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Thermodynamics of vacancies and clusters in high-entropy alloys

Zhijun Wang,^{1,*} C. T. Liu,² and Peng Dou³

¹State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

²Center of Advanced Structural Materials, Department of Mechanical and Biomedical Engineering, College of Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong, China

³Department of Materials Engineering, Chongqing University, Chongqing, China

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By means of thermodynamic analyses, we provide the intriguing evidence that the equilibrium vacancy concentrations and their clusters in high entropy alloys (HEAs) are substantially larger than those in pure metals and simple binary alloys. The increased defect concentrations strongly change the thermodynamic and kinetic properties of the HEAs. With these findings, we predict a strong recombination tendency of vacancies and interstitials after excitation from radiation bombardments, and the results are favorably compatible with very recent experiments on the superior radiation resistance of HEAs. The thermodynamics of vacancies and clusters in HEAs will be of great interest to the design of advanced materials involving many thermodynamic and kinetic properties such as thermal conductivity, diffusivity, precipitation, creep, and irradiation damage.

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I. INTRODUCTION

High entropy alloys (HEAs), or concentrated multicomponent alloys, are attracting much attention recently [1–4]. Solid solutions formed by mixing equiatomic alloying elements are not favorable in traditional physical metallurgy. However, some recent studies of HEAs provide the chance for physical metallurgists and material scientists to seriously reconsider solid solution alloys with concentrated multicomponent elements. Surprisingly, a number of multiple concentrated solid solution alloys with fcc structures exhibit excellent toughness and ductility due to the unusual behavior in twinning and stacking fault at ambient and cryogenic temperatures [5–8]. Now, another amazing feature of an extraordinary radiation tolerance has been confirmed very recently by several papers in 2016 [9–11], indicating the superior resistance to radiation damage of some HEAs, which have the potential to be developed as the next generation radiation tolerant structural materials.

The mechanism of radiation-damage resistance in conventional alloys has been explained by reduced dislocation mobility and tailored interstitial defect cluster motion [4,12]. Besides these possible reasons, some other factors may also play an important role. For instance, it has been confirmed that the intrinsic defective structure of nanoclusters formed in oxide-dispersed strengthening (ODS) alloys can naturally tolerate radiation-induced damage [13]. Accordingly, the intrinsic defects in HEAs are worthy of careful studies for radiation resistance. It is well known that solid solution alloys usually contain intrinsic defects, such as point defects, which play an important role in many phenomena related to the thermodynamic and kinetic properties of alloys. As a result, the equilibrium defects concentration can be altered by changing overall alloy concentration and components, as well as their configuration entropy. Thus, by means of thermodynamic analyses, we are able to reveal a new intriguing phenomenon of vacancy in multiple component alloy systems such as HEAs.

II. VACANCY CONCENTRATION IN HEAs

It is well known that the thermodynamics of intrinsic point defects in pure metals follows the Arrhenius rule of $x_1 = \exp[-u/(kT)]$, where x_1 is the equilibrium concentration of the vacancy, u is the formation energy of a vacancy, k is the Boltzmann constant, and T is the temperature. In an equiatomic multicomponent solid solution system, the equilibrium concentration of vacancy will be written as [14]

$$x_n = \frac{\exp(n - 1 - \frac{u_n}{kT})}{n + \exp(n - 1 - \frac{u_n}{kT})}, \quad (1)$$

where n is the alloying number of the elements and u_n is the formation energy of a vacancy in an equiatomic multicomponent system with n components (different from the u in pure metal). By setting of $n = 1$, Eq. (1) will be reduced to the case of pure metal simply because $\exp[-u/(kT)]$ is much smaller than 1. It is important to point out that the equilibrium vacancy concentration is determined by the alloying number, the vacancy formation energy, and temperature.

First, let us focus on the effect of configuration entropy by simply supposing that the formation energy of a vacancy do not change as the alloying number increases. The variation of vacancy concentration with the alloying number will be given by the equation [14]

$$x_n/x_1 = \frac{\exp(n - 1)}{n + \exp(n - 1 - \frac{u_n}{kT})} \approx \frac{\exp(n - 1)}{n}, \quad (2)$$

the value of which is plotted in Fig. 1 as a function of n . For quinary HEAs, the equilibrium vacancy concentration becomes one order of magnitude larger than that in a pure metal. Even in the binary alloys, the equilibrium vacancy concentration is 1.36 times larger than that in the pure metal. Thus, this plot reveals that the configuration entropy effect in HEAs can greatly enhance the intrinsic vacancy concentration. The variation of equilibrium vacancy concentration in HEAs can be estimated based on Eq. (1). To do so, we should carefully consider the choice of vacancy formation energy in HEAs. It should be noted that even in pure metal it is very difficult to obtain the precise vacancy formation

*Corresponding author: zhjwang@nwpu.edu.cn

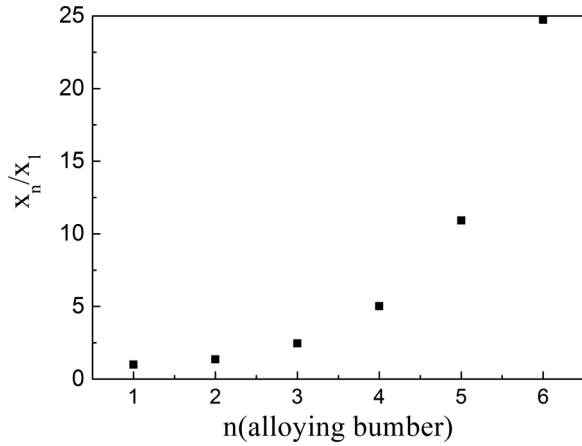


FIG. 1. The increased vacancy concentration from the contribution of configurational entropy compared with the pure metal in equiatomic HEAs with n components.

energy whether by theoretical calculations or experimental measurements [15–17]. The disparate results of the vacancy formation energy have led to a longstanding controversy. In a real system, the data of vacancy formation energy in multicomponent random solid solutions are scarce based on both the experimental and theoretical aspects. The *ab initio* approach has established that the local atomic environment around a vacancy plays a significant role [18–20]. The vacancy complexes in the analyses of binary alloys indicate that the possible configuration around a vacancy may be very different. The vacancy formation energy in alloys is the mean field of vacancy formation energy of different configuration [15]. In HEAs, there are even more configurations around a vacancy. The vacancy complexes imply the preferred configuration surrounded by favorable solute atoms with a lower vacancy formation enthalpy. Figure 2 sketches the atomic configuration around a vacancy in concentrated multicomponent solid solution alloys. The configuration of Fig. 2(b) is more energetically favorable due to a lower binding energy and a lower lattice distortion between the vacancy and solute atoms around it. In the consideration of very small vacancy concentration, the change of the local atomic configuration around vacancy only has a small effect on the whole configuration entropy of the

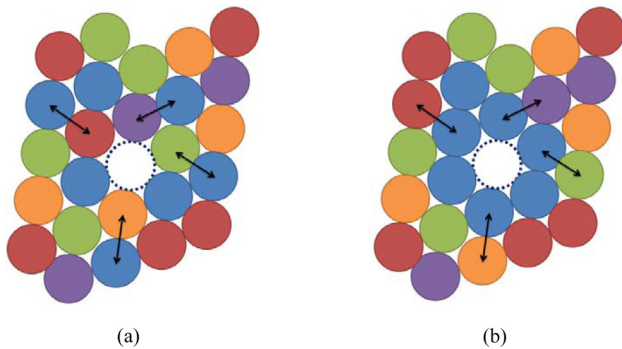


FIG. 2. A sketch of the atomic configuration around a vacancy in concentrated multicomponent solid solution alloys. (a) Random packing around a vacancy and (b) energetic favourable packing.

system, because in that case the vacancy and its local shell can be seen as a cluster in the calculation of the configuration entropy. Therefore, the vacancy formation energy in the concentrated multicomponent alloys can be approximately determined by minimizing the vacancy formation energy u_{\min} . Then u_n in Eq. (1) will be replaced by the energy of u_{\min} and could be smaller than u_n .

Here let us take NiCoFeCrMn for example to show the variation of equilibrium concentration in fcc HEAs. In this HEA alloy, the vacancy formation energy of different elements cannot be directly used because of their different crystal structures. For pure fcc Ni, the vacancy formation energy (VFE) is 1.4 eV by specific heat and electrical conductivity measurements, but 1.79 eV by positron annihilation spectroscopy measurements [15]. The theoretical calculation of VFE for bcc Fe and Cr are 2.3 and 2.8 eV, respectively [15]. For HCP Co, the VFE is 1.34 eV by positron annihilation spectroscopy measurements, but 2.22 eV by theoretical calculation [15]. In the fcc HEAs, without a better choice, we just take the 1.4 eV for all the calculations. The equilibrium vacancy concentrations at different temperatures for different configuration entropy are shown in Fig. 3(a), which shows that the vacancy concentration increases rapidly as the temperature

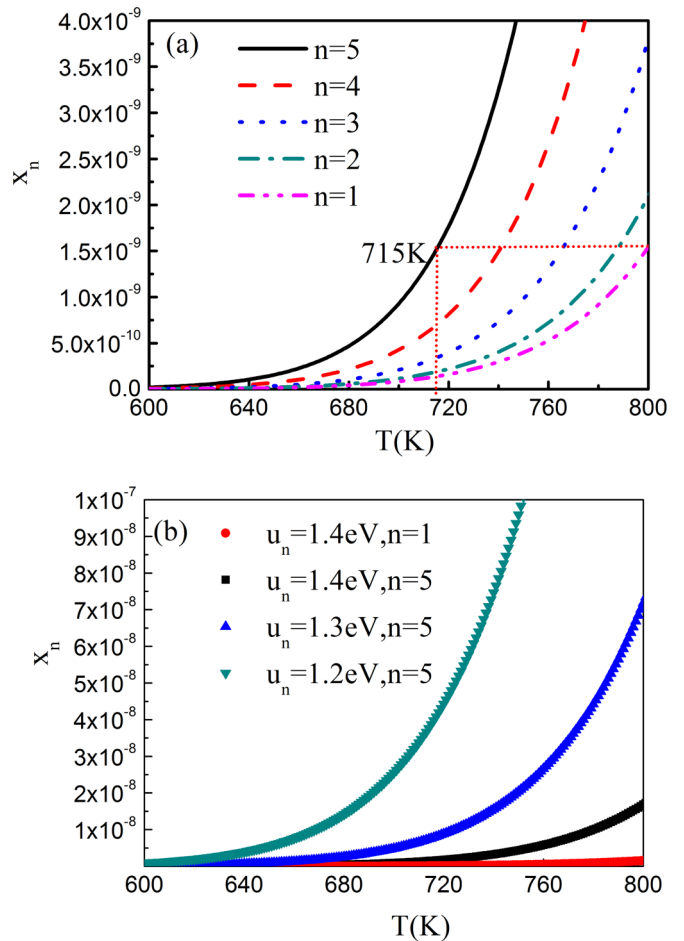


FIG. 3. Equilibrium vacancy concentrations in alloys at different temperatures. (a) The change of vacancy concentration with configuration entropy for $u_n = 1.4$ eV and (b) the change of vacancy concentration with vacancy formation energy.

increases. The increased vacancy concentration from the configuration entropy contribution in quinary alloys is equivalent to the vacancy concentration of pure metal by increasing about 85 K at this temperature range. For NiCoCrFeMn at 800 K, the vacancy concentration will be 1.68×10^{-8} , and vacancy density will be around $10^{15}/\text{cm}^3$, by assuming a molar volume of $8 \text{ cm}^3/\text{mol}$. If the vacancy formation energy can be reduced in HEAs, their vacancy concentration will further increase. As shown in Fig. 3(b), the vacancy concentration will increase by one order of magnitude when the vacancy formation energy decreases from 1.4 to 1.2 eV at the given temperature range.

The large number of equilibrium vacancy concentration may accommodate interstitial atoms generated by radiation damages. These analyses indicate that the equilibrium vacancy concentration in the HEAs will be much higher than that in pure elements, providing a strong recombination tendency of interstitial and vacancy. It will be one of the possible thermodynamic reasons for a better radiation resistance of HEAs. Moreover, the mobility of these vacancies in HEAs will be decreased due to the pinning effect of the potential well in the energetic favorable packing as shown in Fig. 2(b). In that case, the vacancy will jump forward and back near the energetic favorable state for most of the time.

III. VACANCY CLUSTERS IN HEAs

In spite of the large number of vacancies in HEAs, the recombination may not catch up with generation of interstitials and vacancies with increasing radiation damages. There will be supersaturated vacancy in the excited state with a tendency to form the vacancy cluster and void. In HEAs, the fine void distribution after a radiation was solely attributed to the slow kinetics of cluster diffusion [6]. However, the contribution of thermodynamics of defect evolution on the suppression of formation of a large size void should also be evaluated. The radiation or injected helium will make the alloys unstable and supply the driving force for the void/bubble formation. In the thermodynamics of vacancy in radiation, the nucleation of a void in the supersaturated state is the key point. Based on the traditional nucleation theory of phase transformation, the variation of the Gibbs free energy with a nucleus in the unstable state is

$$\Delta G = \Delta G_V + \Delta G_S + \Delta G_E, \quad (3)$$

where ΔG_V is the change of volume free energy, ΔG_S is the change of interface energy, and ΔG_E is the change of elastic energy which can be neglected in the bubble formation. For simplification, considering a nucleus with a radius r ,

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \gamma_{sv}, \quad (4)$$

where Δg is the decrease of Gibbs free energy for a vacancy formation, Ω_v is the volume of a vacancy, and γ_{sv} is the surface energy of a solid and vacancy bubble. The critical bubble radius and variation of Gibbs free energy will be $r_c = \frac{2\gamma_{sv}\Omega_v}{\Delta g}$, $\Delta G_c(r_c) = \frac{16\pi\gamma_{sv}^3\Omega_v^2}{3(\Delta g)^2}$. The free energy analysis does not reveal the independent contribution on the suppression of

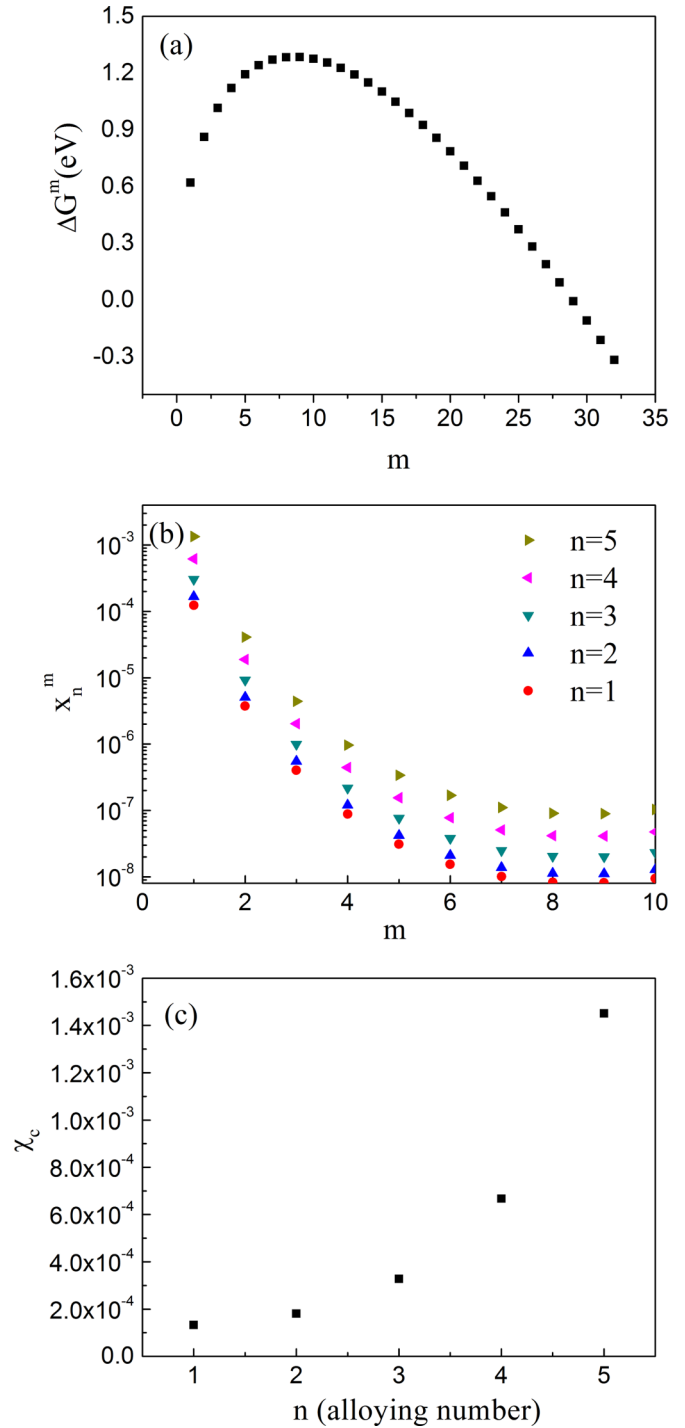


FIG. 4. The thermodynamics of cluster distribution in the HEAs after radiation. (a) The Gibbs free energy of nuclei as a function of vacancy number, (b) the concentrations of cluster with different sizes for alloys with different alloying component number, and (c) the increase of stable vacancy capacity as the alloying component increases. Here m is the vacancy number in the clusters, n is the alloying number of element in the equiatomic alloys, x_n^m is the cluster concentration, and χ_c is the stable vacancy capacity in the supersaturated state. ΔG_n^m is the change of Gibbs free energy by forming a vacancy clusters.

bubble formation by increasing the alloying number in HEAs. However, the vacancy cluster distribution depends on the configuration entropy. The concentrations of stable vacancy clusters will increase with the increasing configuration entropy in the HEAs. The vacancy cluster size distribution in the HEAs with n elements can then be described as

$$x_n^m = \frac{\exp\left(n - 1 - \frac{\Delta G_n^m}{kT}\right)}{n + \exp\left(n - 1 - \frac{\Delta G_n^m}{kT}\right)}, \quad (5)$$

with a similar derivation of Eq. (2). ΔG_n^m is the change of Gibbs free energy by forming vacancy clusters with a vacancy number of m , $\Delta G^m = m4\sqrt{2}r_0^3\Delta g + 4\pi(m4\sqrt{2}r_0^3)^{2/3}\gamma_{sv}$, where r_0 is the average atomic radius.

Even with unknown parameters, Eqs. (4) and (5) can reveal the high entropy effect on the void formation in HEAs. In the empirical analysis, these parameters are estimated as following. As there are a lot of void along the grain boundary and the grain boundary energy of metal is around 500 mJ/m² and the surface energy of metal is around 1000 mJ/m² [21], we suppose that $\gamma_{sv} = 0.06$ eV/ r_0^2 in the cluster, r_0 is the atomic radius. At 800 K, for a driving force $\Delta g = 0.3$ eV/ r_0^3 , the variation of ΔG^m with m is shown in Fig. 4(a) which gives the critical cluster of nine vacancies. The void density in the system is determined by the nucleation rate which is related to the concentration of the nucleus. The concentration distributions of the vacancy cluster for the equiatomic alloying system with different alloying numbers are shown in Fig. 4(b). On the one hand, it shows that the critical cluster number in quinary HEAs is one order of magnitude larger than that in the pure metal. It should be noted that the higher nucleation rate of voids in the HEAs is one of the fundamental reasons for the smaller size of voids in the HEAs after radiation. On the other hand, the stable vacancy concentration in the clusters is given by

$$\chi_c = \int_1^{m < m_c} m x_n^m \quad (6)$$

which indicates the damage tolerance of radiation. Figure 4(c) shows that the HEAs can accommodate many more vacancies than the traditional alloys during the radiation. The large amount of excited vacancy plays the dominant role for the enhanced self-healing effect by annihilation of interstitial atoms and vacancies in radiated HEAs. Therefore, the high entropy effect on the cluster distribution has a great contribution on the radiation resistance. There will be a distinctly higher nucleation rate of void, leading to the fine void and higher vacancy capacity for the self-healing in the HEAs.

IV. DISCUSSIONS

It should also be noted that the supersaturated vacancy can also be introduced by rapid quenching [22,23] during the alloys formation besides the radiation. The alloys are usually prepared at high temperature with a large amount of vacancy. The vacancy will be retained during the cooling. The residual vacancy at low temperature depends on the quenching rate [23]. The residual vacancy was also taken as the primary

contribution of the rapid diffusion in the initial growth of precipitation [16]. Another temperature effect related to the vacancy concentration is the depression of the melting point. The melting point of CoCrFeNi is smaller than all the melting points of single alloying elements. Moreover, the vacancy concentration near the melting point is around 10^{-4} . The contribution of mixing entropy on the freezing points is also an interpretation of its effect on the vacancy. Accordingly, the high entropy effect on the vacancy concentration in HEAs is an intrinsic physical phenomenon.

We have discussed the thermodynamics of the increased equilibrium concentration of vacancies and clusters in the HEAs. It is important to mention that these increased vacancies and clusters may affect many phenomena and thermodynamic and kinetic properties in HEAs, such as thermal conductivity, diffusivity, and precipitation. Due to the complex chemical degrees in the diffusion of HEAs, we only give an empirical discussion here. The increased vacancy concentration is closely connected to the diffusivity. In substitutional diffusion, the diffusion occurs via vacancy migration [24]

$$\begin{aligned} D &= \frac{1}{12} a^2 \frac{1}{\tau} = \frac{1}{12} a^2 Z v x_n \exp\left(\frac{-H_m}{kT}\right) \\ &= \frac{1}{12} a^2 Z v \frac{\exp(n-1)}{n} \exp\left(\frac{-u_{\min}}{kT}\right) \\ &\quad \times \exp\left(\frac{-H_m}{kT}\right) \\ &= D_0 \exp\left(\frac{-(u_{\min} + H_m)}{kT}\right), \end{aligned} \quad (7)$$

where a is the lattice constant, τ is the mean time of stay of an atom in a lattice position, Z is the lattice coordination number, v is the lattice vibration frequency, and H_m is the energy of migration of an atom. In HEAs, there is increased vacancy concentration x_n , enhancing the diffusivity, while the pinning effect of atom around the vacancy indicated by Fig. 2 may increase the H_m to decrease the diffusivity. However, the increased vacancy concentration in HEAs from Eq. (2) is related to the frequency factor D_0 , while the pinning effect is related to the increased diffusion activation energy in the measurement. The pinning effect of vacancy may also have contributions to the reduced dislocation mobility and tailored interstitial defect cluster motion in HEAs as one of the mechanism of radiation-damage resistance [6,11].

V. CONCLUSION

In conclusion, we have found the intrinsic high entropy effects on vacancy formation and void size distribution in HEAs. The equilibrium vacancy concentration is greatly enhanced by the increased configuration entropy in the HEAs. It reveals that the high entropy configuration contribution in quinary alloys is one order of magnitude larger than that in the pure metal. We also extended the analysis to the void formation during radiation damages. The concentrations of the stable vacancy cluster and the critical void nucleus are greatly increased due to the high configuration entropy in HEAs. These analyses present

TABLE I. The notations.

n	alloying number of element	x_n^m	cluster concentration
u	vacancy formation energy	m	vacancy number in the clusters
x_n	vacancy concentration	Ω_v	volume of a vacancy
r_0	average atomic radius	r	radius of void nucleus
γ_{sv}	surface energy of void	Δg	decrease of Gibbs free energy for a vacancy formation in the void
ΔG_n^m	change of Gibbs free energy by forming a vacancy clusters	χ_c	stable vacancy capacity in the supersaturated state
D	diffusivity of vacancy	H_m	energy of migration of an atom

the thermodynamic reason for much better resistance to radiation damages in HEAs. For clear reading, the key notations and their definitions are shown in Table I. Furthermore, many phenomena and properties in HEAs related to the vacancy or cluster should be reconsidered by involving the contribution of configuration entropy in these multicomponent alloy systems.

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