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COMPUTER SIMULATION OF STRUCTURAL RELAXATIONS IN INTERMETALLICS

SYMULACJE KOMPUTEROWE RELAKSACJI STRUKTURALNYCH W ZWIĄZKACH MIĘDZYMETALICZNYCH

The intermetallic compound Ni_3Al , one of the well-known high-temperature L1_2 (γ') superalloys is an excellent model system for the studies of long-range order (LRO) relaxation run by atomic jumps to nn vacancies in a homogeneous superstructure. Experimental studies of "order-order" kinetics in Ni_3Al carried out by means of resistometry revealed that the relaxation isotherms of the Bragg-Williams LRO parameter η were composed of two single exponentials substantially differing in relaxation times. Later investigations suggested that this effect may show up in systems with different types of superlattices.

The origin of the phenomenon was studied by means of Monte Carlo (MC) simulations. Original studies were performed with a model system described by an Ising Hamiltonian with phenomenological pair-interaction energy parameters. Atomic jumps were simulated using the Glauber algorithm, in which their probabilities depend on differences of system energies before and after the jumps. It was concluded that the fast component of the $\eta(t)$ relaxation consists of the efficient elimination/creation of nn antisite pairs resulting from highly correlated ordering/disordering jumps of Al- and Ni-atoms. The process permanently competes with Al-antisite migration within Ni-sublattice, which is a mechanism of a slower elimination/creation of anti sites showing up as the slow η -relaxation component.

An important drawback of the kinetic model based on the Glauber algorithm is the negligence of saddle-point energies, which in any case must be overcome by real atoms when jumping from lattice sites to nn vacancies. In the present paper it is proposed to go beyond the Ising model and to approach the problem by directly implementing the "embedded-atom-method" (EAM) formalism for lattice energy with the "activated-state-rate approximation" and MC simulation.

Assuming that atoms jump only to nn vacancies, "order-order" kinetics (and any other process controlled by atomic migration) is simulated by calculating *on line*

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changes of the system energy ΔE caused by each atomic jump. It is important that, using EAM, it is possible to evaluate ΔE being the difference not only between the system energies before and after the jump, but also between the energy of a system with an atom on the saddle-point and its energy before the jump. Consequently, EAM may be implemented with any algorithm applied in MC simulation of atomic migration and postulating particular formula for the jump probability.

A systematic comparative study of "order-order" kinetics in Ni_3Al is carried out by means of MC simulations involving Glauber and "residence-time" algorithms implemented with EAM formalism. The results yield additional criteria for the evaluation of EAM potentials for Ni_3Al .

Związek międzymetaliczny Ni_3Al , popularny superstop z nadstrukturą typu L_{12} jest doskonałym układem modelowym do badań kinetyki uporządkowania atomowego dalekiego zasięgu, której mechanizmem są zachodzące w jednorodnej nadstrukturze elementarne przeskoki atomów do wakancji w pierwszej strefie koordynacyjnej. Badania rezystometryczne kinetyki procesów „porządek-porządek” w układzie Ni_3Al wykazały, iż w relaksacjach izotermicznych parametru η uporządkowania atomowego dalekiego zasięgu biorą udział dwa procesy znacznie różniące się czasami relaksacji. Późniejsze prace doniosły o wykryciu tego zjawiska również w układach z innymi typami nadstruktur.

Źródła pow. efektu postanowiono szukać metodą symulacji komputerowych Monte Carlo. Początkowo badania prowadzono symulując układ opisany hamiltonianem Isinga z fenomenologicznymi parametrami energii oddziaływań par atomów. Przeskoki atomów do wakancji symulowano w oparciu o dynamikę Glaubera parametryzując ich prawdopodobieństwo różnicą energii układu przed i po realizacji ewentualnego przeskoku. Wyniki symulacji doprowadziły do wniosku, iż szybka składowa relaksacji η pochodzi od bardzo efektywnego procesu eliminacji/tworzenia par defektów antystrukturalnych będących wzajemnie najbliższymi sąsiadami w strukturze układu. Mechanizmem tego procesu są skorelowane w wysokim stopniu przeskoki atomów Al i Ni pomiędzy węzłami różnych podsięci nadstruktury L_{12} . Z procesem tym stale konkuruje inny, polegający na łatwej migracji defektów antystrukturalnych Al pomiędzy węzłami podsięci Ni, w wyniku czego pary defektów antystrukturalnych Ni i Al są ustawicznie łączone i rozłączane a parametru η podlega wolnej ewolucji (wolna składowa relaksacji „porządek-porządek”).

Ważnym niedostatkim stosowanej początkowo dynamiki Glaubera jest zaniebdanie wpływu energii punktu siodłowego na prawdopodobieństwa przeskoków atomów. W niniejszej pracy zaproponowano wyjście poza model Isinga poprzez wkomponowanie metody EAM („embedded atom method”) wyznaczania potencjałów atomów w kryształach do techniki symulacji Monte Carlo.

Zakładając wakacyjny mechanizm migracji atomów, symulowano metodą Monte Carlo relaksacje „porządek-porządek” w układzie Ni_3Al obliczając na bieżąco dla każdego przeskoku związane z nim różnice energii układu. Dzięki zastosowaniu metody EAM różnice te można było liczyć zarówno pomiędzy stanami przed i po przeskoku, jak i pomiędzy stanem układu z atomem w punkcie siodłowym i stanem przed przeskokiem (z atomem w wyjściowym węźle sieci). W konsekwencji, uzyskano możliwość stosowania różnych algorytmów symulacyjnych.

Przeprowadzone badania polegały na porównaniu wyników uzyskiwanych przy użyciu algorytmu Glaubera z uwzględnieniem energii punktu siodłowego oraz lansowanego ostatnio tzw. „algorytmu czasu rezydencji”.

1. Introduction

Experimental studies of “order-order” kinetics in Ni_3Al (i.e. LRO relaxation following an abrupt temperature change from T_i to T_f , both temperatures being lower than the “order-disorder” transition point) carried out by means of resistometry revealed that the relaxation isotherms of the Bragg-Williams LRO parameter η were composed of two single exponentials substantially differing in relaxation times [1].

The present Monte Carlo (MC) simulations aimed at the explanation of the origin of both dominating components of LRO relaxation.

2. Results of MC simulation of an A_3B binary system with Ising Hamiltonian

“Order-order” relaxations following a temperature change within the domain of LRO were simulated in A_3B binary system composed of 256 000 atoms including 10 vacancies. The system relaxed due to atomic jumps to nn vacancies executed with standard Glauber-type probability:

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

where $\Delta E = E_j - E_i$ is the difference between the system energy after and before the jump from “ i -th” to “ j -th” sublattice site, T and k are temperature and Boltzmann’s constant.

The value of ΔE was calculated on line by considering atomic pair-interactions $V_{i-j}^{(\nu)}$ between nearest neighbouring (nn, $\nu = 1$) and next-nearest neighbouring (nnn, $\nu = 2$) “ i ”- and “ j ”-atoms. Interactions of atoms with vacancies were neglected. The corresponding parameters were evaluated by requiring that they yield the value of ordering energy estimated for Ni_3Al , as well as the ordering of thermal vacancies on Ni-sublattice (for details see ref. [2]). The criteria left only two independent pair-interaction energy parameters evaluated finally as $V_{BB}^{(1)} = -0.15 \text{ eV}$ and $-0.06 \text{ eV} < V_{BB}^{(2)} < +0.08 \text{ eV}$.

The simulated system relaxation was analysed by monitoring the MC-time dependence of the Bragg-Williams LRO parameter η and a specific short-range order (SRO) parameter APC: a fraction of B -antisite atoms being nearest neighbours of A -antisite atoms [3].

Laplace analysis of the simulated $\eta(t)$ relaxation isotherms indicated a definite domination of two relaxation times (Fig. 1), which definitely justified the previous fits of weighted sums of two single exponentials:

$$\frac{\eta(t) - \eta_{EQ}}{\eta(t=0) - \eta_{EQ}} \approx C \exp\left(-\frac{t}{\tau_s}\right) + (1 - C) \exp\left(-\frac{t}{\tau_l}\right); \quad \tau_l > \tau_s; \quad 0 \leq C \leq 1. \quad (2)$$

The value of the weight-factor C depended on the set of $V_{ik}^{(\nu)}$ parameters used and was definitely correlated with the shape of the corresponding APC(t) isotherms (Fig. 2).

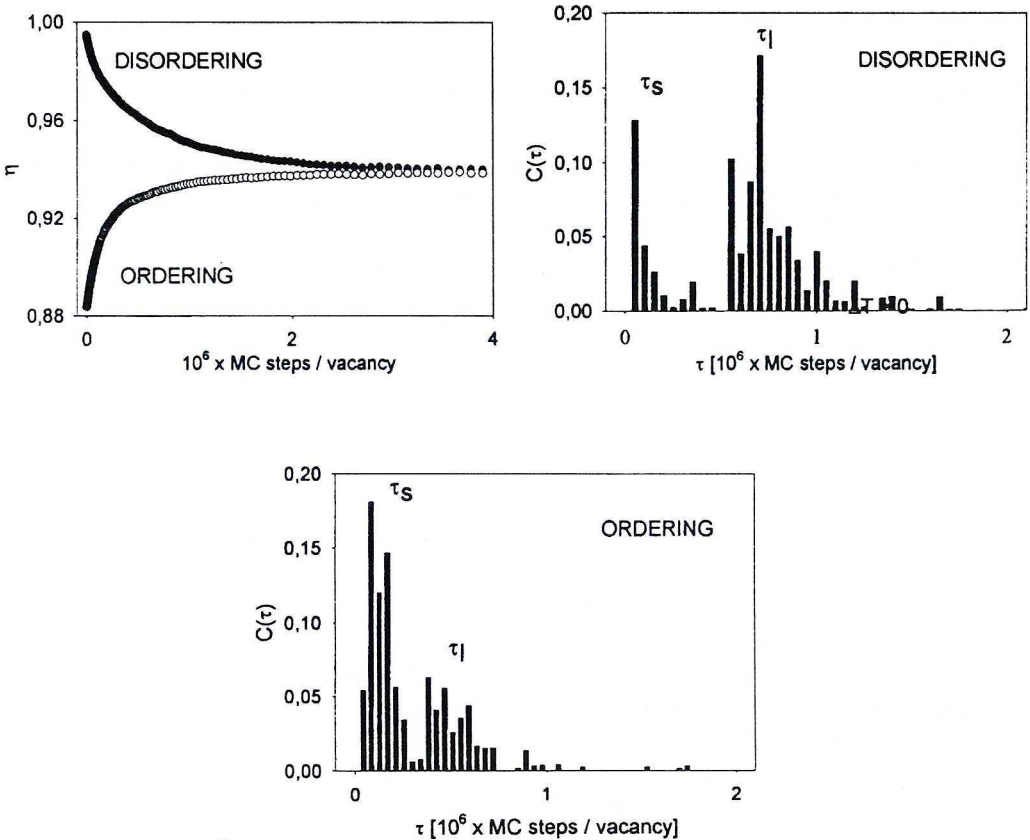


Fig. 1. Examples of $\eta(t)$ isotherms simulated for ordering ($T_i > T_f$) and disordering ($T_i < T_f$) and the corresponding Laplace spectra of relaxation times

A thorough analysis of relations between the frequencies of particular kinds of atomic jumps during LRO relaxations [4] led to the conclusion that the fast component of the $\eta(t)$ relaxation consists of the efficient elimination/creation of nn $A-B$ antisite pairs (initial fast change of APC). It proceeds via highly correlated

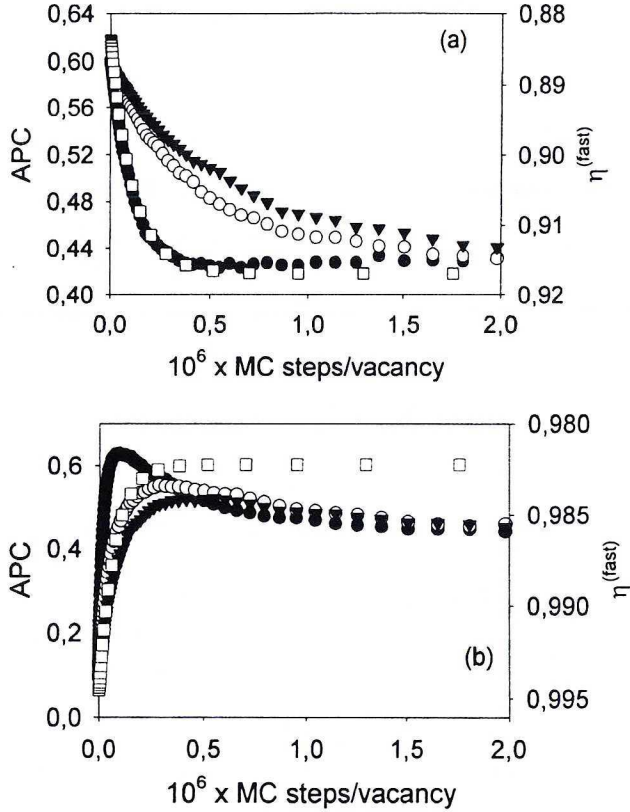


Fig. 2. APC(t) isotherms accompanying “order-order” relaxations: (a) ordering at $T_i = 500$ K and $T_f = 1350$ K; (b) disordering at $T_i = 900$ K, $T_f = 1350$ K with $V_{Al-Al}^{(2)} = -0.04$ eV (●), $+0.06$ eV (○), $+0.08$ eV (▼). Fast component of $\eta(t)$ at $V_{Al-Al}^{(2)} = -0.04$ eV is traced with (□)

ordering/disordering jumps of B and A atoms (Fig. 3). The created B antisites, however, easily migrate within the A sublattice and thus, the nn antisite pairs permanently couple and uncouple. There are two consequences of the process: (i) after reaching an extreme value, APC relaxes to the level of its dynamical equilibrium corresponding to the current temperature value (the fast component of η relaxation completes once APC reaches its extremum); (ii) independently of the fast process, a slow change of η occurs all through the relaxation and finally (after the completion of the fast process) leads to its own equilibrium level.

A choice of particular sets of $V_{ik}^{(\nu)}$ pair-interaction energy parameters controls the balance between the frequencies of the ordering/disordering and “ B -antisite-migration” jumps, which, in turn, determines the value of C (Eq. (2)). Hence, the complex character of experimental $\eta(t)$ relaxation isotherms in Ni_3Al is an evidence of the domination of two coupled relaxation modes: LRO ($\eta(t)$) and SRO (APC(t)).

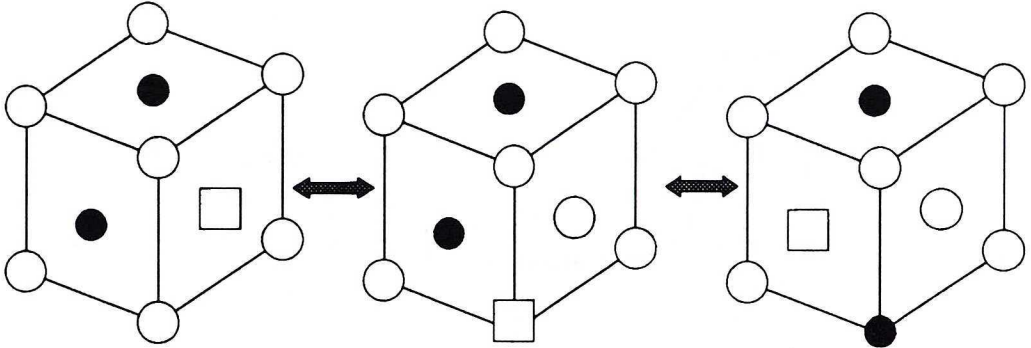


Fig. 3. Scheme of elimination/creation of nn antisite pairs in $L1_2$ - ordered A_3B system:
 • A-atoms, ○ B-atoms, □ vacancy

3. Application of more advanced kinetic models

An important drawback of the standard Glauber dynamics combined with an Ising model is the negligence of saddle-point energies, which in any case must be overcome by real jumping atoms. Estimation of saddle-point energies requires an application of particular atomic pair- (or many-body-) potential. In the presented study, the potential was determined for Ni_3Al within the "embedded atom method" (EAM) [5] and directly implemented with the "activated-state-rate approximation" and MC simulation. Two variants of MC algorithms involving saddle-point energies E^+ were analysed:

(a) Glauber algorithm with $\Pi_{i \rightarrow j}$ given by Eq. (1) and $\Delta E = E^+ - E_i$: each MC step, in which an atomic jump may be executed or suppressed, is considered as MC -time unit,

(b) "Residence-time" algorithm [6] with

$$\Pi_{i \rightarrow j} = \Pi_0 \exp \left[-\frac{E^+ - E_i}{kt} \right], \quad (3)$$

where Π_0 denotes the normalisation factor given by:

$$\Pi_0 = \left[\sum_i \exp \left(-\frac{E^+ - E_l}{kt} \right) \right]^{-1} \quad (4)$$

with summation over all nn positions "l" of a vacancy located on the lattice site "j". A jump chosen at random according to the probability (Eq. (3)) is executed in each MC step, but the corresponding "residence" time increment depends on the current value of Π_0 .

4. MC simulation with EAM potentials

The size of the simulated sample of Ni_3Al was the same as before, but now it contained only one vacancy. The initial state of the sample corresponded to $T_i = 0\text{ K}$ ($\eta = 1$). “Order-order” relaxations were simulated using both MC algorithms defined by Eqs. (1) and (3). The EAM energy differences $E_j - E_i$ and $E^+ - E_i$ were calculated on-line for each atomic jump. According to prior Molecular Statics tests, the “saddle-point” energies E^+ were evaluated by locating the jumping atom half way between its original lattice-site position and the destination nn vacancy. For technical reasons (CPU time), lattice relaxation was not taken into account.

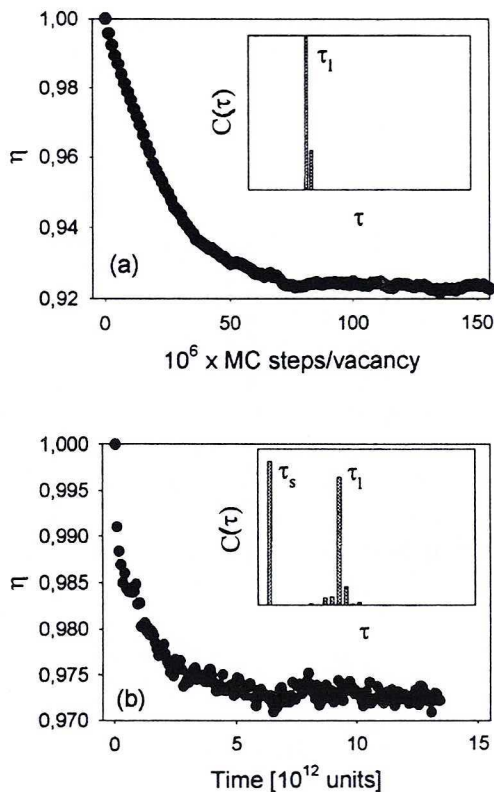


Fig. 4. $\eta(t)$ isotherms and Laplace spectra for Ni_3Al simulated at 1400 K with EAM potentials implemented with Glauber algorithm (a) and with “residence-time” algorithm with saddle-point energies (b)

Figures 4(a) and 4(b) show the $\eta(t)$ disordering isotherms simulated at $T_f = 1400\text{ K}$ by means of Glauber (Eq.(1)) and “residence-time” (Eqs.(3), (4)) algorithms, respectively. Only the “residence-time” algorithm with saddle-point energies yielded an $\eta(t)$ relaxation curve, which fitted Eq. (2) with $\tau_s \neq \tau_l$

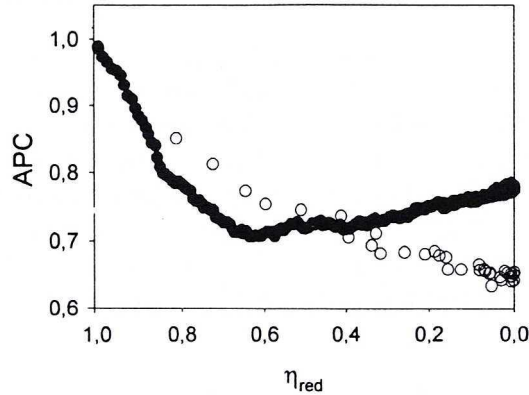


Fig. 5. APC against η_{red} in Ni_3Al simulated with EAM potentials implemented with Glauber algorithm (●) and with “residence-time” algorithm with saddle-point energies (○).

$$\eta_{\text{red}} = 1 - (\eta - \eta_{\text{eq}})/(1 - \eta_{\text{eq}})$$

and $C > 0$. Lack of the fast process in the “Glauber-dynamics” relaxation (in disagreement with experiment) is consistent with the results of MC simulations of an Ising A_3B system [4]: The applied Ni_3Al EAM potentials give considerably different values of $\Delta E = E_j - E_i$ for Al- and Ni-disordering jumps, while, according to the previous analysis, the value of C (Eq. (2)) decreases with an increase of that difference. Figure 5 shows the $\text{APC}(\eta_{\text{red}})$ curves corresponding to the $\eta(t)$ isotherms of Fig. 4(a) and Fig. 4(b). Both curves start at $\text{APC} \approx 1$, which means that the very first antisites in the initially perfectly ordered system form at once as nn pairs. The presence of the fast “order-order” relaxation process is reflected by a slower decrease of the corresponding $\text{APC}(\eta_{\text{red}})$ curve, which again confirms the previous interpretation of the effect [4] and indicates that its mechanism in the present EAM model system is the same as in the one described by an Ising Hamiltonian.

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