

THE HIGHEST ENTROPY PRODUCTION DURING DIFFUSION

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Abstract

In the present paper, the theory of the highest entropy production is discussed. It allows to predict, which phases will grow during the multiphase ternary interdiffusion process. Moreover, the theory says, that phase with the highest entropy production value will nucleate as first in the reaction zone. To verify the theory the mathematical formula for calculating the entropy production was formulated. The formula bases on the generalized Darken method. Two diffusion couples: pure titanium with high purity copper-nickel alloys with different initial composition: Ni₁₀Cu₉₀-Ti and Ni₉₀Cu₁₀-Ti (at at.%) were annealed to obtain the thermodynamic and kinetic data. The integral diffusion coefficients for each component in each phase were determined using Wagners method. The reaction zones in ternary system have been analyzed: the microstructure was observed and chemical compositions were measured. Based on obtained results the entropy production was calculated. It can be expected, that the theory of the highest entropy production can be applied in determining a proper diffusion path in multicomponent, multiphase system.

Key words: diffusion, Cu-Ni-Ti system, entropy production, diffusion path

1. INTRODUCTION

The sequence of structural and compositional changes, which are observed during isothermal annealing of diffusion couple is called a diffusion path (Kizilyalli et al., 1999). Determination of diffusion path in multicomponent and multiphase system enables prediction of microstructure and properties of the alloys after isothermal annealing for particular time. Therefore it helps to design protective coatings and resistant materials in carburizing, nitriding and oxidizing environments (Morral, 2012).

In unlimited binary systems under isothermal-isobaric conditions, all intermediate phases will growth after certain time in diffusion zone. Problem in determination a "proper" diffusion path occurs, when the number of components increases, because the number of possible tracks also increases (Gusak, 2010).

A first reference for understanding diffusion paths in ternary systems was presented by Kirkaldy and Brown (1963). The publication was consisted of 17 theorems, which were further developed by Kirkaldy and Young (1987). Those 17 theorems, with additional 11 were presented recently by Morral (2012). This last publication contains more information about diffusion paths in ternary systems that passes through multiphase fields during reactive diffusion.

The understanding of formation and growth of different phases is slowly developing, but the problem of prediction of diffusion path is still unsolved and the mathematical method for determination "proper" diffusion path does not exist. In the literature one can find a similar approach to solve this problem. Progogine (1961), Gusak (2010) and Wierzba (2016) claim that when more than one diffusion path is possible, the path with the highest entropy production will be chosen. In this paper this hypothesis will be checked, mainly the entropy

production for two different diffusion paths will be calculated and compared.

2. MATHEMATICAL DESCRIPTION

In the simplest case of isothermal - isobaric conditions, the entropy production can be calculated from (Danielewski & Wierzba, 2010):

$$\sigma = \sum_{i=1}^r J_i^d \left(-\text{grad} \frac{\mu_i^{ch}}{T} \right) \quad (1)$$

where: σ - entropy production, J_i^d , μ_i^{ch} - diffusion flux and chemical potential of the i -th component ($i = 1, 2, \dots, r$), respectively, T - temperature. Diffusion flux J_i^d can be calculated, using following form (Darken, 1948):

$$J_i^d = N_i v_i^d \quad (2)$$

where N_i is the molar ratio and v_i^d the diffusion velocity of the i -th component. Diffusion velocity can be expressed using Nernst-Planck formulae (Nernst, 1889; Plank, 1890):

$$v_i^d = -B_i \text{grad} \mu_i^{ch} \quad (3)$$

where B_i is the mobility of the i -th component. Combining Equations (1), (2) and (3), we obtain:

$$\sigma = -\frac{1}{T} \sum_{i=1}^r N_i B_i (\text{grad} \mu_i^{ch})^2 \quad (4)$$

Chemical potential can be calculated by the Gibbs free energy (Wierzba, 2016):

$$\mu_i^{ch} = \frac{\partial g}{\partial N_i} \quad (5)$$

where g is the Gibbs free energy per 1 atom. Equation (4) can be rewritten in the following way:

$$\sigma = \frac{1}{T} \sum_{i=1}^r N_i B_i \left(\sum_{j=1}^r \frac{\partial \mu_i^{ch}}{\partial N_j} \text{grad} N_j \right)^2 \quad (6)$$

Substitution Equation (5) into Equation (6) yields:

$$\sigma = \frac{1}{T} \sum_{i=1}^r N_i B_i \left(\sum_{j=1}^r \frac{\partial^2 g}{\partial N_i \partial N_j} \text{grad} N_j \right)^2 \quad (7)$$

When the concentration of the components in the phases are within a narrow composition range, than is practically impossible to obtain (with satisfactory accuracy) local values of $\text{grad} N_j$.

Supposing, that in the phase (v), the molar fraction of the component and its diffusion coefficient are independent of x , Equation (7) can be formulated as:

$$\sigma_i^{(v)} = \frac{1}{T} \sum_{i=1}^r N_i^{(v)} B_i^{(v)} \left(\frac{d\mu_i^{(v)}}{dx} \right)^2 \quad (8)$$

Afterwards, by multiplying Equation (8) with $(dx)^2$, one gets:

$$\sigma_i^{(v)} (d\mathbf{x})^2 = \frac{1}{T} \sum_{i=1}^r N_i^{(v)} B_i^{(v)} (d\mu_i^{(v)})^2 \quad (9)$$

To minimize the possible errors of derivation, the backward and forward difference of chemical potential over the phase (v) have been applied:

$$\bar{\sigma}^{(v)} = \frac{1}{T} \sum_{i=1}^r N_i^{(v)} B_i^{(v)} \left| \begin{array}{l} \mu_i^{(v-1)} \\ - \mu_i^{(v)} \mid \mid \mu_i^{(v+1)} \\ - \mu_i^{(v)} \mid \end{array} \right. \quad (10)$$

Combining equation (5) with Equation (10), the following form is obtained:

$$\bar{\sigma}^{(v)} = \frac{1}{T} \sum_{i=1}^r N_i^{(v)} B_i^{(v)} \left| \frac{\partial g^{(v-1)}}{\partial N_i^{(v-1)}} - \frac{\partial g^{(v)}}{\partial N_i^{(v)}} \right| \cdot \left| \frac{\partial g^{(v+1)}}{\partial N_i^{(v+1)}} - \frac{\partial g^{(v)}}{\partial N_i^{(v)}} \right| \quad (11)$$

By implementing the backward and forward differences again, the final form of the equation, that enables to calculate the entropy production in the reactive diffusion system is obtained in the following form:

$$\bar{\sigma}^{(v)} = \frac{1}{T} \sum_{i=1}^r N_i^{(v)} B_i^{(v)} \left| \frac{g^{(v)} - g^{(v-1)}}{N_i^{(v)} - N_i^{(v-1)}} - \frac{g^{(v+1)} - g^{(v)}}{N_i^{(v+1)} - N_i^{(v)}} \right| \cdot \left| \frac{g^{(v+1)} - g^{(v)}}{N_i^{(v+1)} - N_i^{(v)}} - \frac{g^{(v)} - g^{(v-1)}}{N_i^{(v)} - N_i^{(v-1)}} \right| \quad (12)$$

In Equation (12) $B_i^{(v)}$ denotes the mobility of the i -th component in the phase (v). One can calculate this mobility using the following equation:

$$B_i^{(v)} = \frac{D_i^{(v)}}{kT} \quad (13)$$



where $D_i^{(v)}$ is the diffusion coefficient of i -th element in the phase (v) and k denotes the Boltzmann constant. In order to calculate the summation of components and phases in Equation (12), it is necessary to have knowledge about diffusion coefficient of all phases that appear in reactive zone. This data is usually lacking in literature for ternary and multicomponent systems. In such a case one can calculate Wagner's diffusion coefficient for each phase.

The Wagner's diffusion coefficient. As it was previously mentioned, in the case of reaction diffusion, it is practically impossible to accurately measure the local values of concentration gradient across very narrow composition range (Paul et al., 2011). In order to avoid that problem, Wagner (1969) formulated so called integrated (integral) diffusion coefficient \tilde{D}_{int}^β , defined as

$$\tilde{D}_{int}^\beta = \int_{N_i'}^{N_i''} \tilde{D}^\beta dN_i \quad (14)$$

where \tilde{D}^β denotes the unknown interdiffusion coefficient in β -phase. The integration limits N_i' and N_i'' , that appear in Equation (14) are the unknown boundaries of homogeneity range in the β -phase (Paul et al., 2010). Wagner made two general assumptions: (1) the end members of the diffusion couple are pure elements or intermetallics, that show negligible solubility; (2) the reaction between those two end members leads to form only intermetallics phases that exhibit the narrow homogeneity range. Taking that into account, Wagner proposed the following formula for calculating integrated interdiffusion coefficient in each phase (Wagner, 1969):

$$\tilde{D}_{int}^\beta = \frac{(N_i^\beta - N_i^-)(N_i^+ - N_i^\beta)}{N_i^+ - N_i^-} \cdot \frac{\Delta x_\beta^2}{2t} + \frac{\Delta x_\beta}{2t} \left[\left(\frac{N_i^+ - N_i^\beta}{N_i^+ - N_i^-} \right) \sum_{v=2}^{v=\beta-1} \left(\frac{V_m^\beta}{V_m^v} (N_i^v - N_i^-) \Delta x_v \right) + \left(\frac{N_i^\beta - N_i^-}{N_i^+ - N_i^-} \right) \sum_{v=\beta+1}^{v=n-1} \left(\frac{V_m^\beta}{V_m^v} (N_i^+ - N_i^v) \Delta x_v \right) \right] \quad (15)$$

where β denotes the phase of interest, N_i^+ and N_i^- are the right- and left-hand side mole fractions of i -th component respectively, Δx is the measured thickness of the v phase, V_m^β and V_m^v denote molar volume of the β and v phase, respectively.

Knowledge about the value of diffusion coefficient gives valuable information about kinetics of the growing phase. It is not enough however to determine which phase will occur in the reaction

zone. For example in Ti-Cu-Ni ternary system at 1073 K there appear 8 different intermetallic phases and 3 different two-phase zones (Effenberg & Ilyenko, 2006) (figure 1). Not all of them would appear during annealing - some of them are more stable than the others, some grow faster, sometimes a metastable phase would also appear (Wierzba, 2016). The information about the diffusion path in such a system is of a crucial importance - Ti-Cu-Ni alloys are widely used as a shape memory metals (Effenberg & Ilyenko, 2006; Li et al., 2016). The properties of such phases have been already studied when it comes to microstructure and properties (Nam et al., 1990; Moberly et al., 1991, Ishida et al. 2013). However the determination of the diffusion path in such a system would allow to predict the properties of a diffusion couple under specific conditions of temperature, time and initial compositions of the alloys. Therefore it will enable to design new materials or new applications of known alloys, depending on the expected properties.

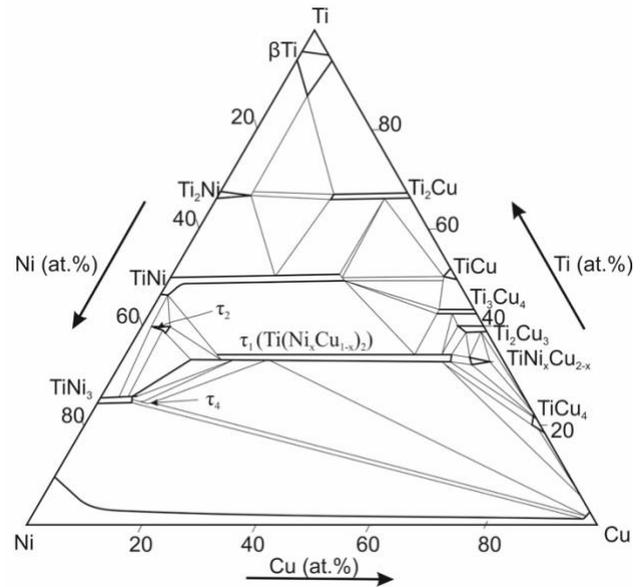


Fig. 1. Ti-Ni-Cu phase diagram at 1073K (Ho et al., 2017)

2. EXPERIMENTS

In this paper two diffusion couples were prepared: high purity Ti (99,7 at.%) were coupled with NiCu alloy with two different compositions: Ni10-Cu90 and Ni90-Cu10. Before diffusion annealing samples were cut to the rectangular shapes with dimensions of about 10 x 10 x 2 mm. The plates were further ground and polished up to obtain mirror-like surface finishing. Diffusion annealing was conducted at 1073K for 160 hours. Before heat treatment the samples were coupled together in a molybdenum frame and put into a glass tube of a



furnace, where there were flushed in the cold zone with high purity argon (5.0). This process enables to avoid unnecessary oxidation of holder and diffusion couple and helps to evacuate air from the furnace. After 5 hours of such treatment couples were inserted into a hot zone of the furnace, where there were annealed for 160 hours at 1073K in the inert gas (again high purity argon).

After the heat treatment, the couples were mounted with the resin. To analyze microstructures of the samples, the metallographic cross-sections were prepared by grinding and polishing. The last mentioned were performed using 0,25 μm granulation of silica suspension. The cross-sections were investigated using scanning electron microscope (SEM, S-3400 Hitachi Scanning Electron Microscope). The microstructure of the reaction zone was observed and the chemical composition of the growing phases were measured.

3. RESULTS

3.1 Ni10-Cu90-Ti

Observation of the microstructure of the diffusion couple Ti-Ni10Cu90 (figure 2) shows, that after annealing at 1073 K for 160 h, the thickest phase is TiCu, which reaches the thickness of about 23 μm . Part the thickness of TiCu is τ_1 , which can be expressed with steichiometric formula of $\text{Ti}(\text{Ni}_{1-x}\text{Cu}_x)_2$. Figure 2 also reveals the existence of very narrow Ti_2Cu phase.

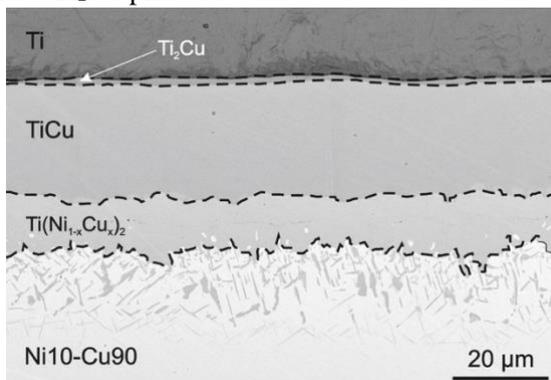


Fig. 2. The microstructure of the Ti-Ni10Cu90 diffusion couple after annealing at 1073K for 160 hours

The thickness of the phases, are presented in table 1. It is clearly visible in figure 2, that between τ_1 and initial alloy of Ni10Cu90, there appears two-phase region. To simplify the calculations, it is assumed that the diffusion path does not cross the conode, but goes across it. The measured concentration profile of Ti, Ni and Cu are presented on figure 3.

The layer sequence, after annealing at 1073K for 160h is as follows: Ni10Cu90 \rightarrow $\text{Ti}(\text{Ni}_{1-x}\text{Cu}_x)_2$ \rightarrow TiCu \rightarrow Ti_2Cu \rightarrow Ti.

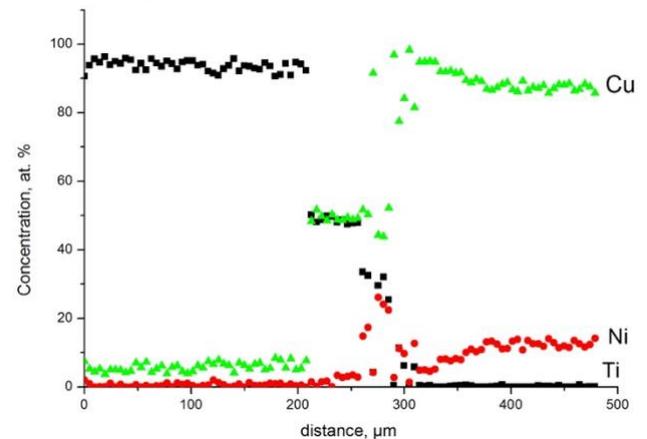


Fig. 3. Concentration profile of the Ti-Ni10Cu90 diffusion couple after annealing at 1073K for 160 hours

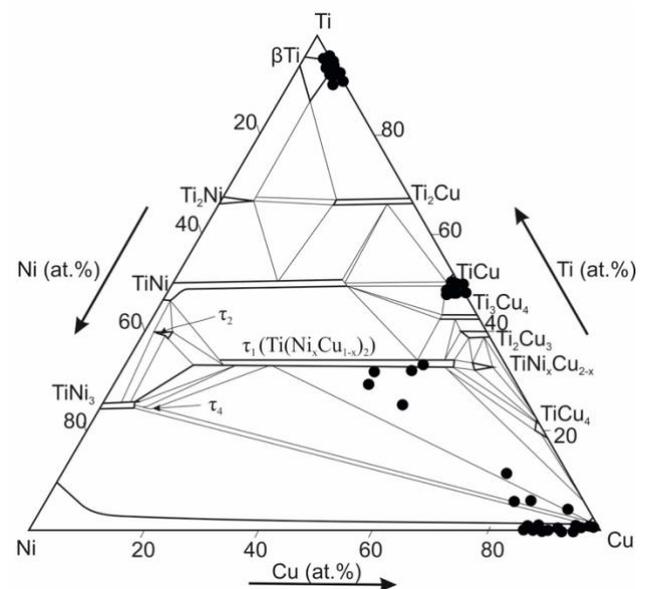


Fig. 4. Diffusion path after diffusion annealing at 1073K for 160h of the Ti-Ni10Cu90 diffusion couple.

Diffusion coefficient in each phase was calculated in accordance with Equation (15), using Wagner's method. Thickness of the phases were measured with the help of digital software. The molar fraction of the components is determined from concentration profile (figure 3).

The value of Gibbs free energy for those phases is known in the literature (Barin, 1995). The results of such calculation is presented in table 1.

Determination of diffusion coefficients in each phase enables also applying Equation (12) to calculated entropy production in each phase (table 1).



Table 1. Results of calculation of Wagner's diffusion coefficient by Equation (15) and entropy production by Equation (12) after annealing at 1073K for 160 h

Phase, j	Thickness Δx , μm	Average molar fraction			Molar volume of the j-th phase, cm^3	Wagner's diffusion coefficient, $\text{cm}^2 \cdot \text{s}^{-1}$			Entropy production, $\frac{J}{K} \cdot \frac{\text{cm}^2}{s}$
		Ti	Ni	Cu		\tilde{D}_{Ti}^j	\tilde{D}_{Ni}^j	\tilde{D}_{Cu}^j	
Ti	---	0,98	0,01	0,01	10,47	---	---	---	---
Ti ₂ Cu	1,608	0,66	0,01	0,33	8,83	$7,99 \cdot 10^{-14}$	$4,18 \cdot 10^{-17}$	$8,56 \cdot 10^{-14}$	$2,36 \cdot 10^{-33}$
TiCu	23,45	0,49	0,02	0,50	8,22	$1,62 \cdot 10^{-12}$	$1,62 \cdot 10^{-15}$	$1,73 \cdot 10^{-12}$	$1,40 \cdot 10^{-30}$
Ti(Ni _{1-x} Cu _x) ₂	12,11	0,32	0,22	0,47	7,63	$6,38 \cdot 10^{-13}$	$4,35 \cdot 10^{-13}$	$8,50 \cdot 10^{-13}$	$8,24 \cdot 10^{-31}$
Ni10Cu90	---	0,01	0,09	0,90	7,06	---	---	---	---

The highest value of entropy production was obtained for TiCu (figure 5). The lowest value of entropy production was calculated for Ti₂Cu.

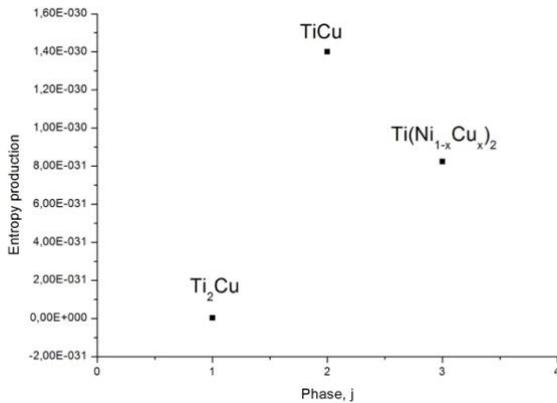


Fig. 5. Representation of entropy production for each phase that appeared after annealing the Ti-Ni10Cu90 diffusion couple for 160 h at 1073K.

4.2 Ni90-Cu10-Ti

The experimental procedure for Ti-Ni90Cu10 was similar to that performed for previous diffusion couple. The microstructure after annealing at 1073K for 160 hours is shown in figure 6.

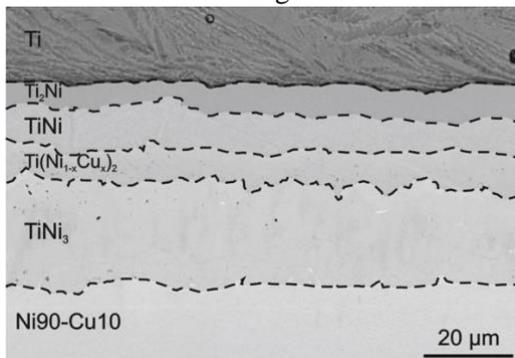


Fig. 6. Microstructure obtained after annealing the diffusion couple Ti-Ni90Cu10 at 1073K for 160 hours.

One can distinguish 4 different phases: Ti₂Ni, TiNi, Ti(Ni_{1-x}Cu_x)₂, TiNi₃ of which TiNi₃ is the thickest (about 20 μm). The thickness of all phases is presented in table 2. The experimental concentration profile after annealing at 1073K for 160 hours is presented in figure 7.

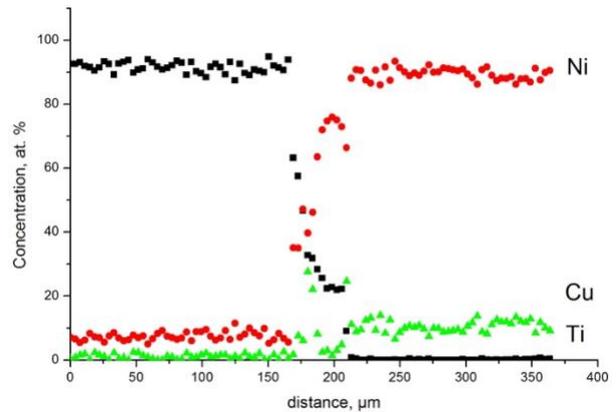


Fig. 7. Experimental concentration profile of components after annealing the Ti-Ni90Cu10 diffusion couple at 1073K for 160 hours.

The diffusion path on ternary phase diagram Ti-Cu-Ni is shown in figure 8.

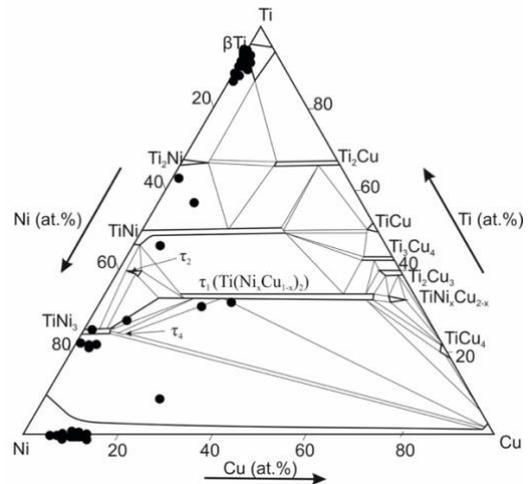
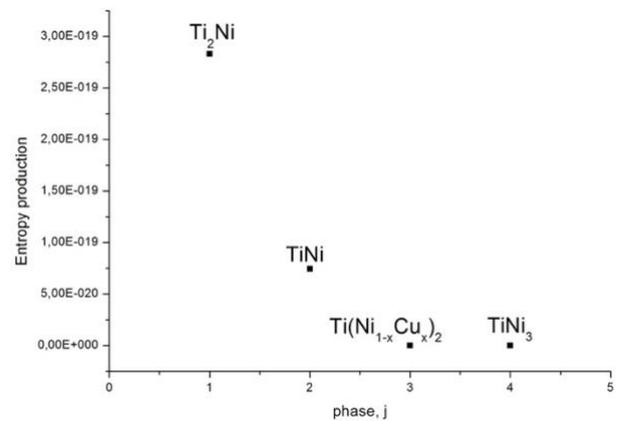


Fig. 8. Diffusion path of Ti-Ni90Cu10 diffusion couple at 1073K

Diffusion path in Ti-Ni90Cu10 diffusion path after annealing at 1073K for 160 hours goes through following phases: Ni90Cu-10 \rightarrow TiNi₃ \rightarrow Ti(Ni_{1-x}Cu_x)₂ \rightarrow TiNi \rightarrow Ni₂Ni \rightarrow Ti.

For each of those intermetallics, the entropy production was calculated. The results are presented in table 2.

The highest value of entropy production was obtained for Ti₂Ni and TiNi (figure 9). Considerably slower value of entropy production was calculated for TiNi₃ and Ti(Ni_{1-x}Cu_x)₂.

**Fig. 9.** Entropy production for each phase, which appeared after annealing Ni90Cu10-Ti diffusion couple for 160 hours at 1073K**Table 2.** Wagner's diffusion coefficient (Equation (15)) and entropy production (Equation (12)) for phases visible after annealing Ti-Ni90 Cu10 at 1073K for 160 hour

Phase, j	Thickness Δx , μm	Average molar fraction			Molar volume of the j-th phase, cm^3	Wagner's diffusion coefficient, $\text{cm}^2 \cdot \text{s}^{-1}$			Entropy production $\frac{J}{K} \cdot \frac{\text{cm}^2}{\text{s}}$
		Ti	Ni	Cu		\tilde{D}_{Ti}^j	\tilde{D}_{Ni}^j	\tilde{D}_{Cu}^j	
Ti	---	0,98	0,01	0,01	10,47	---	---	---	---
Ti ₂ Ni	5,95	0,66	0,33	0,01	8,63	$2,90 \cdot 10^{-13}$	$2,86 \cdot 10^{-13}$	$6,83 \cdot 10^{-29}$	$2,83 \cdot 10^{-19}$
TiNi	8,224	0,49	0,49	0,02	7,95	$4,95 \cdot 10^{-13}$	$4,87 \cdot 10^{-13}$	$3,35 \cdot 10^{-29}$	$7,43 \cdot 10^{-20}$
Ti(Ni _{1-x} Cu _x) ₂	7,575	0,33	0,39	0,28	7,55	$4,59 \cdot 10^{-13}$	$4,12 \cdot 10^{-13}$	$8,74 \cdot 10^{-14}$	$4,10 \cdot 10^{-31}$
TiNi ₃	21,513	0,24	0,75	0,01	7,18	$1,16 \cdot 10^{-12}$	$7,74 \cdot 10^{-13}$	$3,58 \cdot 10^{-13}$	$1,23 \cdot 10^{-30}$
Ni90Cu10	---	0,01	0,9	0,09	6,65	----	---	---	---

5. CONCLUSIONS

In the paper, the method which allow to determine the integral diffusion coefficients by Wagners method was formulated. The calculated mobilities allowed for determination the entropy production in each phase. The reaction zones in ternary Ti-NiCu system have been analyzed and entropy production for diffusion paths was calculated.

It was shown, that the entropy production allows for determination of the sequence of the phase formation in ternary Ti-NiCu system - the phase competition problem. The above mentioned theory has been already discussed in Ti-NiAl ternary system, where it was proved, that maximization of entropy production allows for determination of the diffusion path in such a system (Wierzba, 2016). Therefore, the authors expect, that the theory of the

highest entropy production can be applied in determining a

proper diffusion path in multicomponent, multiphase system.

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NAJWYŻSZA WARTOŚĆ PRODUKCJI ENTROPII W DYFUZJI

Streszczenie

W niniejszej pracy podjęto próbę weryfikacji teorii o najwyższej wartości produkcji entropii w procesie dyfuzji. Umożliwia ona przewidywanie, które fazy wystąpią w trakcie wygrzewania dyfuzyjnego wielofazowego układu trójskładnikowego. Zgodnie z teorią faza o najwyższej wartości produkcji entropii pojawi się w strefie dyfuzyjnej jako pierwsza. W celu zweryfikowania poprawności tej teorii wyprowadzono wzór matematyczny umożliwiający obliczenie wartości produkcji entropii. Równanie zostało wyprowadzone w oparciu o uogólnioną metodę Darkena. W celu uzyskania danych termodynamicznych i kinetycznych przeprowadzono wygrzewanie par dyfuzyjnych: tytan o wysokiej czystości zetknięto ze stopami miedź-nikiel o różnym stężeniu początkowym: Ni10Cu90-Ti i Ni90Cu10-Ti (% at.). Po procesie obserwowano mikrostrukturę stref dyfuzyjnych oraz zbadano skład chemiczny w poszczególnych fazach. Wykazano, że w strefie dyfuzyjnej dla pary Ti-Ni10Cu90 wystąpiły 3 fazy międzymetaliczne: Ti_2Cu , $TiCu$ oraz $Ti(Ni_{1-x}Cu_x)_2$ natomiast dla pary Ti-Ni90Cu10 4 różne fazy: $TiNi_3$, $Ti(Ni_{1-x}Cu_x)_2$, $TiNi$ oraz Ti_2Ni . Na podstawie profilów stężeń obliczono współczynniki dyfuzji Wagnera dla każdego składnika w każdej fazie. Znając wartości współczynnika dyfuzji w każdej z faz międzymetalicznych diagramu równowagi fazowej można wyznaczyć wartość produkcji entropii w całym układzie. Wyniki wykazały, że faza o największej wartości produkcji entropii zostanie utworzona w procesie dyfuzji jako pierwsza - w parze Ni10Cu90-Ti była to faza $TiCu$, natomiast w przypadku pary Ni90Cu10-Ti była to faza Ti_2Ni . Na podstawie badań stwierdzono, że znając wartości maksymalne produkcji entropii można scharakteryzować w jednoznaczny sposób ścieżkę dyfuzji pomiędzy Ti a NiCu.

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