Structural transformations in the NiAl alloys with deviations from the stoichiometric composition during stepwise cooling

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Abstract. The Monte Carlo simulation method shows the formation of B2 superstructure domains in the course of structural phase transitions during stepwise cooling of the Ni-Al intermetallic compound with a deviation from stoichiometry. The effect of the deviation from stoichiometry on the structure and energy characteristics of the alloy during stepwise cooling is analyzed in this article. It is shown that the highest percentage of the ordered phase after stepwise cooling has the alloy with a stoichiometric composition.

1. Introduction
The NiAl intermetallic alloy has the B2 (CsCl) ordering with the Pm3m space group based on a bcc lattice. The Ni–Al system is characterized by large differences in the size of atoms and the electronic structure. Beta-alloys of the Ni–Al system were used in the investigations of low-stability pre-transitional states [1]. It is well known that mono-nickel aluminide is characterized by a high melting temperature (1638 °C) and heat of formation. The crystals of NiAl exhibit stronger elastic anisotropy, and the related anisotropy of properties is compared to the structure with a disordered bcc-lattice [1].

There are two primary methods of computer simulation in condensed matter physics. Currently, the most common method is molecular dynamics, rather than the Monte Carlo method. The method of molecular dynamics is most adequate in the investigation of dynamic processes in materials. However, it has a very important disadvantage: the order-disorder phase transformations are relatively slow to get a certain practical result and require a long experiment time. The use of the Monte-Carlo method can significantly accelerate research. For this reason, the phase transformation in the NiAl alloy is investigated using the Monte Carlo method.

The purpose of this work is to study the structural and phase characteristics of the intermetallic compound NiAl with deviations from the stoichiometric composition during stepwise cooling from the solid solution by the Monte Carlo method.

2. Computer simulation model
The atoms of nickel aluminide are located at the points of the bcc lattice, ordered in accordance with the B2 superstructure (figure 1). The computational cell includes 32×32×32 atomic layers (65536 atoms). Periodic boundary conditions are used for an effective modelling of an infinite system. The starting configuration is a disordered bcc solid solution. To simulate diffusion in a crystal, a single vacancy is introduced in the computational cell; the corresponding concentration of vacancies is $1.53 \times 10^{-5}$. The diffusion of atoms occurs through the mechanism of vacancies, which was previously applied in a similar way in the works [2-11]. The structure of the alloy changes at discrete points in time with an act of diffusion corresponding to the atomic jump in the vacant site. Only atoms from the...
1st, 2nd, or 3rd coordination sphere can jump into the vacant site. The probability of the hopping to the vacant site is determined by the Metropolis algorithm.

![Figure 1. B2 superstructure](image)

The interatomic interactions are described by the Morse potential \( \phi(r_{ij}) = D_{KL} \beta_{KL} \left( \beta_{KL} e^{-\alpha_{KL} r_{ij}} - 2 \right) \), where \( \alpha_{KL}, \beta_{KL}, D_{KL} \) are the potential parameters of bonds between atoms of the \( K \) and \( L \) sorts and \( r_{ij} \) is the distance between the atoms. The configuration energy of the system is calculated as \( E = 1/2 \sum_{i=1}^{N} \sum_{j=1}^{M} \phi(r_{ij} - r_{ij}) \), where \( r_{ij} - r_{ij} \) are the radius-vectors of atoms \( i \) and \( j \), \( N \) is the number of atoms in the system, \( M \) is the number of nearest neighbours, including atoms of three coordination spheres of interaction.

3. Results and discussion

In this study, the structure evolution of Ni-Al alloys having a deviation of \( \pm 5\% \) from stoichiometry is analyzed during stepwise cooling. In the process of stepwise cooling of the alloy, the average configuration energy per atom (figure 2), the long-range order parameter (figure 3 a) and the short-range order parameter (figure 3 b) are analyzed.

![Figure 2. Temperature dependence of the average configuration energy of NiAl alloys without and with deviations from stoichiometry](image)

The lowest configuration energy value has the alloy with 45% Al and the highest value - the alloy with 55% Al, as it is clearly seen from figure 2. The temperature ranges of the disorder-order phase transition are close for the three alloys, but the alloy with a stoichiometric composition moves to the ordered state faster and at a higher temperature.

The behavior of the short-range order parameter in the first coordination sphere (figure 3 a) suggests a tendency of the alloy towards ordering upon cooling, as evidenced by an increase in negativity of the short-range order parameter. At higher temperatures, the degree of ordering is smaller. A system without deviation from stoichiometry shows a stronger tendency towards ordering than systems with deviations from stoichiometry. Changes in the short-range order parameter for all the three studied alloys (figure 3 a) correlate with changes in the configuration energy (figure 2).
The temperature dependence of the long-range order parameter is of particular interest. In the alloy with an equiatomic composition, the long-range order parameter reaches 0.9, and in the alloys having deviations from stoichiometry it reaches 0.89 for 45% Al and 0.72 for 55% Al. In the NiAl alloy without deviation from stoichiometry, the value of the long-range order parameter grows faster than in non-stoichiometric alloys. The maximum value of the long-range order parameter corresponds to the largest volume of the ordered structure.

**Figure 3.** Temperature dependence of the short-range (a) and long-range (b) order parameters in NiAl alloys without and with deviations from stoichiometry

**Figure 4.** Domain structure evolution in NiAl intermetallic alloy with deviation from stoichiometry during stepwise cooling
Let us take a look at the domain structure changes of NiAl with various compositions during stepwise cooling, as presented in figure 4 for different temperatures. At high temperature (1800 K) only small-size domains of the B2 superstructure are observed for all configurations. The size of the antiphase domains with the B2 superstructure increases when cooled down to 1600 K. In an equiatomic alloy, at about 1500 K, the domain structure begins to form with two domains within the computational cell. The process of ordering continues with a decrease in temperature down to 1000 K, keeping disordered areas close to antiphase boundaries. In the alloy with 45% Al, the number of disordered regions decreases with decreasing temperature. The formation of domains is suppressed in the alloy with 55% Al.

4. Summary
Using the Monte Carlo simulation, we have shown the formation of the B2 superstructure antiphase domains after the completion of the disorder - order phase transition in NiAl alloys. Domains are separated by antiphase boundaries in the directions <110> and <100>. The analysis has demonstrated that deviation from stoichiometry exerts a noticeable effect on the structure and energy characteristics of the system. After stepwise cooling, the most ordered phase corresponds to the equiatomic composition and the most disordered one to the 45% Ni-55% Al alloy.

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References
[1] Kositsyn S V and Kositsyna I I 2008 Uspekhi Fiziki Metallov 9 195 (In Russian)
[2] Potekaev A I, Kulagina V V, Chaplygina A A, Chaplygin P A and Starostenkov M D 2017 Russ. Phys. J. 60 1
[3] Kulagina V V and Potekaev A I 2011 Izvestiya VUZov. Fizika 54 369 (In Russian)
[4] Potekaev A I, Kulagina V V, Chaplygina A A, Chaplygin P A and Starostenkov M D 2017 Russ. Phys. J. 59 1532
[5] Chaplygina A A, Chaplygin P A, Starostenkov M D, Potekaev A I and Kulagina V V 2016 Russ. Phys. J. 59 605
[6] Potekaev A I, Grinkevich L S, Chaplygin P A, Starostenkov M D and Chaplygina A A 2015 Russ. Phys. J. 58 485
[7] Starostenkov M D, Chaplygina A A and Romanenko V V 2014 Key Eng. Mater. 592-593 321
[8] Potekaev A I and Kulagina V V 2011 Russ. Phys. J. 54 5
[9] Potekaev A I, Kulagina V V, Chaplygina A A, Starostenkov M D and Klopotov A A 2013 Russ. Phys. J. 55 1248
[10] Chaplygina A A, Starostenkov M D, Kulagina V V and Potekaev A I 2012 Russ. Phys. J. 55 814
[11] Dmitriev S V, Ovcharov A A, Starostenkov M D and Kozlov E V 1996 Phys. Solid State 38 996