

P. ORAMUS *, A. BIBORSKI*, R. KOZUBSKI*, K. PARLIŃSKI **, P. T. JOCHYM **

SUPERSTRUCTURE STABILITY AND SITE PREFERENCES IN β -NiAl DOPED WITH Fe, Co AND Cr. MONTE CARLO SIMULATION

STABILNOŚĆ NADSTRUKTURY ORAZ PREFERENCJE OBSADZEŃ PODSIECI PRZEZ DOMIESZKI Fe, Co i Cr WPROWADZANE DO ZWIĄZKU β -NiAl. SYMULACJE MONTE CARLO

The formation energies of single point defects and pairs of point defects in B2-ordered NiAl-C (C = Fe, Co, Cr) intermetallic compound were calculated “ab initio” within the density functional theory. Subsequently, effective nearest-neighbour (nn) atomic pair-interaction energy parameters in the systems were estimated by interpreting the “ab-initio” calculated energies in terms of Ising Hamiltonian. The parameters were then used in Monte Carlo (MC) simulations of equilibrium distributions of ternary-admixture atoms C over the NiAl-C superstructure at non-zero temperatures. Three variants of C-atom substitution were applied: (i) substitution for Ni atoms; (ii) substitution for Al-atoms; (iii) equivalent substitution for both Ni and Al atoms. Admixture of Fe and Co atoms to NiAl according to variants (i) and (iii) resulted in an increase of B2-superstructure stability; in the remaining cases the superstructure was always destabilised. The simulations showed particular site-occupation preferences of C atoms in NiAl and the competition between chemical ordering and the drift of C-atoms towards preferred lattice sites. Immiscibility of Cr atoms in NiAl showed-up as a strong clusterisation tendency of these atoms.

Keywords: nickel aluminides, based on NiAl; order/disorder transformations; site occupancy; simulations, Monte Carlo

Energie tworzenia pojedynczych defektów punktowych oraz ich par w układach NiAl-C (C = Fe, Co, Cr) z nadstrukturą typu B2 obliczono “z pierwszych zasad” metodą funkcjonału gęstości. Energie te, poprzez przyrównanie ich wartości do odpowiednich formuł wynikających z modelu Isinga, posłużyły do wyznaczenia efektywnych wartości parametrów oddziaływania par atomów w pierwszej strefie koordynacyjnej badanych układów. Parametrów tych użyto następnie w dynamicznych symulacjach Monte Carlo temperaturowych zależności równowagowych rozkładów atomów domieszki C w nadstrukturze układów NiAl-C przy zastosowaniu 3 wariantów podstawiania atomów domieszki: (i) za atomy Ni; (ii) za atomy Al; (iii) w równej proporcji za atomy Ni i Al. Stwierdzono, iż wprowadzenie domieszek do badanych układów wpływa na stabilność nadstruktur: w ogólności stabilność nadstruktury ulega obniżeniu. Wyjątek stanowią przypadki NiAl-Fe oraz NiAl-Co, gdzie domieszki Fe i Co wprowadzane są wg wariantów (i) i (iii). W przypadkach tych obserwuje się zdecydowane wzmocnienie stabilności nadstruktury B2 układu. Symulacje komputerowe wykazały również konkretne preferencje obsadzeń węzłów poszczególnych podsieci nadstruktury NiAl przez atomy domieszki. Obserwowano też współzawodnictwo pomiędzy procesem porządkowania atomowego i dryfem atomów C w stronę preferowanych węzłów sieci krystalicznej. Ograniczona mieszalność atomów Cr w układzie NiAl ujawniła się w postaci silnej tendencji tych atomów do tworzenia klastrów.

1. Introduction

An interest in intermetallic phases based on β -NiAl has for last decade been due to the search for light materials showing high resistance against corrosion, as well as preserving high strength at high temperature. Because of the highly stable B2 superstructure (Fig. 1), the binary system appears, however, extremely hard and brittle and,

therefore, its technical application requires an increase of ductility. It has been found out that this may be achieved by applying ternary admixtures such as Fe, Co or Cr [1-3].

Understanding of the mechanism, by means of which the ternary admixtures improve the mechanical properties of β -NiAl requires that their location in the crystalline structure of the parent phase is recognized.

* INTERDISCIPLINARY CENTRE FOR MATERIALS MODELLING, M.SMOLUCHOWSKI INSTITUTE OF PHYSICS, JAGELLONIAN UNIVERSITY, REYMONTA 4, 30-059 KRAKOW, POLAND

** THE H. NIEWODNICZAŃSKI INSTITUTE OF NUCLEAR PHYSICS, POLISH ACADEMY OF SCIENCES, RADZIKOWSKIEGO 152, 31-342 KRAKOW, POLAND

This problem has recently been a subject of a number of experimental and theoretical studies.

Extensive EXAFS and XANES experiments of Balasubramanian et al. on NiAl-C (C = Fe, Co) [4] suggested a tendency of dilute Fe and Co admixtures to occupy Ni sublattice sites. The same followed for Co from the analysis of the heat of formation and composition of NiAl-Co alloys [5].

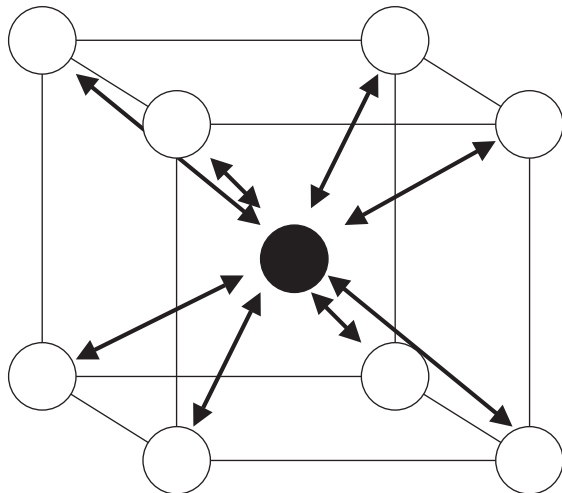


Fig. 1. Scheme of B2-type superstructure of NiAl: ● Ni-atoms, ○ Al-Atoms. Arrows mark nn pairs of atoms: only Ni-Al nn pairs exist

This conclusion has subsequently got strong and definite confirmation by “ab-initio” calculations of Song et al. [6]. On the other hand, several authors reported an influence of particular composition of Ni-Al-Fe on the Fe-atom configuration. In an extensive review Kao et al. [7] analysed the site preference of Fe, Co and Cr in NiAl within a Bragg-Williams-type model with nearest-neighbour (nn) pair interaction energies deduced from a quasi-chemical approach. Considering a triple-defect character of the system they found that Fe, Co and Cr showed the stronger Ni-site preference, the higher was the Al-content in the system. The paper refers to experimental results carried out by means of channeling-enhanced analysis (ALCHEMI), which seem to confirm this anticipation. Nevertheless, Kao et al. suggest that, due to a complete solubility of FeAl and CoAl with NiAl, definite Ni-site occupation preference of Fe and Co in NiAl should be expected for higher concentration of the admixtures. The presumptions have been repeated also in recent papers of Banerjee et al. [8], Bozzolo et al. [9, 10] and Pike et al. [11], where their experimental confirmation mainly by ALCHEMI was reported. The latter authors report also the results of ALCHEMI combined with X-ray diffraction and densitometry revealing defect concentration in Ni-Al-Fe at high temperature (700°C). The analysis of the experimental results was, however, done by assuming perfectly triple-defect

behaviour of the system – i.e. no Al-antisites and no Al-vacancies. With these assumptions it was deduced that ternaries containing not more than 50 at.% Al disordered by creating mostly Fe-antisites - the Ni-antisites being always in minority.

The strong Ni-sublattice site occupation preference of Fe and Co in NiAl has been recently again reported in studies involving “ab initio” calculations [12, 13].

However, in a very interesting “ab initio” study of the effect of Fe and Co on mechanical properties of Ni-rich Ni-Al, Fu et al. [14] showed that while Co always substitutes for Ni, Fe tends merely to the Al-sublattice. The diversity of the reported results has recently been somehow elucidated by Lechermann et al. [15], who succeeded in the “ab initio” elaboration of a phase diagram of the Ni-Al-Fe. The cluster-expansion (CE) calculations revealed the miscibility gap of two B2 phases: one developing along a NiAl-FeAl line with a continuous exchange of Ni and Fe atoms within the Ni(Fe) sublattice and another one developing along the line Fe – NiAl with Fe atoms substituting both for Ni and Al.

In the present work, site occupation preference in NiAl-C (C = Fe, Co, Cr) is studied by means of dynamic Monte Carlo simulation of systems, whose energetics is modelled on the basis of recent “ab initio” calculations of related defect energies in both examined systems [16].

2. Monte Carlo simulation scheme

2.1. Samples

2.1.1. Structure

The simulated samples consisted of 32^3 bcc cells (65536 bcc lattice sites). First, perfect B2 superstructure was created by filling the appropriate lattice sites with equal numbers of Ni and Al atoms.

10 at.% of the admixture C atoms were introduced in three substitution variants:

Variant 1: Generation of a $\text{Ni}_{40}\text{Al}_{50}\text{C}_{10}$ ternary system by randomly replacing 20% of Ni atoms by the C ones.

Variant 2: Generation of a $\text{Ni}_{50}\text{Al}_{40}\text{C}_{10}$ ternary system by randomly replacing 20% of Al atoms by the C ones.

Variant 3: Generation of a $\text{Ni}_{45}\text{Al}_{45}\text{C}_{10}$ ternary system by randomly replacing 10% of Ni atoms and 10% of Al atoms by the C ones.

2.1.2. Energetics

An Ising Hamiltonian of the system was assumed with pair interactions between nearest-neighbouring

(nn) atoms. The values of pair interaction energies V_{Ni-Ni} , V_{Al-Al} , V_{Ni-Al} , V_{Ni-C} , V_{Al-C} and V_{C-C} for B2-type ordered NiAl-C were deduced from the corresponding defect formation energies calculated “ab-initio” [16] by

expressing these energies in terms of V_{i-k} and solving the resulting systems of linear equations ¹⁾. The calculation scheme, as well as the results are presented in Table 1.

TABLE 1
Calculation scheme for effective atomic pair-interaction energy parameters V_{ij} in NiAl-C alloys on the basis of “ab-initio” evaluated defect formation energies in B2-NiAl with antisite defects and admixed C-atoms [16]

Ni-Al-C, B2-type superstructure					
Supercell configurations corresponding to particular defects: projections on (000) plane ○ Al, ● Ni, ■ C					
B2-NiAl Al (000), (00½) Ni (00¼), (00¾)	Ni on Al- sublattice	Al on Ni- sublattice	C on Al- sublattice	C on Ni- sublattice	C on Al- sublattice and C on Ni-sublattice
Defect formation energies: values [16] and relation to nn pair-interaction energies					
	$E_{Ni}^{Al} = 1,08 \text{ eV}$	$E_{Al}^{Ni} = 1,82 \text{ eV}$	$E_{Fe}^{Al} = 2,05 \text{ eV}$ $E_{Co}^{Al} = 1,42 \text{ eV}$ $E_{Cr}^{Al} = 2,16 \text{ eV}$	$E_{Fe}^{Ni} = 0,55 \text{ eV}$ $E_{Co}^{Ni} = -0,02 \text{ eV}$ $E_{Cr}^{Ni} = 1,47 \text{ eV}$	$E_{Fe,Fe}^{Ni,Al} = 2,51 \text{ eV}$ $E_{Co,Co}^{Ni,Al} = 1,47 \text{ eV}$ $E_{Cr,Cr}^{Ni,Al} = 2,85 \text{ eV}$
	$8(V_{Ni-Ni} - V_{Ni-Al})$	$8(V_{Al-Al} - V_{Ni-Al})$	$8(V_{C-Ni} - V_{Ni-Al})$	$8(V_{C-Al} - V_{Ni-Al})$	$-15V_{Ni-Al}$ $-7V_{C-Al} - 7V_{C-Ni}$ $-V_{C-C}$
Calculated relative values of nn pair interaction energies:					
$V_{Ni-Ni} - V_{Ni-Al} = 0.136 \text{ eV}; V_{Al-Al} - V_{Ni-Al} = 0.227 \text{ eV};$					
$V_{Fe-Ni} - V_{Ni-Al} = 0.256 \text{ eV}; V_{Fe-Al} - V_{Ni-Al} = 0.069 \text{ eV}; V_{Fe-Fe} - V_{Ni-Al} = 0.234 \text{ eV}$					
$V_{Co-Ni} - V_{Ni-Al} = 0.178 \text{ eV}; V_{Co-Al} - V_{Ni-Al} = 0.002 \text{ eV}; V_{Co-Co} - V_{Ni-Al} = 0.211 \text{ eV}$					
$V_{Cr-Ni} - V_{Ni-Al} = 0.270 \text{ eV}; V_{Cr-Al} - V_{Ni-Al} = 0.184 \text{ eV}; V_{Cr-Cr} - V_{Ni-Al} = -0.323 \text{ eV}$					

¹⁾ In fact, because of only 5 independent equations being available, only differences ($V_{i-k} - V_{Ni-Al}$) and ($V_{i-k} - V_{Ti-Al}$) were evaluated. This was, however, sufficient to carry out the Monte Carlo simulations (see next section).

The size of a supercell, for which the “ab initio” calculations were carried out, restricted the above procedure to nn pair interactions. Therefore, interactions of atoms in further co-ordination zones were beyond the applied approximation.

2.2. MC simulation algorithm

The “direct exchange” Glauber-type algorithm was applied, in which each Monte Carlo step consisted of:

- (i) Random choice of an “i” atom
- (ii) Random choice of “j” atom
- (iii) Calculation of the increment/decrement ΔE of the configurational energy of the sample caused by an exchange of the positions of atoms “i” and “j”:

$$\Delta E = \sum_{p,q} (N_{pq}^{(f)} - N_{pq}^{(i)}) \times V_{p-q}, \quad (1)$$

where $N_{pq}^{(f)}$ and $N_{pq}^{(i)}$ denote the numbers of nn pairs of atoms “p” and “q” in the sample after and before the “i↔j” exchange, respectively.

It should be noted that for any possible exchange the energy increment/decrement ΔE given by Eq.1 depends effectively on *differences* between particular pair-interaction energies V_{p-q} . Therefore, it is sufficient to know their relative values $V_{p-q} - V_{Ni-Al}$ available from the calculations discussed in section 2.1.2.

- (iv) Calculation of the Glauber-type probability $\prod_{i \leftrightarrow j}$ for the exchange of the positions of atoms “i” and “j”:

$$\prod_{i \leftrightarrow j} = \frac{\exp\left[-\frac{\Delta E}{kT}\right]}{1 + \exp\left[-\frac{\Delta E}{kT}\right]}, \quad (2)$$

where T and k denote absolute temperature and Boltzmann constant, respectively.

- (vi) Generation of a random number $r \in (0, 1)$ and execution of the “i↔j” exchange provided $r \leq \prod_{i \leftrightarrow j}$

The samples generated in the way described in section 2.1.1. were relaxed at particular temperatures T according to the above MC algorithm. The evolution of atomic configuration was monitored in each case by observing MC-time dependences of Bragg-Williams long-range order parameter η and the fraction $C_C^{(Al)}$ of C-atoms occupying Al-sublattice sites.

In order to make η meaningful at any concentration of C admixture the following definition was assumed:

$$\eta = 2 \times \left(\frac{N_{Al}^{(Al)}}{N_{Al}^{(Al)} + N_{Al}^{(Ni)}} - \frac{1}{2} \right) \quad (3)$$

where $N_{Al}^{(v)}$ denotes the number of Al-atoms residing on v -sublattice.

As equilibrium atomic configurations attained by the systems at particular temperatures were of interest, the relaxations were continued until η and $C_C^{(Al)}$ saturated at η_{eq} and $C_{C,eq}^{(Al)}$ levels, respectively.

3. Results

Fig. 2 shows the dependencies of η_{eq} in NiAl, $Ni_{40}Al_{50}C_{10}$, $Ni_{50}Al_{40}C_{10}$ and $Ni_{45}Al_{45}C_{10}$ on temperature reduced with respect to the “order-disorder” transition temperature $T_C^{(NiAl)}$ of binary β -NiAl. The graphs indicate that substitution of any applied element for Al decreases the stability of B2-superstructure of NiAl. While the same effect is observed for both remaining substitutions of chromium, Fe and Co *increase* the B2-superstructure stability when substituted totally or partially for Ni.

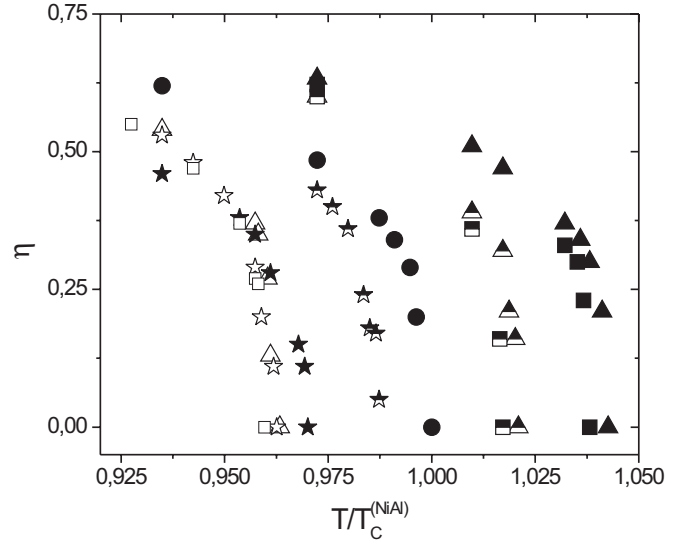


Fig. 2. Reduced-temperature dependence of equilibrium Bragg-Williams LRO parameter η in: NiAl (●), $Ni_{40}Al_{50}Fe_{10}$ (■), $Ni_{45}Al_{45}Fe_{10}$ (■), $Ni_{50}Al_{40}Fe_{10}$ (□), $Ni_{40}Al_{50}Co_{10}$ (▲), $Ni_{45}Al_{45}Co_{10}$ (▲), $Ni_{50}Al_{40}Co_{10}$ (△), $Ni_{40}Al_{50}Cr_{10}$ (★), $Ni_{45}Al_{45}Cr_{10}$ (★), $Ni_{50}Al_{40}Cr_{10}$ (☆)

The site-occupation preference for Fe, Co and Cr in NiAl as a function of reduced temperature is shown in Fig. 3. It is remarkable that both Fe and Co atoms manifest a definite preference for Ni-sublattice, regardless the type of substitution. This becomes especially well marked in the case of $Ni_{50}Al_{40}C_{10}$ and $Ni_{45}Al_{45}C_{10}$ (C = Fe, Co), where already at low temperatures Fe and Co atoms initially located at Al-sublattice sites passed to the Ni-sublattice (low values of $C_C^{(Al)}$).

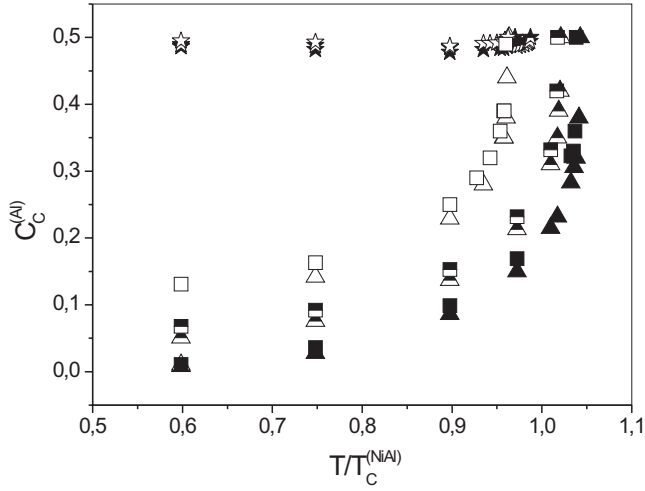


Fig. 3. Reduced-temperature dependence of the fraction $C_C^{(Al)}$ of C-atoms occupying Al-sublattice sites in: $Ni_{40}Al_{50}Fe_{10}$ (■), $Ni_{45}Al_{45}Fe_{10}$ (■), $Ni_{50}Al_{40}Fe_{10}$ (□), $Ni_{40}Al_{50}Co_{10}$ (▲), $Ni_{45}Al_{45}Co_{10}$ (▲), $Ni_{50}Al_{40}Co_{10}$ (△), $Ni_{40}Al_{50}Cr_{10}$ (★), $Ni_{45}Al_{45}Cr_{10}$ (★), $Ni_{50}Al_{40}Cr_{10}$ (☆).

Fig. 4 shows the details of this definite Fe segregation on Ni sublattice (an absolutely analogous process was observed in the case of Co). The curves correspond to the isothermal MC-time evolution of atomic configurations in the initially perfectly long-range ordered ($\eta = 1$) systems at temperature $T = 0.9 \times T_C^{(NiAl)}$. The evolution is additionally illustrated by MC-time dependence of a parameter η' :

$$\eta' = 2 \times \left(\frac{N_{Ni}^{(Ni)}}{N_{Ni}^{(Ni)} + N_{Ni}^{(Al)}} - \frac{1}{2} \right) \quad (4)$$

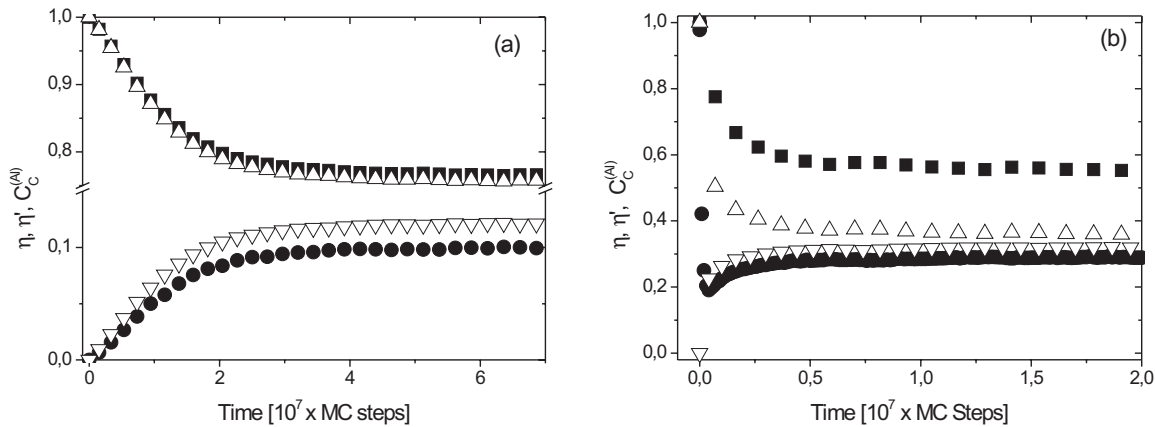


Fig. 4. MC-time dependence of η (■), η' (△), $C_{Fe}^{(Al)}$ (●) and $C_{Ni}^{(Al)}$ (▽) in $Ni_{40}Al_{50}Fe_{10}$ (a) and $Ni_{50}Al_{40}Fe_{10}$ (b) at $T/T_c^{(NiAl)} = 0.9$. The initial configurations as described in Section 2.1.1.

where $N_{Ni}^{(v)}$ denotes the number of Ni-atoms residing on v -sublattice.

In the case of $Ni_{40}Al_{50}Fe_{10}$ (Fig. 4a) the system disordered predominantly due to the formation of Al- and Ni-antisites (perfect coincidence of η and η' isotherms). The contribution of Fe-atoms was definitely smaller, which is clearly illustrated by the $C_{Ni}^{(Al)}(t)$ and $C_{Fe}^{(Al)}(t)$ curves.

More complex process occurred in $Ni_{50}Al_{40}Fe_{10}$, where Fe-atoms were initially located on the Al-sublattice (Fig. 4b). The process of disordering proceeded in two stages: first due to very efficient Ni-Fe exchanges most of Fe atoms were quickly drained from Al- to Ni-sublattice. Consequently, much more Ni- than Al-antisites were produced (see η and η' isotherms). After having reached a minimum the number of Fe-atoms on Al-sublattice again increased (by Fe-Al exchanges) towards the equilibrium level.

Possible role of the evident extreme metastability of the initial configuration of $Ni_{50}Al_{40}Fe_{10}$ (all Fe atoms on Al sublattice) was checked by simulating the relaxation starting from an equilibrium configuration. Such a configuration was produced by first relaxing the system at $T = 0.01 \times T_C^{(NiAl)}$. Even at such a low temperature, most of Fe atoms shifted from Al- to Ni-sublattice.

The $C_{Fe}^{(Al)}(t)$ isotherms following from both simulations performed at $T = 0.9 \times T_C^{(NiAl)}$ (starting from a non-equilibrium and equilibrium configurations) perfectly coincided in the final stage and saturated at similar levels (Fig. 5).

4. Discussion

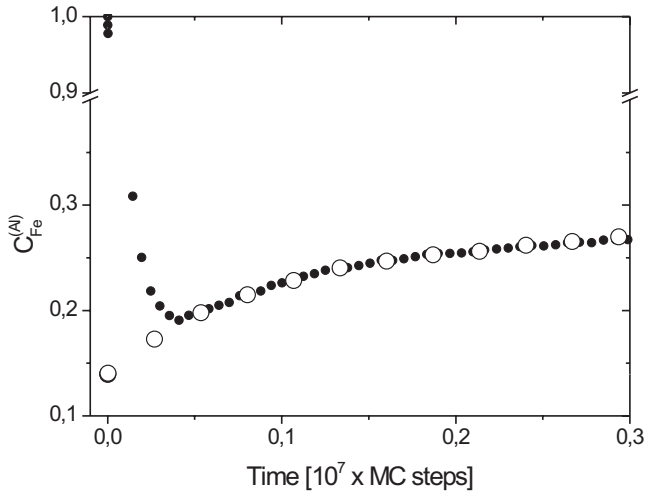


Fig. 5. MC-time dependence of $C_{Fe}^{(A)}$ at $T/T_c^{(NiAl)} = 0.9$ in $Ni_{50}Al_{40}Fe_{10}$ with initial configuration described in Section 2.1.1. (●) and that corresponding to thermodynamic equilibrium at $T/T_c^{(NiAl)} = 0.01$ (○)

In the case of Cr atoms, the simulations revealed a strong tendency for their clusterisation i.e. occupation of nn lattice sites. This is reflected by effectively almost no site-occupation preference with $C_{Cr}^{(A)} \approx 0.5$ at any temperature and directly by the MC-time dependence of the Cr-Cr pair-correlation shown in Fig. 6.

It is obvious that in cases of all three admixtures $C_C^{(A)}$ tended to 0.5 when the “order-disorder” transition point was approached.

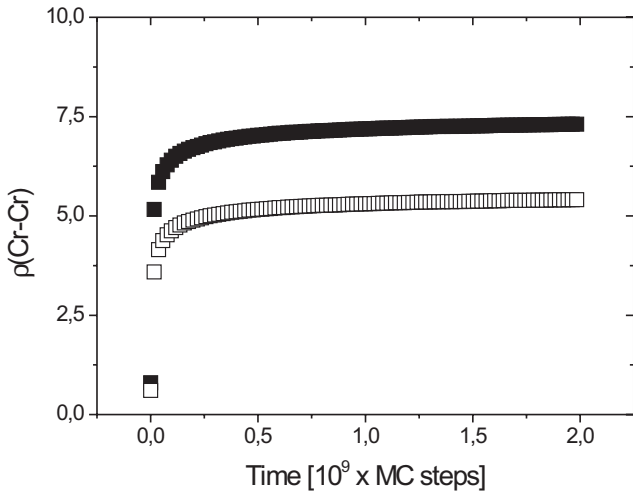


Fig. 6. MC-time dependence of an average number $\rho(Cr-Cr)$ of Cr atoms being nearest (■) and next-nearest (□) neighbours of another Cr-atom in $Ni_{45}Al_{45}Cr_{10}$ at $T/T_c^{(NiAl)} = 0.75$

The reported investigations addressed basic research by challenging to combine “ab-initio” calculations of the cohesive energy of intermetallic systems with MC-simulation of their thermodynamics in terms of pair approximation of the configurational energy. The “ab-initio” calculations referred to in the present paper were performed for limited supercell of the examined system. This on one hand limited the atomic interactions to the 1st co-ordination shell, and on the other hand, because of periodic boundary conditions imposed upon the supercell, determined the lowest concentrations of the admixtures to be reliably treated²⁾.

The negligence of vacancies mediating in reality the atomic jumps in intermetallic crystalline phases was forced by the current state-of-the-art of the MC simulations of atomic migration, which up to now have been run with a fixed number of vacancies introduced to the system (see e.g. [17]). While this scheme is acceptable when applied to $L1_2$ - or $L1_0$ -ordered systems with very low vacancy concentration, there is absolutely no justification for its extrapolation upon the B2-ordered NiAl, where vacancy concentration is correlated with the concentration of antisite defects [18]. The effect requires a substantially new approach to MC simulations, which should be implemented with complete vacancy thermodynamics. The problem is currently extensively studied and the MC simulation results presented in the paper should be considered as a “zeroth approximation” with respect to the effect of vacancy formation.

All the features shown by the performed simulations are explicable in terms of the relationships between pair interaction energies in a system and thus, the study yields a new insight into the atomistic aspects of the phenomena of ordering and clusterisation in binary B2 intermetallics doped with a ternary admixture. Despite some discrepancies, the obtained results are in agreement with many conclusions following from other modelling and experimental examinations.

The following relationships between the nn pair interaction energies (Table 1) may explain the effect of Fe and Co admixtures on the stability of B2 superstructure of NiAl:

$$V_{Ni-Fe} > V_{Fe-Fe} > V_{Al-Al} > V_{Ni-Ni} > V_{Al-Fe} > V_{Al-Ni} \quad (5)$$

$$V_{Al-Al} > V_{Co-Co} > V_{Ni-Co} > V_{Ni-Ni} > V_{Al-Co} > V_{Al-Ni} \quad (6)$$

²⁾ Two atoms of a ternary admixture C introduced to the supercell meant C concentration higher than 10at.%.

The relationships $V_{Ni-Fe} \gg V_{Al-Fe}$ and $V_{Ni-Co} > V_{Al-Co}$ immediately explain the observed definite Ni-site occupation preference of Fe and Co when admixed (in any stoichiometry) to NiAl (Fig. 3). This conclusion is in good agreement with theoretical considerations [6, 9, 10], as well as with EXAFS and XANES experimental results [4], however, does not match ALCHEMI findings of Banerjee et al. [8], as well as the results of Fu et al. [14] concerning Fe.

In $Ni_{40}Al_{50}C_{10}$ ($C = Fe, Co$) the atomic configuration with $\eta = 1$ means that only V_{Al-Ni} and V_{Al-Fe} (V_{Al-Co}) pair interactions are active. As, in view of (5) and (6), the related energies are the lowest, any disordering (decrease of η) producing V_{Ni-Fe} (V_{Ni-Co}), V_{Fe-Fe} (V_{Co-Co}), V_{Al-Al} and V_{Ni-Ni} bonds increases the system energy. This increase is higher than in pure NiAl, where only V_{Al-Al} and V_{Ni-Ni} bonds are formed. Such a situation is still observed in $Ni_{45}Al_{45}C_{10}$ ($C = Fe, Co$) where the Fe (Co) atoms substitute Ni and Al atoms in equal proportion.

In contrary, in $Ni_{50}Al_{40}C_{10}$ ($C = Fe, Co$) with $\eta = 1$ active are V_{Al-Ni} and V_{Ni-Fe} (V_{Ni-Co}) interactions. Again, because of a reduction of the number of Ni-Fe (Ni-Co) bonds, the net energetic cost of a decrease of η is lower than in pure NiAl.

The above predictions are in agreement with the experimental results of Pike et al. [11], who found that the concentration of antisite defects at 700°C was about 17 times higher in $Ni_{50}Al_{40}Fe_{10}$ than in $Ni_{40}Al_{50}Fe_{10}$. It should be noted that the B2 superstructure stabilisation effect of Fe and Co microalloyed in NiAl has been recently indicated in a modelling study of Hao et al. [12]. The following relationships hold for NiAl-Cr:

$$V_{Ni-Cr} > V_{Al-Al} > V_{Al-Cr} > V_{Ni-Ni} > V_{Al-Ni} > V_{Cr-Cr} \quad (7)$$

It is clear that the lowest value of the Cr-Cr pair interaction energy favours the clusterisation of chromium atoms. In addition, because of the high values of Ni-Cr and Al-Cr pair-interaction energies, any admixture of Cr in NiAl decreases the B2-superstructure stability.

The results of the presented study may be related to the experimentally determined ternary phase diagrams of the considered Ni-Al-C systems [19]. It is remarkable that despite the applied rigid lattice approximation excluding the simulation of incoherent precipitation phenomena, the immiscibility of 10 at.% of chromium in B2-ordered NiAl was predicted by the simulations as a strong tendency for clusterisation.

The authors are aware of the roughness of the applied approximation where on one hand only nn pair-interactions are taken into account, and on the other

hand vacancy thermodynamics is neglected. Extension of the model in both directions is in progress.

5. Conclusions

- Superstructure stability and site-occupation preferences of ternary admixtures were studied by means of Monte Carlo simulations in NiAl-C ($C=Fe,Co,Cr$) modelled on the basis of “ab-initio” calculated defect formation energies. Three variants of C-atom substitution were applied: (i) substitution for Ni atoms; (ii) substitution for Al-atoms; (iii) equivalent substitution for both Ni and Al atoms.
- Admixture of C atoms affected the stability of B2 superstructure: Fe and Co atoms admixed to NiAl according to variants (i) and (iii), increased the B2-superstructure stability. In all the remaining cases the superstructure was destabilised.
- The simulations showed particular site-occupation preferences of C atoms in NiAl and the competition between chemical ordering and the drift of C-atoms towards preferred lattice sites. The origin of the effects was explained in terms of the relationships between pair-interaction energies of the system components.
- Immiscibility of Cr atoms in NiAl showed-up as a strong clusterisation tendency of these atoms.

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