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DIFFUSION COEFFICIENTS IN MULTIPHASE Ni80Cr20-Ti SYSTEM

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Abstract

In this paper, the reactive diffusion in Ni80C20r–Ti ternary system is discussed at 1173K. The diffusion couple was prepared and annealed for 100 h. The two intermetallic phases and two two-phase zones occurred, namely: Ti_2Ni, TiNi, TiNi+Cr, and $TiNi_3$+Cr. Based on the experimental results (molar fractions, thicknesses of the intermetallic phases), the intrinsic diffusion coefficients of all components in each phase were numerically approximated. The Wagner method was used in the pure intermetallic phases. In the two phase zones the approximation was based on the generalized Darken and Wagner methods. The presented methods allowed for determination of the effective diffusion coefficients in each presented phase.

Keywords: *Reaction diffusion; Equilibrium; Ni80Cr20–Ti system*

1. Introduction

Diffusion coupling technique is one of the most often used methods of examination of the diffusion phenomena. This method can be used in studying the phase relations (phase diagrams determination) in multicomponent systems and is based on the assumption of local equilibrium in the diffusion zone. The experimental results, obtained on annealed diffusion couple in the form of the concentration profile, help in determination of the diffusion path, which is a mapping of the stationary concentrations onto the isothermal section of the equilibrium phase diagram [1]. The diffusion path is a common way of presenting the sequence of the layers growth and their compositions on the phase diagram. The experimental determination of the diffusion (reaction) path during the diffusion coupling experiments allows for determination of many phenomena, such as the order of the product layers, their morphology and compositions, however, the information about their spatial distribution is lost. The diffusion path connects initial compositions of the diffusion couple and can go across the single-, two-, and three-phase fields (in ternary systems). It starts at the composition of one alloy and ends at the other [1]. Kirkaldy and Brown [2], in one of their seventeen theorems, show the possibility of mapping the concentration profiles (diffusion path) onto the ternary isotherm.

One of the most important kinetic data in high temperature alloys characterization is the diffusion coefficient. The diffusion coefficient describes the speed of atom interaction - entropy and enthalpy in the alloy. There are some experimental methods allowing for determination of these material constants, however, they are limited to the binary [3] or ternary alloys [4,5]. Such methods are based on insertion of the markers between the alloys that create the diffusion couple. Then, based on the position of the markers after the annealing, the diffusion coefficient can be determined [6]. Such experimental approach is time- and cost-consuming, and that is why the numerical methods are presently widely used for determination of the diffusivity data. One of the most known methods of this kind, based on the experimental results after annealing of the binary diffusion couple, is Boltzmann-Matano analysis [7,8], further generalized by Sauer-Freise by introduction of different molar volumes [9]. However, such approach is limited to the binary one-phase systems. There were some attempts to modify the Boltzmann-Matano method into ternary systems [10], but these modifications allow for determination of the intrinsic diffusion coefficients only in multicomponent one-phase systems. None of the above mentioned approaches could determine the diffusion coefficient in multi-phase alloys, which is essential in many applications as the diffusion coefficients help to

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understand the mechanical properties of heat-treated materials, i.e. stress induced diffusion [11] or phase transformation [12].

There were many theoretical as well as experimental studies describing the phase diagrams for the Ni-Cr-Ti system [13-15]. Knowledge of phase equilibrium in such a system is of great importance as addition of Ti into Ni-Cr alloys improves their high-temperature corrosion resistance and mechanical properties [16-17]. However, those properties depend strongly on the order and morphology of the intermetallic phases that form in the interdiffusion zone which in turn depend on initial alloy compositions.

In this paper, the annealing process of the Ni80Cr20-Ti diffusion couple at 1173K for 100h was conducted. The alloy composition was chosen to check what intermetallic phases will form (one and two phase regions) during annealing under these conditions – such data is lacking in the literature. The experimental results will be used to verify if it is possible to determine the diffusion coefficients of particular elements (Ni, Cr, and Ti) in each phase of the multicomponent ternary systemby the proposed approach.The procedure of determination of diffusion coefficients is based on the Wagner approximation [19] and generalization of the Darken method into the two-phase systems [20]. Ultimately, the diffusion coefficients in the whole system were approximated.

2. Experimental

In this paper, two materials were connected to create a diffusion couple, namely Ni80Cr20 (Ni – 80 at. %, Cr – 20 at. %) alloy and Ti (99.9% purity from Sigma Aldrich supplier). Before diffusion annealing, the samples were cut to the rectangular shapes of the dimensions 20 x 10 x 1 mm. The surface of the samples were further ground and polished up till 1 μm grain size of SiO_2 particles in a polishing suspension to obtain mirror-like surface finishing. The diffusion couple was inserted into the molybdenum holder (Figure 1) and placed into the glass tube of the Carbolite STF 16/450 tube furnace. Initially the holder with the samples was flushed with high purity argon (5.0 purity) in the cold zone of the furnace to extract the ambient atmosphere. After the flushing time, the holder was moved to the hot zone of the furnace. The proper heat treatment experiment was performed at 1173K for 100h also in an argon atmosphere to prevent the oxidation of the diffusion couple. After annealing and standard preparation of metallographic cross-sections, the diffusion couple was examined using scanning electron microscopy (SEM) Hitachi S3400 N coupled with energy dispersive spectrometer (EDS). Images were taken in back-scattered electron (BSE) mode, which enabled the increase of the contrast between the phases. Concentration profiles of diffusion couple's cross-section were measured using EDS and the qualitative analysis of the elements that occurred in the diffusion zone was made using EDX (energy dispersive X-Ray spectroscopy). Thicknesses of identified phases were determined by means of NIS-Elements software based on SEM/BSE images.

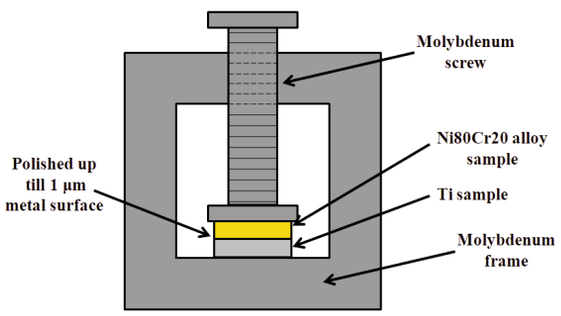

Figure 1. *A schematic image showing the connection of Ni80Cr-Ti diffusion couple in molybdenum frame*

3. Results and discussion

3.1. Experimental results

The SEM/BSE image of diffusion zone that was created between pure titanium and Ni80Cr20 alloy after annealing at 1173 K for 100 hours is presented in Figure 2. The SEM/EDX analysis was performed (Figure 3, Table 1) and enabled the identification of the phases that were distinguished and named in Figure 2. During the diffusion, the Ti_2Ni and TiNi phases (points 2, 3 and 4, 6 in Figure 3, Table 1, respectively) were generated as well as two-phase zones: TiNi+Cr and TiNi+Cr and $TiNi_3$+Cr. The formation of such phases wasvisible in the cross-section: TiNi created a brighter matrix (point 8 in Figure 3, Table 1) within which a darker chromium precipitates (point 7 in Figure 3, Table 1) were present. Similarly, dark chromium spots

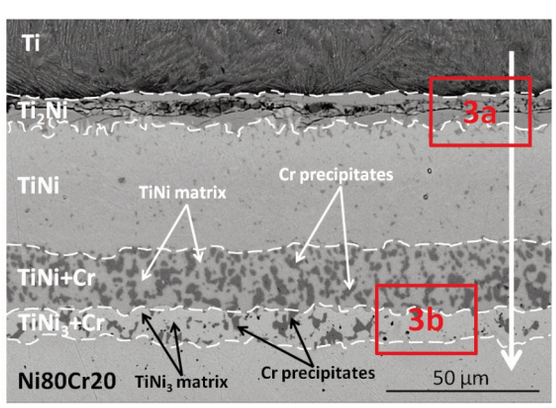

Figure 2*. SEM/BSE image showing the cross-section of Ni80Cr20-Ti diffusion couple after annealing for 100 h at 1173 K. Red boxed are magnified in Figure 3*

(point 10 in Figure 3, Table 1) were distinguishable from a brighter $TiNi_3$ matrix (point 9 in Figure 3, Table 1).The SEM/BSE image revealed also, that there were many pores and cracks visible within the Ti_2Ni phase (Figure 2). It is probably an effect of the cross-section preparation, mainly grinding steps – $TiNi_2$ was brittle and therefore, it was very likely that some of it broke away while preparation.

The concentration profile of the elements as a function of distance, following the direction of the line-scan marked by a white arrow in Figure 2, is shown in Figure 4. The concentration profile may be also drawn as a ternary diagram where concentration of chromium, nickel, and titanium are x, y, and z-axis, respectively. Diffusion path, obtained by placing the mentioned ternary form of concentration profile onto isothermal section of the equilibrium phase diagram of Ni–Cr–Ti system at 1123K is presented in Figure 5. Based on such a diagram, an occurrence of $TiNi_2$ and TiNi phases, that were observed on SEM/BSE images (Figure 2 and 3a), may be confirmed. Moreover, as it is visible in Figure 5, diffusion path crossed the conodes in two points, which resulted in generation of two two-phase regions, namely TiNi+Cr and $TiNi_3$+Cr – such observation is also in a good agreement with metallographic observations (Figure 2 and 3b).

All the presented results allow for determination of the phases which were created after annealing of the diffusion couple at 1173K for 100 h. Summarizing, diffusion path between pure Ti and Ni80Cr20 alloy in the given conditions went through the following phases: Ti → $TiNi_2$ → TiNi → TiNi + Cr → $TiNi_3$+Cr → Ni80Cr20.

The phases mentioned above possessed different thickness. It was clearly visible that TiNi intermetallic phase was characterized by greater thickness than $TiNi_2$ intermetallic phase. Also, the two-phase zone TiNi + Cr was substantially thicker than $TiNi_3$ + Cr zone. The exact values of a thickness Δx_i of the distinguished phases – measured based on Figure 2, are collected in Table 2. The molar fractions of the elements in the phases as well as molar volume of the phases are also presented in Table 2.

Table 1. *SEM/EDX quantitative point analysis of elements present in Ni80Cr20-Ti diffusion couple after annealing for 100h at 1173K, as marked in Figure 3*

Point	Elements content / at. %		
	Ti	Cr	Ni
1	93.7	0.3	6.0
2	66.9	0.1	33.0
3	66.9	0.3	32.8
4	49.2	0.5	50.3
5	62.0	0.4	37.6
6	46.9	2.7	50.3
7	2.3	95.7	2.0
8	44.4	4.4	51.2
9	25.2	1.6	73.2
10	4.0	90.5	5.5
11	0.8	13.5	85.7

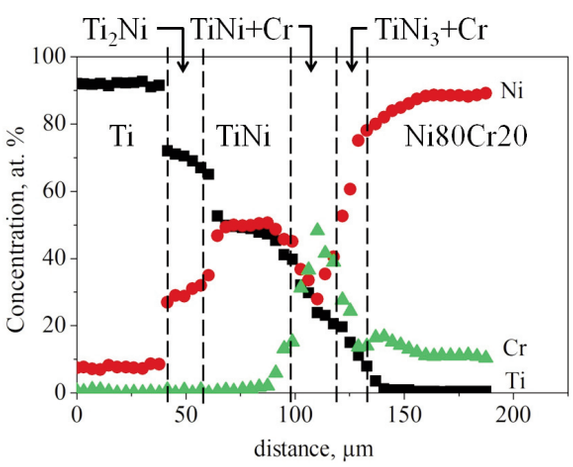

Figure 4. *The composition profile of reactive diffusion between Ni80Cr20 and Ti at 1173 K after 100 h*

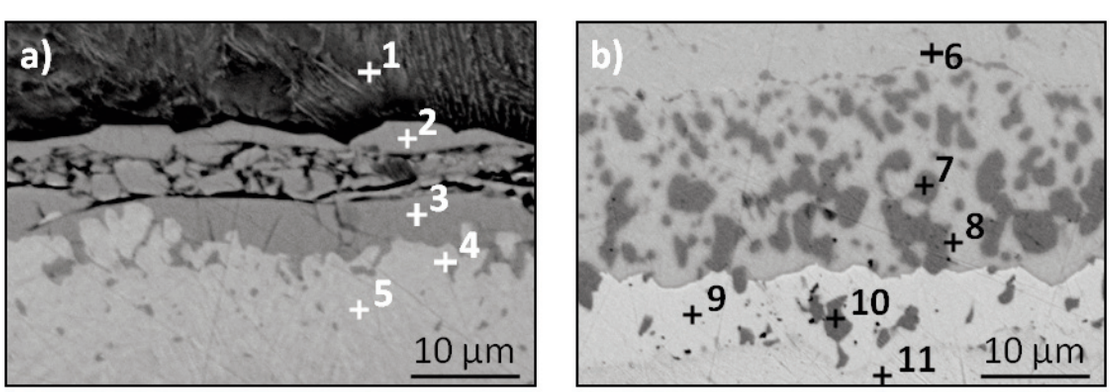

Figure 3*. SEM/BSE images showing the magnifications of cross-sections of Ni80Cr20-Ti diffusion couple after annealing for 100 h at 1173 K marked by framed boxes in Figure 2. Points indicate the location of SEM/EDX qualitative analysis*

Table 2. *Experimental and thermodynamical data after annealing of Ni80Cr20-Ti diffusion couple for 100h at 1173K*

Phase, *j*	**Ti**	**Ti_2Ni**	**TiNi**	**TiNi+Cr**	**$TiNi_3$+Cr**	**Ni80Cr20**
Thickness, Δx_j, μm	---	9.71	42.26	20.85	8.81	---
Molar fraction, N_{Ti}^j	0.98	0.67	0.50	0.27	0.19	0.00
Molar fraction, N_{Ni}^j	0.02	0.34	0.51	0.28	0.55	0.80
Molar fraction, N_{Cr}^j	0.00	0.00	0.02	0.45	0.26	0.20
Molar volume, V_j, cm^3	10.46	8.60	7.91	7.62	7.21	6.70

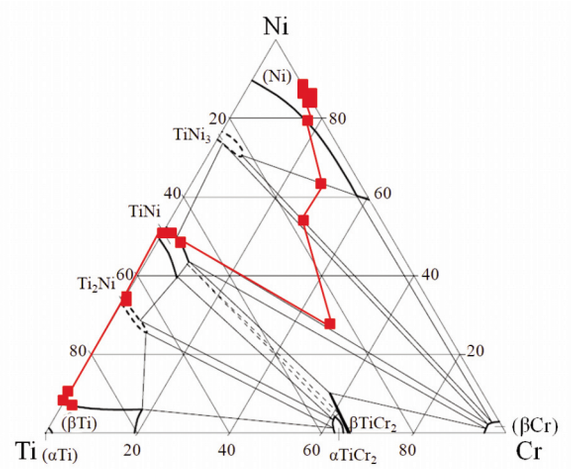

Figure 5. *The phase diagram of the ternary Ni–Cr–Ti system [17]. The points represent the experimental results of diffusion between Ni80Cr20 and Ti at 1173 K depicted previously on concentration profile visible in Fig. 4*

3.2. Diffusion coefficients approximation

Determination of diffusion path, sequence of growth, and thickness of appearing phases in ternary systems during diffusion process is still an unsolved problem. One of the greatest obstacles that restrain the progress in understanding of diffusion phenomena in such systems is lacking of kinetic data, namely diffusion coefficients of the elements in particular phases and systems under specific temperature conditions. The experimental diffusion path observed after annealing of the Ni80Cr20-Ti diffusion couple for 100h at 1173K (Figure 5) revealed which phases and regions were formed in the diffusion zone. Therefore, the diffusion coefficients (D_i^j) of the *i*-th element (*i*= Ni, Cr, Ti) in each phase (*j*) may be calculated – initially only the diffusion coefficients for the high purity Ti ([21]) were known (Table 3).

3.2.1. Wagner's diffusion coefficients

One of presently available ways of calculation of diffusion coefficients in multiphase, multicomponent systems was proposed by Wagner. The formula for calculation of intrinsic diffusion coefficients had been presented as follows [12]:

$$D_i^{\beta} = \left| \frac{\left(N_i^{\beta} - N_i^{-}\right)\left(N_i^{+} - N_i^{\beta}\right)}{\left(N_i^{+} - N_i^{-}\right)} \frac{\Delta x_{\beta}^2}{2t} + \left[\left(\frac{N_i^{+} - N_i^{\beta}}{N_i^{+} - N_i^{-}} \right) \sum_{v=2}^{v=\beta-1} \left(\frac{V_m^{\beta}}{V_m^{v}} \left(N_i^{v} - N_i^{-} \right) \Delta x_v \right) + \left(\frac{N_i^{\beta} - N_i^{-}}{N_i^{+} - N_i^{-}} \right) \sum_{v=\beta+1}^{v=n-1} \left(\frac{V_m^{\beta}}{V_m^{v}} \left(N_i^{+} - N_i^{v} \right) \Delta x_v \right) \right] \right| \frac{\Delta x_{\beta}}{2t} \quad (1)$$

where: $N_i^{\pm}$ is the molar fraction of the element *i*on the left hand-side (-) and right-hand side (+) of the diffusion couple, N_i^{β} – molar fraction of the *i*-th element in the β-phase, Δx_j and V_m^j – thickness and molar volume of the *j*-th phase ($j = \beta$ or v where β - the phase of interest and v– currently calculated phase), respectively, t – time of diffusion annealing.

The Wagner diffusion coefficients rely strongly on the neighboring phases, namely on concentration of particular elements and thicknesses of the phases. The above mentioned experimental data (phase thickness and molar fraction of elements, time of annealing) as well as molar volume of all the phases have to be known to apply Equation 1. The required data for calculation of diffusion coefficients for Ni80Cr20-Ti diffusion couple after annealing at 1173K for 100 hours are presented in Table 3. Results of calculations of intrinsic diffusion coefficients by Wagner method (Equation 1) are gathered in Table 4.

Table 3. *Summary of the unknown diffusion coefficients in Ni80Cr20-Ti system at 1173K*

Phase, j	**Ti**	**Ti_2Ni**	**TiNi**	**TiNi+Cr**	**$TiNi_3$+Cr**	**$TiNi_3$**	**Ni80Cr20**
D_{Ti}^j / $cm^2\ s^{-1}$	**$4.34 \cdot 10^{-13}$**	?	?	?	?	?	?
D_{Ni}^j / $cm^2\ s^{-1}$	**0**	?	?	?	?	?	?
D_{Cr}^j / $cm^2\ s^{-1}$	**0**	?	?	?	?	?	?

Table 4. *Diffusion coefficients in ternary Ni-Cr-Ti system calculated by Wagner's method (Equation 1)*

Phase, j	Ti	Ti_2Ni	TiNi	TiNi+Cr	$TiNi_3$+Cr	$TiNi_3$	Ni80Cr20
D_{Ti}^{j} / cm^2 s^{-1}	$4.34\cdot10^{-13}$	**$1.63\cdot10^{-12}$**	**$1.13\cdot10^{-11}$**	**$3.34\cdot10^{-12}$**	**$1.00\cdot10^{-12}$**	?	?
D_{Ni}^{j} / cm^2 s^{-1}	0	**$1.80\cdot10^{-12}$**	**$1.84\cdot10^{-11}$**	**$5.61\cdot10^{-12}$**	**$1.22\cdot10^{-12}$**	?	?
D_{Cr}^{j} / cm^2 s^{-1}	0	**0**	**$5.57\cdot10^{-14}$**	**$4.05\cdot10^{-12}$**	**$4.38\cdot10^{-12}$**	?	?

3.2.2. Determination of diffusion coefficients in the two-phase region

In the previous section of the paper, the two-phase regions, namely TiNi+Cr and $TiNi_3$+Cr were treated as regular intermetallic phases, thus the Wagner formula could be applied for calculation of diffusion coefficients. However, the Wagner formula enables for calculation of diffusion coefficients only in the phases that appear in the diffusion zone while annealing – it is impossible to calculate diffusion coefficients in the phases that are missed by diffusion path. Therefore, even if the diffusion coefficient in the $TiNi_3$+Cr has been calculated, the diffusion coefficient of the $TiNi_3$ phase is still missing.

Diffusion coefficients, that are presented in Table 4 for these phases are effective diffusivities that are influenced by diffusion coefficients of phases that appear in the two-phase regions, molar fraction of the phases and the gradient of component's concentration over displacement. Therefore, for the two-phase region $TiNi_3$+Cr, the equation describing the flux of the *i*-th component may be formulated as follows:

$$J_i\left(TiNi_3+Cr\right)=f\left(TiNi_3\right)D_i\left(TiNi_3\right)\frac{\partial N_i}{\partial x}+ +f\left(Cr\right)D_i\left(Cr\right)\frac{\partial N_i}{\partial x} \quad (2)$$

where: $f(TiNi_3)$ and $f(Cr)$are the molar fractions of the $TiNi_3$ and Cr phases in the two-region zone and $D_i(TiNi_3)$ and $D_i(Cr)$ are diffusion coefficients of *i*-th component in the $TiNi_3$ and Cr phase, respectively.

A problem arises in determination of the gradient of component's concentration over displacement, as only one point is visible on diffusion path between the $TiNi_3$ and Cr phases. Nevertheless, from the properties of derivative, the above mentioned gradient may be rewritten in the following form:

$$\frac{\partial N_i}{\partial x}=\frac{\partial N_i}{\partial \overline{N_i}}\cdot\frac{\partial \overline{N_i}}{\partial x} \quad (3)$$

where $\overline{N_i}$ is the average molar fraction in the two-phase region.

For the NiCrTi system, when the conodes between the $TiNi_3$ and Cr phases are almost parallel and restrain a thin two-phase region, the first derivative may be simplified to:

$$\frac{\partial N_i}{\partial \overline{N_i}}\approx\frac{N_i+0.1}{\overline{N_i}+0.1}\approx\frac{N_i}{\overline{N_i}} \quad (4)$$

Thus, Equation 2 may be rewritten in the following form:

$$D_i\left(TiNi_3+Cr\right)\frac{\partial \overline{N_i}}{\partial x}=f\left(TiNi_3\right)D_i\left(TiNi_3\right)\cdot \cdot\frac{N_i\left(TiNi_3\right)}{\overline{N_i}}\cdot\frac{\partial \overline{N_i}}{\partial x}+ +f\left(Cr\right)D_i\left(Cr\right)\frac{N_i\left(Cr\right)}{\overline{N_i}}\cdot\frac{\partial \overline{N_i}}{\partial x} \quad (5)$$

and the equation for effective diffusion coefficient can be approximated as:

$$D_i\left(TiNi_3+Cr\right)=f\left(TiNi_3\right)D_i\left(TiNi_3\right)\frac{N_i\left(TiNi_3\right)}{\overline{N_i}}+ +f\left(Cr\right)D_i\left(Cr\right)\frac{N_i\left(Cr\right)}{\overline{N_i}} \quad (6)$$

Finally, the diffusion coefficients in $TiNi_3$ can be calculated as:

$$D_i\left(TiNi_3\right)=\frac{D_i\left(TiNi_3+Cr\right)\overline{N_i}-\left(1-f\left(TiNi_3\right)\right)D_i\left(Cr\right)N_i\left(Cr\right)}{N_i\left(TiNi_3\right)f\left(TiNi_3\right)} \quad (7)$$

Molar fractions of components in particular phases that appear in Equation 7 have been depicted on schematic representation of Ni80Cr20-Ti diffusion path after annealing at 1173K in Figure 6**.**

Calculation of diffusion coefficient in the $TiNi_3$ phase by Equation 7 is possible, when diffusion coefficients in the Cr phase are known. To calculate their values the analogous approximation can be used in the TiNi+Cr two-phase zone, as diffusion coefficients in the TiNi phase had been previously calculated by the Wagner method (Equation 1, Table 4). Thus, the Cr intrinsic diffusion coefficient and the impurities diffusion coefficients in Cr can be approximated as:

$$D_i\left(Cr\right)=\frac{f\left(TiNi\right)D_i\left(TiNi\right)N_i\left(TiNi\right)}{\left(1-f\left(TiNi\right)\right)N_i\left(Cr\right)} \quad (8)$$

Results of calculation of $D_i(Cr)$ by Equation 8 are used for calculation of $D_i(TiNi_3)$ by Equation 7. The required data for calculation of above mentioned diffusion coefficients in the two-phase zone after annealing at 1173K for 100 hours are presented in Table 5. Results of calculations are gathered in Table 5.

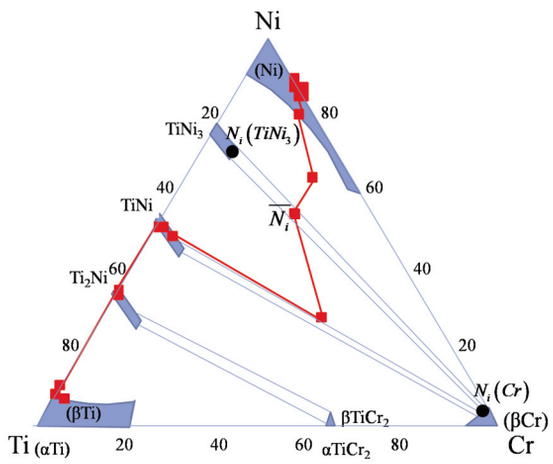

Figure 6. *Schematic representation of Ni80Cr20-Ti diffusion path after annealing at 1173K for 100h with marked concentrations in the $TiNi_3$+Cr two-phase region.*

Table 5. *Experimental and thermodynamical data after annealing of Ti-Ni80Cr20 diffusion couple for 100h at 1173K.*

Phase, *j / molar fraction*	N_{Ti}^j	N_{Ni}^j	N_{Cr}^j
TiNi	0.45	0.49	0.06
TiNi+Cr	0.27	0.28	0.45
Cr	0.03	0.02	0.95
f(TiNi)	0.03		
$TiNi_3$	0.23	0.71	0.06
$TiNi_3$+Cr	0.19	0.55	0.26
Cr	0.01	0.03	0.96
f($TiNi_3$)	0.27		

3.2.3. Diffusion coefficient of pure components inNi80Cr20 alloy

Lack of diffusion coefficients in the literature is not the only obstacle that inhibits description of diffusion phenomena. Problem of determination of ternary interdiffusion coefficients may be solved based on thermodynamic models, which present interdiffusion coefficients depending on binary and ternary interaction parameters. Therefore, for ternary system, one obtains main and cross interdiffusion coefficients for dependent components. The Wagner method enables for calculation of intrinsic diffusion coefficients of particular elements in particular phases, thus it is an effective diffusivity. Therefore, it is impossible to directly compare the values of diffusion coefficients obtained in such different ways.

So even though the Ni-Cr-Ti ternary system, especially in its fcc phase, was already compressively studied by Huang et al. [15] it is impossible to use the Huang's method for calculation of the diffusion coefficients of particular elements in the alloy what is the subject of this study as the Huang's method is based on thermodynamical data (namely gradient of chemical potential), which is lacking in the literature.

Nevertheless, these diffusion coefficients, namely diffusion coefficients of elements in Ni80Cr20 alloy may be estimated thanks to their correspondence to atomic mobility:

$$D_i = RTM_i \tag{9}$$

where R – gas constant and T – absolute temperature. Atomic mobility $M_i$may be further defined as:

$$M_i = \frac{1}{RT}\exp\left(\frac{\Phi_i}{RT}\right) \tag{10}$$

where Φ_i is a property that depends on the composition and temperature. It may be calculated thanks to Redlich-Kister polynomials:

$$\Phi_i = \sum_p x_p \Phi_i^p + \sum_p \sum_{q>p} x_q x_p \left[\sum_{r=0,1,2,\ldots} {}^r\Phi_i^{p,q}\left(x_p - x_q\right)^r\right] + \\ + \sum_p \sum_{q>p} \sum_{v>q} x_p x_q x_v \left[\sum_s v_{pqv}^s \, {}^s\Phi_i^{p,q,v}\right], (s = p,q,v) \tag{11}$$

where ${}^p\Phi_i$ denotes the value of Φ_i for i-th element in p-th phase, ${}^r\Phi^{p,q}_i$ and ${}^s\Phi^{p,q,v}_i$ are parameters of

Table 6. *Diffusion coefficients in ternary Ti-Ni-Cr system calculated by Wagner's method and by separation of the effective diffusivity in the two-phase region(Equation 7 and Equation. 8)*

Phase, j	**Ti**	**Ti_2Ni**	**TiNi**	**TiNi+Cr**	**$TiNi_3$+Cr**	**$TiNi_3$**	**Ni80Cr20**
D_{Ti}^j / cm^2 s^{-1}	$4.34\cdot10^{-13}$	$1.63\cdot10^{-12}$	$1.13\cdot10^{-11}$	$3.34\cdot10^{-12}$	$1.00\cdot10^{-12}$	**$1.9\cdot10^{-13}$**	?
D_{Ni}^j / cm^2 s^{-1}	0	$1.80\cdot10^{-12}$	$1.84\cdot10^{-11}$	$5.61\cdot10^{-12}$	$1.22\cdot10^{-12}$	**$6.7\cdot10^{-13}$**	?
D_{Cr}^j / cm^2 s^{-1}	0	0	$5.57\cdot10^{-14}$	$4.05\cdot10^{-12}$	$4.38\cdot10^{-12}$	**0**	?

interaction for binary and ternary systems, respectively.

In case of calculation of diffusion coefficients of pure components in Ni80Cr20 system, Equation 11 may be simplified only to the first addend. Values of Φ_i were calculated by equations given by Zhu et al. [22], which are presented in Table 7.

Table 7. *Equations for calculation of parameter Φ for pure components in Ni80Cr20 alloy*

Component *i*	Mobility of i-th component
Nickel	$\Phi_{Ni}^{Ni} = -276860 + R \cdot T \cdot \ln\left(8.5 \cdot 10^{-5}\right)$
Titanium	$\Phi_{Ti}^{Ti} = -143640 + R \cdot T \cdot \ln\left(5.98 \cdot 10^{-5}\right)$
Chromium	$f_{Cr}^{Cr} = -235000 + R \cdot T \cdot \ln\left(5.21 \cdot 10^{-5}\right)$

Results of calculations of parameter Φ and atomic mobilitiesM_i of pure components along with molar fractions with these components for Ni80Cr20 alloyat 1173K are presented in Table 8.

Based on the data collected in Table 8, it is finally possible to calculate diffusion coefficients of Ti, Ni, and Cr in Ni80Cr20 alloy at 1173K by Equation 9. Results are presented in Table 9.

4. Conclusions

In the present paper, an attempt to determine the diffusion coefficients in Ni80Cr20-Ti had been made based on the experimental results of annealing of such a diffusion couple at 1173K for 100h. Diffusion coefficients were calculated by various possible methods, mainly by the Wagner formula ($TiNi_2$, TiNi, TiNi+Cr, $TiNi_3$+Cr), separation of effective diffusivity in the two-phase region ($TiNi_3$), and thermodynamic data (Ni80Cr20). Summary of the obtained results is presented in Table 10.

It was shown, that a single diffusion experiment enabled the determination of all the diffusion coefficients in the ternary Ni80Cr20 system at 1173K, however, three different methods of calculations had to be used, as each of them had its own limitations. An experimental study had to be performed, because the kinetic information, namely the thickness of the phases that occurred in the diffusion zone, was needed for implementation of the Wagner formula. However, once calculated, the results, summarized in Table 10, may be further applied in determination of the phases and their thicknesses that appear while annealing of the ternary Ti-Ni-Cr diffusion couple at 1173 K.

Table 8. *Results of calculations of parameter Φ (simplified Equation 11) and atomic mobility M_i (Equation 10) for Ni80Cr20 alloy at 1173K*

Component *i*	Molar fraction of i-th component	Parameter Φ_i^i of i-th component / J·mol^{-1}	Atomic mobility M_i of i-th component /mol·J^{-1}
Nickel	0.8	$-2.67 \cdot 10^5$	$1.34 \cdot 10^{-16}$
Titanium	0.0	$-3.48 \cdot 10^5$	$3.30 \cdot 10^{-20}$
Chromium	0.2	$-3.56 \cdot 10^5$	$1.40 \cdot 10^{-20}$

Table 9. *Diffusion coefficients in ternary Ti-Ni-Cr system calculated by Wagner's method, by separation of the effective diffusivity in the two-phase region and by using thermodynamic data (Equation 9)*

Phase, j	Ti	Ti_2Ni	TiNi	TiNi+Cr	$TiNi_3$+Cr	$TiNi_3$	Ni80Cr20
D_{Ti}^j / cm^2 s^{-1}	$4.34 \cdot 10^{-13}$	$1.63 \cdot 10^{-12}$	$1.13 \cdot 10^{-11}$	$3.34 \cdot 10^{-12}$	$1.00 \cdot 10^{-12}$	$1.9 \cdot 10^{-13}$	**$1.31 \cdot 10^{-12}$**
D_{Ni}^j / cm^2 s^{-1}	0	$1.80 \cdot 10^{-12}$	$1.84 \cdot 10^{-11}$	$5.61 \cdot 10^{-12}$	$1.22 \cdot 10^{-12}$	$6.7 \cdot 10^{-13}$	**$3.22 \cdot 10^{-16}$**
D_{Cr}^j / cm^2 s^{-1}	0	0	$5.57 \cdot 10^{-14}$	$4.05 \cdot 10^{-12}$	$4.38 \cdot 10^{-12}$	0	**$1.37 \cdot 10^{-16}$**

Table 10. *Summary of the diffusion coefficients in Ni80Cr20-Ti system at 1173K.*

Phase, j	Ti	Ti_2Ni	TiNi	TiNi+Cr	$TiNi_3$+Cr	$TiNi_3$	Ni80Cr20	Cr
D_{Ti}^j / cm^2 s^{-1}	$4.34 \cdot 10^{-13}$	$1.63 \cdot 10^{-12}$	$1.13 \cdot 10^{-11}$	$3.34 \cdot 10^{-12}$	$1.00 \cdot 10^{-12}$	$1.9 \cdot 10^{-13}$	$1.31 \cdot 10^{-12}$	0
D_{Ni}^j / cm^2 s^{-1}	0	$1.80 \cdot 10^{-12}$	$1.84 \cdot 10^{-11}$	$5.61 \cdot 10^{-12}$	$1.22 \cdot 10^{-12}$	$6.7 \cdot 10^{-13}$	$3.22 \cdot 10^{-16}$	0
D_{Cr}^j / cm^2 s^{-1}	0	0	$5.57 \cdot 10^{-14}$	$4.05 \cdot 10^{-12}$	$4.38 \cdot 10^{-12}$	0	$1.37 \cdot 10^{-16}$	$7.8 \cdot 10^{-14}$

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KOEFICIJENTI DIFUZIJE U VIŠEFAZNOM Ni80Cr20-Ti SISTEMU

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Apstrakt

U ovom radu je razmatrana reaktivna difuzija u Ni80C20r–Ti trojnom sistemu na temperaturi od 1173K. Difuzioni par je pripremljen, a zatim je narednih 100 časova podvrgnut žarenju. Pojavile su se dve intermetalične faze, kao i dve dvofazne zone Ti_2Ni, TiNi, TiNi+Cr i $TiNi_3$+Cr. Na osnovu rezultata eksperimenata (molarna frakcija i debljina intermetaličnih faza), približno su numerički određeni koeficijenti unutrašnje difuzije za sve komponente u svakoj fazi. Vagnerova metoda je korišćena kod čistih intermetaličnih faza. Kod dvofaznih zona su za aproksimaciju korišćene uopštene Darkenova i Vagnerova metoda. Predstavljene metode su omogućile određivanje efikasnih koeficijenata difuzije za svaku prikazanu fazu.

Ključne reči: *Reakciona difuzija; Ravnoteža; Ni80Cr20–Ti sistem*