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Experimental and numerical studies on the sluggish diffusion in face centered cubic Co-Cr-Cu-Fe-Ni high-entropy alloys

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ABSTRACT

On purpose of studying the sluggish diffusion of high-entropy alloys, three different face centered cubic Co-Cr-Cu-Fe-Ni high-entropy alloys were prepared, and assembled into three groups of sandwich-type diffusion multiple annealed at 1273, 1323, and 1373 K respectively. By means of the electron probe microanalyzer technique and recently developed numerical inverse method, the composition-dependent interdiffusivities at different temperatures were effectively evaluated by minimizing the residual between the model-predicted compositions/interdiffusion fluxes and the respectively experimental ones. After that, the tracer diffusivities were predicted based on the assessed mobility parameters and thermodynamic descriptions with the simplified ideal solution model. The comprehensive comparison between the interdiffusivities/tracer diffusivities in the Co-Cr-Cu-Fe-Ni high-entropy alloys and those in sub-binary, ternary, quaternary and other quinary alloys indicates that the sluggish diffusion exists in interdiffusion instead of tracer diffusion for the present Co-Cr-Cu-Fe-Ni high-entropy alloys.

1. Introduction

Of great significance in recent novel alloys are high entropy alloys (HEAs) which were firstly reported by Yeh et al. [1]. Distinct from the conventional alloys which focus on *X*-rich corners (*X* = Cu, Fe, or Al, etc.), HEAs contain at least 5 equimolar or near-equimolar elements ranging from 5 to 35 at.%. So far, the study of HEAs has been drawing many attentions throughout the world, because of its so-called four "core effects" [1,2], namely, high entropy, sluggish diffusion, severe lattice distortion and cocktail effects, which lead to their most comprehensive mechanical properties, like, good hardness, yield strength, creep strength, plastic strain, ductility, wear resistance, and so on [3–5]. More importantly, only a low-cost heat-treatment and simple approach can inspire these potentials to a dramatic scale [6].

Sluggish diffusion in HEAs is strongly relevant to their outstanding thermal stability, creep strength, etc. Hence, it is extraordinarily essential to validate its low diffusion kinetics. However, the traditional Matano-Kirkaldy method can merely calculate the interdiffusivities of the intersection point in ternary systems and is of little use in higher order systems, which leads to the lack of experimental data in multicomponent alloys. Thus, the determination of diffusion coefficients of HEAs is challenging. So far, only a limited number of studies have been reported on the diffusion kinetics of HEAs. Tsai et al. [7] firstly studied and reported to observe the sluggish diffusion in face centered cubic (fcc) Co-Cr-Fe-Mn-Ni alloys. By combining the Sauer-Fraise method with quasi-binary diffusion couples and hypothesizing that the correlation effect resulting from the alloy structure is neglected, the interdiffusivities were concluded to be approximately equal to the tracer diffusivities. Kulkarni and Chauhan [8] investigated the interdiffusion in fcc Co-Cr-Fe-Ni system by using a single diffusion couple, but only obtained the average interdiffusivities. Beke and Erdélyi [9] re-analyzed the data presented in Ref. [7]. By calculating the Fe and Ni tracer diffusivities, they confirmed the sluggish diffusion in fcc Co-Cr-Fe-Ni HEAs. Recently, Dabrowa et al. [10] reported the tracer diffusivities in the fcc Al-Co-Cr-Fe-Ni alloys and also re-analyzed the experimental data presented in Ref. [7]. Vaidya et al. [11] measured the tracer diffusivities of Ni in the equiatomic fcc Co-Cr-Fe-Ni and Co-Cr-Fe-Mn-Ni alloys by means of the radiotracer technique. Very recently, by combining diffusion multiples with developed numerical inverse method, Chen and Zhang [12] from our research group determined the composition-dependent interdiffusivities and tracer diffusivities of Ni in Co-Cr-Fe-Mn-Ni HEAs and compared with the reported data available in the literature. Moreover, Zhang et al. [13] demonstrated that sluggish diffusion

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Table 1
Summary of literature reports on diffusion in different HEAs.

Phase	System	Method[a]	Type of Diffusivity	Code[b]	Refs.
fcc	CoCrFeMnNi	QBDC & S-F	Tracer diffusivity	√	[7]
	CoCrFeNi	TMM	Interdiffusivity	√	[8]
	CoCrFeMnNi	Semi-empirical rules & Re-analyses of Ref. [7]	Tracer diffusivity	√	[9]
	AlCoCrFeNi	DMA & LM	Tracer diffusivity	√	[10]
	CoCrFeMnNi	DMA, LM & Re-analyses of Ref. [7]		√	
	CoCrFeNi & CoCrFeMnNi	Radiotracer technique & Gaussian solution	Tracer diffusivity	×	[11]
	CoCrFeMnNi	DM & NIM	Interdiffusivity	√	[12]
			Tracer diffusivity	×	
	CoCrFeMnNi	CALPHAD assessment	Tracer diffusivity	×	[13]
	CoCrCuFeNi	DM & NIM	Interdiffusivity	√	This work
			Tracer diffusivity	×	

[a] QBDC: Quasi-binary diffusion couple; S-F: Sauer-Fraise method; TMM: Transfer matrix method; DMA: Darken-Manning Approach; LM: Levenberg-Marquardt method; DM: Diffusion Multiple technique; NIM: Numerical Inverse Method.
[b] Indicates the conclusion in the reference whether it has sluggish diffusion or not: √ yes; × no.

was not found even with homologous temperature (T_m/T) by both experimental and computational approach. A brief summary of all their methods and conclusions are listed in Table 1. In Table 1, well-grounded is the conclusion that although interdiffusion in HEAs has been investigated, the composition-dependent interdiffusivities are still rare and retain missing in many other HEAs, like Co-Cr-Cu-Fe-Ni system etc. Therefore, it is quite urgent and exigent that we need to remedy this circumstance where a highly effective and efficient method to determine diffusivities is needed.

Recently, a house-made code, also known as HitDIC (High-throughput Determination of Interdiffusion Coefficients, https://www.hitdic.com) [14–16], has been realized to evaluate the composition-dependent interdiffusivities of multicomponent systems. With the validation in several multicomponent systems, to demonstrate, fcc Co-Ni [17] binary system, fcc Co-Cr-Nb, Co-Cr-Ta, Co-Nb-Ta, and Co-Fe-Ni [14], fcc Ni-Al-Ta [18], Ni-Al-Mo [19], Cu-Ag-Sn [20] and Al-Cu-Ni [21] ternary system, bcc_A2 Fe-Mn-Si [22] ternary system, and fcc Co-Cr-Fe-Mn-Ni [12] quinary system, this method is applicable to the high-throughput determination of the composition-dependent interdiffusivities in HEAs.

Aiming at the authentication of sluggish diffusion in HEAs, fcc Co-Cr-Cu-Fe-Ni quinary system is chosen as the target in the present work. The major research objectives are: (*i*) to evaluate the composition-dependent interdiffusivity matrices in fcc Co-Cr-Cu-Fe-Ni HEAs at different temperatures by using the numerical inverse method in combination with diffusion multiple technique; (*ii*) to predict tracer diffusivities based on the thermodynamic descriptions with the simplified ideal solution model together with the evaluated interdiffusivity matrices, and (*iii*) to validate whether sluggish diffusion exists in fcc Co-Cr-Cu-Fe-Ni HEAs by comprehensively comparing the evaluated interdiffusivities/tracer diffusivities in HEAs with those in different sub-systems.

2. Experimental procedure

Three different alloys (denoted as 1, 2 and 3) were synthesized by arc-melting of Cobalt (purity: 99.98 wt%), Chromium (purity: 99.95 wt%), Copper (purity: 99.98 wt%), Iron (purity: 99.98 wt%) and Nickel (purity: 99.995 wt%) simultaneously under an Argon atmosphere. In order to ensure homogeneities, all the samples were re-melted four times. The nominal and actual compositions of the alloys are listed in Table 2, respectively. Then, all the ingots were cut into blocks of approximate 4 mm × 4 mm × 10 mm, polished and finally sealed into vacuum quartz tubes. Furthermore, all the alloys were homogenized at 1373 K for 168 h, followed by water quenching to retain their microstructures and homogeneities. Later on, all the annealed alloys were detected through X-ray diffraction (XRD), and the results are exhibited in Fig. 1. In all cases only the single fcc phase was observed. Moreover, the scanning electron microscope (SEM) technique was taken into use and again only single fcc phase was also observed in all the samples, as shown in Fig. 2. Additionally, as shown in Fig. 3, the diffusion multiples were assembled in the schematic order and pressed in a vacuum hot-pressing furnace for 2 h at 1273 K, 1323 K and 1373 K accordingly. After that, the multiples were further annealed in the same furnace but without any pressure at 1273 K, 1323 K and 1373 K for another 70 h. Then, all the diffusion multiples were quenched in water and metallographically polished afterwards. Finally, the concentration profiles of each diffusion multiple were determined by means of electron probe microanalyzer (EPMA).

Table 2
Nominal and actual compositions of the presently prepared alloys.

Alloy	Nominal compositions (in at.%)	Actual compositions (in at.%)
1#	$Co_{22.5}Cr_{22.5}Cu_{5.5}Fe_{22.5}Ni_{27.0}$	$Co_{22.5}Cr_{22.8}Cu_{5.4}Fe_{22.7}Ni_{26.6}$
2#	$Co_{25.0}Cr_{25.0}Fe_{25.0}Ni_{25.0}$	$Co_{24.9}Cr_{25.3}Fe_{25.2}Ni_{24.6}$
3#	$Co_{26.4}Cr_{22}Cu_{3.2}Fe_{22}Ni_{26.4}$	$Co_{26.4}Cr_{22.3}Cu_{3.0}Fe_{22.4}Ni_{25.9}$

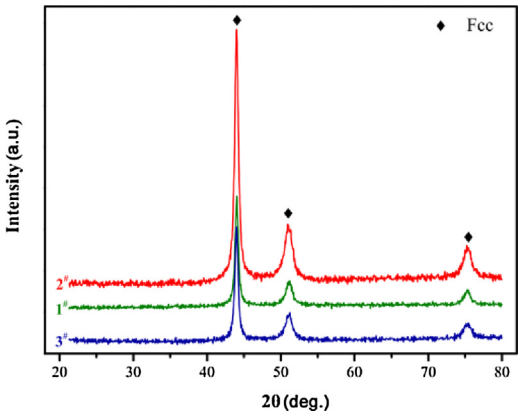

Fig 1. XRD patterns of the alloys $Co_{22.5}Cr_{22.8}Cu_{5.3}Fe_{22.7}Ni_{26.6}$ (1#), $Co_{24.9}Cr_{25.3}Fe_{25.2}Ni_{24.6}$ (2#), and $Co_{26.4}Cr_{22.3}Cu_{3.0}Fe_{22.4}Ni_{25.9}$ (3#).

3. Models

The composition evolution of an element *i*, in a given system with ***N*** components, is subjected to Fick's second law,

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left(\sum_{j}^{N-1} \tilde{D}_{ij}^{N} \frac{\partial c_j}{\partial x}\right) \quad (i = 1, 2, \ldots, N-1) \tag{1}$$

where c_i is the concentration of element *i*, *t* is the diffusion time and *x* is the diffusion distance. $\tilde{D}_{ii}^{N}$ are referred to as diagonal inter-