Molecular dynamics simulation of diffusion in a (110) B2-NiAl film

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ABSTRACT

We report on the first direct molecular dynamics study of diffusion in B2-NiAl using one of the most reliable embedded-atom method potentials for this phase. The simulation is performed for near the stoichiometric composition at a temperature just below the melting temperature of the model. In the molecular dynamics simulation, an equilibrium point-defect concentration is generated and maintained by using a film sample with periodic boundary conditions only in two directions and free surfaces in the third direction. Two types of point defects − Ni vacancies and Ni antisites − are found in the bulk of the model. It is demonstrated that isolated Ni vacancies strongly dominate in concentration over all of their bound complexes with Ni antisites. Although we predict that some attractive interactions should occur between point defects to form bound Ni vacancy-Ni antisite pairs and bound Ni antisite-Ni vacancy-Ni antisite complexes, only about 2% of Ni vacancies and 1% of Ni antisites statistically randomly associate to form bound Ni vacancy-Ni antisite-Ni vacancy complexes (the so-called bound triple-defect complex). As a result, it is deduced that the triple-defect diffusion mechanism is not likely to be the dominant diffusion mechanism in the bulk of the model because this diffusion mechanism effectively requires that the Ni vacancies and Ni antisites must form bound triple-defect complexes. Furthermore, it is found that Ni atoms diffuse in the bulk of the model on average about 2.5 times faster than Al atoms. Therefore, we suggest that isolated Ni vacancies are likely to play a key role in atomic diffusion of both Ni and Al near the stoichiometric composition of B2-NiAl and, consequently, the most plausible and widely accepted candidate for dominant diffusion mechanism in B2-NiAl can be considered to be six-jump cycles of a Ni vacancy. Furthermore, we can suppose that additional next-nearest-neighbor jumps of a Ni vacancy may cause that Ni atoms diffuse faster than Al atoms.

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1. Introduction

NiAl is a B2-ordered intermetallic compound (CsCl prototype) which retains its crystal structure up to the melting temperature of about 1911 K [1,2]. Furthermore, it exhibits quite a wide homogeneity range: up to 10 at.% on either side of the stoichiometric composition [1,2]. This compound has attracted much attention as a high temperature structural material for a wide range of engineering applications in automotive, aircraft, space, and other industries [2—4]. The significant technological importance of the compound has motivated strong interest in its fundamental properties. In particular, a detailed knowledge of diffusion in B2-NiAl has been shown to play a remarkable role in understanding its high temperature properties [5].

According to experimental data [6,7], B2-NiAl is considered to be a triple-defect compound. In particular, deviations from the exact stoichiometric composition toward Al-rich compositions are predominantly accommodated by vacancies on the Ni sublattice, whereas Ni-rich compositions are dominated by antistructural Ni atoms (Ni antisites) on the Al sublattice [8—10]. This means that atomic disorder in stoichiometric B2-NiAl should be strongly dominated by triple defects consisting of two Ni vacancies and one Ni antisite. Triple-defect disorder does not change the bulk composition of the compound. However, it should be emphasized that it is by no means clear whether the point defects group into triple-defect complexes physically or the triple-defect complexes should be viewed only conceptually in a totally dissociated form so that interactions between their constituents can be neglected. For example, in Ref. [11] on the basis of experimental diffusion data and supporting zero-temperature atomistic simulations, it was concluded that the triple-defect diffusion mechanism [12] should mainly operate on both sides of stoichiometry in B2-NiAl. This diffusion mechanism suggests that the vacancies and antisite defects must form bound triple-defect complexes. On the other hand, in [13] on the basis of zero-temperature atomistic simulations with a reliable embedded-atom method (EAM) potential developed by Mishin et al. [14] and supporting first-principle calculations, the previously mentioned conclusion of [11]

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was critically analyzed. In particular, it was noted in Ref. [13] that several atomic mechanisms of diffusion can operate in $B2$-NiAl concurrently and may depend on the composition around the stoichiometric composition. For example, in the perfectly ordered stoichiometric structure of $B2$-NiAl at least two diffusion mechanisms can operate concurrently: (i) six-jump cycles of a Ni vacancy [15,16] in the [110] direction, which were shown in [13] to occur in fact by three vacancy jumps (because of mechanical instability of the arising configurations involving a Al vacancy) and (ii) next-nearest-neighbor jumps of a Ni vacancy [17]. Furthermore, it was pointed out in Ref. [13] that the idea of a multiplicity of diffusion mechanisms in $B2$-NiAl is supported by the early experimental diffusion measurements [18]. Therefore, the findings of Ref. [13] suggest that triple-defect complexes need not be grouped into triple-defect complexes physically in order to provide long-range diffusion in $B2$-NiAl. More recent zero-temperature first-principles calculations [19] showed that next-nearest-neighbor jumps of a Ni vacancy, the triple-defect diffusion mechanism and the [110] six-jump cycles of a Ni vacancy initially are plausible mechanisms for Ni diffusion in stoichiometric $B2$-NiAl. In good agreement with previous authors [13], it was also concluded in Ref. [19] that the pathway for the [110] six-jump cycle of a Ni vacancy occurs in three steps and not six, due to mechanical instability of the arising configurations involving a Al vacancy. At the same time, the authors of Ref. [19] ruled out next−nearest−neighbor jumps, since an increase in Ni diffusivity was not observed in experimental work [11] in the Al-rich deviations from stoichiometry and also because the next-nearest-neighbor jump distance is larger than the nearest-neighbor jump distance in the other two mechanisms. Later, the same authors, using similar calculations, also concluded [20] that the triple-defect diffusion mechanism should be the dominant mechanism for Al diffusion in stoichiometric $B2$-NiAl.

The common approach which was used in the described theoretical studies of diffusion mechanisms in $B2$-NiAl invokes the harmonic approximation to transition state theory [21] to estimate different jump rates and then to compare their activation energies and pre-exponential factors with experimental data. In those calculations, the minimum energy path and the saddle point of a jump are determined at zero temperature. Lastly, we should note that zero-temperature first-principles calculations were also used in Ref. [22] to reveal the most important jump mechanisms in $B2$-NiAl. However, in Ref. [22], instead of individual comparisons of the activation energy and pre-exponential factor of each jump with experimental data, the results were simultaneously incorporated within a Kinetic Monte Carlo simulation at 1300 K. This allowed the authors [22] both to track the frequency with which the various jumps occur as functions of composition and to calculate tracer diffusion coefficients. According to the data, around stoichiometry the most frequent jump mechanism, which contributes to macroscopic transport, is the triple-defect jump sequence. Furthermore, since experimental Al tracer diffusion coefficients are not available, it was predicted, in particular, that at stoichiometry the Al tracer diffusion coefficient is larger that of Ni.

We should emphasize here, however, that the approaches described above rely on the assumption that the activation energy and pre-exponential factor of a jump rate (as well as a point defect formation energy, which is also important for a proper diffusion coefficients calculations) are temperature independent. In contrast, recent molecular dynamics (MD) simulations with semi-empirical interatomic potentials indicate that this assumption is not realistic [23,24]. Moreover, MD simulations offer the most direct approach to diffusion calculations, automatically capturing the anharmonicity of atomic vibrations and all other sources of temperature effects [25]. On the other hand, lattice diffusion in solids is presently very difficult of access on MD simulation time scales even using semi-empirical interatomic potentials [23−25]. This is mostly

due to the low point-defect concentrations and the slow jump rates of point defects in crystals. Nonetheless, theoretical calculations [10] show that at high temperatures, the concentration of thermal vacancies on the Ni sublattice in stoichiometric $B2$-NiAl can be high enough, about 1% or even more, to make possible a long-time scale MD simulation of diffusion in this phase. Accordingly, in this paper, for the first time, we estimate the mutual Ni vacancy and Ni antisite distribution as well as the Ni and Al self-diffusion coefficients ratio in near stoichiometric $B2$-NiAl directly from MD simulation using one of the most reliable EAM potentials [14] for this phase. In the MD simulation, an equilibrium point-defect concentration is generated and maintained by using a film sample with periodic boundary conditions only in two directions and free surfaces in the third direction. The free surfaces in the model serve as sources and sinks of point defects. The main reason for choosing the simulation geometry is that such a film sample provides the most direct approach to generate and maintain an equilibrium point-defect concentration inside the sample at high temperatures [23,24], which is crucial for proper diffusion calculations.

2. Calculation methods

A film sample of stoichiometric $B2$-NiAl was constructed using slab geometry to provide (110) exposed surfaces on opposing sides of the slab in the z-direction. To simulate the free surfaces, vacuum layers of length ∼1 nm were placed at the lower and upper limits of the simulation block in the z-direction. Periodic boundary conditions were imposed in the x and y-directions parallel to the surface. The dimensions of the simulation block were chosen to provide an approximately square shape of the repeat unit of the surface and 14 layers across the slab. The resulting slab contained 1512 atoms (each layer consisted of 54 Ni and 54 Al atoms) and was ∼2.9 nm thick (we consider that the film thickness is equal to 14 interlayer distances).

The interatomic interactions in $B2$-NiAl were modeled using the EAM potential developed by Mishin et al. [14]. The EAM potential was constructed by fitting to experimental data and a large set of *ab initio* structural energies. This potential accurately reproduces lattice properties of $B2$-NiAl, including elastic constants, thermal expansion and phonon frequencies. It also predicts reasonable values of point-defect energies, planar fault and surface energies. In particular, the combination of the point-defect energies obtained at zero-temperature correctly predicts $B2$-NiAl to be a triple-defect compound [10,14]. Furthermore, it was demonstrated [26,27] that the EAM potential not only accurately reproduces lattice and defect properties of $B2$-NiAl but also gives a realistic description of the principal properties of the liquid $Ni_{50}Al_{50}$ alloy, even though no liquid data were included in the fitting of the potential. In addition, the EAM potential is able to describe crystallization of an amorphous $Ni_{50}Al_{50}$ phase into $B2$-NiAl phase directly within the framework of the MD method [28,29].

In Ref. [27], we found that the film model melts at 1550 K (the bulk lattice parameter is ∼2.94 Å) starting from the surface of the film after ∼56 ns of isothermal MD annealing, while MD annealing at 1500 K (the bulk lattice parameter is ∼2.937 Å) for a much longer time of 300 ns did not reveal any substantial changes of the internal energy of the model that could be associated with a phase transformation, i.e. the crystal structure of the film is stable at 1500 K (see Fig. 1). These data allow us to conclude that the melting temperature of the film is in the range: 1500−1550 K. These data are in accordance with results of other MD simulations [26]. In Ref. [26], by applying a two-phase method wherein the solid (100) $B2$-NiAl and liquid $Ni_{50}Al_{50}$ phases separated by two interfaces were simulated in direct coexistence in an all-periodic simulation block, it was shown that the bulk melting temperature of the MD