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Assessment of Mobilitiesof the B2Phase in the Nickel-Chromium-Aluminum System

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Abstract. A model for diffusion is applied to the nickel-chromium-aluminum (Ni-Cr-Al) system to optimize the mobility parameters for the B2 phase by fitting the experimentally obtained inter-diffusivities. In the model, the activation energy for diffusion is expressed as a function of the degree of ordering which is evaluated from thermodynamic data. These data are used to evaluate the thermodynamic factors of the B2 phase in the Ni-Cr-Al ternary system. The interdiffusivities from the model are used to simulate diffusion experiments. The results are generally agreed with the experimental data.

Introduction

It is well known that MCrAlY-type coatings widelyused for improving the high temperature properties and the oxidation resistance of turbine blades are degraded due to depletion of Al from the coating [1]. The loss of Al occurs by diffusion toward the surface of the coatings to form Al_2O_3 scale and by interdiffusion with the superalloy substrates [2]. Several studies [3,4] have shown that the interdiffusion between the coatings and the substrates may contribute more to the overall Al depletion than the Al depletion caused by oxidation.The driving force for interdiffusionof Al is generally the chemical potential gradientbetween the coatings and the substrates. The inter-diffusion between the coatings and the substrates decreases the integrity of the coating system, and severely accelerates the degradation of the coatings [5]. Since the B2 phase of the Ni-Cr-Al ternary system is a fundamental phase for MCrAlY-type coatings, a number of studies on the properties of the phase have thus been conducted, among which, the diffusion behavior is a property of key importance to consider. A quantitative knowledge of diffusivities is especially attractive when predicting the lifetime of the coatings and modeling the inter-diffusion processes on the basis of the multicomponent thermodynamic and mobility database [6]. Just because of these, several multicomponent thermodynamic database for Ni-base superalloys have been developed [7~9] while rare mobility database for the B2 phase in the Ni-Cr-Al ternary system have been reported.

The quantitative models of diffusivities are essential to perform a simulation of the diffusion-controlled phase transformations. To perform diffusion simulations using the DICTRA software [10,11], both thermodynamic and kinetic descriptions of the simulated system are needed. Moreover the results and the accuracy of the simulations critically depend on the quality of these descriptions. Compared with the thermodynamic descriptions available from the Thermo-Calc database [8,9], diffusivities have to be evaluated from experimental measurements, and moreover, they are generally functions of alloy composition. Diffusion database becomes thus very complex. A superior alternative is to store mobilities in the database rather than diffusivities. The number of parameters that need to be stored in a kinetic database will be substantially reduced and the parameters are independent. Diffusivities to be used in the simulations can be obtained as a product of a thermodynamic factor and a kinetic factor. The thermodynamic factor is essentially the second derivatives of the molar Gibbs energy with respect to the concentrations. The kinetic factor contains

the mobilities. It is clear that the quality of mobilities is critically important for the evaluation of diffusivities. Therefore, the objective of this work is to assess the mobilities of B2 phase of the Ni-Cr-Al system by fitting the experimentally obtained diffusivities and then to test the assessedmobilities by comparing with diffusion experiments.

Model for diffusion mobility

The B2 phase in the Ni-Al-Cr system is an ordered phase on the basis of a bcc structure. The thermodynamics of the Ni-Al-Cr system have been assessed by Dupin et al. [12,13], which uses a two-sublattice order-disorder description to model the B2 phase. Vacancies are included in the description of the B2 phase. The disordered fcc and bcc solid solution phases are described using a single sublattice model.Composition-dependent diffusion mobility descriptions are needed to include the possible matrix diffusion in the ordered B2 phases. Helander and Ågren [14,15] proposed a phenomenological model to assess the diffusion mobilities in ordered phases using a CALPHAD-type approach [16,17]. The model was successfully used to assess Fe-Ni-Al B2 phase using the available experimental data [14].

The diffusion mechanism has been briefly summarized in the literatures [18~22]. Here will represent a review of the model for diffusion mobility. If it is assumed that diffusion occurs in a crystalline phase by a vacancy exchange mechanism only, in which the equilibrium vacancy concentration can be maintained, diffusivities, D_{kj}^{L}, are defined in the lattice-fixed frame of reference as the product of a mobility term and a thermodynamic factor.

$$D_{kj}^{L} = \sum_{i=1}^{n} M_{ki}^{L} \frac{\partial \mu_i}{\partial x_j}. \tag{1}$$

If the partial molar volumes are assumed to be constants, diffusivities in Eq.(1) D_{kj}^{L} can be transformed to be D_{ij}^{V} in the volume-fixed frame of reference,

$$D_{kj}^{V} = \sum_{i=1}^{n} (\delta_{ik} - x_k) x_i M_i \frac{\partial \mu_i}{\partial x_j}. \tag{2}$$

where*j* and *i* are the diffusion species and gradient species, respectively. δ_{ki} is the Kronecker delta, equaling to 1 when $i = k$ and 0 otherwise. μ_i and x_i are the chemical potential and the mole fraction of the species i, respectively. The partial derivative of the chemical potential, μ_i, with respect to the mole fraction, x_i, defines the thermodynamic factor which can be calculated by a CALPHAD-based description of the thermodynamics for the given systems.The M_{ki}^{L} matrix, which is both composition and temperature dependent, defines the mobility in the lattice-fixed frame of reference and assumes that the off-diagonal terms are zero, i.e. the correlation effects are negligible [18,23,24], which is valid when the vacancy concentration is in local equilibrium.This reduces the number of parameters needed to describe the diffusion in a multicomponent system, as only the diagonal terms of the mobility matrix, M_{ki}^{L}, must be evaluated. The diagonal terms of the mobility matrix, M_{ki}^{L}, are assumed to have a form as follows:

$$M_{ki}^{L} = \delta_{ki} x_i M_i, \quad M_i = \frac{\Theta_i}{RT} \cdot \exp\left(\frac{-\Delta Q_i^{*}}{RT}\right). \tag{3}$$

where Θ_i is a frequency factor with the units of m^2/sand ΔQ_i^{*} is diffusion activation energy of species*i* in a given phasewith units of J/mol. As Θ_i and ΔQ_i^{*} can be combined into one parameter, it is customary to assume that Θ_i is experimentally dependent on the composition and thus can be evaluated with ΔQ_i^{*}, which is expressed by Ågren*et al* in terms of a Redlich-Kister polynomials [14,15, 25],

$$\Delta Q_i^* = \sum_j x_j Q_i^j + \sum_p \sum_{j>p} x_j x_p [\sum_{r=0} {}^r Q_i^{pj} (x_j - x_p)^r] + \sum_j \sum_{p>i} \sum_{k>p} x_j x_p x_k [v_{jpk}^s \cdot {}^s Q_i^{jpk}] \; (s = j, p, k). \quad (4)$$

where Q_i^j, ${}^r Q_i^{pj}$ and ${}^s Q_i^{jpk}$ are linear functions of temperature. ${}^k Q_i^{pj}$ and ${}^s Q_i^{jpk}$ are binary and ternary interaction parameters, respectively. The parameters v_{jpk}^s are given by

$$v_{jpk}^s = x_s + (1 - x_j - x_p - x_k)/3 \quad (5)$$

For an ordered B2 phase, the composition dependence of the diffusion activation energy mustinclude the effect of chemical ordering. Based on the modelby Girifalco [26], which assumes that the activation energyfrom chemical ordering is dependent on a long-range orderparameter, Helander and Ågren [15] suggested incorporatingthe effect of chemical ordering by dividing the activationenergy into two terms. The activation energy, ΔQ_i^*,if the effect of the chemical ordering on diffusion activation energy is considered, can thus be written as

$$\Delta Q_i^* = \Delta Q_i^{dis} + \Delta Q_i^{ord} \quad (6)$$

where ΔQ_i^{dis} is the activation energy for diffusion in the disordered state and ΔQ_i^{ord} is the contribution to the activation energy from chemical ordering given by

$$\Delta Q_i^{ord} = \sum_k \sum_{j \neq k} \Delta Q_{ikj}^{order} [y_k^\alpha y_j^\beta - x_k x_j] \quad (7)$$

where ΔQ_{ikj}^{order} is the contribution to the activation energy for species*i* due to the chemical ordering of the *k*-*j* atoms, y_k^α is the site fraction of the species*k* on the α site, and y_j^β the site fraction of the species*j* on the β site. In this study, the contribution from chemical ordering from Eq.7 is included in activation energy, ΔQ_i^*, used in Eq.4.

Experimental information

The diffusion behavior of ordered phases was initiated by the experimental observation on β brass by Kuper*et al.*[27]. Since then a majority of the work on ordered phases has been performed from the scientific point of view. Among them, selfdiffusioncoefficients [28], tracer coefficients [29] and chemical diffusion coefficients [30,31] in binary β-NiAl phase have been thoroughly investigated and some important observations related to the effect of defects [32] and impact of ordering [33] on diffusion have also been highlighted. Diffusion data of the B2 phase in the Fe-Ni-Al system was investigated with solid-solid diffusion couples and found that the interaction among the components was strongly dependent on composition [34]. Diffusion data of the β-phase in the Ni-Al-Cr systems were estimated by the modified Boltzmann-Matano method on the basis of the experimental data [35]. It is observed to be composition dependence of the main interdiffusion coefficients. The cross inter-diffusion coefficients are smaller than the main inter-diffusion coefficients in the examined composition range. Thermodynamic calculation shows that the thermodynamic interaction between Al and Cr in Al-rich β-Ni(Al,Cr) is possibly negligible. Hopfe et al. [36] used the square root diffusivity analysis to measure the interdiffusion coefficients of the B2 phase in the Ni-Cr-Al ternary system by four single-phase B2/B2 diffusion couples andfound that the addition of Cr to the $Ni_{1.28}Al_{0.72}$ alloy could tend to reduce the values of D_{AlAl} in the B2 phase. Inter-diffusion coefficients of the B2 phase in the Ni-Co-Cr-Al quaternary system were estimated by the square root diffusivity analysis [37]. The obtained results indicated that the cross interdiffusivities other than D_{AlCo} were less than the main interdiffusivities and that the values of D_{Ali} were greater than those of D_{Cri} and D_{Coi}. This finding suggests that the addition of Cr decreases the interdiffusion coefficients of Al and Co, but the addition of Co did not cause an obvious change in the interdiffusion coefficients of Al and Cr in the β-phase region. The different effects associated with the additions of Cr and Co could be attributed to the stronger thermodynamic interactions

between Al and Co compared with that between Al and Cr.The experimental information from Hou*et. al.* [35], Hopfe*et. al*. [36] and Wei*et. al*. [37] is the main source of data for the present study and is shown in Tables1 and 2.

Table 1 Source of the experimental data from the literature [35]

Comp. (at. fraction)		logD[m^2/s]			
Al	Cr	$logD_{AlAl}$	$logD_{AlCr}$	$logD_{CrAl}$	$logD_{CrCr}$
		1123K			
0.5338	0.0196	-14.1778	-15.6968	-15.7878	-14.7328
0.5327	0.0206	-14.2000	-15.7033	-15.6656	-14.7100
0.5318	0.0220	-14.2248	-15.6990	-15.5528	-14.6904
0.5301	0.0226	-14.2848	-15.6737	-15.4609	-14.6840
0.5298	0.0230	-14.3054	-15.6968	-15.4023	-14.6716
		1223K			
0.5280	0.0165	-14.0146	-15.2798	-14.9393	-14.6180
0.5277	0.0171	-14.0182	-15.2902	-14.9318	-14.6126
0.5272	0.0183	-14.0250	-15.2612	-14.9031	-14.6108
0.5258	0.0189	-14.0526	-15.2993	-14.8729	-14.6003
0.5200	0.0209	-14.1421	-15.2782	-14.8539	-14.5768
0.517	0.0220	-14.2000	-15.2823	-14.7825	-14.5670
		1323K			
0.5453	0.0196	-13.6202	-15.1278	-14.6778	-14.4776
0.5434	0.0198	-13.6256	-15.0926	-14.6778	-14.4673
0.5423	0.0211	-13.6366	-15.1179	-14.6497	-14.4647
0.5382	0.0227	-13.6457	-15.1226	-14.6537	-14.4535
0.5373	0.0237	-13.6574	-15.0888	-14.6308	-14.4461
0.5354	0.0254	-13.6872	-15.1169	-14.6144	-14.4498
0.5345	0.0271	-13.7038	-15.0883	-14.6021	-14.4473
0.5305	0.0275	-13.7310	-15.0931	-14.6108	-14.4342
0.5253	0.0298	-13.7815	-15.0980	-14.5950	-14.4353
0.5234	0.0276	-13.8027	-15.1226	-14.5772	-14.4318
0.5221	0.0309	-13.8517	-15.1203	-14.5756	-14.4237

Table 2 Source of the experimental data from the literatures [36] and [37]

Temp. / K	Aver. Comp.	[D_{ij}]	Al	Cr	Co	Note
1323	33.37at% Al 5.19at% Cr 6.21at% Co	Al Cr Co	38.12 17.29 14.09	8.08 24.41 7.08	23.34 13.35 15.52	[37]
1223	32.50 at% Al 5.18 at% Cr 6.07 at% Co	Al Cr Co	18.43 4.40 2.84	0.47 10.43 0.36	8.25 2.54 7.42	[37]
1123	32.50 at% Al 5.18 at% Cr 6.07 at% Co	Al Cr Co	2.82 0.47 0.39	0.039 3.43 0.015	0.39 0.11 0.34	[37]
1473	34.6 at% Al 4.8 at% Cr	Al Cr	770 80	370 330	- -	[36]
	33.5 at% Al 7.5 at% Cr	Al Cr	640 230	420 420	- -	[36]

Optimization procedure

It is known that the structural vacancies formed in a B2 phase can be governed by the thermodynamic properties of the phase and have an important effect on its diffusion behavior [38,39]. In the Ni-Al binary system, on the Al-rich side of the B2 phase, the Al sublattice is almost completely occupied by Al, and the Ni sublattice by Ni and Va (Vacancy). The vacancy concentration increases as the Al content increases [40](Fig.1). On the Ni-rich side, the Al sublattice is occupied by Al and the excess Ni by forming so-called anti-structure defects, and the Ni sublattice is occupied by Ni. Based on the structural characteristics of the B2 phase, its diffusion model becomes practically a Ni-Al-Vaternary system. It means that the ternary terms in Eq. 4 should be included.For the B2 phase of the Ni-Cr-Al system, it has been acceptable that the site preference of Cr depends strongly on both alloy composition and temperature [41]. In the work of Jiang et. al. [41,42], the first-principles calculations based on the density functional theory were performed to study the site preference of 3d, 4d and 5d transition-metal elements in B2 NiAl alloys by adopting a statistical-mechanical Wagner-Schottky model. The obtained results reveal that: (1) in the Al-rich B2 NiAl, Cr prefers the Ni sublattice at lower temperature but prefers the Al sublattice at higher temperature. It can be observed from Fig.2a in the literature [41] and Fig.4a in the literature [42] that when temperature is greater than about 1075K, Cr starts to show a preference for the Al sublattice; (2) in the Ni-rich B2 NiAl, Cr has a predominant preference for the Al sublattice at the temperature range examined; (3) the stoichiometric B2 NiAl, only at very low temperature, Cr partitions equally between Al and Ni sublattices. It can also be observed from Fig.2c in the literature [41] and Fig.4c in the literature [42] that when temperature is more than about 450K, Cr starts to show a preference for the Al sublattice. It can be concluded that Cr shows a preference for Al sublattice irrespective of the stoichiometry when temperature is more than about 1100K. Combining the available experimental data [35~37], it can thus be acceptable that the B2 phase in the Ni-Cr-Al system can be described as β-Ni(Al,Cr).It indicates that its diffusion model should be described as being (Ni,Va)(Al,Cr).Regretfully, the positron lifetime measurement[43] (Fig.2) shows that the positron lifetime annihilated at defects in the β-Ni(Al,Cr) phase is clearly less than that in the binary NiAl phase, and also markedly less than that in the $Ni_{50}Al_{50}$ phase (τ_m=240ps). It can be speculated that the addition of Cr may be responsible for the decrease in vacancy concentration of the β-Ni(Al,Cr) phase in the Ni-Cr-Al ternary system. In addition, the broad solubility range of Cr in the B2 single phase region couldnot be explained readily by Cr only entering the Al sites without evoking excess vacancies even for low Al alloys (Al<50%). Considering the influence of Va on its diffusion behavior, the diffusion model for B2 phase of the Ni-Cr-Al system can be treated as Ni-Al-Cr-Vaquaternary system. Therefore, it should be reasonable that the diffusion model for B2 phase in the Ni-Cr-Al ternary system can be described as (Ni,Cr,Va)(Al,Cr).

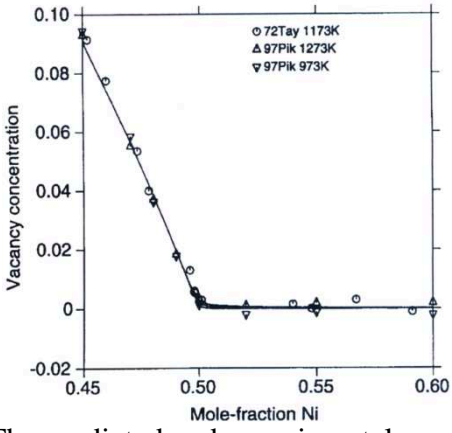

Fig.1 The predicted and experimental vacancy concentration per lattice site of the B2 phase in the Ni-Al binary system [40]

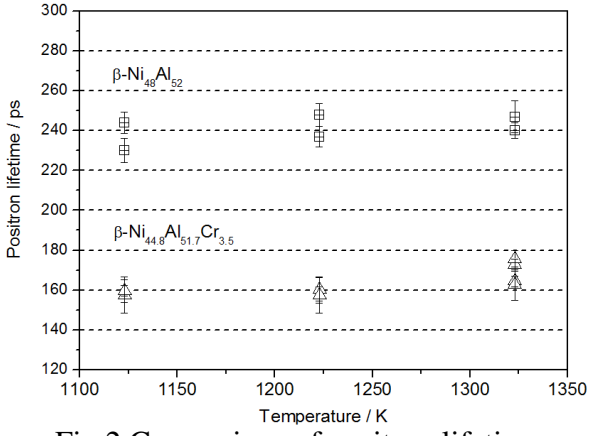

Fig.2 Comparison of positron lifetimes experimentally in the binary β-NiAl and ernary t β-Ni(Cr,Al) phases at various temperatures [43]

It is worth noting, however, that Huang and Chang [13], when assessing a thermodynamic description of the B2 phase in the Ni-Al-Cr system, used the model (Al,Cr,Ni)(Cr,Ni,Va) which is a natural extension of the model (Al,Ni)(Ni,Va) for the binary Ni-Al B2 phase by adding Cr to both sublattices [39]. Since Huang and Chang [13] neglected some of the possible constituents in their model, aimprovement of the assessment by Huang and Chang was subsequently made by Dupin etal [12], who applied the model (Al,Cr,Ni,Va)(Al,Cr,Ni,Va) to re-assess a thermodynamic description of the B2 phase in the Ni-Al-Cr system. Comparing these proposed thermodynamic models for the B2 phase in the Ni-Al-Cr systems, we can easily find that the model (Al,Cr,Ni,Va)(Al,Cr,Ni,Va) used by Dupin et al [12] is also a natural extension of the model (Al,Ni,Va)(Al,Ni,Va) used by Helander and Ågren [14], for the binary Ni-Al B2 phase by adding Cr to both sublattices, but this model is the most general model for the B2 phase in the Ni-Cr-Al system compared to the models (Ni,Cr,Va)(Al,Cr) and (Al,Cr,Ni)(Cr,Ni,Va). At the same time, this model was adopted by Campbell [44] to assess the diffusion mobilities of the B2 phase in the Ni-Al-Cr system. The assessed mobility descriptions are validated by comparing calculated and measured composition profiles for a variety of Ni-Al and Ni-Al-Cr diffusion couples, including B2/B2 and γ/B2 couples. For consistency, we extend our model (Ni,Cr,Va)(Al,Cr) to the general model (Al,Cr,Ni,Va)(Al,Cr,Ni,Va) in this investigation.

The parameters in Eqs.4 and 7 can be optimized to yield a best fit to the experimental data using the PARROT module [45,46] in the DICTRA software [10,11]. The experimental data are written as a set of equilibriums which are comparedwith the equilibrium calculated using the mobilityfunctions given in Eq.6. PARROT optimizes the mobilityfunctions using a least-squares method to minimize theerror between the experimental and calculated values foreach equilibrium.

It is well known that the crystal structure of B2 NiAl is primitive cubic CsCl structure. Its space group is *Pm3m* (Z=1). It can be described in terms of two inter penetrating cubic cells where Al atoms occupy one sublattice and the Ni atoms occupy the second sublattice if any defects are neglected. Due to the inter penetration of the two unit cells,diffusion in the B2 phase occurs through jumps between equivalent simple cubic metal sublattices. We thus follow the assessment of the B2 phase in the Ni-Al system by Helander and Ågren [14,15] and assume that the order contributions to diffusion mobilities of the B2 phase is be symmetric about the stoichiometric composition, e.g $\Delta Q_{A:B} = \Delta Q_{B:A}$, consistent with the thermodynamic description of the B2 phase. This assumption also makes the mobility description easier to extrapolate to multicomponent systems.

The parameters for the Ni-Al system have been assessed [15,47] and thereafter kept fixed. The Cr interactions in the Ni-Al-Cr B2 phase are optimized using the experimentally obtained diffusion data. It is worth noting that the Al and Cr atoms are not randomly distributed in the B2 phase in the Ni-Cr-Al ternary system. The probability of finding a Cr atom on the Al- and Ni-sublatticesis generally different. This means that from ternary diffusion information, it has been possible to assess parameters such as, ΔQ^{ord}_{CrCrNi}, i.e the contribution to the activation energy for the mobility of Cr from the ordering of Cr-Ni atoms in the B2 phase.In addition, using the CALPHAD approach to describe the composition dependence of mobility terms generally requires the determination of mobilities for fictive metastable end-member phases. Regretfully, neither pure Al nor pure Ni is stable in the B2 structure at any temperature. To optimize diffusion mobilitiesusing the PARROT module, it is necessary to make some assumptionsas follows:

(1)Since the B2 phase only exists as an intermediate phase in the Al-Ni system, it is not possible to get any experimental information regarding the self-diffusion of the elements in the hypothetical states of pure Al and Ni in b.c.c. form. This makes it necessary to assume physically reasonable values for the mobilities of Al in the b.c.c.-Al and of Ni in b.c.c.-Ni.

(2) The contribution from the Ni-Vanearest neighbor ordering is assumed to be zero because the vacancies are usually formed at x_{Al}>0.5 [48,49], indicating that they are formed on the sublattice preferentially occupied by Ni atoms so that the Ni-Va ordering is negligible. Similarly, the Cr-Al ordering can't be taken into account.

Based on the above assumptions,an optimization procedure [45,46] is used to extract the composition and temperature dependence of the activation energy in Eq.4 from the experimental data. In the optimization, Eq.2 is used to calculate the chemical diffusivity from the mobility. The derivatives of chemical potentials in Eq.2 are calculated from the thermodynamic data for the Ni-Cr-Al system. These data are the results of a CALPHAD assessment using independent experimental information on the thermodynamic properties of the Ni-Cr-Al system. The thermodynamic description for the Ni-Al-Cr system comes from the literature [12],The optimization begins with initial estimations of the mobility parameters followed by a calculation of the diffusion coefficients corresponding to the known experimental data. By comparing the experimental with calculated diffusivities, the mobility parameters are optimized to achieve the best agreement.

Results and discussion

It is worth noting that the role of vacancies in the B2 phases was discussed [48] and high vacancy concentrations have been experimentally observed in the Al-Fe [49] and Al-Ni [40] systems (i.e. Fig.1).The effect of vacancy on the diffusion can generally be qualitatively understood as a way of compensating for off-stoichiometric compositions. When adding an Al atom into the off-stoichiometric B2 phase in the Ni-Cr-Al ternary system, the sublattice occupied by Cr or Ni atoms can be expanded by vacancies if it is unfavorable for Al to reside on this sublattice. Little is known about the effect of the solute atoms on the formation of vacancies in the ternary Ni-Cr-Al system.

Themeasured positron lifetimes are shown in Fig.2. The positron lifetime annihilated at defects in the β-Ni(Al,Cr)phase is clearly less than that in the binary NiAl phase, and also markedly less than that in the $Ni_{50}Al_{50}$ phase (τ_m=240ps). It can be speculated that the addition of Cr may be responsible for the decrease in vacancy concentrationof the β-Ni(Al,Cr) phase in the Ni-Cr-Al ternary systemregardless of its site occupancy behavior. In the optimization, the effect of vacancy is thus taken into account and the parameters such as ΔQ^{ord}_{CrAlVa}, ΔQ^{ord}_{CrCrVa}, ΔQ^{ord}_{AlAlVa}, ΔQ^{ord}_{AlCrVa}, ΔQ^{ord}_{NiAlVa} and ΔQ^{ord}_{NiCrVa} are assessed. The optimized mobility parameters are summarized in Table 3. Fig.3 shows the calculated and measured chemical diffusivities. Fig.4 reveals the experimentally measured chemical diffusivities and the iso-diffusivity curves calculated on an isothermal section from thermodynamic data. It is observed that the calculated chemical diffusivities agree reasonably well with the experimental data.

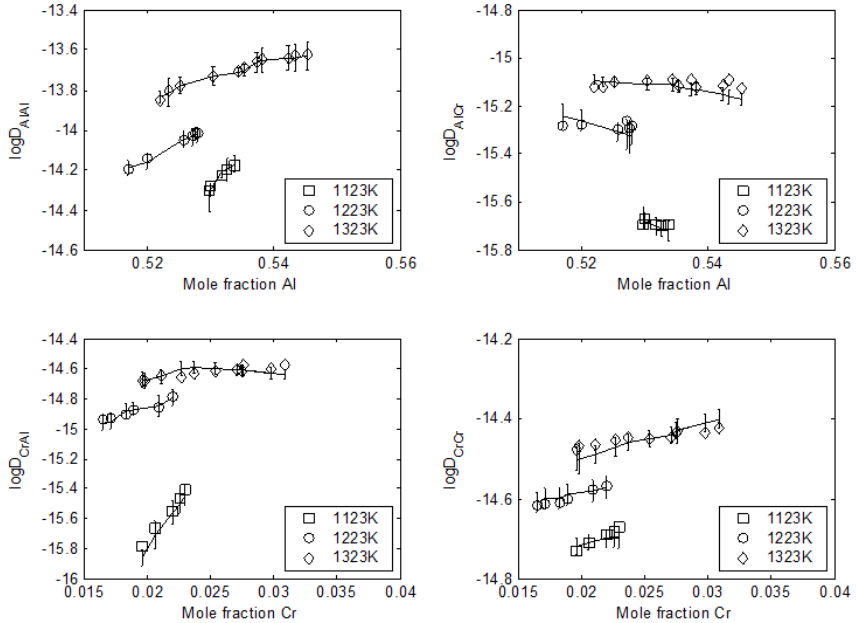

Fig. 3 Comparison of the calculated and measured chemical diffusivities for the B2 phase in the Ni-Cr-Al ternary system. The symbol shows experimental values from Hou *et a*l [35]

Table 3 Assessed mobility parameters for the B2 phase in the Ni-Cr-Al system

mobility parameters	ΔQ_i^* [J/mol]	Θ_i [m^2/s]		mobility parameters	ΔQ_{ikj}^{ord} [J/mol]	
			Mobility of Al			
Q_{Al}^{Al}	-215000	-80.2	Assessed in Ref.16	ΔQ_{AlAlNi}^{ord}	359700	Assessed in Ref. 16
Q_{Al}^{Cr}	-215000	-80.2	Assumed in this report	ΔQ_{AlAlVa}^{ord}	-1071200	Assessed in Ref. 16
Q_{Al}^{Ni}	-215000	-80.2	Assessed in Ref. 16	ΔQ_{AlNiVa}^{ord}	0	Assessed in Ref. 16
${}^{o}Q_{Al}^{Al,Ni}$	-327400		Assessed in Ref. 16	ΔQ_{AlCrNi}^{ord}	360600	Assessed in this report
${}^{o}Q_{Al}^{Al,Cr}$	-143276		Assessed in this report	ΔQ_{AlCrVa}^{ord}	-53800	Assessed in this report
${}^{o}Q_{Al}^{Al,Cr,Ni}$	-87313		Assessed in this report	ΔQ_{AlCrAl}^{ord}	0	Assumed in this report
${}^{o}Q_{Al}^{Cr,Ni}$	-128781		Assessed in this report			
			Mobility of Cr			
Q_{Cr}^{Al}	-407000	-35.6	Assumed in this report	ΔQ_{CrAlNi}^{ord}	-57312	Assessed in this report
Q_{Cr}^{Cr}	-407000	-35.6	Assessed in Ref.31	ΔQ_{CrAlVa}^{ord}	-14400	Assessed in this report
Q_{Cr}^{Ni}	-407000	-35.6	Assumed in this report	ΔQ_{CrNiVa}^{ord}	0	Assessed in this report
${}^{o}Q_{Cr}^{Al,Ni}$	76177		Assessed in this report	ΔQ_{CrCrNi}^{ord}	39700	Assessed in this report
${}^{o}Q_{Cr}^{Al,Cr}$	-78214		Assessed in this report	ΔQ_{CrCrAl}^{ord}	0	Assumed in this report
${}^{o}Q_{Al}^{Al,Cr,Ni}$	-40989		Assessed in this report	ΔQ_{CrCrVa}^{ord}	-14400	Assessed in this report
${}^{o}Q_{Crl}^{Cr,Ni}$	-143800		Assessed in this report			
			Mobility of Ni			
Q_{Ni}^{Al}	-204000	-90.837	Assessed in Ref. 16	ΔQ_{NiAlVa}^{ord}	-107000	Assessed in Ref. 16
Q_{Ni}^{Cr}	-204000	-90.837	Assumed in this report	ΔQ_{NiNiAl}^{ord}	314400	Assessed in Ref. 16
Q_{Ni}^{Ni}	-204000	-90.837	Assessed in Ref. 16	ΔQ_{NiNiVa}^{ord}	0	Assessed in this report
${}^{o}Q_{Ni}^{Al,Ni}$	-327400		Assessed in Ref. 16	ΔQ_{NiCrAl}^{ord}	0	Assumed in this report
${}^{o}Q_{Ni}^{Al,Cr}$	41600		Assessed in this report	ΔQ_{NiCrVa}^{ord}	-58000	Assessed in this report
${}^{o}Q_{Ni}^{Al,Cr,Ni}$	-77600		Assessed in this report	ΔQ_{NiCrNi}^{ord}	-121000	Assessed in this report
${}^{o}Q_{Ni}^{Cr,Ni}$	-670		Assessed in this report			

The optimized results in this investigation are also compared withthose reported in the literature [44]. It was seen that there existed evident differences in the optimized results, especially the ordering parameters of Al, though the optimization approach and the model used were the same in

the two investigations. The ordering parameters of Ni are basically comparable to those of Cr. This difference is possibly because the optimized results using PARROT module in the DICTRA software are sometime sensitive to the initial setting of the parameters which are to be optimized, in particular interaction parameters and ordering parameters. The contribution of Cr-Va ordering tomobilities of the B2 phase was negligible in the work of Campbell [44], but was taken into account in this investigation. At the same time, the contribution of Cr-Al ordering was considered in the work of Campbell [44] but was set to be zero in this investigation. Our recent works [37,50]partially support the assumption. The different data resources and the very limited set of the available experimental data for B2 phase in the Ni-Cr-Al ternary system are also responsible partially for the differences.

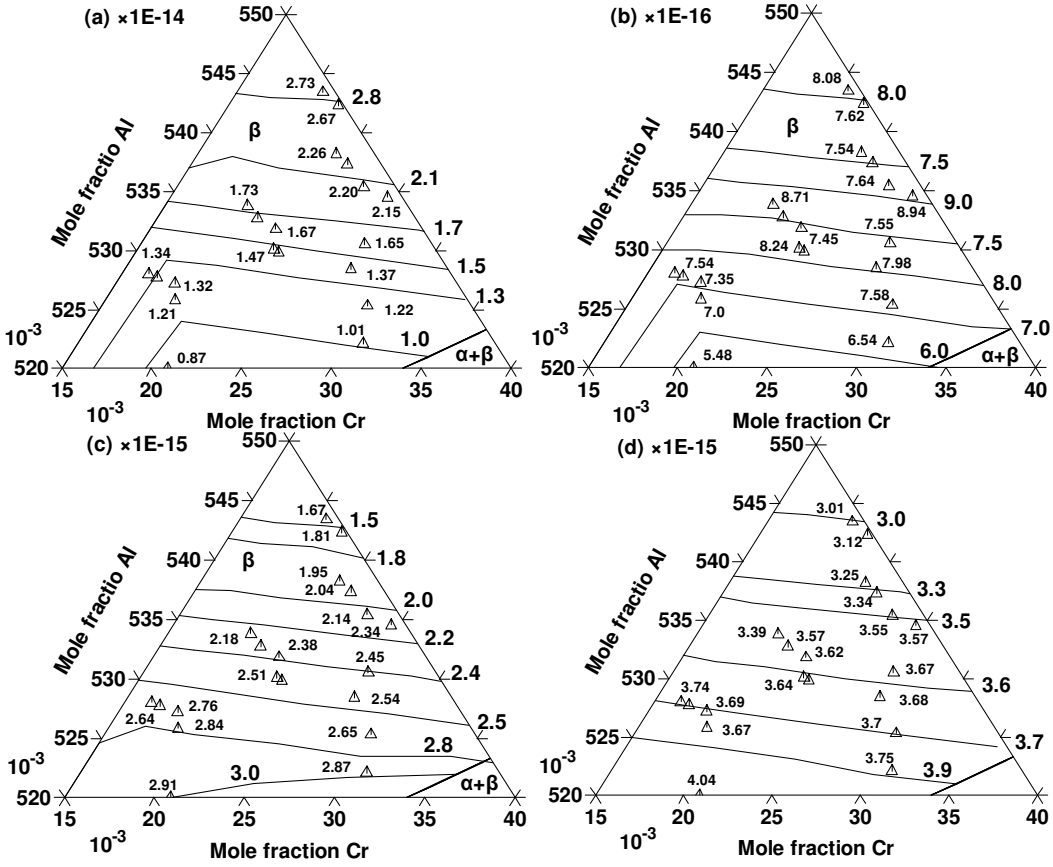

Fig. 4 An isothermal section of the Ni-Cr-Al system at 1323K where (a) $\tilde{D}^{Ni}_{AlAl}$, (b) $\tilde{D}^{Ni}_{AlCr}$, (c) $\tilde{D}^{Ni}_{CrAl}$ and (d) $\tilde{D}^{Ni}_{CrCr}$ are shown. The solid lines are calculated iso-diffusivity lines. The symbol shows experimental values from Hou *et a*l [35]

The Ni-52Al-1.7Cr and Ni-12Al-8Cr (at.%)alloys were prepared as a rod in vacuum induction furnace. Samples of 10×10×20mm^3 were cut from the rod and then homogenized at 1273K for 20h in the furnace with a vacuum of 1×10^{-2}Pa. A JSM-6301F electron probe micro-analyzer (EPMA) was used to analyze the composition of the heat-treated alloys. The given composition of the alloy was the average value of the concentrations obtained for 15 points in each heat-treated alloy sample. Sheets of 10 mm thickness were cut from the heat-treated samples and were polished with 300m diamond paste. The Sheets were placed by facing each other and were joined in a hot-press furnace at 1323K and 20MPa for 5min under an Ar protective atmosphere. Subsequently, the diffusion couple was given a diffusion anneal at 1323K for 10h in the furnace with a vacuum of 1×10^{-2}Pa. After diffusion experiment, concentration profiles were obtained from a JSM-6301F EPMA which was carried out on the specimens at an acceleration voltage of 15KV. Concentrations were measured with pure element standards and the experimental errors were corrected by a PAP correction program. In order to improve the accuracy, the concentration values reported at the same distance were the average value of concentrations obtained for no less than 5 points parallel to the joining interface.

The experiment is simulated by DICTRA software. In the simulation, the parameters for diffusion in the fcc phase (γ-Ni) are taken from the literature [12]. The result of the diffusion simulation is shown in Fig.5. The simulated concentrations profiles for Ni, Cr and Al elements are compared to the profiles measured. There is a satisfactory agreement with the experimental observation.

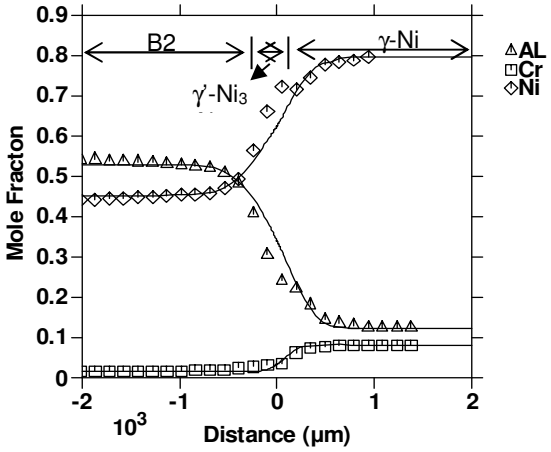

Fig. 5 Ternary diffusion couples heat treated at 1323K for 10h. The symbols are experimental data. The solid lines are results of DICTRA simulations using the diffusivities assessed in the present report.

Conclusions

Based on thermodynamic description of the B2 phase in the Ni-Cr-Al ternary system, the mobility parameters for diffusion in this phase are optimized by fitting the previous experimentally obtained diffusion data with the help of a model for diffusion. The results reveal that the optimized mobility parameters can represent the experimental data for this system reasonably well. Using the optimized mobility parameters, the diffusivities can be calculated and compared with our EPMA experimental observation in this paper. There is a general agreement between the calculated diffusivities with the experimental observations.

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References

[1] A. Maricocchi, A. Bartz, D. Wortman. J: Therm. Spray Technol.Vol. 6 (1997), p.193.

[2] Y. Zhang, J.A. Haynes, W.Y. Lee, I.G. Wright, B.A. Pint, K.M. Cooley, P.K. Liaw: Metall. Mater. Trans. A. Vol. 32 (2001), p.1727.

[3] K.A. Ellison, J.A. Daleo and D.H. Boone. Interdiffusion Behavior in NiCoCrAlYRe-Coated IN-738 at 940°C and 1050°C. Superalloys 2000, Proc. Ninth International Symposium on Superalloys (Seven Springs, PA), (Sept 17-21, 2000), T.M. Pollock et al., Ed, p. 649.

[4] B. Gleeson, E. Basuki and A. Crosky, Interdiffusion Behavior of an Aluminide Coated Nickel-Base Alloy at 1150°C, Elevated Temperature Coatings: Science and Technology IV, N.B. Dahotre, J.M. Hampikian, and J.E. Morral, Ed., TMS, (2001), p.119.

[5] B.A. Pint, K.L. More, I.G. Wright:Oxid. Met. Vol. 59 (2003), vol. p.257.

[6] J.P. Simmons, Y. Wen, C. Shen, Y.Z. Wang: Mater. Sci. Eng. A. Vol. 365 (2004), p.136.

[7]. N. Saunders, Phase Diagram Calculations for Ni-Based Superalloys, Superalloys 1996, R.D. Kissinger, Ed., The Materials Society, 1996, pp.101-110

[8] U.R. Kattner, Construction of a Thermodynamic Database for Ni-base Superalloys: A Case Study, CALPHAD and Alloy Thermodynamics, P.E.A. Turchi, A. Gonis, and R.D. Shull, Ed., The Materials Society, 2002, pp.147-164

[9] N. Dupin, B. Sundman, Scand: J. Metall.Vol. 30 (2001), p.184.

[10] DICTRA. Stockholm, Sweden: Thermo-Calc AB. (2003).

[11] J-O. Andersson, T. Helander, L. HÖglund, P. F. Shi, B. Sundman: CALPHAD. Vol.26, (2001), p.273.

[12] N. Dupin, I. Ansara, B. Sundman: CALPHAD. Vol. 25 (2001), p.279.

[13] W Huang, Y A Chang: Intermetallics. Vol. 7, (1999), p.863.

[14] T. Helander, J. Ågren: Acta Mater. Vol. 47, (1999),p.3291.

[15] T. Helander, J. Ågren:Acta Mater. Vol. 47, (1999),p.1141.

[16] L. Kaufman, H, Bernstein. Computer calculation of phase diagrams. London: Academic Press.(1970).

[17] N. Saunders, A.P. Miodownik: CALPHAD calculation of phase diagrams: a comprehensive guide. New York: Elsevier Science.(1998).

[18] J-O. Andersson, J. Ågren: J. Appl. Phys.Vol.72, (1992), p.1350.

[19]J. Kucera, B. Million: Metall. Trans. A. Vol.1 (1970), p.2603.

[20] B. Jönsson, Z. Metallkd:Vol.85 (1994), p.502.

[21] A. Engström, J. Ågren, Z. Metallkd:Vol.87 (1996), p.92.

[22] A. Borgenstam, A. Engström, L. Höglund, J. Ågren: J. Phase Equilib.Vol.21 (2000), p.269.

[23] I V Belova and G E Murch: Defect and Diffusion Forum. Vol.237-240 (2005), p. 291.

[24] G E Murch, in: Diffusion Kinetics in Solids, in Phase Transformation in Materials edtiedby G Kostorz, Wiley Chapter 3 (2001),p.171-238.

[25] O. Redlich, A. Kister:Ind. Eng. Chem.Vol.40 (1948), p.345.

[26] L.A. Girifalco: J.PhysChem Solids.Vol.24 (1964),p.323.

[27] A.B. Kuper, D. Lazarus, J.R. Manning, C.T. Tomizuka: Phys. Rev. Vol.140 (1956), p.1436.

[28] A. Paul, A. A. Kodentsov, F-J-J. Van Loo: J. Alloys Compd. Vol.403 (2005), p.147.

[29] S. Frank, S.V. Divinski, U. Södervall U, C. Herzig:Acta Mater. Vol.49 (2001),p.1399.

[30] S. Shankar, L.L. Seigle: Metall. Trans.Vol. 9A (1997), p.1467.

[31] H. Wei, X.F. Sun, Q. Zheng, H.R. Guan, Z.Q. Hu:Acta Mater. Vol.52 (2004), p.2645.

[32] I.V. Belova, G.E. Murch： Intermetallics. Vol. 6 (1998) p.115.

[33] R. Kozubski, D. Kmiec, E. Partyka, M. Danielewski:Intermetallics. Vol.11 (2003) p.897.

[34] G.H. Cheng, M.A. Dayananda: Metall. Trans A. Vol. 10 (1979), p.1415.

[35] G. C. Hou, H. Wei, N. R. Zhao, X. F. Sun, H. R. Guan, Z. Q. Hu:Scripta Mater. Vol.58, (2008) p.57.

[36] W.D. Hopfe, Yoon-Ho Son, J.E. Morral, A.D Romig Jr. In: B. Fultz, R. Cahn, D. Gupta, editors. Diffusion in ordered alloys: TMS; (1993) p.69.

[37] H. Wei, H. Y. Zhang, X. F. Sun, M. S. Dargusch, X. Yao: J. Alloys Compd. Vol.493 (2010), p.507.

[38] L. Pike, Y.A. Yang and C.T. Liu:Acta Mater. Vol.45 (1979), p.3709.

[39] W. Huang and Y.A. Chang:Intermetallics. Vol.6 (1998), p.487.

[40] A. Taylor and N.J. Doyle: J. Appy. Crystallogr. Vol.5 (1972), p.201.

[41] C. Jiang, D.J. Sordelet, B. Gleeson:Scripta Mater. Vol.54 (2006), p.405.

[42] C Jiang:Acta Mater.Vol. 55 (2007), p.4799.

[43] H. Wei, X. F. Sun, Q. Zheng, Z. Q. Hu, X. Yao and M. S. Dargusch. PAT study on the vacancy defect in the B2 phase in the Ni-Cr-Al System, to be published.

[44] C E Campbell:Acta Mater. Vol. 56 (2008), p.4277.

[45] B. Jansson. PARROT. Stockholm, Sweden: Royal Institute of Technology. (1984).

[46] B. Jansson: Report, Royal Institute of Technology, Stockholm, Sweden, (1984)

[47] H. Wei, G.C. Hou, X.F. Sun, H.G. Guan and Z.Q. Hu: J. Alloys Compd. Vol.454 (2008), p.400.

[48] T. Haraguchia, F. Horib, R. Oshimab, M. Kogachia: Intermetallics. Vol.9 (2001), p.763.

[49] M Kogachi, T. Haraguchi, S.M. Kim: Intermetallics. Vol.6 (1998), p.499.

[50] H. Wei, J.J. Liang, B.Z.Sun, P. Peng, Q.Zheng, X.F. Sun, M.S.Dargusch, X. Yao: Intermetallics. Vol.18 (2010), p.1062.

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Assessment of Mobilities of the B2 Phase in the Nickel-Chromium-Aluminum System
10.4028/www.scientific.net/MSF.789.477

DOI References
[1] A. Maricocchi, A. Bartz, D. Wortman. J: Therm. Spray Technol. Vol. 6 (1997), p.193.
http://dx.doi.org/10.1007/s11666-997-0012-x
[2] Y. Zhang, J.A. Haynes, W.Y. Lee, I.G. Wright, B.A. Pint, K.M. Cooley, P.K. Liaw: Metall. Mater. Trans. A. Vol. 32 (2001), p.1727.
http://dx.doi.org/10.1007/s11661-001-0150-6
[6] J.P. Simmons, Y. Wen, C. Shen, Y.Z. Wang: Mater. Sci. Eng. A. Vol. 365 (2004), p.136.
http://dx.doi.org/10.1016/j.msea.2003.09.019
[11] J-O. Andersson, T. Helander, L. HÖglund, P. F. Shi, B. Sundman: CALPHAD. Vol. 26, (2001), p.273.
http://dx.doi.org/10.1016/S0364-5916(02)00037-8
[12] N. Dupin, I. Ansara, B. Sundman: CALPHAD. Vol. 25 (2001), p.279.
http://dx.doi.org/10.1016/S0364-5916(01)00049-9
[13] W Huang, Y A Chang: Intermetallics. Vol. 7, (1999), p.863.
http://dx.doi.org/10.1016/S0966-9795(98)00138-1
[14] T. Helander, J. Ågren: Acta Mater. Vol. 47, (1999), p.3291.
http://dx.doi.org/10.1016/S1359-6454(99)00174-3
[15] T. Helander, J. Ågren: Acta Mater. Vol. 47, (1999), p.1141.
http://dx.doi.org/10.1016/S1359-6454(99)00010-5
[25] O. Redlich, A. Kister: Ind. Eng. Chem. Vol. 40 (1948), p.345.
http://dx.doi.org/10.1021/ie50458a036
[26] L.A. Girifalco: J. PhysChem Solids. Vol. 24 (1964), p.323.
http://dx.doi.org/10.1016/0022-3697(64)90111-8
[28] A. Paul, A. A. Kodentsov, F-J-J. Van Loo: J. Alloys Compd. Vol. 403 (2005), p.147.
http://dx.doi.org/10.1016/j.jallcom.2005.04.194
[29] S. Frank, S.V. Divinski, U. Södervall U, C. Herzig: Acta Mater. Vol. 49 (2001), p.1399.
http://dx.doi.org/10.1016/S1359-6454(01)00037-4
[31] H. Wei, X.F. Sun, Q. Zheng, H.R. Guan, Z.Q. Hu: Acta Mater. Vol. 52 (2004), p.2645.
http://dx.doi.org/10.1016/j.actamat.2004.02.012
[34] G.H. Cheng, M.A. Dayananda: Metall. Trans A. Vol. 10 (1979), p.1415.
http://dx.doi.org/10.1007/BF02812005
[37] H. Wei, H. Y. Zhang, X. F. Sun, M. S. Dargusch, X. Yao: J. Alloys Compd. Vol. 493 (2010), p.507.
http://dx.doi.org/10.1016/j.jallcom.2009.12.146
[38] L. Pike, Y.A. Yang and C.T. Liu: Acta Mater. Vol. 45 (1979), p.3709.
http://dx.doi.org/10.1016/S1359-6454(97)00028-1
[39] W. Huang and Y.A. Chang: Intermetallics. Vol. 6 (1998), p.487.
http://dx.doi.org/10.1016/S0966-9795(97)00099-X
[40] A. Taylor and N.J. Doyle: J. Appy. Crystallogr. Vol. 5 (1972), p.201.
http://dx.doi.org/10.1107/S0021889872009203
[41] C. Jiang, D.J. Sordelet, B. Gleeson: Scripta Mater. Vol. 54 (2006), p.405.

http://dx.doi.org/10.1016/j.scriptamat.2005.10.023
[42] C Jiang: Acta Mater. Vol. 55 (2007), p.4799.
http://dx.doi.org/10.1016/j.actamat.2007.04.049
[44] C E Campbell: Acta Mater. Vol. 56 (2008), p.4277.
http://dx.doi.org/10.1016/j.actamat.2008.04.061
[47] H. Wei, G.C. Hou, X.F. Sun, H.G. Guan and Z.Q. Hu: J. Alloys Compd. Vol. 454 (2008), p.400.
http://dx.doi.org/10.1016/j.jallcom.2006.12.119
[48] T. Haraguchia, F. Horib, R. Oshimab, M. Kogachia: Intermetallics. Vol. 9 (2001), p.763.
http://dx.doi.org/10.1016/S0966-9795(01)00061-9
[49] M Kogachi, T. Haraguchi, S.M. Kim: Intermetallics. Vol. 6 (1998), p.499.
http://dx.doi.org/10.1016/S0966-9795(97)00097-6
[50] H. Wei, J.J. Liang, B.Z. Sun, P. Peng, Q. Zheng, X.F. Sun, M.S. Dargusch, X. Yao: Intermetallics. Vol. 18 (2010), p.1062.
http://dx.doi.org/10.1016/j.intermet.2010.02.004