

Study and simulations of quick diffusion in Zr-based alloys



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HIGHLIGHTS

- An improved database for fast diffusion paths was obtained.
- The diffusion parameters in type C kinetic on fast paths in α -Zr for Cr and Co were used.
- Simulated diffusion profiles were compared with previous experimental results. This comparison and the adequacy of the improved database are discussed.
- Diffusion parameters for fast diffusion paths in Zr at low temperature were assessed for Co and Cr.
- Diffusion profiles on grain boundaries in α -Zr for Cr and Co are presented in the temperature range of 380–460 K.

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ABSTRACT

Zirconium and its alloys are widely used in the nuclear industry. Under normal conditions, Zr-alloys are polycrystalline and contain a high density of grain and interphase boundaries. These boundaries function as paths for accelerated matter movement. The movement of fast diffusing elements (Co, Fe, Cr, Ni) in Zr alloys along boundaries produces technologically important changes in the materials in nuclear reactors at normal temperatures (~550 K) e.g.: segregation, phase precipitation, hydrogen absorption, etc.

In this work, diffusion parameters for fast diffusion in Zr at low temperature were assessed for Co and Cr. An improved database for DICTRA (Diffusion-Controlled-TRANSformation) software for fast diffusion was obtained. The diffusion parameters in grain boundaries of α -Zr for Cr and Co were used from a particular kinetic diffusion model [1]. Simulated profiles were compared with previous experimental work [2]. The results of the comparison and the adequacy of the improved database are discussed.

Diffusion profiles on grain boundaries in α -Zr for Cr and Co are presented in the temperature range of 380–460 K.

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1. Introduction

Zirconium based materials are widely used in nuclear power reactors in view of their special properties: good corrosion resistance, adequate mechanical properties and a low capture cross section for thermal neutrons. These materials are usually found in service with a high density of grain and interphase boundaries. Albeit the operating temperatures are not extremely high, these

alloys undergo important changes during operation, associated with irradiation, corrosion and the movement of alloy solutes by diffusion. This is especially important with the interest in increased burn-up fuels and other measurements to keep the alloys inside the reactors for longer periods of time. Understanding the changes that can happen to these alloys in the reactor environment is, thus, of paramount importance. Several of these changes are associated with the change of position of atoms in the lattice and one of the important mechanisms for this is diffusion.

In other technological sense, the CANDU (CANada Deuterium Uranium) reactor uses hundreds of pressure tubes (Zr based alloys) to contain the fuel and coolant. These tubes are in contact with

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alloy steels (with Cr, Co and other possible elements) at 300 °C under normal conditions. Finally a diffusion process is suggested between the Zr based alloys and the alloys steel with metallurgical process associated: segregation, hydrogen absorption, etc [2,3].

The study of the diffusion of different alloying elements as well as the possible impurities present in a multi-component system is useful in the characterization of the mobility of such atoms in the studied alloy and thus supports the development of kinetic databases. These databases are useful in the prediction of atom movements caused by chemical potential gradients such as, for instance, phase transformation, generation of concentration profiles at different times and temperatures, growth of oxide layers, etc.

Besides bulk diffusion, grain boundary diffusion can also be important. The relative importance of both bulk and boundary diffusion depends, among other aspects, on the temperature of the material [4].

A grain boundary (GB) is defined as the transition region between two adjacent crystals in a single-phase material, which are in contact and only differ in the crystallographic orientation. Most boundaries are considered as a two-dimensional zone (approx. 5–10 wide) and highly disordered compared with the adjacent crystallographic regions. This classical definition applied to the so-called “high angle” or “incoherent” grain boundary. There are also less common grain boundaries where special orientations of the adjacent grains give significantly different characteristics to the boundary, especially with respect to disorder: these are normally termed coherent interfaces. An interface boundary (IB) is a two-dimensional region between two adjacent zones with different crystal structures. Partially coherent or “low-angle” interface boundaries are also possible, especially in the initial stages of second-phase nucleation. As a consequence of the high disorder in incoherent boundaries, both GBs and IBs are regions in which diffusion can be increased by several orders of magnitude in relation to the volume diffusion in the adjacent matrix either side of the boundary. At temperatures in which volume diffusion can be considered practically zero, an appreciable, although localized amount of material can be moving rapidly in the boundary plane, accelerating not only the diffusion itself, but also phenomena associated with it: discontinuous precipitation, phase transformation, corrosion, etc.

Previous results [2] indicate that both Cr and Co, are fast diffusing elements in the grain boundaries of α -Zr consistent with their behavior as fast diffusers also observed in volume diffusion.

Harrison classified the diffusion kinetics along dislocations and grain boundaries in three groups, namely A, B and C kinetics [1] as discussed in the next section. This classification makes it possible to perform a comprehensive evaluation of the diffusive process; it is possible, as will be shown, to derive an independent evaluation of the segregation factor of Cr and Co to GBs, in addition to the GB diffusion coefficient itself.

Previous work at the Diffusion Division of the Materials Department–CNEA focused mostly on the experimental aspects of quick path diffusion [2,3,5–7]. In particular, this work has focused on the numerical simulations of fast diffusing elements in Zr nuclear alloys. The studies at CNEA have indicated that if one can characterize the diffusion parameters for various solutes in these alloys, it may be possible to predict phase transformations, segregation factor and mechanical behaviors, etc.

In this work, experimentally measured segregation values and grain boundary diffusion coefficients were used to derive mobility data to use in DICTRA. The diffusion profiles calculated using DICTRA and these mobilities are compared to profiles obtained experimentally to evaluate the quality of the derivation of the mobility data.

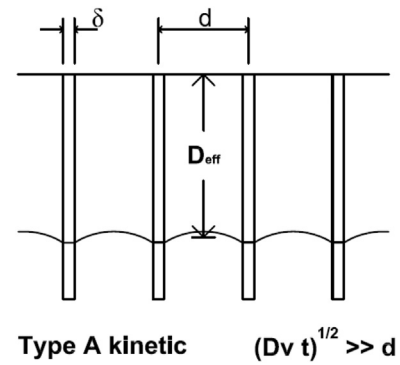


Fig. 1. Schematic illustration of type A kinetic condition according to Harrison classification. D_v : volume diffusion coefficient; D_{gb} : grain boundary diffusion coefficient; d : grain size; t : annealing time; δ : grain boundary size. D_{eff} is a weighted average given by $D_{eff} = f D_{gb} + (1 - f)D$ where D_{gb} is the grain boundary diffusion coefficient and D is the matrix diffusion coefficient.

2. Grain boundary diffusion models

Grain boundary (GB) diffusion in polycrystalline materials is a complex process that involves a series of elementary processes: volume diffusion coming from the grain surfaces, diffusion along the GB and volume diffusion through the GB. According to the relative importance of each of this processes, different kinetics are distinguished.

The so-called Harrison classification, initially derived for the diffusion along dislocations [1] includes, in a polycrystal, three regimes named A, B and C as reviewed below.

2.1. Type A kinetic

The most important elemental process in this kinetic condition is the volume diffusion in the grains. It is observed in high temperature limit cases (for GB diffusion) and/or long annealing time. In this situation, the diffusion length $(D_v t)^{1/2}$ is much larger than the distance between the grain boundaries (d , in Fig. 1). In type A kinetics an average tracer atom will travel through many grains and GBs during the annealing time t , resulting in a planar interfaces [8] and [1]. Experimentally the system behaves according to Fick's law and an effective diffusion coefficient is measured.

The condition for this regimen is: $(D_v t)^{1/2} \gg d$.

2.2. Type B kinetic

There are two important elemental processes in this kinetic condition: GB diffusion and volume diffusion. The volume diffusion

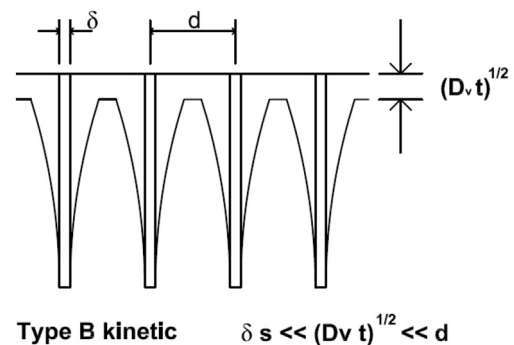


Fig. 2. Schematic illustration of type B kinetic according to Harrison classification. D_v : volume diffusion coefficient; D_{gb} : grain boundary diffusion coefficient; d : grain size; t : annealing time; $(D_v t)^{1/2}$: volume diffusion length; δ : grain boundary size.

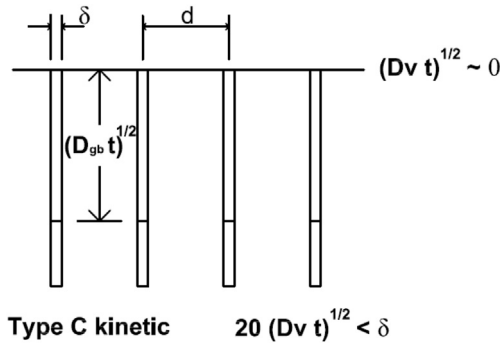


Fig. 3. Schematic illustration of type C kinetic according to Harrison classification. D_v : volume diffusion coefficient; D_{gb} : grain boundary diffusion coefficient; d : grain size; t : annealing time; $(D_v t)^{1/2}$: volume diffusion length; $(D_{gb} t)^{1/2}$: effective diffusion length; δ : grain boundary size.

field coming from one GB does not overlap the diffusion field coming from the other GB, so each of them can be treated as an isolated GB. Therefore, the mathematical solutions for isolated GBs [9–11] are valid for polycrystals.

This regime is observed when temperatures are below those of type A kinetic and/or when annealing times are shorter. Experimentally, an apparent diffusion coefficient, P_{gb} , is measured, in which the segregation factor is reflected. $P_{gb} = s \delta D_{gb}$.

The condition for this regime is: $\delta s \ll (D_v t)^{1/2} \ll d$ (Fig. 2).

2.3. Type C kinetic

In this kinetic regime the most important process is GB diffusion. It is observed at low temperatures and/or extremely short annealing time.

The condition for this kinetic regime is: $(D_v t)^{1/2} \ll \delta$.

This means that diffusion only happens inside the GB. This kinetic regime is the only one that allows experimentally measuring the grain boundary diffusion coefficient (Fig. 3).

3. Kinetic and thermodynamic theory

3.1. Kinetic

In the presence of a concentration gradient, a net flux is established for the specie evaluated. The law which relates the flux and the concentration gradient is Fick's first law. Considering a case at constant temperature and pressure, on a given phase of an alloy, with the k specie diffusing on z direction, it is expressed as:

$$J_k = -D_k \frac{\partial C_k}{\partial z}$$

The basic model for only one active diffusive phase was used in this work. In this case, the flux in a multicomponent system is defined as:

$$J_k = - \sum_{j=1}^{n-1} D_{kj}^n \frac{\partial C_j}{\partial z} \quad (1)$$

where equation (1) is solved using numerical methods [12]. DICTRA [13] software was used for the corresponding numerical simulations based on the databases generated with the diffusion parameters previously established in different kinetic regimes [2,14].

3.2. Thermodynamic

For pure elements, the following thermodynamic model is normally used to describe the Gibbs energy at sufficiently high temperatures [15].

$$G_m - H_m^{SER} = a + b \cdot T + c \cdot T \cdot \ln(T) + \sum d_i \cdot T^i$$

where:

$G_m - H_m^{SER}$ is the Gibbs energy relative to the Standard Element Reference (SER) state. H_m^{SER} is the enthalpy of the mechanical mixture of the pure elements in their stable phase at $T = 298.15$ K and $P = 10^5$ Pa (SER), and is normally taken as zero for pure elements. The coefficients a , b , c , and d_i are model parameters.

In the case of the solution phases and compounds with various elements the following Gibbs free energy expression is used:

$$G = G^\circ + {}^{id}G_{mix} + {}^{xs}G_{mix} + G_{mag}$$

where:

G° is the Gibbs energy due to the mechanical mixing of the phase constituents,
 ${}^{id}G_{mix}$ is the ideal contribution to the mixing Gibbs energy,
 ${}^{xs}G_{mix}$ is the excess mixing Gibbs Free energy,
 G_{mag} is the magnetic contribution to the Gibbs free energy for ferromagnetic or antiferromagnetic phases

Developing a database for the composition and temperature dependence of all the D_{kj}^n , including the cross terms can be very complex. To avoid this complication a database of mobilities is created. The diffusion coefficients used for the simulation are the product of a thermodynamic and a kinetic factor. The thermodynamic factor is basically the second derivative of the Gibbs energy with respect to concentration and the kinetic factor contains the atomic mobilities. For a detailed discussion see Refs. [17,18]. Thermodynamic data used for GB diffusion are the ones corresponding to the materials volume, then the thermodynamic factor that affects the diffusion coefficient may not be exact for GB.

Table 1
Chemical analysis of the Zr used in this work. Values are in mass ppm.

Element	B	C	Ca	Cd	Cl	Co	Cr	Cu	Fe	H	Hf	Mg	Mn	Mo
Al	<20	<0.25	31	<10	<5	<10	<50	<17	138	<3	74	<10	<25	<10
Element	Na	Nb	Ni	O	P	Pb	Si	Sn	Ta	Ti	U	V	W	
N	<20	<50	<36	423	<3	<25	<10	<10	<50	<25	<1	<25	<25	

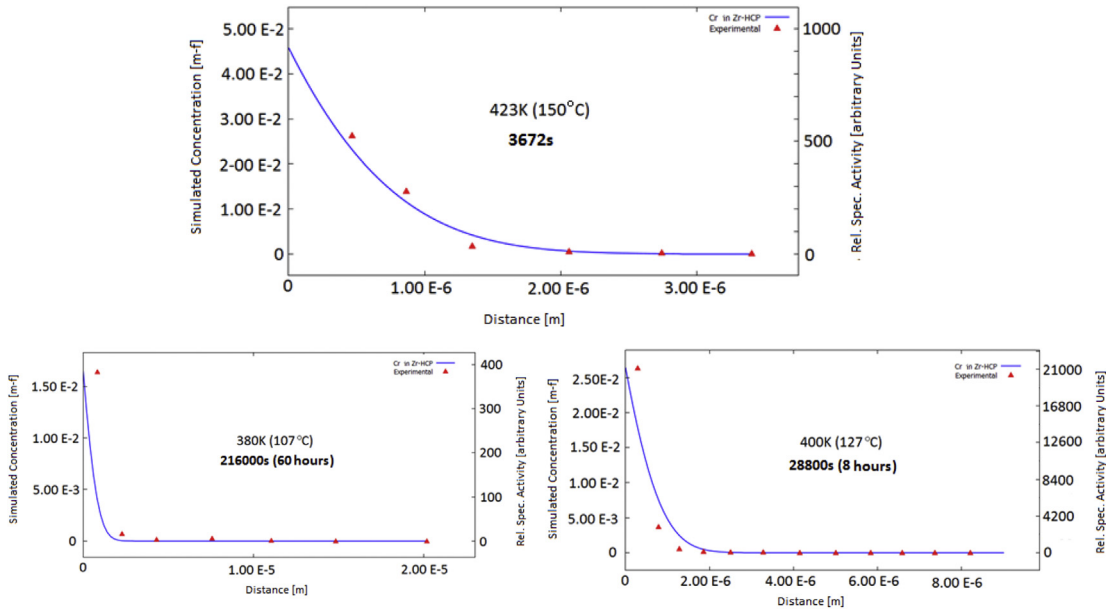


Fig. 4. Cr diffusion on GB of α -Zr. Simulations and experimental data [2].

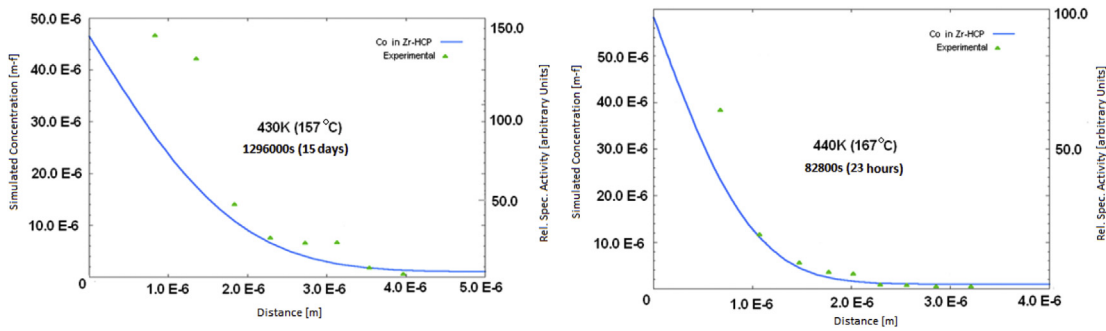


Fig. 5. Co diffusion on GBs of α -Zr. Simulations and experimental data [2].

4. Experimental and theoretical calculations

Annealing treatments with conditions leading to type C kinetic were designed and performed [2]. In this case, the diffusion volume can be calculated based on the thickness of the grain boundary (taken as 5×10^{-10} m in the present case) (Table 1).

This allows one to guarantee that matter found at a distance of $\sim 3 \times 10^{-6}$ m from the surface has moved solely through the grain boundary. The boundary conditions to define a constant source of the diffusing element at different temperatures are the solubility values for Co and Cr in α -Zr. The solubility of Cr and Co in α -Zr (alpha phase) is very small at temperatures below 300 °C. However we focus the analysis in the intermetallic phase near to the alpha phase ($ZrCr_2$ in the Zr–Cr system and Zr_5Co in the Zr–Co system). In the fact that $ZrCr_2$ phase needs more Cr to form herself than the Co concentration needed to form Zr_5Co , we propose that the alpha phase for the ZrCr system (at thermodynamic equilibrium) has less Cr concentration than the Co concentration in the alpha phase from ZrCo system. This is coherent with the solubility calculations at different temperatures performed. Kinetic parameters used for the simulations came from the experimental data of [2] and the thermodynamic parameters for GB adopted are equivalent to those applicable to bulk volume, obtained from Refs. [19] and [20].

Thus, different diffusion experiments of Co and Cr in α -Zr were

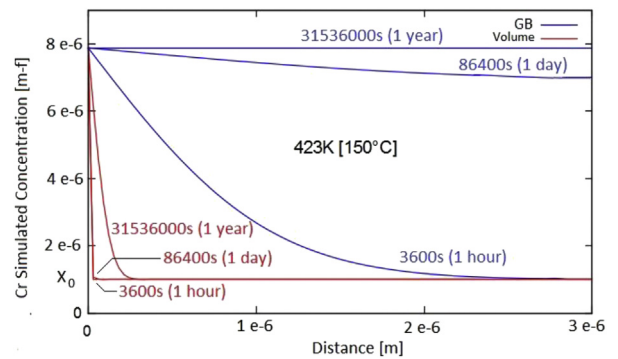


Fig. 6. Diffusion simulations for volume and GB diffusion of Cr in α -Zr at 150 °C, for different times.

performed [2] and simulated using DICTRA. The results of these simulations are presented in Figs. 5 and 6. The simulation conditions for these cases are presented in Table 2.

5. Results and discussion

Particularly for the Co diffusion on GB of α -Zr [2], no differences

Table 2
Input data used for the simulations of grain boundary diffusion presented in Figs. 4 and 5.

Thermodynamic data				Kinetic data	
T [K]	X(Cr) [at.]	Xo [at.]	Hr.	T [K]	D_{gb-Cr} [m ² /s]
380	2.17 E-6	1.0 E-6	60	380	1.27 E-18
400	4.09 E-6	1.0 E-6	8	400	1.11 E-17
423	7.87 E-6	1.0 E-6	1.02	423	1.04 E-16

Thermodynamic data				Kinetic data	
T [K]	X(Co) [at.]	Xo [at.]	Hr.	T [K]	D_{gb-Co} [m ² /s]
430	4.65 E-5	1.0 E-6	360	430	8.2 E-19
440	5.83 E-5	1.0 E-6	23.18	440	3.6 E-18

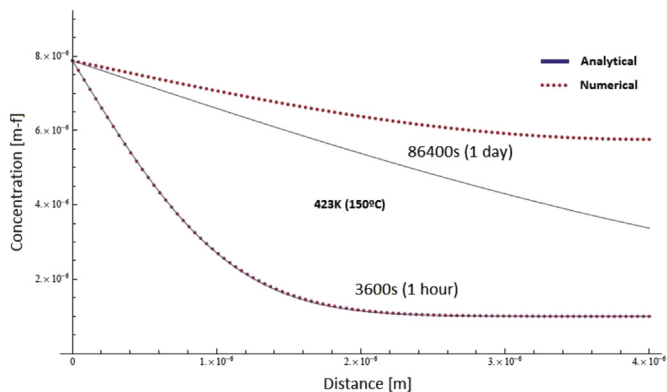


Fig. 7. Cr diffusion on GB of α -Zr. Numerical and analytical concentration profiles. 423 K (150 °C)- 1 h, 1 day.

were found between the diffusion performed with different purity grades of Zr (comparing [16] and [2]). Quick path diffusion does not seem depend on concentration or interaction with other possible elements in the material (impurities). Then, no optimization of the GB mobility coefficients as function of the composition is proposed. In exchange, GB thermodynamic factor is an issue to develop, in view of the results shown in Fig. 6.

5.1. GB diffusion vs. volume diffusion

Fig. 6 shows comparative simulations performed for grain boundary diffusion and volume diffusion. They were performed based on GB diffusion similar to type C kinetic. It is possible to observe that for equal temperatures and times, diffusion profiles on grain boundaries show an important increment in concentration, in relation to that corresponding for volume coefficients. Particularly for the 150°C-1hs profile, when the volume diffusion is nearly zero, the GB matter movement could be clearly appreciated. The GB concentration gradient is visible at approx. 2 μ m from the diffusive surface.

Measurement of GB diffusion usually presents greater difficulties than volume diffusion, and can be performed only on very narrow temperature and time ranges, particularly applicable to type C kinetic. This highlights the importance of numerical solutions, in providing results for diffusion at times and temperatures not accessible experimentally.

5.2. Numerical vs analytical solutions for GB diffusion

Diffusion parameters used for GB kinetic databases were those obtained using type C kinetic: the diffusing element moved exclusively along the GB and was confined to it. This type of diffusion presents analytical solutions equivalent to those applied to volume diffusion. In particular, in the case of quick path diffusion, the conditions imposed by analytical solutions are not compatible with technological processes, hence numerical solutions are more adequate. Fig. 7 compares both solutions: at the same temperature, both solutions are equivalent for short periods of time. For larger periods, numerical solution results in a larger concentration on the right end of the curve due to the lack of the semi-infinite condition imposed in the analytical solution.

6. Conclusions

- A database for fast-paths diffusion at low temperatures has been improved for Co and Cr in Zr grain boundaries.
- Simulated diffusion profiles when the grain boundary conditions predominate, show a very good agreement with the experimental results, for both Cr and Co in α -Zr.
- Quick path diffusion is a phenomenon to be particularly considered in low temperature technological processes, given the existence of ultra-fast diffusers that can generate important movement of matter in localized zones.

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References

- [1] L.G. Harrison, *Trans. Faraday Soc.* 57 (1961) 1191–1199.
- [2] C. Corvalán, M. Iribarren, N. Di Lalla, F. Dymont, *Def. Diff. Forum* 283–286 (2009) 669–674.
- [3] M. Iribarren, O.E. Agüero, F. Dymont, *Def. Diff. Forum* 194–199 (2001) 1211–1216.
- [4] D.A. Porter, K.E. Easterling, *Phase Transformations in Metals and Alloys*, second ed., Chapman & Hall, London, 1992.
- [5] F. Dymont, M. Iribarren, K. Vieregge, *Chr. Herzig, Mater. Sci. Forum* 126–128 (1993) 395–398.
- [6] F. Dymont, M. Iribarren, K. Vieregge, *Chr. Herzig, Phil. Mag. A* 63 (1991) 959–966.
- [7] M. Iribarren, M. Iglesias, F. Dymont, *Metallurgical Mater. Trans. A* 04 33 (3) (2012) 797–800.
- [8] Y. Mishin, Chr. Herzig, J. Bernardini, W. Gust, *Grain boundary diffusion: fundamentals to recent developments*, *Int. Mater. Rev.* 42 (4) (1997) 155–178.
- [9] J.C. Fisher, *Appl. Phys.* 22 (1951) 74–84.
- [10] R.T.P. Whipple, *Philos. Mag.* 45 (1954) 1225–1237.
- [11] T. Suzuoka, *J. Phys. Soc. Jpn.* 19 (1964) 839–850.
- [12] J. Agren, *J. Phys. Chem. Solids* 43 (1982) 385–391.
- [13] J.-O. Andersson, L. Höglund, B. Jönsson, J. Ågren, *Fundamentals and Applications of Ternary Diffusion*, 270–76, Pergamon Press, New York, NY, 1990, pp. 153–163.
- [14] C. Corvalán, M. Iribarren, N. Di Lalla, F. Dymont, *J. Nucl. Mater.* 382 (1) (2008) 35–38.
- [15] A.T. Dinsdale, *SGTE data for pure elements*, *Calc. Phase Diagrams* 15 (1991) 317–425.
- [16] K. Vieregge, Chr. Herzig, *J. Nucl. Mater.* (1990) 175–229.
- [17] TCAB, *DICTRA User's Guide 27*, Thermo-calc Software AB, Stockholm, 2013.
- [18] C.E. Campbell, W.J. Boettinger, U.R. Kattner, *Acta Mater.* 50 (4) (2002) 775–792.
- [19] J. Pavlík, Vřest'sál, M. Šob, *CALPHAD* 33 (2009) 382–387.
- [20] X.J. Liu, H.H. Zhanga, C.P. Wanga, K. Ishidab, *J. Alloys Compd.* 482 (2009) 99–105.