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Guillermo Bozzolo
Analex Corporation
Brook Park, Ohio

Carlos Amador
Universidad Nacional Autónoma de México
Ciudad Universitaria
Distrito Federal, México

John Ferrante and Ronald D. Noebe
Lewis Research Center
Cleveland, Ohio

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GUILLERMO BOZZOLO*, CARLOS AMADOR**, JOHN FERRANTE*** AND RONALD D. NOEBE***

* Analex Corporation, 3001 Aerospace Parkway, Brook Park, OH, 44142-1003

** Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 Distrito Federal, México.

***National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135.

ABSTRACT

The semiempirical BFS method for alloys is generalized by replacing experimental input with first-principles results thus allowing for the study of complex systems. In order to examine trends and behavior of a system in the vicinity of a given point of the phase diagram a search procedure based on a sampling of selected configurations is employed. This new approach is applied to the study of the β phase of the Ni-Al system, which exists over a range of composition from 45-60 at. % Ni. This methodology results in a straightforward and economical way of reproducing and understanding the basic features of this system. At the stoichiometric composition, NiAl should exist in a perfectly ordered B2 structure. Ni-rich alloys are characterized by antisite point defects (with Ni atoms in the Al sites) with a decrease in lattice parameters. On the Al-rich side of stoichiometry there is a steep decrease in lattice parameter and density with increasing Al content. The presence of vacancies in Ni sites would explain such behavior. Recent X-ray diffraction experiments suggest a richer structure: the evidence, while strongly favoring the presence of vacancies in Ni sites, also suggests the possibility of some vacancies in Al sites in a 3:1 ratio. Moreover, local ordering of vacant sites may be preferred over a random distribution of individual point defects.

During the last decade, there has been tremendous progress in the development and implementation of several theoretical tools for the analysis and description of metals and their alloys. Each one of these techniques, mainly first-principles approaches (i. e. those which require only the identity of the constituent elements as input [1]) and semiempirical methods (i. e. those which require various degrees of experimental information as input [2]), are somehow limited in their range of applications in that they either involve prohibitive computational effort for realistic cases (first-principles) or suffer a lack of physical accuracy and detail in their predictions (semiempirical calculations). These limitations are clearly apparent when applying these techniques to alloys, therefore restricting their usefulness for theoretical alloy design. Current needs in materials development require theoretical support able to provide, with computational simplicity and physical consistency, information on new materials ranging from basic knowledge of their defect structure to a complete description of their mechanical properties and processing.

Among the semiempirical methods currently available, the BFS method for alloys [3] distinguishes itself in that it does not have any *a priori* limitation on the number and type of elements and their alloys to which it can be applied. However, this necessary flexibility which allows its implementation to a wide variety of systems, is based on the somewhat restrictive assumption that each alloy constituent exists in the alloy phase under study. For example, the β -NiAl alloy is taken as an alloy of bcc-nickel and aluminum, although Ni and Al are fcc elements and therefore no experimental data is available for the bcc phases of these elements. There is a relatively small number of situations where the alloy and its constituents exist in the same phase (for example, the fcc based

CuAu ordered alloy). In order to free the BFS method from this restriction, which would obviously limit its usefulness to those cases where experimental information is available, we have replaced the experimental input to the method by pure element parameters determined by first-principles *Linear Muffin-Tin Orbitals* (LMTO) method calculations. Moreover, greater consistency is achieved by also using the corresponding LMTO results for the alloy under study: the BFS parameters (Δ_{AB} , Δ_{BA}) [3] for the AB alloy are analytically determined so as to reproduce the corresponding LMTO-determined heat of formation and lattice parameter. By doing so we also avoid the potential problem of inconsistency and ambiguity in data obtained from different experimental techniques.

While these BFS parameters might not necessarily be transferable to other portions of the phase diagram (i. e. to a different phase, even if it is based on the same structure), they should necessarily be a suitable choice for analyzing the vicinity of the phase under consideration, making this approach particularly useful for studying the defect structure of such alloys for the range of compositions for which that phase exists. Moreover, following this generalized version of the BFS method, it is particularly easy to include the effect of additions of any number of impurity elements on the basic properties of the alloy. A more detailed presentation of the theoretical procedure and applications to ternary systems will be the subject of a forthcoming publication. In this work, we concentrate on the implementation of this scheme to an alternative way of performing atomistic simulations, as will be described below, and apply this procedure to the relevant example of the defect structure of B2 NiAl. The computational efficiency of the BFS method and its simple formulation based on the concepts of BFS strain and chemical energies [3], allow for an alternative way of performing atomistic simulations based on surveying a large number of candidate configurations. This is particularly convenient if the goal is to gain understanding not only of the ground state properties of the system but knowledge on metastable states, thus giving us insight on the trends found experimentally. Instead of searching for an absolute energy minimum for a given concentration, we construct a large number of candidate configurations to obtain information on the energetics of the system close to the equilibrium state. These configurations are, to a certain extent, arbitrary, and do not necessarily correspond to the equilibrium state for a given composition. While most are experimentally unaccessible, they serve the purpose of determining trends in the bulk properties of the actual alloys. If the set of configurations sampled is sufficiently large and the structures are chosen respecting the symmetries underlying the studied phase, one would expect to find the equilibrium state or states sufficiently close to it for each composition. This approach is not meant to substitute large scale Monte-Carlo simulations which would provide the full description of the composition and temperature dependence of the ground state. On the contrary, it could be taken as a supplementary set of calculations which could enhance the somehow limited information provided by Monte-Carlo simulations. This sampling algorithm follows in spirit the comprehensive searches of ground states method [4]. The ideal thermodynamical equilibrium state theoretically determined is rarely achievable in the laboratory in the process of making the actual alloy. Knowledge of other low-lying states (i. e. states close in energy to the equilibrium state), combined with the results of Monte-Carlo simulations can only enhance our understanding of the basic features and behavior of the actual alloy.

The parameters for the BFS method are obtained from results of first-principles, all-electron, density- functional based calculations of the elemental constituents and ordered binary compounds of these elements. The particular implementation used in this work is the Linear Muffin-Tin Orbitals method [1] in the Atomic Sphere Approximation. As mentioned above, in order to provide parameters to the BFS method, we need to calculate the equilibrium properties of the elemental solid for the same symmetry of the compound to be studied. Thus, for this case we have calculated *bcc* Al and *bcc* Ni, as well as B2 ordered NiAl. Calculations were done for different values of the lattice constant, and total energies were then fitted to the universal equation of state of Rose *et al.*[5]. The LMTO method uses a minimal basis set, accordingly we have used only *s*, *p* and *d* orbitals in the calculation. All calculations were done with equivalent sampling of the Brillouin zone using, for the *bcc* lattice,

	a_0 (Å)	E_C (eV/atom)	B_0 (GPa)	E_v (eV/atom)
Al(bcc)	3.192	3.945	77.3	1.8
Ni(bcc)	2.752	5.869	249.2	3.0

Table 1: LMTO parameters for pure bcc Al and Ni

120 k - points in the irreducible wedge. Apart for the parameters describing the equation of state of the element, the parameterization of the BFS approach requires the formation energy of a vacancy. We have also calculated this quantity with the LMTO method using a supercell approach. Studies of the convergence of this property as a function of the supercell size showed that, for the required precision in the calculation (± 0.1 eV/atom) and within practical computational limits, a supercell of 8 atoms is necessary. As BFS is parameterized without considering the relaxation caused by the formation of a vacancy, no relaxation is allowed in the LMTO calculations.

As mentioned above, the consistent parameterization of the BFS method requires also the calculation of the formation energy and lattice constant of an ordered binary compound. We have chosen the *bcc* based B2 structure. This calculation for the compound is equivalent in the basis set and sampling of the Brillouin zone used for the elements.

The results from the LMTO calculation used in the parameterization of the BFS method for the present work are shown in Table 1. The equilibrium lattice parameter determined for β -NiAl is $a_{LMTO} = 2.85$ Å, and the formation energy of the ground state B2 structure is $\delta h = -0.6092$ eV/atom. The BFS parameters thus obtained are $\Delta_{AlNi} = 0.0840$ Å⁻¹ and $\Delta_{NiAl} = -0.0581$ Å⁻¹.

The BFS method is based on the idea that the energy of formation of an alloy is the superposition of individual contributions ε_i of non-equivalent atoms in the alloy [3]:

$$\varepsilon_i = \varepsilon_i^S + g_i(\varepsilon_i^C - \varepsilon_i^{C_0}). \quad (1)$$

ε_i has two components: a *strain* energy ε_i^S , computed with equivalent crystal theory (ECT) [6], that accounts for the actual geometrical distribution of the atoms surrounding atom i , computed as if all its neighbors were of the same atomic species, and a *chemical* energy $\varepsilon_i^C - \varepsilon_i^{C_0}$, which takes into account the fact that some of the neighbors of atom i may be of a different chemical species. For ε_i^C we interpret the chemical composition as a defect of an otherwise pure crystal. We represent this defect by ‘perturbing’ the electronic density in the overlap region between dissimilar atoms and locating them at equilibrium lattice sites of atom i . The ideas of ECT [6] are used to develop a procedure for the evaluation of the energy associated with this ‘defect’. To free the chemical energy of structural defect energy which should only be included in the strain energy, we reference ε_i^C to a similar contribution where no such perturbation is included ($\varepsilon_i^{C_0}$). The coupling function g_i , which ensures the correct asymptotic behavior of the chemical energy, is defined as $g_i = e^{-a_i^S}$, where a_i^S is a solution of $\varepsilon_i^S = -E_C^i [1 - (1 + a_i^S) \exp(-a_i^S)]$ (see ref. [5]), and where E_C^i is the cohesive energy for atom i . In the context of BFS, the terms ‘strain’ and ‘chemical’ represent quite different effects than the usually assigned meanings. For a clear understanding of this paper, we direct the reader to ref. 3 where a detailed description of the calculation of the strain and chemical energy contributions is provided. Except for two parameters determined by fitting to experimental or theoretical alloy properties, the method relies on pure element properties. The BFS parameters used in this work, as well as the ECT parameters are listed in refs. 3 and 6, respectively. These parameters have been previously used, with a great degree of success, in previous BFS applications to the Cu-Au system, including surface segregation as well as multilayer surface relaxation studies.

The BFS calculation was done on a 72 atoms cell, allowing for isotropic lattice relaxation induced by the presence of vacancies and substitutional atoms. A comparison of the modeled results with experimental data is displayed in Fig. 1. The theoretical results, shown as a continuous line,

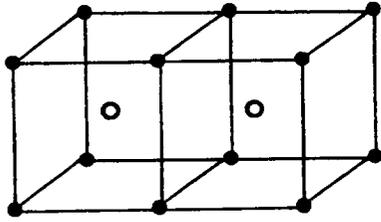
consist of the calculated lattice parameter and density for the lowest energy configuration (within the configuration set used in this simulation) for each composition. There is good agreement with experiment, particularly for Ni-rich alloys. The lowest energy states correspond to antisite point defects (Ni atoms occupy sites in the Al sublattice) for Ni-rich alloys and vacant Ni sites for Al-rich alloys. The departure from the experimental behavior, more noticeable in the Al-rich side of stoichiometry, could be partially due to the absence of computed local relaxations due to the presence of vacancies.

The availability of information regarding configurations close to the lowest energy state for each composition indicates that the defect structure could be richer than what was described above: very close in energy to the minimum energy states, one finds configurations that include vacancies both in the Ni and Al sublattice. For example, within the family of configurations composed of Al-vacancies plus Ni-vacancies, the values (hexagons in Fig. 2) with lattice parameters closest to those of the lowest energy states (solid triangles) consisted of locally ordered arrangements of vacancies (i.e. an Al vacancy shared by two Ni-vacancies at the nearest-neighbor distance) while those points further away consisted of more random distributions. This feature is independent of composition. Energetically, marked differences exist between different types of point defects, regardless of their relative location: Al antisite atoms, for example, not only increase the lattice parameter with increasing Al content but also introduce a noticeable energy difference with respect to alternative states characterized by combinations of Ni and Al vacancies. A more detailed discussion of the simulation can be found in Ref. 8.

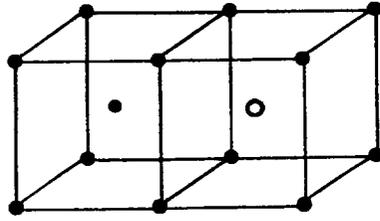
The present paper shows the feasibility of this combined first-principles plus semi-empirical approach for the study of the role of complex defects in the stability of metallic alloys. Results for the system studied showed very good agreement with experimental information, essentially confirming the previously suggested explanation for the contraction of the equilibrium lattice constant of B2 NiAl off-stoichiometry alloys, but indicating also a more complex arrangement of defects. This method allows the study of complex systems which are unaccessible to first-principles calculations such as defects in ternary systems and defects in binary and ternary surfaces.

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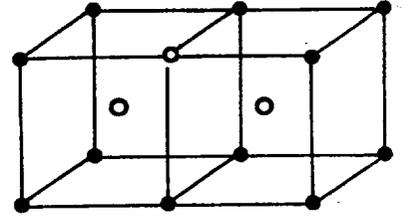
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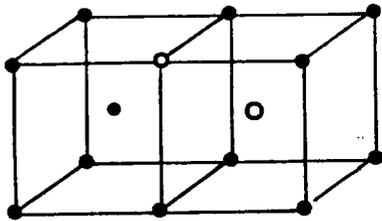
B2 NiAl



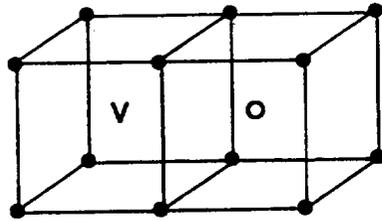
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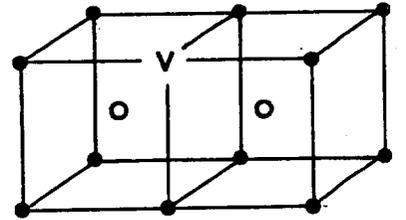
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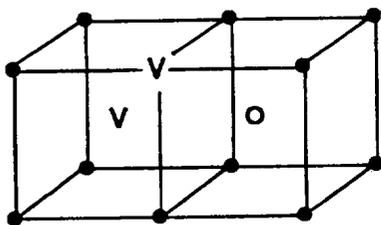
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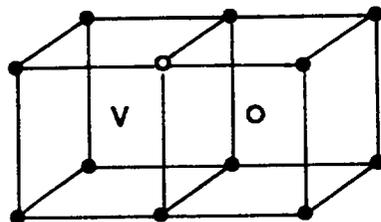
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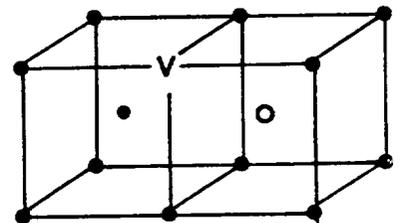
Al vacancies



Ni and Al vacancies



Ni antisite + Ni vacancies



Al antisite + Al vacancies

Fig. 1

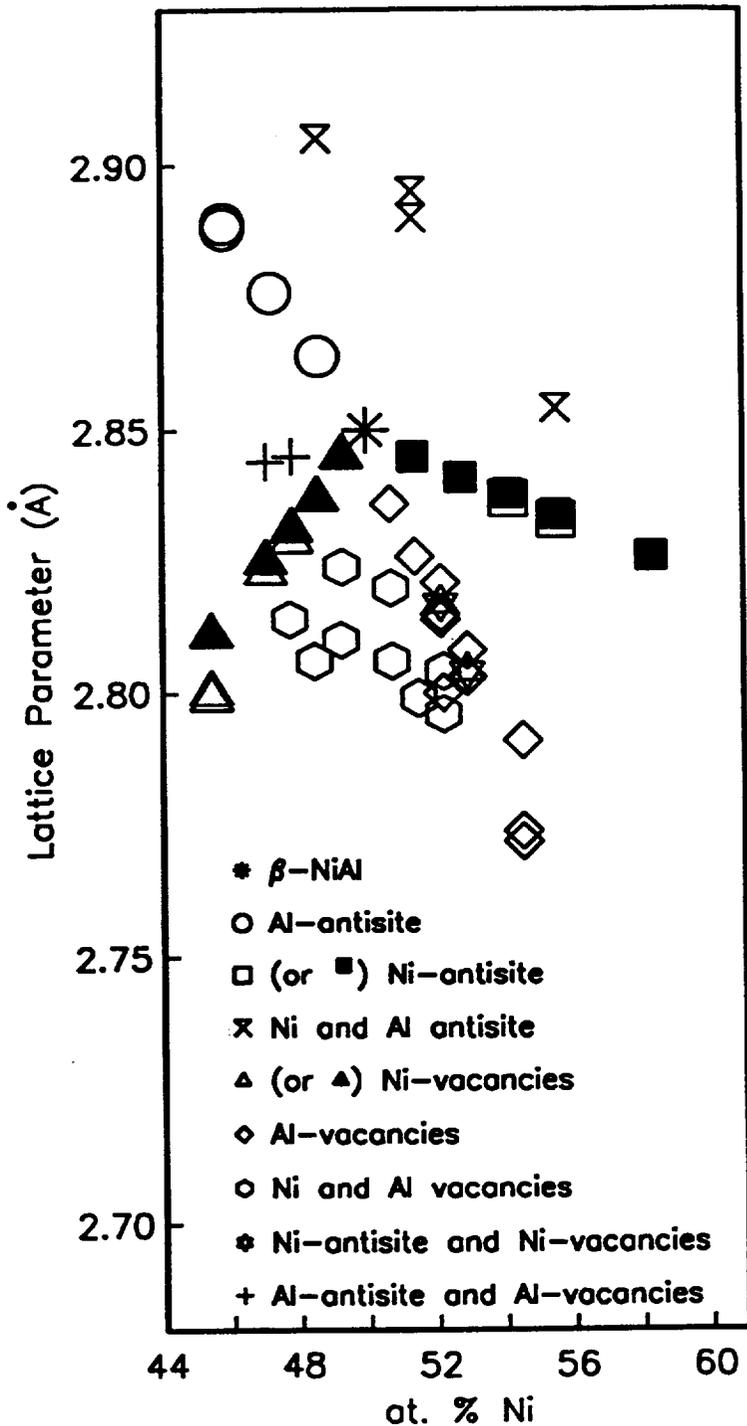


Fig. 2

Lattice parameter (in Å) as a function of Ni concentration for several NiAl structural forms. Different symbols denote alloys with Ni and/or Al antisite defects as well as Ni and/or Al vacancies. The shaded triangles and squares indicate the lowest energy configurations at each composition. Similar symbols for the same composition correspond to different distributions of the same defect within the computational cell.

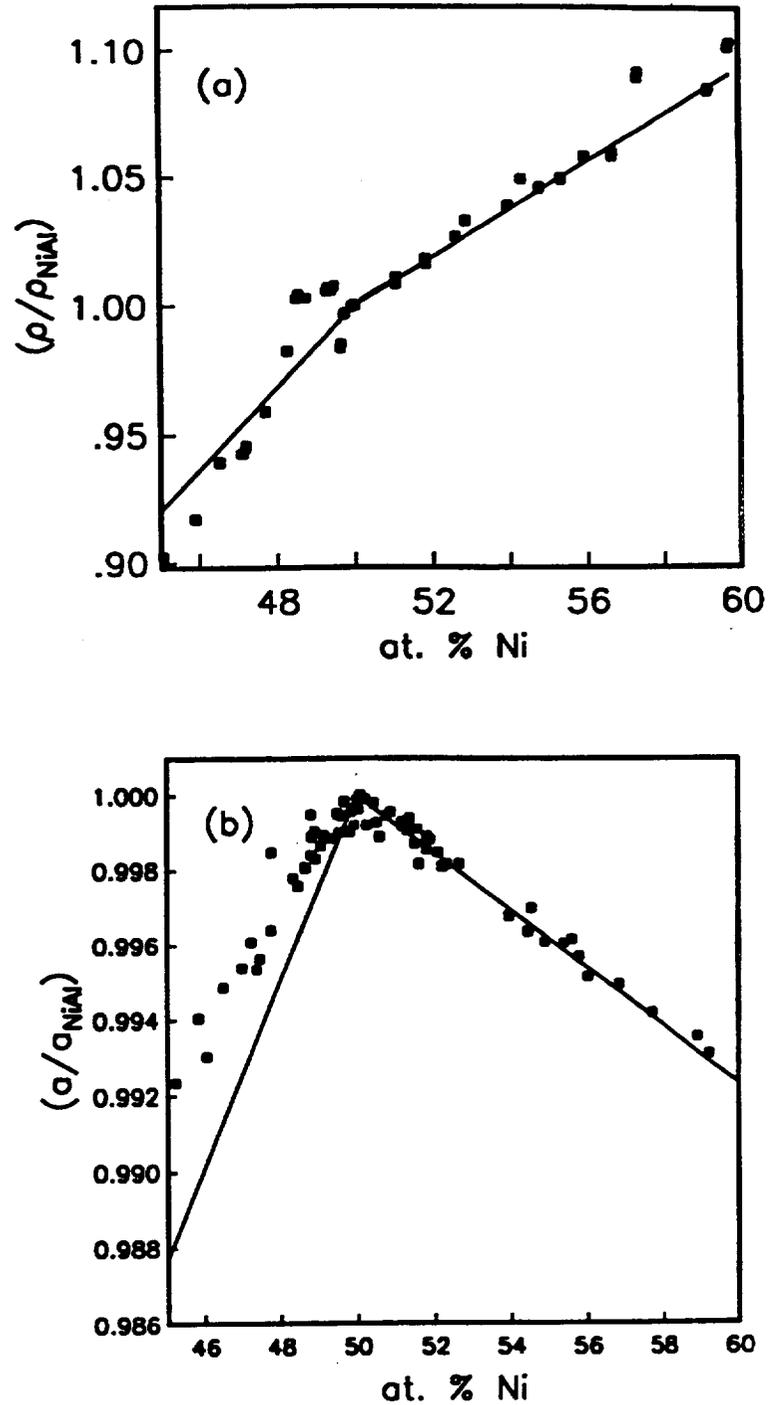


Fig. 3

(a) Density and (b) lattice parameter of non-stoichiometric NiAl alloys as a function of Ni concentration, normalized to their stoichiometric values. The solid squares denote results from different investigators (see ref. 7). The lines denote the BFS predictions, corresponding to the lowest energy states (solid squares and triangles) in Fig. 2.

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