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## Tracer Diffusion of Cobalt in High-Entropy Alloys $\text{Al}_x\text{FeNiCoCuCr}$

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The Co diffusion in the as-cast high-entropy alloys  $\text{Al}_x\text{FeNiCoCuCr}$  ( $x = 1, 1.5, 1.8$ ) is studied by means of the tracer-diffusion method using the  $^{60}\text{Co}$  isotope. As shown, the Co diffusion in the high-entropy alloys occurs by means of the vacancy mechanism and the diffusion coefficient decreases approximately in three times (from  $3.21 \cdot 10^{-16}$  to  $0.98 \cdot 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$ ) with the increasing Al concentration. The decelerated Co diffusion is explained in terms of relatively large and negative enthalpy of mixing.

**Keywords:** high-entropy alloys,  $^{60}\text{Co}$  diffusion coefficient, structure, activation energy, melting temperature.

Методом радіоактивних ізотопів досліджено дифузію  $^{60}\text{Co}$  у литих високоентропійних стопах  $\text{Al}_x\text{FeNiCoCuCr}$  ( $x = 1, 1.5, 1.8$ ). Показано, що дифузія Co у високоентропійних стопах відбувається за вакансійним механізмом, і зі збільшенням концентрації Al значення коефіцієнта дифузії зменшується приблизно втричі (від  $3,21 \cdot 10^{-16}$  до  $0,98 \cdot 10^{-16} \text{ м}^2 \cdot \text{с}^{-1}$ ). Уповільнена дифузія Co пояснюється за рахунок відносно великої і негативної ентальпії змішання.

**Ключові слова:** високоентропійний стоп, коефіцієнт дифузії  $^{60}\text{Co}$ , структура, енергія активації, температура топлення.

Методом радиоактивных изотопов изучена диффузия  $^{60}\text{Co}$  в литых высокоэнтропийных сплавах  $\text{Al}_x\text{FeNiCoCuCr}$  ( $x = 1, 1.5, 1.8$ ). Показано, что диффузия Co в высокоэнтропийных сплавах происходит по вакансионному ме-

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ханизму, и с увеличением концентрации Al значение коэффициента диффузии уменьшается примерно в три раза (от  $3,21 \cdot 10^{-16}$  до  $0,98 \cdot 10^{-16} \text{ м}^2 \cdot \text{с}^{-1}$ ). Замедленная диффузия Co объясняется за счёт относительно большой и отрицательной энтальпии смешения.

**Ключевые слова:** высокоэнтропийный сплав, коэффициент диффузии  $^{60}\text{Co}$ , структура, энергия активации, температура плавления.

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## 1. INTRODUCTION

Development of new engineering materials with the high properties is a requirement of the present time. The high-entropy alloys (HEAs), which attracted attention of a number of scientists, can be attributed to these materials [1–5]. These alloys belong to multicomponent metallic systems containing constituents in equimolar or nearly equimolar relationship being between 5 and 35 at.%. According to Yeh *et al.* [2], the HEAs do not have the element as host and are characterized by high configurational entropy of mixing ( $\Delta S_{\text{mix}}$ ) providing formation of simple solid solutions. Subsequent studies were followed this determination, however, the name HEA was unchanged.

The HEA possess unique practically important properties, for instance, high heat resistance, corrosion resistance [6], low electrical conductivity and thermal conductivity [7, 8]. The low growth of grains [9] and high thermal stability [10] are attributed also to the HEA. One can assume that sluggish diffusion kinetics even at high temperatures is an important contributor to the outstanding properties of the HEA.

Nevertheless, currently there is no enough diffusion data for HEAs. For example, M. H. Tsai *et al.* [11] have applied the diffusion pair method and measured the diffusion parameters in the CoCrFeMnNi HEA, and the obtained data were compared with the self-diffusion. It was found that the diffusion rates of each element in the CoCrFeMnNi HEA were low, which was attributed to a higher activation energy of diffusion. To explain the sluggish diffusion in the HEA, the quasi-chemical model was proposed in which the essential fluctuations of the lattice potential energy (LPE) in different matrixes create the effect of trap and obstacles for atomic mobility resulting in high diffusion-activation energy.

Recently M. Dabrowa *et al.* [12] have studied interdiffusion parameters in non-equimolar HEA AlCoCrFeNi and determined the tracer diffusion coefficients of the components using two methods of optimisation. The results confirmed the theory of sluggish diffusion in HEAs.

Very recently, M. Vaidya *et al.* [13] have reported the results upon tracer ( $^{63}\text{Ni}$ ) diffusion obtained for the first time in CoCrFeNi and CoCrFeMnNi alloys by the radiotracer technique in the temperature range of 1073–1373 K. A tendency to a successive slow down on the

tracer diffusion rate with an increased number of components in the HEAs was established. They concluded that diffusion in HEAs is not inevitably decelerated.

Taking into account the limited number of works upon diffusion in HEA as well as the fact that the knowledge upon diffusion and kinetic parameters are the key data in study of crystallization processes, phase transformations, and atomic ordering, the new studies in this direction are required. At the same time, in order to enhance the reliability of the diffusion data, it is necessary to extend a set of the experimental methods. Therefore, the diffusion processes in the  $\text{Al}_x\text{FeNiCoCuCr}$  HEA with the third chemical compositions  $x = 1, 1.5, 1.8$  has been studied by means of the tracer-diffusion method using the  $^{60}\text{Co}$  isotope.

## 2. MATERIAL AND METHODS

The as-cast high-entropy alloys  $\text{Al}_x\text{FeNiCoCuCr}$  with the Al concentrations  $x = 1$  ( $A_1$ ),  $x = 1.5$  ( $A_2$ ), and  $x = 1.8$  ( $A_3$ ) were studied (Table 1). The samples of the HEA were the  $10 \times 10 \times 1.2$  mm plates. To study the diffusion of cobalt in HEA, the tracer diffusion method was applied, which is more effective to study the diffusion processes in metals and alloys. The radioactive isotope  $^{60}\text{Co}$  was chosen as diffusant which was deposited on the plate surface at room temperature. This isotope has the  $\sim 5.3$  years half-life time and irradiates electrons ( $\beta$ ) resulting from  $\beta$  decay. The plates with the deposited layer of the radioactive isotope were aged in vacuum ( $p = 10^{-5}$  Pa) at 1473 K during 10 hrs.

The phase composition and the microstructure of the as-cast HEA were studied by means of the X-ray diffraction (XRD) analysis using diffractometer DRON-3M with the  $\text{CoK}_\alpha$  irradiation and the scanning electron microscope Jeol JCM-5000 (Neoscope). All the X-ray powder diffractograms of the HEA in initial as-cast state were measured with the same exposure of  $0.05^\circ/2''$ . The surface layer of the  $0.2\text{--}0.25$   $\mu\text{m}$  in thickness was removed by etching before measurements in order to exclude the effect of stresses appeared after mechanical treatment.

In order to estimate the tracer diffusion coefficient of Co, the methodology described in [14] was applied. The concentration distribution of

**TABLE 1.** Chemical composition of the high-entropy alloys  $\text{Al}_x\text{FeCoNiCuCr}$ .

Alloy	$x$	Element, [wt.%]/[at.%]					
		Al	Fe	Co	Ni	Cu	Cr
$A_1$	1	8.8/17.2	18.1/17.1	18.3/16.3	18.9/16.9	19.7/16.3	16.0/16.2
$A_2$	1.5	12.2/23.0	17.4/15.9	17.3/14.9	18.6/16.1	19.4/15.5	14.9/14.6
$A_3$	1.8	14.9/27.3	16.8/14.9	17.1/14.4	17.7/14.8	18.7/14.6	14.7/14.0

the  $^{60}\text{Co}$  isotope in the studied sample was determined by layer-by-layer analysis. This methodology is used in case of diffusion from a thin layer (1–3  $\mu\text{m}$ ) into infinite body at stationary isothermal ageing. In this method, the concentration of the radioactive isotope penetrated in a sample is detected upon irradiation intensity  $I_n$  (a number of pulses per minute) from  $n$ -th layer. Generally, the dependence of irradiation intensity  $I_n$  on a coordinate after  $n$ -th layer stripping is expressed by formula:

$$I_n = \int_{d_n}^{\infty} c(d, \tau) \exp[-\mu(d_0 - d_n)] dd, \quad (1)$$

where  $d_n$  is the coordinate of  $n$ -th layer,  $c(d, \tau)$  is the function expressed the dependence of a radioactive isotope concentration on coordinate,  $\mu$  is the absorption coefficient of an isotope irradiation by a sample material;  $\tau$  is the durability of diffusion annealing.

If to accept the premise that solution of the Fick's second equation for the above-mentioned conditions is as follows:

$$c(d, \tau) = \frac{A}{\sqrt{\pi D \tau}} \exp\left(-\frac{d^2}{4D\tau}\right), \quad (2)$$

and, moreover, substituting Eq. (2) in Eq. (1), after transformations, one obtains:

$$\mu I_n + \frac{\partial I_n}{\partial d_n} = \frac{A}{\sqrt{\pi D \tau}} \exp\left(-\frac{d_n^2}{4D\tau}\right). \quad (3)$$

After taking a logarithm of the expression (3) and neglecting  $\mu I_n$  (through a smallness of  $\mu$  for this case), one obtains:

$$\ln\left(\frac{\partial I_n}{\partial d_n}\right) = -\frac{1}{4D\tau} d_n^2 + A. \quad (4)$$

Since  $\ln(\partial I_n / \partial d_n)$  is linear function of  $d_n^2$  Eq. (4), the  $\text{tg}\alpha$  equals to  $1/(4D\tau)$  ( $\alpha$  is the angle between this dependence and coordinate  $d^2$ ) that characterises a bulk diffusion. Deviation from linear dependence  $\ln(\partial I_n / \partial d_n) = f(d_n^2)$  is an attribute of existence of other contributions into diffusion process from grain boundaries, dislocations, interphase boundaries, *etc.* [15].

Thus, according to Eq. (4), the following relationship for diffusion coefficient determination is obtained:

$$D = -\frac{1}{4\tau \text{tg}\alpha}, \quad (5)$$

or, in decimal logarithm:

$$D = -\frac{0.1086}{\tau \operatorname{tg} \alpha}. \quad (6)$$

This approach is usually used in diffusion studies at isothermal ageing of an alloy with the accuracy in diffusion coefficient determination of approximately 5%.

### 3. RESULTS

The XRD analysis at room temperature has shown that one bcc ( $\alpha$ ) and two f.c.c. ( $\gamma_1$  and  $\gamma_2$ ) phases were identified in the as-cast equimolar  $\text{AlFeCoNiCuCr}$  alloy ( $A_1$ ) (Fig. 1), which is consistent with the data of works [1–3, 16]. The lattice parameters of these phases are  $a_\alpha = 0.2871$  nm,  $a_{\gamma_1} = 0.3624$  nm and  $a_{\gamma_2} = 0.3592$  nm, respectively. The phases  $\alpha$  and the  $\gamma_1$  were detected in the as-cast HEA having a higher concentration of Al ( $x = 1.8$ ), whereas the  $\gamma_2$  phase was not revealed. The lattice constants of the  $\alpha$  and  $\gamma_1$  phases grow to the values of 0.2882 nm and 0.3648 nm, respectively, with increasing concentration of Al, which suggests dissolution of Al in both phases and is consistent with the concentration dependences of the lattice parameter of the b.c.c. and f.c.c. phases in the  $\text{Al}_x\text{FeCoNiCuCr}$  HEA shown in [2, 3]. At the same time, the width of diffraction lines of  $\alpha$ -phase increases approximately by 13%. As there is no evidence for dispersion of crystal structure, the broadening of the linewidth is attributed to growing microstresses.

The linewidth of diffraction lines from the  $\gamma$ -phase, particularly for the HEA with the higher Al concentration, has been not estimated correctly through its weak intensity because of the low content of this phase. According to the X-ray diffraction data, the concentration of the

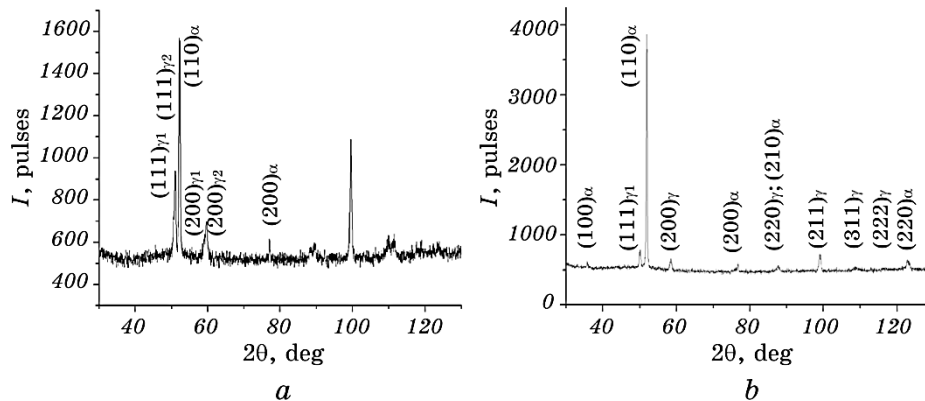


Fig. 1. XRD patterns of the as-cast  $\text{Al}_x\text{FeCoNiCuCr}$  HEAs for  $x = 1$  ( $A_1$ ) (a) and  $x = 1.8$  ( $A_3$ ) (b).

$\gamma$ -phase was reduced from 35% to 8% by opposite to that of the  $\alpha$ -phase, which increases from 65% to 92% with the increasing Al content.

Figure 2 represents the SEM images of the as-cast  $\text{Al}_x\text{FeCoNiCuCr}$  HEA. The typical dendrite (DR) structure with the interdendrite (ID) zones is observed in the HEA that is consistent with works [3, 16]. The dimensions and morphology of the DRs and IDs are diverse in these alloys and the sizes of individual DR reach of 100–500 nm and ID zones of 1–10  $\mu\text{m}$ . This indicates on inhomogeneity of the crystallization reaction through a difference in local composition and inhomogeneous distribution of atoms in the melt and, as a result, in the solid solution. Moreover, with it, the increase of Al content results in refinement of DRs and IDs, excepting for individual large ID zones (Fig. 2, *b*). The inhomogeneous atomic distribution in the  $\text{Al}_x\text{FeCoNiCuCr}$  HEA was detected in [16–18]. Particularly Cu tends to segregate in ID–DR boundaries [16, 18], which results from a high positive enthalpy of mixing of Cu in the mixture with the other elements [16, 19]. Taking into account the spatial inhomogeneities in the as-cast  $\text{Al}_x\text{FeCoNiCuCr}$  HEA [16–18], their multiphase composition and dendritic microstructure [1–3] (see Fig. 1 and Fig. 2) as well as the competing affinity of each element with other ones (negative and positive enthalpy of mixing in binary systems  $A$ – $B$ , where  $A, B = \text{Cu}, \text{Ni}, \text{Cr}, \text{Al}, \text{Co}, \text{Fe}$  [19]), one can assume abnormal behaviour of the diffusion characteristics.

The concentration profiles of the  $^{60}\text{Co}$  tracer diffusion in the equimolar  $\text{AlFeNiCoCuCr}$  HEA are presented in Fig. 3. The pronounced exponential behaviour of the concentration profiles for this alloy points to the fact that the Co tracer diffusion at 1473 K occurs in the bulk due to the vacancy mechanism. The diffusant  $^{60}\text{Co}$  penetrates on the depth of 50  $\mu\text{m}$ . At this temperature, the diffusion coefficient of

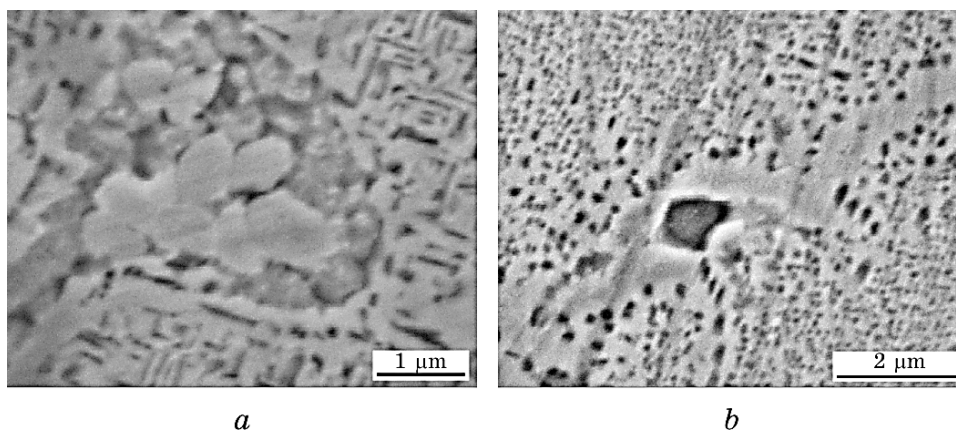
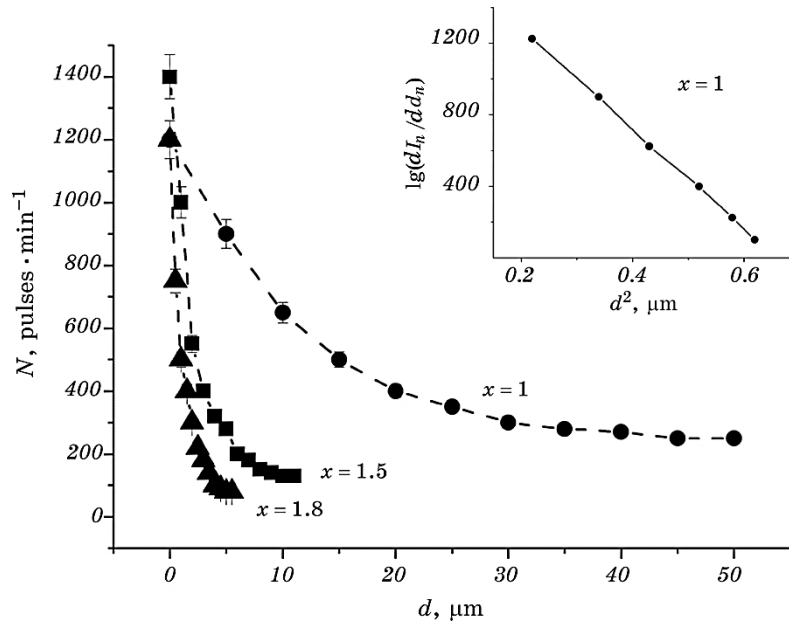


Fig. 2. SEM images of microstructures of the as-cast  $\text{Al}_x\text{FeCoNiCuCr}$  HEAs with different aluminium contents ( $x$ -value): 1.0 ( $A_1$ ) (*a*) and 1.8 ( $A_3$ ) (*b*).

cobalt in the equimolar HEA, as estimated upon (6), is equal to  $3.21 \cdot 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$  (Table 2).

In order to correct compare the obtained value with the Co diffusion coefficient in CoCrFeMnNi HEA obtained by M. H. Tsai *et al.* [11], the melting point  $T_m$  of the equimolar  $A_1$  HEA was measured by means of the DTA analysis ( $T_m = 1600 \text{ K}$ ; Fig. 4, *a*) and the inverse homologous temperature was determine  $T_m/T \cong 1.1$ . Extrapolating the data of M. H. Tsai *et al.* on this homologous temperature, the Co diffusion coefficient for CoCrFeMnNi HEA,  $D_{\text{Co}}^{\text{HEA}} \cong 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ , differs from that obtained in our experiment and higher by two orders of magnitude. One can assume that this difference results from effect of Al.

The increase of Al concentration confirms this hypothesis. The diffusion curve for the  $\text{Al}_{1.5}\text{FeNiCoCuCr}$  HEA ( $A_2$ ) is near the exponential shaped one, although it differs from that for the equimolar HEA ( $A_1$ ) by abrupt decreasing depth ( $\cong 11 \mu\text{m}$ ) of the  $^{60}\text{Co}$  penetration at  $1473 \text{ K}$  (Fig. 3). The exponential behaviour of the curve means also the bulk diffusion of Co in the  $A_2$  HEA and, at the same time, this diffusion process is slower than in the equimolar  $A_1$  alloy. The estimated Co diffusion coefficient in this case is  $1.1 \cdot 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$ , which approximately



**Fig. 3.** The concentration profiles of the  $^{60}\text{Co}$  isotope tracer diffusion in the equimolar ( $x = 1.0$ ) high-entropy alloy  $\text{Al}_x\text{FeNiCoCuCr}$  ( $A_1$ ) and in the HEAs with  $x = 1.5$  ( $A_2$ ) and  $x = 1.8$  ( $A_3$ ) after diffusion ageing at  $T = 1473 \text{ K}$  during  $\tau = 3.6 \cdot 10^4 \text{ sec}$ . Insert shows the diffusion curve for  $A_1$  in coordinates  $\ln(\partial I_n / \partial d_n) = f(d_n^2)$  ( $x = 1$ ).

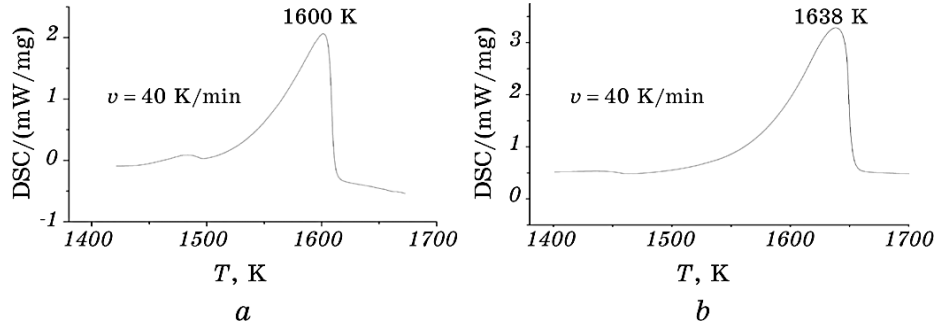
**TABLE 2.** Diffusion characteristics of the  $\text{Al}_x\text{FeNiCoCuCr}$  HEAs for 1473 K.

Alloy	$x$	$D_{\text{Co}}^{\text{HEA}}$ , [ $\text{m}^2\cdot\text{s}^{-1}$ ]	$D_{\text{Co}}^{\text{shield}}$ , [ $\text{m}^2\cdot\text{s}^{-1}$ ]	$D_{\text{Co}}^{\text{shield}} / D_{\text{Co}}^{\text{HEA}}$	$D_0$ , [ $\text{m}^2\cdot\text{s}^{-1}$ ]	$Q$ , [ $\text{kJ}\cdot\text{mol}^{-1}$ ]
$A_1$	1	$3.21\cdot 10^{-16}$	–	18	–	351.4
$A_2$	1.5	$1.1\cdot 10^{-16}$	–	52	–	364.5
$A_3$	1.8	$0.98\cdot 10^{-16}$	–	59	–	365.9
CoCrFeMnNi [11]	–	$\sim 10^{-14}$ (1473 K)	–	–	$9.26\cdot 10^{-4}$	306.9
Co [14]	–	–	$57.6\cdot 10^{-16} \text{ m}^2\cdot\text{s}^{-1}$ (1448 K)	–	–	–

three times of magnitude smaller than in the equimolar HEA (Table 2). The melting point of this alloy increases by 16 K ( $T_m = 1616$  K) and does not change essentially the  $T_m/T \cong 1.1$  value. Therefore, the comparison of  $D$  values for  $A_1$  and  $A_2$  alloys is correct.

In case of the  $\text{Al}_{1.8}\text{FeNiCoCuCr}$  HEA ( $A_3$ ) with the higher Al content ( $x = 1.8$ ), the  $^{60}\text{Co}$  penetration depth at the same temperature (1473 K) is approximately by one order smaller than in equimolar HEA ( $A_1$ ) and does not exceed 6  $\mu\text{m}$  (Fig. 3). This one points onto a still smaller Co diffusion rate in the alloy. The diffusion curve shows also exponential behaviour (Fig. 3), although its slope is greater than that for the  $\text{AlFeNiCoCuCr}$  ( $A_1$ ) and the  $\text{Al}_{1.5}\text{FeNiCoCuCr}$  ( $A_2$ ) HEAs. The estimated diffusion coefficient in the  $\text{Al}_{1.8}\text{FeNiCoCuCr}$  HEA ( $A_3$ ) is smaller and equal to  $0.98\cdot 10^{-16} \text{ m}^2\cdot\text{s}^{-1}$  (Table 2). This  $D_{\text{Co}}^{\text{HEA}}$  value should be still smaller since the melting of the  $A_3$  HEA occurs at higher temperature, 1638 K (Fig. 4, *b*) (the corresponding inverse homologous temperature  $T_m/T$  is increased). Consequently, the addition of Al reduces the tracer diffusion rate.

Thus, in accordance with the data obtained by M. H. Tsai *et al.* [11], the Co diffusion coefficient for Al free CoCrFeMnNi HEA at identical

**Fig. 4.** Heat flow for the  $\text{Al}_x\text{FeCoNiCuCr}$  HEA:  $x = 1$  ( $A_1$ ) (*a*) and  $x = 1.8$  ( $A_3$ ) (*b*).



temperature conditions (the same inverse homologous temperature) is higher by approximately two orders in magnitude. Moreover, the  $D_{\text{Co}}^{\text{HEA}}$  values determined in our tracer diffusion experiment (Table 2) are approximately by one order of magnitude smaller than Co self-diffusion coefficient at 1448 K,  $D_{\text{Co}}^{\text{self}} = 57.6 \cdot 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$ , in [14] (Table 2). Thus, it can be concluded that aluminium decelerates diffusion process in as-cast high-entropy alloys  $\text{Al}_x\text{FeNiCoCuCr}$  ( $x = 1, 1.5, 1.8$ ).

The activation enthalpy of the diffusion  $Q$  was estimated by means of the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (7)$$

where  $D_0$  is the pre-exponential factor,  $RT$  has its usual meaning. We are aware that diffusion experiment at different temperatures is required, which will be fulfilled in the near future. However, just to estimate  $Q$  value and its change with the Al increase, the pre-exponential factor,  $D_0 = 9.26 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ , as obtained for Co in the multicomponent CoCrFeMnNi alloy, was taken from [11]. The estimated activation enthalpy for the studied equimolar AlFeNiCoCuCr HEA equals  $Q = 351.4 \text{ kJ} \cdot \text{mol}^{-1}$ . The enthalpy of activation for the studied HEA equals  $Q = 333.6 \text{ kJ} \cdot \text{mol}^{-1}$  in case of pre-exponential factor,  $D_0 = 2.16 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ , as obtained by J. Dabrowa *et al.* for the Co tracer diffusion in AlCoCrFeNi system [12]. The obtained  $Q$  values are by 15% higher than those reported in [11, 12]. The differences between  $Q$  value obtained in the present work and those reported in [11, 12] can be explained by the effect of Al, except for proximity in  $D_0$  for studied values. The presence of Mn in the multicomponent CoCrFeMnNi alloy [11] and the considerable deviation from equimolar composition of HEA [12] may also have an impact upon differences between  $Q$  values.

#### 4. DISCUSSION

The activation enthalpy for studied HEAs estimated in the same way using the pre-exponential factor taken from [11] turned out an increasing value with the increasing Al content to  $x = 1.5$  and  $x = 1.8$  (Table 2). The higher diffusion activation enthalpy, the slower is diffusion process [14]. This one supports a statement that Al suppresses diffusion in the  $\text{Al}_x\text{FeNiCoCuCr}$  HEAs, and this process is sluggish.

One can assume that such an essential effect of Al on tracer diffusion of Co is due to significant interaction between Al and Co atoms. The calculation results of the mixing enthalpy of different binary systems [19] support this assumption. The negative enthalpy of mixing  $\Delta H_{\text{mix}}$  of the Al–Co binary system ( $-19 \text{ kJ} \cdot \text{mol}^{-1}$ ) is larger in contrast to other binary systems ( $-1 \text{ kJ} \cdot \text{mol}^{-1}$  for Al–Cu;  $-10 \text{ kJ} \cdot \text{mol}^{-1}$  for Al–Cr;

$-11 \text{ kJ}\cdot\text{mol}^{-1}$  for Al–Fe). An exception is only for the Al–Ni system where  $\Delta H_{\text{mix}} = -22 \text{ kJ}\cdot\text{mol}^{-1}$  [19]. One can expect also the sluggish diffusion of Ni in the  $\text{Al}_x\text{FeNiCoCuCr}$  HEA. It correlates with the EDS/TEM data regarding the existence of the dendritic Al–Ni zones with the *B2* crystal structure enriched principally with Co in the as-cast equimolar  $\text{AlCoCrCuFeNi}$  HEA [20].

Possible mechanisms of the diffusion of Co in the HEAs were considered in [11–13]. A quasi-chemical model for calculation of fluctuations of the lattice potential energy (LPE) in different principle metals and particularly Al-free  $\text{CoCrFeMnNi}$  HEA was proposed by M. H. Tsai *et al.* [11]. Greater LPE fluctuation between the lattice sites produces more significant atomic traps and leads to higher activation enthalpy, which accounts for the decelerated diffusion in HEA [11]. However, it could be noted that the single phase in  $\text{CoCrFeMnNi}$  HEA did not contain Al, which essentially distorts crystal lattice [2, 3], and the approach [11] does not take into consideration the possible different interaction in pairs of atoms.

According to [21], the grain-boundary diffusion in polycrystals is the main contribution to mass transfer only within the temperature interval  $(0.5\text{--}0.7)T_m$ . At temperatures higher than denoted interval, the bulk tracer diffusion is dominated. The grain-boundary contribution at  $0.85T_m$  in  $^{63}\text{Ni}$  tracer diffusion in homogeneous equimolar HEAs  $\text{CoCrFeNi}$  and  $\text{CoCrFeMnNi}$  (with relatively developed grain structure at room temperature) was studied in [13], although, the authors underlined a need of more detailed investigation of this point at relatively high temperatures as the subject of a separate study.

Our experiment has been done at even greater temperature 1473 K that corresponds to  $(0.90\text{--}0.92)T_m$  and excludes grain-boundary contribution. Moreover, the as-cast Al-containing  $\text{Al}_x\text{FeNiCoCuCr}$  HEAs ( $x = 1, 1.5, 1.8$ ) represent the dendrites formed during crystallization of the melt and do not contain grain boundaries (Fig. 2). Thus, a grain boundary diffusion mechanism in the studied HEAs with  $T_m = 1600\text{--}1638 \text{ K}$  can be excluded.

In addition, in case of two-phase system [15], the second phase exists as an isolated inclusion and phase boundaries do not form the uniform system similar to grain boundary one. Therefore, the whole mass transfer upon phase boundaries at high temperature should be still lower than along grain boundaries. A contribution of DR–ID boundaries to diffusion process remains open, although, taking into account high temperature (1473 K) and linear dependence  $\ln(\partial I_n / \partial d_n) = f(d_n^2)$  Eq. (4) (Fig. 3, insert), the contributions to diffusion process from boundaries of different structural elements, particularly from DR–ID boundaries, are not sufficient [15].

According to [14], the exponential-like concentration curves (Fig. 3) and linear dependence Eq. (4) mean that diffusion of Co in the as-cast

$\text{Al}_x\text{FeNiCoCuCr}$  HEA at high temperature occurs preferably in the bulk by a vacancy mechanism. The vacancies in their sufficient concentration for diffusion in HEAs can be generated at high temperatures by a theoretically forecasted mechanism based on local distortion of the interatomic distances due to considerable differences of the atomic radii [22]. In the studied HEAs, the atomic radius of Al (0.143 nm) is higher than that for the rest metals (for example, 0.125 nm of Co).

## 5. CONCLUSIVE REMARKS

The  $^{60}\text{Co}$  tracer diffusion in the as-cast  $\text{Al}_x\text{FeNiCoCuCr}$  ( $x = 1, 1.5, 1.8$ ) HEAs at the temperature of 1473 K ( $(0.90\text{--}0.92)T_m$ ) turned out to be abnormally low more than one order as compared to the Co self-diffusion process.

Increase in the concentration of Al in the as-cast  $\text{Al}_x\text{FeNiCoCuCr}$  HEAs from  $x = 1$  to  $x = 1.8$  decreases the  $^{60}\text{Co}$  tracer diffusion coefficient  $D_{\text{Co}}^{\text{HEA}}$  by three times from  $0.98 \cdot 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$  to  $3.21 \cdot 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$  and increases the activation enthalpy of the diffusion approximately by 4% (from 351.4 to 365.9  $\text{kJ} \cdot \text{mol}^{-1}$ ). The tracer diffusion of Co in the Al containing HEAs at given homologous temperatures  $(0.90\text{--}0.92)T_m$  is decelerated one provided by Al that is explained in terms of relatively high and negative enthalpy of mixing of the Al and Co system.

The exponentially shaped  $^{60}\text{Co}$  concentration profiles correspond certainly to the bulk tracer diffusion in the as-cast  $\text{Al}_x\text{FeNiCoCuCr}$  HEAs via more probable vacancy mechanism.

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