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Experimental assessment of the thermodynamic factor for diffusion in CoCrFeNi and CoCrFeMnNi high entropy alloys

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ABSTRACT

The present work provides a first experimental assessment of the product of thermodynamic factor (Φ) and the cross correlation term (S) for high entropy alloys. Following a pseudo-binary approach, the concentration-dependent interdiffusion coefficients are determined for CoCrFeNi and CoCrFeMnNi high-entropy alloys at 1423 K using four different diffusion couples. Combining the data with the measured previously tracer diffusion coefficients, the value of ΦS for the equiatomic compositions is found to be close to unity for CoCrFeNi while a value of 3 to 5 is obtained for CoCrFeMnNi indicating deviations from the ideal solid solution. The interdiffusion coefficients are higher for CoCrFeMnNi substantiating the fact that an increased configurational entropy need not result in decelerated rates of the atomic transport.

High entropy alloys (HEAs) are a new class of multicomponent alloys, where constituents are combined in equiatomic or near equiatomic ratios [1]. An intriguing aspect of HEAs is the diffusion kinetics in such a multi-element matrix and there is still a lack of consensus on the factors governing the atomic transport rates in HEAs. Activation barrier [2], correlation effects [3,4] and crystallographic structure [5] have been found to influence the diffusion rates in HEAs. Recently, self-diffusion rates in crystalline bulk [6–8] or along grain boundaries [9] in CoCrFeNi and CoCrFeMnNi HEAs were measured using the radiotracer method. An anticipated deceleration of diffusivities with increased configurational entropy could not be observed. A cross-over temperature appeared, above which the diffusion rates in quinary HEA were higher than those in the quaternary one. However, the experimental reports on diffusivities in HEAs are still very limited, see e.g. a recent review [10], and therefore more reliable measurements of diffusion at various temperatures in different HEA systems are required.

In many processes, like oxidation, corrosion, etc., where chemical driving forces for diffusion are present, a basic knowledge of the interdiffusion coefficients for the alloys is required. However, the interdiffusion coefficients are very difficult to measure at lower and intermediate temperatures due to very long annealing times required inevitably. The presence of a multicomponent matrix makes it further complicated. For binary alloys, the product of the thermodynamic factor, Φ, and the cross correlation term, S, i.e. $\Phi \cdot S$, is provided via the relation between the tracer and interdiffusion coefficients, i.e. well-known Darken-Manning equation [11], $\tilde{D} = (N_A D^*_B + N_B D^*_A)\phi S$. Here D^*_A and D^*_B are the tracer diffusion coefficients of the components. The term S called the vacancy-wind term, too, was introduced by Manning [11] to account for the cross correlations in element diffusion. This relation can be extended to multi-component systems using the pseudo-binary approach suggested by Paul [13]. Nevertheless, to the best of our knowledge, this approach has never been applied to HEAs.

Therefore, in the present work we aim to determine for the first time the product $\Phi \cdot S$, providing an assessment of the thermodynamic factor, too, through dedicated interdiffusion measurements in conjunction with the available tracer diffusion coefficients [7]. With the tracer diffusion coefficients being available at several temperatures, the product $\Phi \cdot S$ will provide a straightforward and reliable way to derive the interdiffusion coefficients at any temperature of interest. Furthermore, the extent of a deviation from the random solid solution (as indicated by the values of the product $\Phi \cdot S$) can help in fine tuning the extrapolated Gibbs energy functions obtained for these HEAs and thus improve the quality of phase predictions.

As it was stated above, while the interdiffusion technique has been well established for measuring diffusivities in binary alloys [12], its use is greatly limited for the multicomponent systems. Pseudo-binary approach in multicomponent systems has been proposed in [13] to overcome this problem, where diffusion couples are designed in such a way that n-component alloy end members have compositional gradient for only 2 constituents, while remaining n-2 have same composition in both end members. To illustrate, one of the diffusion couples studied

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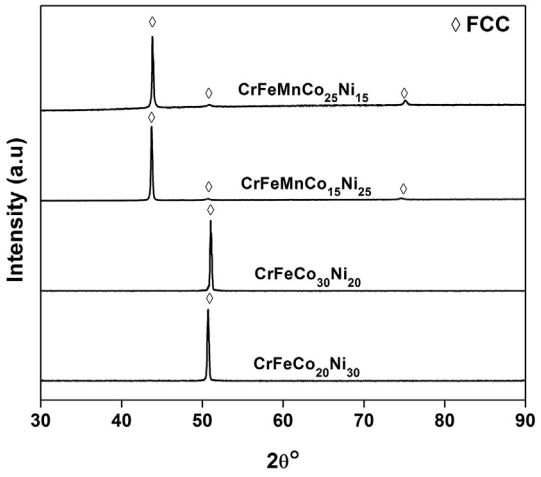

Fig. 1. XRD patterns of quaternary and quinary Co—Ni diffusion couples.

in the present work is $Cr_{25}Fe_{25}Co_{20}Ni_{30}$ – $Cr_{25}Fe_{25}Co_{30}Ni_{20}$, which has composition gradient of only Co and Ni across the interface and the composition at mid-point of the gradient corresponds to equiatomic CoCrFeNi. From here onwards, for the sake of brevity, such a couple would be referred as $(Co—Ni)_{CrFe}$ diffusion couple. The elements in bracket are the ones for which a concentration gradient exists in the diffusion couple, whereas subscript denotes the elements which have constant compositions.

The end members of all diffusion couples were produced by arc melting and subsequent homogenization at 1473 K for 50 h. Samples of 1 mm thickness were cut from each end member and mechanically polished. The samples were put in mechanical contact in a special fixture, which was subsequently annealed at 1423 K. Y_2O_3 suspension containing micrometer-large particles, was added to the contact surface as Kirkendall markers. The fixture was made from stainless steel (SS316). Mo spacers were placed between samples and fixture to avoid diffusion of elements across them. The quaternary diffusion couples were annealed in a vacuum furnace having alumina tube for holding samples and SiC heating coils. Vacuum levels of 10^{-6} mbar were maintained and temperature was controlled within ±5 K. Mn, due to its low vapor pressure, has a high tendency for evaporation loss. Therefore, quinary diffusion couples were sealed in Ar-filled quartz tube and annealed in muffle furnace with SiC heating coils. After diffusion annealing, the concentration profiles were obtained by performing compositional line-scans (step size – 1 μm) across the interface using energy dispersive spectrometry (EDS). Compositional analysis of EDS was also confirmed by electron probe microanalyzer (EPMA) for few representative samples.

The interdiffusion analysis becomes more complicated if the end members exhibit multiple phases. A two phase region provides multiple lattice paths for the diffusing element. Therefore, diffusion couples in the present work are chosen such that a single phase structure is present in binary phase diagrams of diffusing elements at the temperature of interest. To illustrate, the equiatomic CoNi binary alloy shows a single phase FCC solid solution at all temperatures [14] and therefore the $(Co—Ni)_{CrFe}$ and $(Co—Ni)_{CrFeMn}$ diffusion couples are selected for the presented study.

Fig. 1 presents the XRD patterns of end members of quaternary and quinary Co—Ni diffusion couples. Both $Cr_{25}Fe_{25}Co_{20}Ni_{30}$ and $Cr_{25}Fe_{25}Co_{30}Ni_{20}$exhibit single phase FCC structure. End members of the quinary $(Co—Ni)_{CrFeMn}$ diffusion couple, i.e., $Cr_{20}Fe_{20}Mn_{20}Co_{15}Ni_{25}$ and $Cr_{20}Fe_{20}Mn_{20}Co_{15}Ni_{25}$, crystallize in the FCC structure, too. Similar structure is shown by all the alloys used for the interdiffusion measurements in this study. Table 1 exemplifies that the composition of the end members of Co—Ni diffusion couple conform to the nominal values within acceptable deviations.

After interdiffusion annealing of a diffusion couple, the composition profile across the interface is determined from the EDS and/or EPMA analysis. It may be noted that the agreement of EDS and EPMA results have been verified (not shown here) for these alloys and it falls within the experimental error (<8%). Fig. 2a and b depict the typical concentration profiles obtained after interdiffusion annealing of quaternary $(Co—Ni)_{CrFe}$ diffusion couple for 100 and 240 h, respectively. The diffusion zone length obtained after 100 h of annealing is 85 μm, which increased to 140 μm when time of heat treatment was increased to 240 h. The overall composition towards the right and left extremes of diffusion couple does not change significantly during annealing, with deviations being <1%. Fig. 2c shows a BSE image of the $(Co_{20}Ni_{30}–Co_{30}Ni_{20})_{Cr25Fe25}$ couple after annealing. A reasonably smooth interface is seen and the dashed line indicates a region where a line scan was taken to obtain the compositional profile. Three such line scans have been taken for each diffusion couple studied to ensure statistically reliable profile. The Y_2O_3 powder (average particle size of 10 μm) used as Kirkendall markers, however, could not be found by SEM inspection. Further, no second phase is seen in the region of interdiffusion. The remaining constituents display almost horizontal profile confirming the applicability of the ideal pseudo-binary couple [10]. All the diffusion annealing treatments in the present work, for both quaternary and quinary diffusion couples, were performed for 240 h to get a wider interdiffusion zone and hence more reliable determination of diffusivities.

According to the pseudo-binary approach the diffusion parameters for a multicomponent system can be determined using a single experiment [13] and the following equation was used to calculate the interdiffusion coefficient [15]:

$$D\sim(Y_i^*) = \left(\frac{1}{2t\frac{dY_{M_i}}{dx}}\right)_{Y^*}\left[(1-Y_{M_i}{}^*)\int_{x^{-\infty}}^{x^*} Y_{M_i}dx + Y_{M_i}{}^*\int_{x^*}^{x^{+\infty}}(1-Y_{M_i})dx\right] \quad (1)$$

Here t is time of annealing and x is the position variable. M is a variable used to normalize the composition of diffusing species in terms of mole fraction (N) of other constituents, $M_i = N_j + 0.5^*\sum N_c$, where i and j refer to the elements having concentration gradient in a diffusion couple and c refers to the elements whose composition remains constant during diffusion annealing [9]. Y is the another normalization variable, defined as

$$Y_i = \frac{M_i - M_i^-}{M_i^+ - M_i^-}$$

where M_i^+ and M_i^- are the values for end members on the right hand side and left side of diffusion couple, respectively. The limits $x^{-\infty}$ and $x^{+\infty}$ refer to the end member compositions which are lean and rich,

Table 1
Composition (at.%) of CoNi diffusion couple end members obtained from EPMA (Total no. of readings taken for each alloy, n = 5).

Alloy	Co	Cr	Fe	Mn	Ni
$Cr_{25}Fe_{25}Co_{20}Ni_{30}$	19.5 ± 0.7	25.7 ± 0.6	25.5 ± 0.3	–	29.1 ± 0.6
$Cr_{25}Fe_{25}Co_{30}Ni_{20}$	29.2 ± 0.2	25.7 ± 0.5	25.8 ± 0.3	–	19.2 ± 0.3
$Cr_{20}Fe_{20}Mn_{20}Co_{15}Ni_{25}$	15.5 ± 0.6	20.6 ± 0.5	20.4 ± 0.6	18.9 ± 0.6	24.6 ± 0.4
$Cr_{20}Fe_{20}Mn_{20}Co_{25}Ni_{15}$	25.1 ± 0.3	20.2 ± 0.7	20.0 ± 0.5	20.0 ± 0.8	14.7 ± 0.1