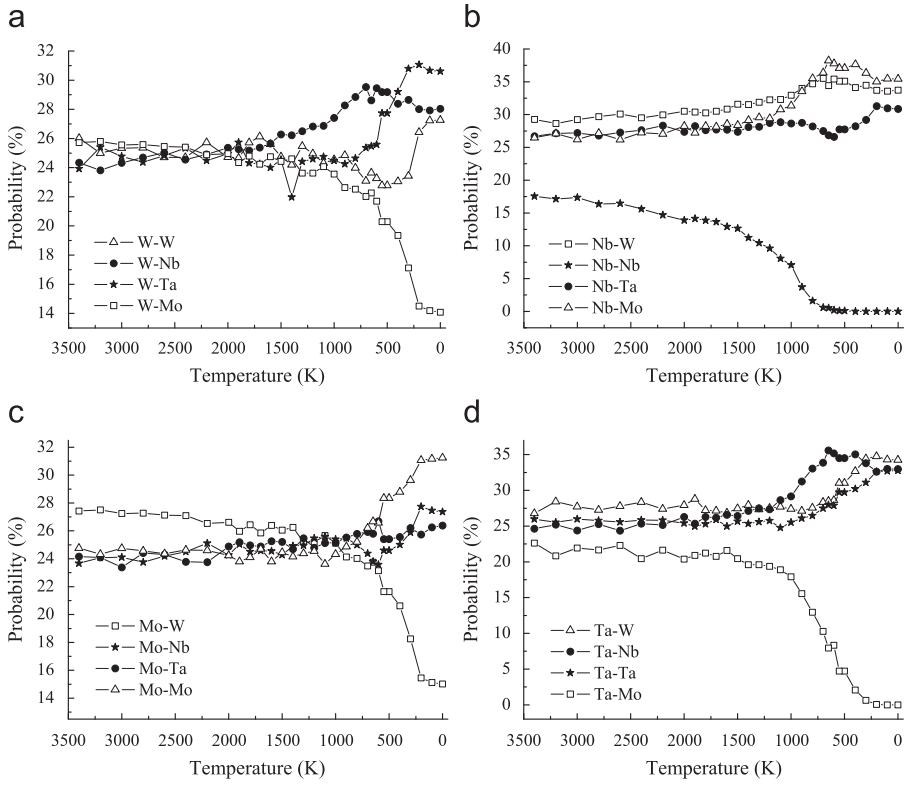

Fig. 1. Short-range order matrix elements ρ (see text) between nearest-neighbors for (a) W, (b) Nb, (c) Mo and (d) Ta as a function of temperature.

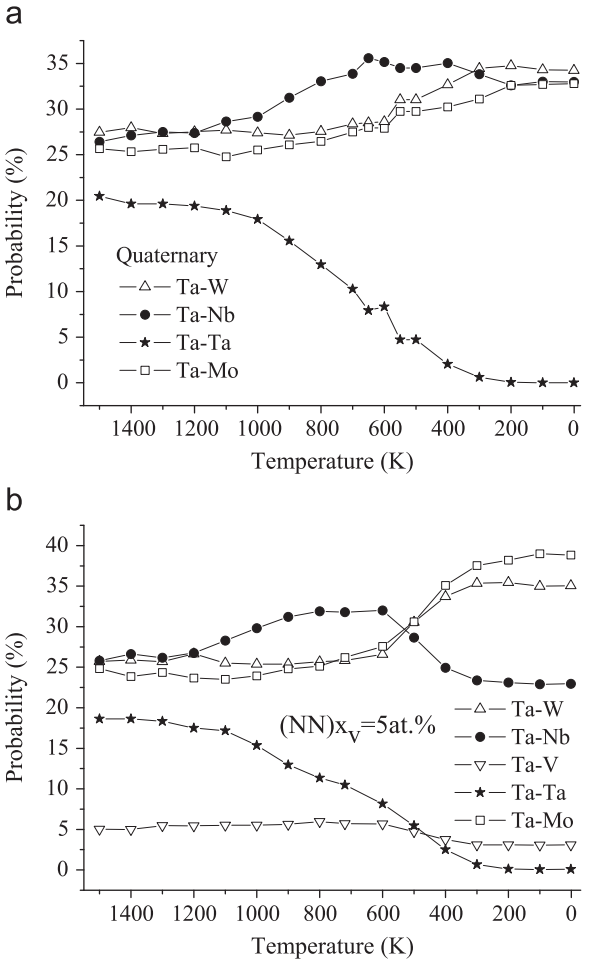

Fig. 2. Short-range order matrix elements ρ_{TaX} for the (a) quaternary (X=W, Nb, Mo) and (b) 5-element (X=W, Nb, Mo, V) alloys as a function of temperature (for $T < 1500$ K).

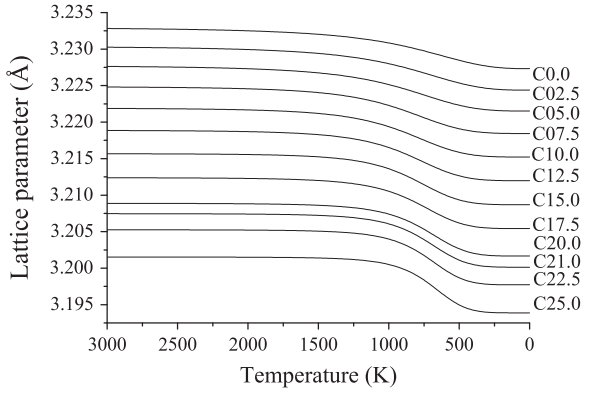

Fig. 3. Lattice parameter (in Å) as a function of temperature (in K) for C_n alloys ($0 < n < 25$) where n denotes the concentration of V.

for which the system transitions to a regime where the concentration of V is sufficiently high to let the high entropy behavior dictate the structure of the alloy. Not surprisingly, the values of T_C are highly dependent on the onset of Ta–V interactions leading to the elimination of the solid solution regime with descending temperature, as can be seen in Fig. 1a.

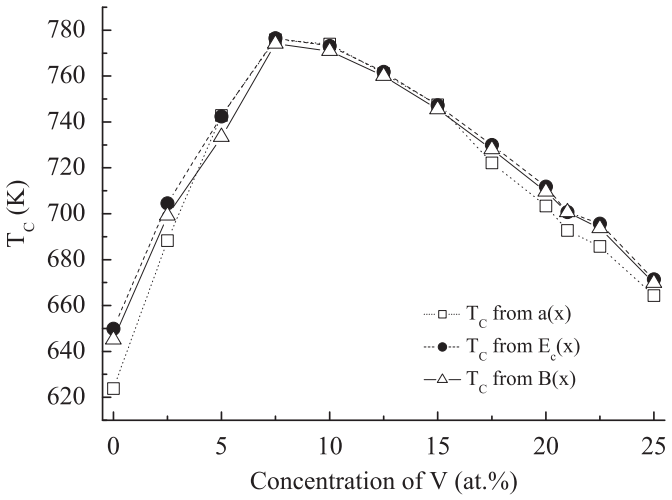

Fig. 4. Critical temperature T_C as a function of V concentration, obtained from the temperature dependence of the (a) lattice parameter, (b) cohesive energy, and (c) bulk modulus of the corresponding C_n alloys.

Summarizing, atomistic modeling of 4- and 5-elements alloys suggests that it is possible to quantify the transition to a high entropy regime characterized by the formation of a continuous solid solution, to a great extent regardless of the individual interactions which would otherwise lead to the formation of precipitates. Based on a simple analysis, a critical concentration can be determined to establish such transition.

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