Critically Percolated States in High-Entropy Alloys with Exact Equi-Atomicity

Akira Takeuchi1*, Kunio Yubuta2 and Takeshi Wada2

1Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
2Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The formation of site-percolated states of exact equiatomic high-entropy alloys (HEAs) with body-centered-cubic (bcc) and face-centered-cubic (fcc) structures was investigated where their critical concentrations \( (p_{\text{crit}}) \) are given as 0.245 and 0.198, respectively, from conventional percolation theory. Molecular dynamics simulations were performed for WNbMoTa and WNbMoTaV HEAs with a bcc structure and AuCuNiPdPt and AuCuNiPdPdPt HEAs with an fcc structure. The simulation conditions included a generalized embedded atom method potential under N\( T_p \) ensemble where the number of elements \( (N) \), absolute temperature \( (T) \), and pressure \( (p) \) were maintained constant. N-element alloys \( (N = 4 \text{ and } 5) \) with a fraction of constituent elements \( (x = 1/N) \) were initially prepared in \( 10 \times 10 \times 10 \) supercells randomly in terms of chemical species and were simulated under atmospheric pressure at \( T = 1000 \text{ K} \). The total pair-distribution functions of the alloys revealed that the nearest neighbor distance \( (d_{\text{nn}}) \) for fcc ranged from 0.20 to 0.33 nm, whereas \( d_{\text{nn}} \) and the second neighbor distance \( (d_{\text{nnn}}) \) for bcc ranged from 0.235 to 0.305 nm and 0.305 to 0.370 nm, respectively. A 3-dimensional topological analysis for atomic correlations revealed that the alloys were in percolated and isolated states, respectively, when \( x < p_{\text{crit}} \) and \( x > p_{\text{crit}} \) and that the values of \( 1/p_{\text{crit}} \) correspond to the ideal values of \( N \) for exact equi-atomic HEAs. Furthermore, it was observed that exact equi-atomic quaternary alloys \( (N = 4) \) with a bcc structure and quinary alloys \( (N = 5) \) with an fcc structure are in the critically percolated states. [ doi:10.2320/matertrans.M2018216]

(Received July 2, 2018; Accepted November 5, 2018; Published December 14, 2018)

Keywords: high-entropy alloys, alloy design, phase stability, prediction

1. Introduction

Recently, significant scientific interest has been paid to high-entropy alloys (HEAs), which are exact or near-equatomic multicomponent alloys in the form of solid solutions. Specifically, HEAs form simple solid solutions of face-centered-cubic (fcc), body-centered-cubic (bcc) or hexagonal close-packed (hcp) structures such as pure metals and primary solid solutions containing minor solute elements. Some HEAs exhibit a mixture of fcc and bcc phases. Single and dual solid solutions without intermetallic compounds are formed in HEAs when the constituent elements are selected carefully, even in multicomponent alloys without primary constituent elements. For instance, single-phase HEAs include WNbMoTa and WNbMoTaV alloys with a bcc structure and AuCuNiPd and AuCuNiPdPdPt alloys with an fcc structure. The crystallographic structures of these HEAs are slightly affected by those of the constituent elements. This effect is simply interpreted by the fact that W, Nb, Mo, Ta and V elements exhibit bcc structure and are frequently called as bcc-forming elements (bcc-formers), whereas noble metals are considered fcc-formers. According to the above interpretation, it is assumed that HEAs may be formed owing to the extension of the complete solid solutions from binary to multicomponent systems.

Analogically, an extendable tendency also can be observed in percolation theory where its generalization has been performed from a two-species (black-and-white) random process to a multispecies (polychromatic) process. Initially, a fundamental percolation theory based on a “black-and-white” model has been constructed for simple lattices, such as simple cubic, bcc, and fcc lattices in binary systems. This basic model corresponds to binary alloys with two constituent elements in the field of metallurgy. Subsequently, the percolation theory has been extended so that it can be applied to complicated systems by introducing the concept of “color”. Here, the number of colors can be interpreted as the number of constituent elements (chemical species) in metallurgy. Thus, it is worth examining the applicability of polychromatic percolation theory to HEAs by utilizing the analogy underlying the percolation theory and metallurgical alloying.

Hereafter, only exact equi-atomic HEAs are considered to simplify and derive the essence of the percolation phenomena in multicomponent systems. As for the exact equi-atomic HEAs with \( N \)-elements, the fraction of each constituent element \( (x) \) is readily calculated to be \( x = 1/N \), which corresponds to 100/N atomic percent (at%). Here, the WNbMoTa and WNbMoTaV alloys refer to W25Nb25Mo25-Ta25 and W20Nb20Mo20Ta20V20 alloys (at%), respectively. These exact equiatomic HEAs encouraged us to perform theoretical and computational studies on percolation phenomena in HEAs. Specifically, the motivation of the present study resulted from early studies of percolation in which a critical concentration of site percolation \( (p_{\text{crit}}) \) of the nearest neighbor is given as 0.198 (19.8 at%) for fcc and 0.245 (24.5 at%) for bcc structures. The authors realized that these values of \( p_{\text{crit}} \) are considerably close to \( x = 1/N \) of exact equiatomic quaternary and quinary alloys. This led to an early report by Zallen in which the percolation phenomena in multi-species were discussed systematically as polychromatic percolation for a close-packed structure (fcc) and a simple cubic structure for 3- and higher-dimensional lattices. These results obtained by Zallen should be ideal data of percolation for multicomponent HEAs. However, there remain uncertainties about the validity of \( p_{\text{crit}} \) in actual HEAs. For instance, the actual HEAs possess slightly-different atomic sizes and weak negative heat of mixing among the constituent elements. In addition, the actual HEAs are affected by thermal fluctuations at a given temperature. To investigate these effects of HEAs on the formation of percolated states, it is convenient to use...
molecular dynamics (MD) simulations for actual HEAs at a certain temperature using realistic MD potentials.

The purpose of the present study is to investigate the possibility of WNbMoTa and WNbMoTaV HEAs with a bcc structure and the AuCuNiPt and AuCuNiPdPt HEAs with an fcc structure to form percolated states through a computational method utilizing MD simulations.

2. Methods

2.1 MD simulations

Classical MD simulations were performed using the commercial software SCIGRESS ME Ver. 2.3 (Fujitsu).\(^{14}\) The target alloys were the WNbMoTa and WNbMoTaV alloys\(^{6}\) with a bcc structure and HEAs comprising noble metals, represented by the AuCuNiPt and AuCuNiPdPt alloys\(^{9}\) with an fcc structure.

Crystal lattices of \(10 \times 10 \times 10\) supercells composed of randomly-distributed constituent elements were constructed computationally for bcc and fcc structures by using the commercial software. The supercells contained 2000 and 4000 atoms for bcc and fcc structures, respectively, and periodic boundary conditions were imposed in all directions while maintaining the shape of the cubic structure during the MD simulations. Subsequently, the alloys were structurally relaxed at \(T = 100\) K for a certain time while monitoring the changes in pressure \((p)\) and volume of the supercell \((V)\) to obtain the initial structures stabilized and optimized for MD simulations. Subsequently, these relaxed alloys were annealed at 1000 K computationally under an isothermal-isobaric \((NTP)\) ensemble at a pressure of 0.1013 MPa for 100 ps to homogenize them using equilibrium MD simulations. The annealing temperature of 1000 K was selected experimentally that realistic MD potentials.

First, the ranges of the primary peak in the PDF profiles for total pairs were measured. The atomic correlations of the MD in the supercells were analyzed by selecting an appropriate element and its connection of atoms in the nearest neighbor distance \(d_{\text{nn}}\). The selected elements can be exemplified by W for the bcc HEAs and Pt for the fcc HEAs, as W and Pt possess intermediate atomic radius \((r_{\text{elem}})\) among the constituent elements and total values. The MD potentials were carefully selected from the “Generalized Embedded Atom Method” (GEAM) library equipped in the software.\(^{14}\) The GEAM potential\(^{14}\) based on the Embedded Atom Method (EAM) scheme\(^{15}\) enables us to deal with 16 metallic elements and their mixtures as alloys with bcc, fcc, and hcp structures. The actual elements available in GEAM are Cu, Ag, Au, Ni, Pd, Pt, Al, and Pb with fcc, Fe, Mo, Ta, and W with bcc, and Mg, Co, Ti, and Zr with hcp structures. Notably, the above elements and the resultant alloys could be handled with the GEAM potential of the software.\(^{14}\) The GEAM potential\(^{14}\) lacks the data for V and Nb with a bcc structure, and thus, they were acquired from the data of Ta by differentiating the inter-atomic distances of V and Nb separately.

Furthermore, supplemental MD simulations for bcc structure were also performed to compare the percolated and un-percolated for simple binary alloys with compositions of Mo\(_{20}\)Ta\(_{80}\), Mo\(_{25}\)Ta\(_{75}\), Mo\(_{80}\)Ta\(_{20}\) and Mo\(_{75}\)Ta\(_{25}\). These binary alloys with the solute contents of 25 at\% and 20 at\%, respectively, corresponded to percolated and un-percolated states.

2.2 Analysis of percolation

First, the ranges of the primary peak in the PDF profiles for total pairs were measured. The atomic correlations of the MD in the supercells were analyzed by selecting an appropriate element and its connection of atoms in the nearest neighbor distance \(d_{\text{nn}}\). The selected elements can be exemplified by W for the bcc HEAs and Pt for the fcc HEAs, as W and Pt possess intermediate atomic radius \((r_{\text{elem}})\) among the constituent elements in each system as summarized in Table 1.

The connections of atoms in \(d_{\text{nn}}\) and in the largest cluster were highlighted in the ball-and-stick view by utilizing the graphical functions equipped in commercial software CrystalMaker® X for Windows,\(^{17}\) Version 10.2.1 by considering the periodic boundary conditions. Specifically, the procedure to determine the largest cluster by utilizing the software was to first select an arbitrary atom, followed by “extend selection” of “molecule” by trial and error repeatedly using the software.

In addition, the length of mean square displacements \((L_{\text{MSD}})\) was calculated using the MD software as reported in a previous literature.\(^{18}\) Specifically, \(L_{\text{MSD}}\) is defined by eq. (1)

| Table 1 Atomic number accompanied by its atomic symbol, group in the periodic table, atomic radius \((r_{\text{elem}})\) and atomic weight \((M_{\text{elem}}/\mu\text{mol}^{-1})\) of the constituent elements acquired from literature.\(^{16}\) |
|-----------------|----------|----------|----------|----------|----------|
| **Element** | \(r_{\text{elem}} / \text{nm}\) | \(M_{\text{elem}} / \mu\text{mol}^{-1}\) | 21\(\text{V}\) | 41\(\text{Nb}\) | 42\(\text{Mo}\) | 73\(\text{Ta}\) | 74\(\text{W}\) |
| **Group** | 5 | 5 | 6 | 5 | 6 |
| \(r_{\text{elem}} / \text{nm}\) | 0.132 | 0.143 | 0.136 | 0.143 | 0.137 |
| \(M_{\text{elem}} / \mu\text{mol}^{-1}\) | 50.9415 | 92.90638 | 95.94 | 180.9479 | 183.84 |
| **Element** | \(r_{\text{elem}} / \text{nm}\) | \(M_{\text{elem}} / \mu\text{mol}^{-1}\) | 28\(\text{Ni}\) | 29\(\text{Cu}\) | 45\(\text{Pd}\) | 78\(\text{Pt}\) | 79\(\text{Au}\) |
| **Group** | 10 | 11 | 10 | 10 | 11 |
| \(r_{\text{elem}} / \text{nm}\) | 0.125 | 0.128 | 0.137 | 0.139 | 0.144 |
| \(M_{\text{elem}} / \mu\text{mol}^{-1}\) | 58.6934 | 63.546 | 106.42 | 195.078 | 196.96655 |
3. Results and Discussion

3.1 Atomic arrangements of the MD results

The present MD simulations under the conditions described in Section 2 were successfully performed without overshooting as shown in Fig. 1 as ball-and-stick views. Figure 1 demonstrates that the simulated atomic arrangements of (a) WNbMoTa and (b) WNbMoTaV alloys with a bcc structure and (c) AuCuNiPt and (d) AuCuNiPdPt alloys with an fcc structure appear to maintain their crystalline structures without transforming to other crystalline phases. It appears that the WNbMoTa and WNbMoTaV alloys with a bcc structure exhibited higher crystallinity close to their ideal bcc structure than AuCuNiPt and AuCuNiPdPt alloys did to an fcc structure. This difference in degree of crystallinity between the simulated bcc and fcc alloys was presumably due to the reproducibility of the GEAM potential.

3.2 PDF and percolation analysis of the AuCuNiPt and AuCuNiPdPt alloys with fcc structure

The \( d_0 \) was determined by the total PDF, \( g_{\text{total}}(r) \). Figure 2 revealed that the \( g_{\text{total}}(r) \) functions of the AuCuNiPt and AuCuNiPdPt alloys exhibit a sharp primary peak with a peak distance of approximately \( r = 0.265 \) nm. The primary peak profiles of \( g_{\text{total}}(r) \) are distributed in the range approximately 0.20 to 0.33 nm, which correspond to the \( d_0 \) of the fcc structure with the coordination number (Z) of 12. The partial PDF, \( g_{ij}(r) \), of the constituent atomic pair, i-j, slightly differs from the \( g_{\text{total}}(r) \) in terms of intensity and the range of distance of the first peak, but \( g_{ij}(r) \) functions of the first peaks are also almost plotted over the range approximately 0.20 to 0.33 nm. From Fig. 2, the authors determined that \( d_0 = 0.20 \) to 0.33 nm. The correlations of the constituent elements were analyzed in a 3-dimensional view as hypothetical bonds by selecting the atomic connections within \( d_0 \). The results are shown in Figs. 3 and 4, where the balls (atoms) within 0.20 \( \leq d_0/\text{nm} \leq 0.33 \) are drawn with stick bonds in the supercell denoted by dotted lines, whereas those forming the largest cluster are highlighted. Figure 3, representing the AuCuNiPt alloy, shows that the highlighted balls and sticks are distributed over the supercells and they penetrate the boundaries of the supercell through three sets of two parallel planes of the supercell along the x-, y-, and z-directions. Thus, it was interpreted that the AuCuNiPt alloy was in a percolated state. Figure 4, representing the AuCuNiPdPt alloy, shows that the highlighted balls and sticks occupy a part of the whole supercells. For instance, the connections of the highlighted balls and sticks in Fig. 4(c) narrowly penetrate the y-z parallel planes along the x-direction, but they do not pass through the x-z planes along the y-direction. Overall, the highlighted balls and sticks barely penetrate the supercell because of the presence of the other clusters comprising the non-highlighted balls and sticks. Thus, the status of connections of the constituent elements shown in Fig. 4 can be understood to be close to the critically percolated state. Thus, it was observed that the AuCuNiPt and AuCuNiPdPt alloys were in completely

\[
L_{\text{MSD}} = \langle (r(t_{\text{interval}}) - r(0))^2 \rangle = \frac{1}{NM} \sum_{i=1}^{N} \sum_{k=1}^{M} |r_i(t_k + t_{\text{interval}}) - r_i(t_k)|^2
\]
3.3 PDF and percolation analysis of the WNbMoTa and WNbMoTaV alloys with bcc structure

The features of profiles of $g_{\text{total}}(r)$ of the WNbMoTa and WNbMoTaV alloys shown in Fig. 5 demonstrates a primary peak and a secondary peak as a shoulder to the primary one. These peaks correspond, respectively, to $d_a$ and the second nearest distance ($d_{nn}$), which is a considerably short distance in a bcc structure. In ideal pure metals with a bcc structure, the ratio $d_a/d_{nn}$ is as small as 1.15. Thus, $d_a$ and $d_{nn}$ in the profiles of $g(r)$ are hardly separated completely. In other words, it is difficult to deconvolute $d_a$ and $d_{nn}$ because of a mixture of the profiles caused by thermal fluctuations around the ideal site positions of atoms in an actual alloy and in an alloy simulated using MD with a bcc structure. Thus, $d_a$ and $d_{nn}$ were determined carefully. Figure 5 reveals that the profiles exhibit a sharp primary peak at a peak distance approximately $r = 0.28$ nm and the peaks spread in the range $0.235$ to $0.305$ nm. The secondary peaks are observed at a peak distance approximately $r = 0.32$ nm and the peaks spread in the range $0.305$ to $0.37$ nm. Thus, the subsequent analysis was performed with the distances $d_a = 0.235$ to $0.305$ nm and $d_{nn} = 0.305$ to $0.37$ nm. The latter correspond to $Z_a = 8$ and $Z_{nn} = 6$, respectively. Here, it should be noted that comparison of the $g_{\text{v}}(r)$ profiles between Figs. 5(a)–(b) at $r$ ranging $0.235$ to $0.370$ nm revealed the presence of sharp subpeaks (shoulder peaks) in $g_{\text{f}}(r)$ profiles, such as subpeaks in Mo–Mo and Nb–Nb pairs.

Fig. 3 Ball-and-stick views at $t = 100$ ps for the AuCuNiPt HEA for Pt atoms on (a) (100), (b) (010), (c) (001), and (d) (111) projections where the dotted lines indicate the boundary of the supercell. The view directions are along the three axial vectors [(100), (010) and (001)] and (111) from the upward direction symbolized as “©”. The sticks within the nearest neighbor distance, $0.20 \leq d_{nn} \leq 0.33$ only are drawn. The balls and sticks forming the largest cluster are highlighted from the analysis utilizing the software by considering the periodic boundary conditions. The authors have confirmed the same tendency by selecting other elements than Pt. The completely and near-critically percolated states, respectively, are characterized by their differences in intensity from $g_{\text{total}}(r)$ profiles. These subpeaks that deviate from $g_{\text{total}}(r)$ may be a symptom of the un-percolation observed from PDF profile. Such apparent difference in the $g_{\text{v}}(r)$ from $g_{\text{total}}(r)$ generally observed in alloys with fcc structure shown in Figs. 2(a) and (b) where both alloys are in percolated states. This symptom will be discussed in the next Sub-Section.
The correlations of the constituent elements were analyzed in a 3-dimensional view by selecting the atomic connections within $d_n = 0.235$ to $0.305$ nm in Fig. 6 for the WNbMoTa alloy and Fig. 7 for the WNbMoTaV alloy where W was representatively selected in the analysis because of its intermediate atomic radius among the constituent elements. The atomic arrangements of the WNbMoTa alloy shown in Fig. 6(c) indicate that the highlighted balls and sticks barely penetrate the x-z parallel planes along the y-axis from $y = 0$ to 1. This situation in Fig. 6 is similar to Fig. 4 for the AuCuNiPdPt HEA. The highlighted balls and sticks of the WNbMoTaV alloy shown in Fig. 7 demonstrate the presence of completely-isolated clusters. Thus, it was interpreted that the WNbMoTa and WNbMoTaV alloys formed near-critically percolated and un-percolated states, respectively. The presence of the isolated percolated cluster shown in Fig. 7(a)–(d) was interpreted from the relationships between $x$ and $p_{csite}$ in that $x = 0.20$ and $p_{csite} = 0.245$ for the WNbMoTaV alloy. Subsequently, the authors considered the effects of $d_{nn}$ on the percolations by extending the threshold length to $d_{nn} = 0.305$ to $0.37$ nm from the PDF analysis shown in Fig. 5. This extension was according to the early study, which demonstrated that increasing $Z$ tends to decrease $p_{csite}$ for a close packed (cp) structure at a dimension ($d$) from 3 to 8 as given in eq. (2).

$$p_{cp}^Z(d)Z_{cp}(d) \approx 2.4, \quad 3 \leq d \leq 8$$  \hspace{1cm} (2)$$

The authors applied eq. (2) for a bcc structure, although bcc is not a cp structure, to examine the relationships between $p_{csite}$ and $Z$. Specifically, the length of the nearest and the second nearest distance, $d_{nn}$, was considered in the analysis of percolations for the bcc alloys as demonstrated in Fig. 8. Consequently, it was observed that the constituent elements of the WNbMoTaV alloy form a percolated state again when considering $d_{nn}$ ranging from 0.235 to 0.37 nm. Thus, it was expected that the classical percolation theory regarding a black-and-white model and the resultant values of $p_{csite}$ can be applied to exact equiatomic HEAs with $N = 4$ for bcc and
$N = 5$ for fcc structures, whereas a polychromatic model was adopted for exact equiatomic HEAs with $N \geq 5$ for a bcc structure.

### 3.4 Analysis of the alloys with $L_{\text{MSD}}$ and PDF

First, the atomic displacements of the MD simulations were quantitatively analyzed for $L_{\text{MSD}}$. Figure 9 depicts $L_{\text{MSD}}$ of the alloys calculated during $t$ up to 100 ps. Figure 9 shows that (a) AuCuNiPt and (b) AuCuNiPdPt alloys with fcc structure exhibit $L_{\text{MSD}} > 0.002$ nm$^2$, whereas $L_{\text{MSD}}$ of (c) WNbMoTa and (d) WNbMoTaV alloys with bcc structure is in the range of 0.001 to 0.002 nm$^2$. Thus, the present MD simulations for the alloys with fcc structure tended to provide larger $L_{\text{MSD}}$ than those with the bcc structure. In details, the values of $L_{\text{MSD}}$ of (a) AuCuNiPt and (b) AuCuNiPdPt alloys with fcc structure demonstrate that the magnitude of $L_{\text{MSD}}$ was approximately in the order of Cu $\sim$ Ni $>\$ Pd $>\$ Au $>\$ Pt. Thus, they roughly tended to decrease with increasing atomic number or atomic weight of the constituent elements that are summarized in Table 1. On the other hand, the magnitude of $L_{\text{MSD}}$ in (c) WNbMoTa and (d) WNbMoTaV alloys with bcc structure was approximately in the order of Nb $>$ Ta $\sim$ V $>$ Mo $>$ W, and thus, they did not vary consistently in the order of atomic number or atomic weight of the constituent elements. This inconsistency observed in the alloys with bcc structure may presumably be due to the assumption of GEAM parameters of Nb and V from Ta. Excepting for Nb and V, the magnitude of $L_{\text{MSD}}$ of the Mo, Ta and W did not exhibit to decrease with decreasing atomic number or atomic weight because of higher $L_{\text{MSD}}$ value of Ta. There remains uncertainty that this inconsistency including the assumption of GEAM parameters of Nb and V may influence the percolation or un-percolation states. However, authors think that inconsistency does not provide completely and drastically different states between percolated and un-percolated states, since the present MD results for WNbMoTa and WNbMoTaV alloys were provided as stable bcc structures as shown in Figs. 1(a) and (b). In other words, this inconsistency will not provide percolated state for the alloys that should be un-percolated state in fact, and vice versa.

Incidentally, the decreasing tendency of $L_{\text{MSD}}$ with decreasing atomic number or atomic weight found in the present MD simulation for alloys with fcc structure was supported by a previous study$^{19}$ in a CrMnFeCoNi HEA where the average mean-square atomic displacements (MSADs) are evaluated to be $25.2 \times 10^{-6}$ nm$^2$. Here, it should be noted that MSAD $= 25.2 \times 10^{-6}$ nm$^2$ is approximately 100 times smaller than $L_{\text{MSD}}$ in the present results. In part, this disagreement in magnitude between $L_{\text{MSD}}$ and MSAD might be due to the inclusions of thermal expansion and fluctuation of the supercells at $T = 1000$ K in the present MD simulations under $N\text{T}_p$ ensemble. However, supplemental MD simulations for alloys with bcc structure (WNbMoTa and WNbMoTaV) and fcc structure (AuCuNiPt and AuCuNiPdPt) denied this possibility. Specifically, supplemental MD simulations with superlattice constants acquired from $T = 1000$ K and $t = 100$ ps from Fig. 1 with initial ideal atomic arrangements provided almost the same order of $L_{\text{MSD}}$ ($L_{\text{MSD}} > 0.002$ nm$^2$ and 0.001 to 0.002 nm$^2$ for bcc). Furthermore, other supplemental MD simulations with the same lattice constants of the supercell under $N\text{T}_V$ ensemble also gave almost 100 times larger $L_{\text{MSD}}$ value than MSAD. Thus, the authors came to conclude that present MD simulation essentially give the larger $L_{\text{MSD}}$ than MSAD from the previous study$^{19}$ in a CrMnFeCoNi HEA. At any event, the present MD simulation revealed that alloys with bcc structure exhibited the smaller deviations of the atomic displacements from their ideal sites than alloys with fcc structure.

Next, the percolation was analyzed with the characteristics of the PDF profiles. In principle, the PDF gives the probability of the constituent elements that are found at a distance around an atom, as a coordination number of the
coordination polyhedral. When the solvent and solute atoms are apparent in the conventional alloys, such as medium- and low-high entropy alloys (MEA and LEA), the formation of clusters in MEAs and LEAs or dispersion of solute atoms in the matrix comprised of solvent atoms in LEA gives different shape in PDFs to the complete chemically disordered solid solutions. In contrast, the HEAs are the alloys with characteristics of the absence of the concept of solvent and solute atoms, in particular, for the HEAs with exact equiatomicity. With this concept, it is expected that the absence of percolated state in HEAs, such as the WNbMoTaV alloy in an un-percolated state among the four alloys simulated in the present study, may lead to change in intensity of the $g_{ij}(r)$ profile from $g_{total}(r)$. In reality, the authors pointed out a symptom of the un-percolation observed from PDF profile for Mo–Mo and Nb–Nb pairs in Fig. 5(b) in the previous Sub-Section.

To investigate the difference more precisely, PDFs of the Mo–Ta binary systems are shown in Fig. 10. As a result, it is shown that $g_{total}(r)$ profiles do not exhibit apparent difference between percolated and un-percolated states, as shown in Figs. 10(a) and (b) as well as in Figs. 10(c) and (d). However, the $g_{ij}(r)$ profiles demonstrates the difference in the intensity at distances denoted by upward and downward arrows. As a whole, there is a weak tendency denoted by three connected arrows that alloys in percolated states shown in Figs. 10(a) and (c) give difference in the intensity of all the $g_{ij}(r)$ profiles. On the other hand, alloys in un-percolated states shown in Figs. 10(b) and (d) give difference in the intensity of the $g_{ij}(r)$ from $g_{total}(r)$ at distanced denoted by arrows for the solute atomic pairs of Mo–Mo in Fig. 10(b) and Ta–Ta in Fig. 10(d). Thus, Fig. 10 shows that occurrence of percolation could barely be detected by analyzing $g_{ij}(r)$ profiles in Mo–Ta binary alloys. This detectability of percolation in binary alloys was presumably due to the decrease in contents of solute elements from 25 to 20 at% as a compensation of increase in the contents of solvent elements from 75 to 80 at%. In contrast, such apparent changes in $g_{ij}(r)$ profiles were not clearly observed in Fig. 5(b) for all $g_{ij}(r)$ in HEAs. Presumably, this is due to the fact that all the constituent elements decrease in their contents from 25 to 20 at% due to the compositional characteristic in HEAs in Fig. 5. The detection of percolated state from $g_{ij}(r)$ profile will be examined in the authors future researches by performing MD simulations for other HEAs, such as Al$_x$CoCrFeNi alloys$^{20)}$ that exhibit transitions from fcc, fcc + bcc and bcc with increasing Al content.

4. Conclusions

MD simulations using the GEAM scheme were performed for quaternary bcc WNbMoTa and fcc AuCuNiPt and quinary bcc WNbMoTaV and fcc AuCuNiPdPt HEAs. The MD results analyzed for PDFs revealed the percolated and isolated states, respectively, when $x \geq p_{site}^{fcc}$ and $x < p_{site}^{bcc}$ where $p_{site}^{bcc}$ of the nearest neighbor of the bcc and fcc structures is given as $p_{site}^{bcc} = 0.245$ and 0.198, respectively, from the conventional percolation theory. Further investigation revealed that the exact equi-atomic alloys in quaternary alloys ($N = 4$) with a bcc structure and quinary alloys ($N = 5$) with an fcc structure are in a critically-percolated state in terms of site percolation.
Acknowledgments

This research was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS): Grant Program of Scientific Research (B) with the program title of “Alloy Design of High-Entropy Alloys (HEAs) Based on Screening Hypothesis and Statistical Decision Theory and Fabrication of New HEAs” (Grant No. 17H03375).

REFERENCES