Diffusion coefficients in multiphase Ni80Cr20-Ti system

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Abstract: In this paper, the reactive diffusion in Ni80Cr20r–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 occur, namely: Ti2Ni, TiNi, TiNi+Cr and TiNi3+Cr. Based on
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 zone 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 exists 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 base on insertion of the markers between the alloys that create the diffusion
couple. Then, basing on the position of the markers after the annealing, the diffusion coefficient
can be determined [6]. Such experimental approach is time- and cost-consuming, that's 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 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, Ti) in each phase of the multicomponent ternary system by 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 SiO₂ 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 for increasing 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

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. SEM/EDX analysis was performed (Figure 3, Table 1) and enabled for identification of the phases that are distinguished and named in Figure 2. During the diffusion, the Ti₂Ni 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 TiNi₃+Cr. The formation of such phases is visible in cross-section: TiNi creates a brighter matrix (point 8 in Figure 3, Table 1) within which a darker chromium precipitates (point 7 in Figure 3, Table 1) are present. Similarly, dark chromium spots (point 10 in Figure 3, Table 1) are distinguishable from a brighter TiNi₃ matrix (point 9 in Figure 3, Table 1). SEM/BSE image revealed also, that there are many pores and cracks visible within the Ti₂Ni phase (Figure 2). It is probably an effect of cross-section preparation, mainly grinding steps – TiNi₂ is brittle and therefore, it is very likely that some of it broke away while preparation.

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.
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 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|

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. Basing on such a diagram, an occurrence of TiNi₂ 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 crosses the conodes in two points, which results in generation of two two-phase regions, namely TiNi+Cr and TiNi₃+Cr – such observation is also in a good agreement with metallographic observations (Figure 2 and 3b).
Figure 4. The composition profile of reactive diffusion between Ni80Cr20 and Ti at 1173 K after 100 h.

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.

All the presented results allow for determination of the phases which were created after annealing of the diffusion couple at 1173 K for 100 h. Summarizing, diffusion path between pure Ti and Ni80Cr20 alloy in the given conditions goes through the following phases: Ti → TiNi2 → TiNi → TiNi + Cr → TiNi3 + Cr → Ni80Cr20.

The phases mentioned above possess different thickness. It is clearly visible that TiNi intermetallic phase is characterized by greater thickness than TiNi2 intermetallic phase. Also, the two-phase zone TiNi + Cr is substantially thicker than TiNi3 + Cr zone. The exact values of
a thickness $\Delta x_j$ 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 2.** Experimental and thermodynamical data after annealing of Ni80Cr20-Ti diffusion couple for 100h at 1173K.

| Phase, $j$ | Ti  | Ti$_2$Ni | TiNi | TiNi+Cr | TiNi$_3$+Cr | Ni80Cr20 |
|-----------|-----|----------|------|---------|-------------|----------|
| Thickness, $dx_j$, $\mu$m | --- | 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 |

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) reveals 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 ($[21]$) are known (Table 3).

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

| Phase, $j$ | Ti  | Ti$_2$Ni | TiNi | TiNi+Cr | TiNi$_3$+Cr | TiNi$_3$ | Ni80Cr20 |
|-----------|-----|----------|------|---------|-------------|-----------|----------|
| $D_{Ti}^j$, cm$^2$s$^{-1}$ | 4.34x10$^{-13}$ | ? | ? | ? | ? | ? | ? |
| $D_{Ni}^j$, cm$^2$s$^{-1}$ | 0 | ? | ? | ? | ? | ? | ? |
| $D_{Cr}^j$, cm$^2$s$^{-1}$ | 0 | ? | ? | ? | ? | ? | ? |

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]:

$$D_i^\beta = \left( \frac{(N_i^\beta - N_i^\alpha)(N_i^\alpha - N_i^\beta)}{(N_i^\alpha - N_i^\gamma)} \right) \Delta x_i^\alpha + \left( \frac{V_i}{V_i^\alpha} \right) \left( \frac{\sum_{\beta=1}^{\beta-1} (N_i^\beta - N_i^\gamma) \Delta x_i^\gamma}{2t} \right) + \left( \frac{V_i}{V_i^\alpha} \right) \left( \frac{\sum_{\gamma=1}^{\gamma-1} (N_i^\alpha - N_i^\gamma) \sum_{\beta=1}^{\beta-1} (V_i^\beta/N_i^\beta) (N_i^\beta - N_i^\gamma) \Delta x_i^\gamma}{2t} \right)$$

(1)
where: $N^+_{i}$ is the molar fraction of the element $i$ on the left hand-side (-) and right-hand side (+) of the diffusion couple, $N^-_{i}$ – molar fraction of the $i$-th element in the $\beta$-phase, $\Delta x_j$ and $V^+_j$ – thickness and molar volume of the $j$-th phase ($j = \beta$ or $\nu$ where $\beta$ - the phase of interest and $\nu$ – 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 4. Diffusion coefficients in ternary Ni-Cr-Ti system calculated by Wagner’s method (Equation 1).

| Phase, $j$ | Ti  | Ti$_2$Ni | TiNi | TiNi+Cr | TiNi$_3$+Cr | TiNi$_3$ |
|------------|-----|----------|------|---------|-------------|---------|
| $D^+_j/\text{cm}^2\text{s}^{-1}$ | 4.34$\times$10$^{-13}$ | 1.63$\times$10$^{-12}$ | 1.13$\times$10$^{-11}$ | 3.34$\times$10$^{-12}$ | 1.00$\times$10$^{-12}$ | ? |
| $D^-_j/\text{cm}^2\text{s}^{-1}$ | 0 | 1.80$\times$10$^{-12}$ | 1.84$\times$10$^{-11}$ | 5.61$\times$10$^{-12}$ | 1.22$\times$10$^{-12}$ | ? |
| $D^+_j/\text{cm}^2\text{s}^{-1}$ | 0 | 0 | 5.57$\times$10$^{-14}$ | 4.05$\times$10$^{-12}$ | 4.38$\times$10$^{-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:

$$J_i (\text{TiNi}_3 + \text{Cr}) = f (\text{TiNi}_3)D_i (\text{TiNi}_3) \frac{\partial N_i}{\partial x} + f (\text{Cr})D_i (\text{Cr}) \frac{\partial N_i}{\partial x}$$

(2)

where: $f(\text{TiNi}_3)$ and $f(\text{Cr})$ are the molar fractions of the TiNi$_3$ and Cr phases in the two-region zone and $D_i (\text{TiNi}_3)$ and $D_i (\text{Cr})$ are diffusion coefficients of $i$-th component in the TiNi$_3$ and Cr phase, respectively.

A problem arises in determining 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:

$$\frac{\partial N_i}{\partial x} = \overline{N_i} \frac{\partial \overline{N_i}}{\partial x}$$

(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:

\[
\frac{\partial N_i}{\partial N_i} \approx \frac{N_i + 0.1}{N_i + 0.1} \approx \frac{N_i}{N_i}
\]  

(4)

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

\[
D_i(TiNi_3 + Cr) \frac{\partial N_i}{\partial x} = f(TiNi_3)D_i(TiNi_3) \frac{N_i(TiNi_3)}{N_i} \cdot \frac{\partial N_i}{\partial x} + f(Cr)D_i(Cr) \frac{N_i(Cr)}{N_i} \cdot \frac{\partial N_i}{\partial x}
\]  

(5)

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

\[
D_i(TiNi_3 + Cr) = f(TiNi_3)D_i(TiNi_3) \frac{N_i(TiNi_3)}{N_i} + f(Cr)D_i(Cr) \frac{N_i(Cr)}{N_i}
\]  

(6)

Finally, the diffusion coefficients in TiNi$_3$ can be calculated as:

\[
D_i(TiNi_3) = \frac{D_i(TiNi_3 + Cr)N_i - (1 - f(TiNi_3))D_i(Cr)N_i(Cr)}{N_i(TiNi_3)f(TiNi_3)}
\]  

(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.

**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.

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:

\[
D_i^{(Cr)} = \frac{D \left( TiNi + Cr \right) N_i - f \left( TiNi \right) D_i \left( TiNi \right) N_i \left( TiNi \right)}{\left( 1 - f \left( TiNi \right) \right) N_i \left( Cr \right)}
\] (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.

### 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 |

### 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\(\times\)10\(^{-13}\) | 1.63\(\times\)10\(^{-12}\) | 1.13\(\times\)10\(^{-11}\) | 3.34\(\times\)10\(^{-12}\) | 1.00\(\times\)10\(^{-12}\) | 1.9\(\times\)10\(^{-13}\) | ? |
| \(D_{Ti}^{(j)}\) cm\(^2\)s\(^{-1}\) | 0 | 1.80\(\times\)10\(^{-12}\) | 1.84\(\times\)10\(^{-11}\) | 5.61\(\times\)10\(^{-12}\) | 1.22\(\times\)10\(^{-12}\) | 6.7\(\times\)10\(^{-13}\) | ? |
| \(D_{Cr}^{(j)}\) cm\(^2\)s\(^{-1}\) | 0 | 0 | 5.57\(\times\)10\(^{-14}\) | 4.05\(\times\)10\(^{-12}\) | 4.38\(\times\)10\(^{-12}\) | 0 | ? |

3.2.3. Diffusion coefficient of pure components in Ni80Cr20 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 is such different ways.

So even though the Ni-Cr-Ti ternary system, especially in its fcc phase, has been 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 bases 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:

\[ D_i = RTM_i \]  \hspace{1cm} (9)

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

\[ M_i = \frac{1}{RT} \exp \left( \frac{\Phi_i}{RT} \right) \]  \hspace{1cm} (10)

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

\[
\Phi_i = \sum_{p} x_p \Phi_i^p + \sum_{p < q} x_p x_q \left[ \sum_{s=0,1,2} \Phi_{p,q}^s (x_p - x_q)^s \right] + \\
+ \sum_{p < q < r} x_p x_q x_r \left[ \sum_s \psi_{p,q,r}^s \Phi_{p,q,r}^s \right] (s = p,q,v)
\]  \hspace{1cm} (11)

where \( \Phi_i^p \) denotes the value of \( \Phi_i \) for \( i \)-th element in \( p \)-th phase, \( \Phi_{p,q}^{s} \) and \( \Phi_{p,q,r}^{s} \) are parameters of 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 \( \Phi_i \) were calculated by equations given by Zhu et al. [22], which are presented in Table 7.

**Table 7.** Equations for calculation of parameter \( \Phi \) 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         | \( \Phi_{Cr}^{Cr} = -235000 + R \cdot T \cdot \ln \left( 5.21 \cdot 10^{-5} \right) \) |

Results of calculations of parameter \( \Phi \) and atomic mobilities \( M_i \) of pure components along with molar fractions with these components for Ni80Cr20 alloy at 1173K are presented in Table 8.

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

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

Based on 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.

**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 | Ti₂Ni | TiNi | TiNi+Cr | TiNi₂+Cr | TiNi₃ | Ni80Cr20 |
|----------|---|-------|------|---------|---------|-------|----------|
| D_{Ti} / cm² s⁻¹ | 4.34·10⁻¹³ | 1.63·10⁻¹² | 1.13·10⁻¹¹ | 3.34·10⁻¹² | 1.00·10⁻¹² | 1.9·10⁻¹³ | 1.31·10⁻¹² |
| D_{Ni} / cm² s⁻¹ | 0 | 1.80·10⁻¹² | 1.84·10⁻¹¹ | 5.61·10⁻¹² | 1.22·10⁻¹² | 6.7·10⁻¹³ | 3.22·10⁻¹⁶ |
| D_{Cr} / cm² s⁻¹ | 0 | 0 | 5.57·10⁻¹⁴ | 4.05·10⁻¹² | 4.38·10⁻¹² | 0 | 1.37·10⁻¹⁶ |

4. Conclusions

In the present paper, an attempt of determination of 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 using various possible methods, mainly by the Wagner formula (TiNi₂, TiNi, TiNi+Cr, TiNi₃+Cr), separation of effective diffusivity in the two-phase region (TiNi₃) and by using thermodynamic data (Ni80Cr20). Summary of the obtained results is presented in Table 10.

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

| Phase, j | Ti | Ti₂Ni | TiNi | TiNi+Cr | TiNi₂+Cr | TiNi₃ | Ni80Cr20 | Cr |
|----------|---|-------|------|---------|---------|-------|----------|---|
| D_{Ti} / cm² s⁻¹ | 4.34·10⁻¹³ | 1.63·10⁻¹² | 1.13·10⁻¹¹ | 3.34·10⁻¹² | 1.00·10⁻¹² | 1.9·10⁻¹³ | 1.31·10⁻¹² | 0 |
| D_{Ni} / cm² s⁻¹ | 0 | 1.80·10⁻¹² | 1.84·10⁻¹¹ | 5.61·10⁻¹² | 1.22·10⁻¹² | 6.7·10⁻¹³ | 3.22·10⁻¹⁶ | 0 |
| D_{Cr} / cm² s⁻¹ | 0 | 0 | 5.57·10⁻¹⁴ | 4.05·10⁻¹² | 4.38·10⁻¹² | 0 | 1.37·10⁻¹⁶ | 7.8·10⁻¹⁴ |

It was shown, that a single diffusion experiment enables for 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 has its own limitations. An experimental study had to be performed, because the kinetic information, namely the thickness of the phases that occur in the diffusion zone, is needed for implementation of the Wagner formula. However, once calculated 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.
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**Figure 1.** A schematic image showing the connection of Ni80Cr-Ti diffusion couple in molybdenum frame.

**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.

**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.

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

**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.

**Figure 6.** Schematic representation of Ni80Cr20-Ti diffusion path after annealing at 1173K for 100h with marked concentrations in the TiNi3+Cr two-phase region.
**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.

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

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

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

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

**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)

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

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

**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)

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