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Body-Diagonal Diffusion Couples for High Entropy Alloys

John E. Morral[1]

Abstract Body-diagonal diffusion couples provide a systematic way to investigate the diffusivity of high entropy alloys, a.k.a. HEAs. By definition these alloys contain 5-elements or more. All independent concentration differences in a body-diagonal couple are equal, except for being positive or negative. They are similar to diagonal diffusion couples for 3-element alloys, but the term body-diagonal applies only to couples with 4-elements or more. Composition vectors for these couples are aligned with body-diagonals in cubes located in the multi-element composition space of HEAs. The body-diagonals can be represented with a simple vector notation. The notation and other properties of body-diagonals are given in this work, including the number of diagonals and the angles between them. An advantage for HEAs is the fact that there are more diagonal directions and, therefore, more potential diffusion couples than needed to measure or validate diffusivity databases. That advantage gives flexibility to avoid 2-phase regions and, when validating databases, to avoid eigenvector directions of the diffusivity matrix. When body-diagonal diffusion couples are compact, their diffusion paths cross at the same composition, making it possible to measure an HEA diffusivity using the Boltzmann–Matano–Kirkaldy method.

Keywords body-diagonals · diffusion couples · diffusivity database validation · diffusivity measurement · high entropy alloys

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1 Introduction

A body-diagonal diffusion couple contains four or more elements and has the same differences in the independent concentration variables between elements in the couple, except that the differences can be positive or negative. The dependent concentration variable makes up the difference to reach 100% and is not necessarily equal to the other differences.

These characteristics have been used before in a 4-element body-diagonal diffusion couple by Kulkarni et al.[1] Similar diffusion couples can be made from 3-element alloys. These are diagonal diffusion couples because, as shown in Fig. 1, their composition vectors correspond to diagonals on a square in 2-dimensional composition space.

When there are 4-elements in a diffusion couple, their composition vectors lie along the body-diagonals of cubes in 3-dimensional composition space. Cubes have eight corners and four diagonals that cross inside the cube and connect two cube corners. When there are five or more components, as in high entropy alloys (HEAs), the composition space is 4-dimensional and, by definition, the cubes are hypercubes in a composition hyperspace. See, for example, https://en.wikipedia.org/wiki/Hypercube. The objective of this paper is to extend the idea of diagonal diffusion couples in ternary systems to body-diagonal diffusion couples in n-element systems and apply them specifically to the measurement and validation of diffusivities for HEAs.

In Fig. 1 the diagonal directions of the composition vectors are separated by an angle of 90°. A previous analysis of constant diffusivity equations showed that the uncertainty of ternary diffusivity measurements obtained from two diffusion couples was smallest when their composition vector directions were 90° apart and was largest as

52

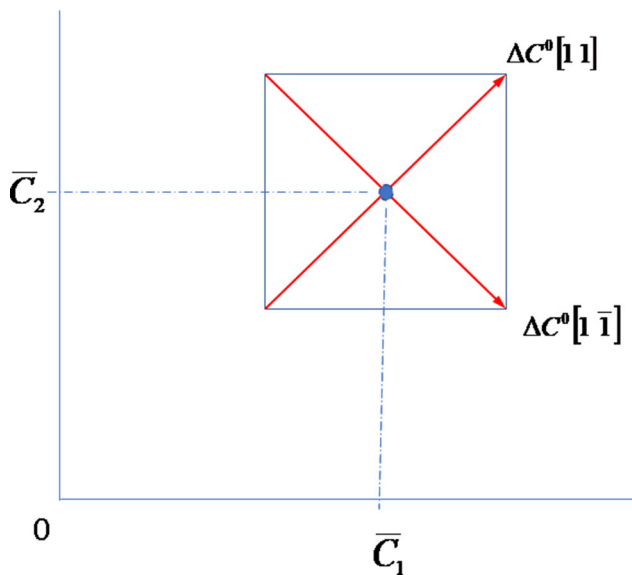J. Phase Equilib. Diffus. (2018) 39:51–56

Fig. 1 A square in a 2-dimensional, ternary 3-element composition space. The center of the square is the average composition of two diagonal diffusion couples, while corners of the square are at compositions of alloys in the two couples. Composition vectors connect opposite corners to represent the two diagonal diffusion couples

their acute angle approached 0°,[2] i.e. when the composition vectors coincided. In this work, it is assumed that the same is true for the directions of body-diagonal diffusion couples when used for measurements on HEAs.

In early work on multi-element alloys, semi-empirical databases were validated by comparing measured and predicted concentration profiles. In a 2003 study of a 7-element alloy system by Campbell et al.[3] the composition vector directions were dictated by the composition of commercial alloys. It is, however, more common to use directions dictated either by the method used or other factors like the size and shape of the single-phase region in which the diffusivity database applies.

Another sound method of studying HEAs uses quasibinary diffusion couples. It is similar to using body-diagonal diffusion couples in that it dictates the directions of composition vectors. Those directions lie along the concentration axes of the multi-element composition space. They were used by Tsai et al.[4] in their seminal study of sluggish diffusion in HEAs. Tsai's concentration profiles on the Co-Cr-Fe-Mn-Ni system were later used by Zhang et al.[5] to verify their HEA diffusivity database. In addition Zhang's work included comparisons with their own quasibinary experiments on Co-Cr-Fe-Ni diffusion couples and with the work by Kulkarni et al.[1] on body-diagonal Co-Cr-Fe-Ni diffusion couples. Kulkarni's diffusion couples were somewhat unique, because both diagonal and body-diagonal diffusion couples have been uncommon in recent

multi-element diffusivity measurements, see for example Ref 6-9.

Reasons why composition vectors in body-diagonal directions are desirable for studies of HEAs include their simple vector notation, their uniform distribution in hyperspace and their large numbers, offering more flexibility when making measurements or validating diffusivity databases. In the following, the notation for composition vectors will be introduced first and then diagonals will be described for ternary thru n-component systems. Examples will be given specifically for 5 and 6-element HEAs. Then it will be discussed how to select body-diagonal diffusion couples for measurement and validation studies.

2 Composition Vector Notation and Directions

The co-ordinates of a diffusion couple composition vector are given by the initial concentration differences of each element i between the right and left end of the couple:

$$\Delta C_i^0 = C_i^R - C_i^L \qquad (Eq\ 1)$$

The composition vector for a 5-element HEA can be written as:

$$[\Delta C^0) = [\Delta C_1 \Delta C_2 \Delta C_3 \Delta C_4] \qquad (Eq\ 2)$$

Equation 2 reflects the fact that there are only four independent concentration variables in a 5-element system. Another way of writing Eq 2 is:

$$[\Delta C^0) = \Delta C^{max}[f_1 f_2 f_3 f_4] \qquad (Eq\ 3)$$

In which the f_i are concentration differences divided by the maximum difference:

$$f_i = \frac{\Delta C_i}{\Delta C^{max}} \qquad (Eq\ 4)$$

Accordingly, the notation for a composition vector in a 5-elementt, HEA, body-diagonal diffusion couple can be written as:

$$[\Delta C^0) = \Delta C^0[1\ 1\ \bar{1}\ 1] \qquad (Eq\ 5)$$

in which $\bar{1} = -1$ and ΔC^0 is the absolute value of all initial concentration differences:

$$\Delta C^0 = |\Delta C_i^0| \qquad (Eq\ 6)$$

Equation 5 is an example of the simple vector notation possible for body-diagonal composition vectors. It is simple because all the initial concentration differences are given by ΔC^0, the diagonal direction is given by the bracket, and the sign of each concentration difference is given by components in the bracket. The only additional

information needed is to connect the name of the elements with the individual components in the bracket.

3 Body-Diagonals in Hyperspace

The notation and vocabulary needed to discuss body-diagonals in HEAs are similar to those used for ternary and quaternary systems. These will be discussed first, because they are easier to visualize than body-diagonals in HEA hyperspace.

3.1 Diagonals for a Ternary System

For a ternary system, the diagonals for a specific alloy composition were illustrated in Fig. 1. The center of the square is at the average composition of the diffusion couple:

$$\bar{C}_i = \frac{C_i^R + C_i^L}{2} \tag{Eq 7}$$

The body-diagonals in Fig. 1 each contain two vectors as illustrated in Fig. 2. These additional vectors are obtained by considering all possible permutations of 3-element directions; $\Delta C^0[1\ 1]$, $\Delta C^0[1\ \bar{1}]$, $\Delta C^0[\bar{1}\ \bar{1}]$ and $\Delta C^0[\bar{1}\ 1]$. Each of these vectors is drawn from the center to a corner of the square. Of the two vectors contained in one diagonal, one is the negative of the other. Since composition vectors point in only one direction, only the first two vectors in Eq 8 are
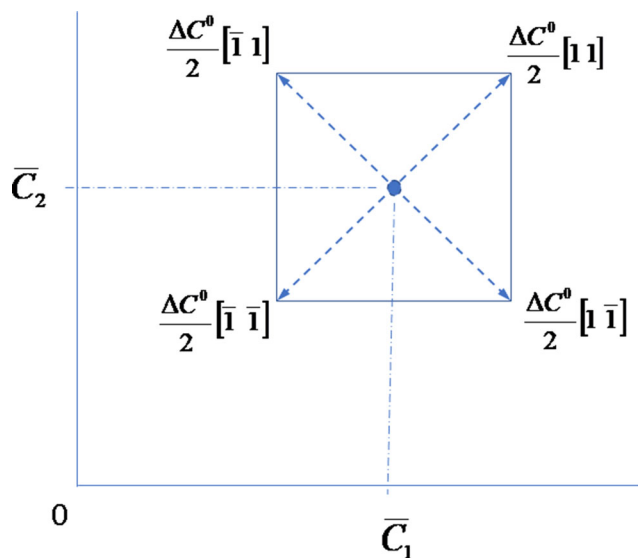

Fig. 2 A square in a 2-dimensional, ternary, composition space illustrating vectors with directions corresponding to all permutations of plus and minus concentration differences. By comparing Fig. 1 and 2 one sees that a composition vector is along a diagonal that has two directions, one of which is the negative of the other. In this work it is not necessary to consider the negative directions. Therefore they are ignored in the text except to indicate they exist

needed to define the two composition vectors in the square. In what follows the negative directions will be omitted.

3.2 Body-Diagonals for Quaternary and HEA Systems

The composition space for a quaternary system is 3-dimensional and the body-diagonal directions are associated with a 3-dimensional unit cube: a cube with edges that are one unit long. As in any cube, it has eight corners and four body-diagonals. The four body-diagonal directions for composition vectors can be expressed as permutations of three positive and negative ones as given by; $[1\ 1\ 1]$, $[1\ 1\ \bar{1}]$, $[1\ \bar{1}\ \bar{1}]$, $[\bar{1}\ 1\ \bar{1}]$. Note that the negative of these vector directions were not listed.

It follows that extending the number of body-diagonals to a 5-element HEA involves increasing the dimension of the vectors to correspond to a 4-dimensional unit hypercube. The various permutations of body-diagonal directions for that case are given by; $[1\ 1\ 1\ 1]$, $[1\ 1\ 1\ \bar{1}]$, $[1\ 1\ \bar{1}\ 1]$, $[1\ \bar{1}\ 1\ 1]$, $[\bar{1}\ 1\ 1\ 1]$, $[1\ 1\ \bar{1}\ \bar{1}]$, $[1\ \bar{1}\ 1\ \bar{1}]$, $[\bar{1}\ 1\ 1\ \bar{1}]$. As before, no negative directions were listed.

The examples given above demonstrate well-known relationships between squares, cubes and hypercubes (see again https://en.wikipedia.org/wiki/Hypercube). These relationships are that, for "m" dimensions (m equal to $n-1$ elements), the number of corners is 2^m and, the number of body-diagonals is 2^{m-1}. The number of body-diagonals is half the number of corners, because body-diagonals have a corner at each end. Also, one can calculate that the length of a body-diagonal in a unit cube or hypercube is $\sqrt{m}$ using the Pythagorean Theorem. These relationships are summarized in Table 1.

4 Selecting Best Body-Diagonals for Experimental HEA Research

A strategy for selecting the best body-diagonal directions for composition vectors is to select those that form the largest acute angle with other selected diagonals.[2] Although this relationship was proved for ternaries, it makes sense that if the smallest uncertainty is at the largest angle, then the largest uncertainty will be at the smallest angle, i.e. when the vectors coincide and the acute angle is zero.

The angle between body-diagonals is given by the dot product of vectors. For example, using two vectors for a 5-element system the dot product is:

$$[1\ 1\ 1\ 1] \cdot [1\ 1\ \bar{1}\ 1] = \sqrt{4}\sqrt{4}\cos\theta \tag{Eq 8}$$

or

$$1 + 1 - 1 + 1 = 4\cos\theta \tag{Eq 9}$$

Table 1 Body-diagonals as a function of number of alloy elements

Number of alloy elements	n	3	4	5	6
Number of independent variables and diffusion couples needed to measure [D].	$m = n - 1$	2	3	4	5
Corners on a unit concentration square, cube or hypercube	2^m	4	8	16	32
Number of body-diagonals	2^{m-1}	2	4	8	16
Body-diagonal length	$\sqrt{m}\Delta C^0$	$\sqrt{2}\Delta C^0$	$\sqrt{3}\Delta C^0$	$\sqrt{4}\Delta C^0$	$\sqrt{5}\Delta C^0$

Table 2 Method for determining best-angles between body-diagonal directions for 5-element HEAs

Directions	1111	111$\bar{1}$	11$\bar{1}$1	1$\bar{1}$11	$\bar{1}$111	11$\bar{1}\bar{1}$	1$\bar{1}$1$\bar{1}$	$\bar{1}$11$\bar{1}$
1111	0	60	60	60	60	90	90	90
111$\bar{1}$	60	**0**	**90**	**90**	**90**	60	60	60
11$\bar{1}$1	60	**90**	**0**	**90**	**90**	60	60	60
1$\bar{1}$11	60	**90**	**90**	**0**	**90**	60	60	60
$\bar{1}$111	60	**90**	**90**	**90**	**0**	60	60	60
11$\bar{1}\bar{1}$	90	60	60	60	60	0	90	90
1$\bar{1}$1$\bar{1}$	90	60	60	60	60	90	0	90
$\bar{1}$11$\bar{1}$	90	60	60	60	60	90	90	0

Note that directions are given as vector components. The m vector components contain all permutations of $\pm$ 1 s, but exclude negatives of these directions. Angles in degrees are determined from the dot product between directions. Mutually perpendicular directions can be found in the table e.g. in bold

Solving Eq 9 yields an angle of $\theta = 60°$, which is not the best body-diagonal, because other diagonals have acute angles of 90°. For comparison, in Ref 2 the sample studied had an inherent uncertainty of 10% for an acute angle of 90° and 14% for an acute angle of 60°.

A method for selecting best-directions, i.e. those directions with the largest acute angles, is illustrated in Tables 2 and 3 for 5 and 6-element alloys, respectively. In the Tables, all possible directions are listed along both the columns and rows. Then the dot product is used to determine angles between directions associated with each coefficient in the table.

As shown in Table 2, the only acute angles for 5-element HEAs are 60° and 90°. There are two groups of directions in which all the directions are mutually perpendicular, i.e. each direction in the group makes an angle of 90 degrees with every other direction in the group. These groups of best-directions have their angles written in bold type and are the groups [1 1 1 1], [1 1 $\bar{1}\bar{1}$], [1 $\bar{1}$ 1 $\bar{1}$], [$\bar{1}$ 1 1 $\bar{1}$] and [1 1 1 1], [1 1 $\bar{1}\bar{1}$], [1 $\bar{1}$ 1 $\bar{1}$], [$\bar{1}$ 1 1 $\bar{1}$].

As shown in Table 3, the only acute angles for 6-element HEAs are 78° and 53°. In this Table, five directions,[1 1 1 1$\bar{1}$], [1 1 1$\bar{1}$1], [1 1$\bar{1}$ 1 1], [1$\bar{1}$ 1 1 1], [$\bar{1}$1 1 1 1], have mutual angles of 78°. These directions have angles written in bold type and are best-directions for measuring a 6-element HEA diffusivity with the least inherent uncertainty.

5 Discussion

This work combines what is well known about the geometry of hypercubes with a symmetric model for diffusion couples. The center of the hypercube in composition space is the average composition of the body-diagonal diffusion couples. The body-diagonals radiate from the center of the cube in multiple, systematic directions. Differences in the directions are different permutations of plus and minus concentration differences.

An important difference between HEA and ternary diffusion couples is the concentration ranges that equi-element alloys can have. For example in a single-phase, ternary diffusion couple, the difference in concentration between the equi-element alloy and its corners is 30 at.%, while for a 5-element HEA the difference is 10 at.% as seen in Ref 5, 6. However in practice the difference may be smaller and closer to 5 at.% as in Ref 6.

With smaller concentration differences, variations in the diffusivity with composition become less important. With smaller differences the diffusion couples can be "compact"[2] i.e.; act as if their diffusivity is constant[10] and, thereby, their predicted concentration profiles follow error function solutions to Fick's Second Law, within the experimental error, as was seen, for example, in Ref 11 and 12. According to the properties of error functions, compact diffusion couples have diffusion paths that cross the initial interface at their average composition given by Eq 7. In that case, all m^2 diffusion coefficients in an n-element diffusivity, [D], can be measured using the Boltzmann–Manato–Kirkaldy (B–M–K) method.[13]

Note that the B–M–K method is applicable in general to an n-element system when diffusion paths from m diffusion couples obtained from the B–M Analysis cross at the same composition. At the crossing point all B–M Analysis equations apply to that same composition and, therefore, can be solved analytically for all diffusion coefficients in [D]. In the limit as ΔC_i goes to zero, [D] is a constant and the B–M–K method is exact. As ΔC_i increases and [D] begins to vary, the crossing points will start to drift

Table 3 Angles between body-diagonal directions for 6-element HEAs. The table has been cut into two parts. (a) is the left side of the table and (b) is the right side

Directions	11111	1111$\bar{1}$	111$\bar{1}$1	11$\bar{1}$11	1$\bar{1}$111	$\bar{1}$1111	111$\bar{1}\bar{1}$	11$\bar{1}$1$\bar{1}$
(a)								
11111	0	53	53	53	53	53	78	78
1111$\bar{1}$	53	**0**	**78**	**78**	**78**	**78**	53	53
111$\bar{1}$1	53	**78**	**0**	**78**	**78**	**78**	53	78
11$\bar{1}$11	53	**78**	**78**	**0**	**78**	**78**	53	53
1$\bar{1}$111	53	**78**	**78**	**78**	**0**	**78**	78	78
$\bar{1}$1111	53	**78**	**78**	**78**	**78**	**0**	78	78
111$\bar{1}\bar{1}$	78	53	53	78	78	78	0	78
11$\bar{1}$1$\bar{1}$	78	53	78	53	78	78	78	0
1$\bar{1}$11$\bar{1}$	78	53	78	78	53	78	78	78
$\bar{1}$111$\bar{1}$	78	53	78	78	78	53	78	78
11$\bar{1}\bar{1}$1	78	78	53	53	78	78	78	78
1$\bar{1}$1$\bar{1}$1	78	78	53	78	53	78	78	53
$\bar{1}$11$\bar{1}$1	78	78	53	78	78	53	78	53
1$\bar{1}\bar{1}$11	78	78	78	53	53	78	53	78
$\bar{1}$1$\bar{1}$11	78	78	78	53	78	53	53	78
$\bar{1}\bar{1}$111	78	78	78	78	53	53	53	53

Direction	1$\bar{1}$11$\bar{1}$	$\bar{1}$111$\bar{1}$	11$\bar{1}\bar{1}$1	1$\bar{1}$1$\bar{1}$1	$\bar{1}$11$\bar{1}$1	1$\bar{1}\bar{1}$11	$\bar{1}$1$\bar{1}$11	$\bar{1}\bar{1}$111
(b)								
11111	78	78	78	78	78	78	78	78
1111$\bar{1}$	53	53	78	78	78	78	78	78
111$\bar{1}$1	78	78	53	53	53	78	78	78
11$\bar{1}$11	78	78	53	78	78	53	53	78
1$\bar{1}$111	53	78	78	53	78	53	78	53
$\bar{1}$1111	78	53	78	78	53	78	53	53
111$\bar{1}\bar{1}$	78	78	78	78	78	53	53	53
11$\bar{1}$1$\bar{1}$	78	78	78	53	53	78	78	53
1$\bar{1}$11$\bar{1}$	0	78	53	78	53	78	53	78
$\bar{1}$111$\bar{1}$	78	0	53	53	78	53	78	78
11$\bar{1}\bar{1}$1	53	53	0	78	78	78	78	53
1$\bar{1}$1$\bar{1}$1	78	53	78	0	78	78	53	78
$\bar{1}$11$\bar{1}$1	53	78	78	78	0	53	78	78
1$\bar{1}\bar{1}$11	78	53	78	78	53	0	78	78
$\bar{1}$1$\bar{1}$11	53	78	78	53	78	78	0	78
$\bar{1}\bar{1}$111	78	78	53	78	78	78	78	0

apart and an error is introduced. However if they drift apart less than the experimental error then the analysis is as accurate as when it is applied to a ternary system. As clearly shown in Fig. 5 of Ref [8], the actual crossing point cannot be known for ternary diffusion couples. The difference in the actual crossing points may be on the order of the experimental error, as is the case for multicomponent compact diffusion couples.

Information on possible body-diagonals and angles between them were given in this work for both 5 and 6-element HEA's. Extension to more components is straightforward by calculating the necessary combinations and permutations of plus and minus direction components. What remains before experiments can be performed is to decide on a suitable ΔC^0 and on which body-diagonal directions to use for the body-diagonal diffusion couples.

If the objective is to validate a composition dependent diffusivity database, the first step should be to verify the composition dependence of the database. That can be determined by calculating concentration profiles using both

56

J. Phase Equilib. Diffus. (2018) 39:51–56

the database in question and a constant value of the diffusivity. The constant diffusivity should be calculated by the database at the average composition of the intended body-diagonal diffusion couples. When concentration profiles overlap or the differences seem insignificant for a given body-diagonal, one can assume that they would be the least important directions to test with experiments. If only a few diffusion couples are planned, the focus should be on directions in which the difference between the database and constant diffusivity profiles is the greatest.

When validating databases, one should calculate eigenvector directions of the diffusivity, as well. These directions should be avoided, because such directions and other nearby directions do not contain sufficient information to detect even very large errors in certain of the m^2 components in an n-element diffusivity matrix.[2,14] Such preliminary calculations on a computer can save time in experimental investigations by identifying the most productive body-diagonals to test. However, the caveat is that predictions made by the database will be no better than the database making them. The more accurate the database, the more help it will be in selecting best directions to pursue.

6 Conclusions

Body-Diagonal diffusion couples provide a systematic method of designing HEA diffusion couples to measure diffusivities or validate diffusivity databases. They are an alternative to using quasi-binary couples, which is another sound and systematic method. Other conclusions are:

1. Body-diagonal diffusion couples can be described using a simple vector notation.
2. Body-diagonal diffusion couples are in directions that are distributed uniformly throughout the multi-dimensional composition space of HEA and are greater in number than needed to measure experimental HEA diffusivities or to fully validate their diffusivity databases.
3. The excess number of body-diagonals facilitates designing diffusion couples that can avoid phase boundaries and, in the case of diffusivity database validation, avoid eigenvector directions of the diffusivity matrix.
4. Body-diagonals can be grouped according to the angles they make with other body-diagonals. The angles are associated with an inherent measurement uncertainty that is least when the angle is 90° and increases as the angle is smaller.

5. When body-diagonal diffusion couples are compact, their diffusion paths cross at a single composition and the diffusivity can be measured using the Boltzmann–Matano–Kirkaldy method.

References

1. K. Kulkarni and G.P.S. Chauhan, Investigations of Quaternary Interdiffusion in a Constituent System of High Entropy Alloys, *AIP Adv.*, 2015, **5**, p 097162
2. W.D. Hopfe and J.E. Morral, Uncertainty Analysis of Ternary Diffusivities Obtained From One Versus Two Compact Diffusion Couples, *J. Ph. Equilib. Diffus.*, 2016, **37**, p 210-218
3. C.E. Campbell, J.-C. Zhao, and M.F. Henry, Comparison of Experimental and Simulated Ni-Base Superalloy Diffusion Couples, *J. Ph. Equilib. Diffus.*, 2004, **25**, p 6-15
4. K.-Y. Tsai, M.-H. Tsai, and J.-W. Yeh, Sluggish Diffusion in Co-Cr-Fe-Mn-Ni High Entropy Alloys, *Acta Mater.*, 2013, **61**, p 4887-4897
5. C. Zhang, F. Zhang, K. Jin, H. Bei, S. Chen, W. Cao, J. Zhu, and D. Lv, Understanding of the Elemental Diffusion Behavior in Concentrated Solid Solution Alloys, *J. Ph. Equilib. Diffus.*, 2017, **38**, p 434-444
6. V. Verma, A. Tripathi, and K.N. Kulkarni, On Interdiffusion in FeNiCoCrMn High Entropy Alloy, *J. Ph. Equilib. Diffus.*, 2017, **38**, p 446-456
7. W. Chen and L. Zhang, High-Throughput Determination of Interdiffusion Coefficients for Co-Cr-Fe-Mn-Ni High-Entropy Alloys, *J. Ph. Equilib. Diffus.*, 2017, **38**, p 457-465
8. K.-W. Moon, C.E. Campbell, M.E. Williams, and W.J. Boettinger, Diffusion in FCC Co-Rich Co-Al-W Alloys at 900 and 1000 °C, *J. Ph. Equilib. Diffus.*, 2016, **37**, p 402-415
9. B. Gao, Y. Gu, Q. Wu, Y. Guo, and Y. Cui, Diffusion Research in BCC Ti-Al-Ni Ternary Alloys, *J. Ph. Equilib. Diffus.*, 2017, **38**, p 502-508
10. J.S. Kirkaldy and D.J. Young, *Diffusion in the Condensed State*, The Institute of Metals, London, 1987, p 176
11. M.S. Thompson, J.E. Morral, and A.D. Romig, Jr., Applications of the Square Root Diffusivity to Diffusion in Ni-Al-Cr Alloys, *Metall. Trans.*, 1990, **21A**, p 2679-2685
12. M.K. Stalker, J.E. Morral, and A.D. Romig, Jr., Application of the Square Root Diffusivity to Diffusion in Ni-Cr-Al-Mo Alloys, *Metall. Trans*, 1992, **23A**, p 3245-3249
13. J.S. Kirkaldy and J.E. Lane, Diffusion in Multicomponent Metallic Systems IX. Intrinsic Diffusion Behavior and the Kirkendall Effect in Ternary Substitutional Solutions, *Can. J. Phys.*, 1966, **44**, p 2059-2071
14. A.V. Jaques and J.C. LaCombe, A Stable and Efficient Regression Approach for Determination of Coefficients in Linear Multicomponent Diffusion, *J. Ph. Equilib. Diffusion*, 2012, **33**, p 181-188