COMPUTATIONAL MODELING METHOD FOR SUPERALLOYS

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Introduction

Computer modeling based on theoretical quantum techniques has been largely inefficient due to limitations on the methods or the computer needs associated with such calculations, thus perpetuating the notion that little help can be expected from computer simulations for the atomistic design of new materials. In a major effort to overcome these limitations and to provide a tool for efficiently assisting in the development of new alloys, we developed the BFS method for alloys (ref. 1), which together with the experimental results from previous and current research that validate its use for large-scale simulations, provide the ideal grounds for developing a computationally economical and physically sound procedure for supplementing the experimental work at great cost and time savings.

Background

The BFS method for alloys succeeds over other competing techniques in that it is not limited to any specific number of elements and it is not restricted to any particular crystallographic structure. These are major obstacles for other techniques, usually limited to the treatment of a few elements and just binary alloys. Moreover, other techniques only provide reliable results for bulk calculations offering little confidence in applications to extended defects (surfaces, interfaces). The BFS method is based on quantum perturbation theory and the solution of trascendental equations for each atom in the sample, in order to compute their contribution to the total energy. Thus, the computational requirements are trivial, favoring the use of BFS for large-scale simulations. The method relies on first-principles determined parameters with general transferrability to any situation, as opposed to competing techniques that have the additional disadvantage that their parameters or potentials should be determined and optimized for each specific application.

Based on the idea of determining the energy of formation of arbitrary atomic configurations (ΔH), the method determines the energy contribution of each atom (ε_i), partitioning this contribution into a strain (ε_i^{strain}) and a chemical component (ε_i^{chem}), providing separate information on the structural and compositional features of the sample (ref. 1). The two contributions are linked by a coupling function g_i so that $\Delta H = \sum_i \varepsilon_i = \sum_i (\varepsilon_i^{strain} + g_i \varepsilon_i^{chem})$. The three terms ($\varepsilon^{strain}$, ε^{chem}, g) are evaluated by solving perturbation theory-based equations which require input parameters determined for each element and each binary combination of elements via first-principles calculations. This amounts to solving three trascendental equations for each atom in the sample.

The BFS method has been recently applied to assist in HITEMP projects investigating the role of alloying additions to NiAl. Due to its simplicity and physically sound foundation, the method provides detailed atomistic information regarding fundamental properties (i.e. solubility limit of such additions, their site preference, metastable structures, formation of precipitates, interfacial segregation, physical properties, etc). The method is meant to provide a useful tool in the process of alloy design, by giving much needed insight in the basic mechanisms at the atomic level that guide the formation of the alloy and its ensuing properties. Due to its minimal hardware, time and cost requirements, it gives an alternative source of information that can only enhance the knowledge gained through experimental work.

Figs. 5-10 summarize the work done for NiAl-based alloys. In essence, the same procedure is now being applied to the study of partitioning ratios in superalloys, by individually examining the role of each alloying component and the interaction between them. In this study, we built a large set of sufficiently large atomic configurations, considering almost every possible atomic distribution in a given lattice. With the advance knowledge that all the alloys studied experimentally are bcc-based, we restricted the calculation to such crystallographic structure. First, we examined the defect structure of non-stoichiometric NiAl alloys (ref. 2), succesfully reproducing every known experimental fact: substitutional defects, triple defects, vacancies and their location, dependence of the lattice parameter with concentration, etc. (Fig. 6). We later added, separately, Ti, Cr, and Cu atoms, examining in each case the site preference of each element as a function of concentration and in the presence of other alloying additions, as well as the solubility limit and the formation of precipitates.

For Ti, it was found that it forms Heusler Ni_2AlTi precipitates above $x_{Ti} \sim 5\%$, in agreement with experiment. This was found by analyzing a large number of possible atomic configurations and defining the ground state structures for each concentration as the minimum energy states, finding that below 5 at. % Ti, disordered configurations are energetically favorable, but with a clear departure of ordered states (Heusler) beyond that value (Fig. 7). For Cr, a similar analysis determined that the solubility limit is approximately 1 at. % Cr, with the formation of α-Cr precipitates beyond that value. This is in excellent agreement with experiment (Fig. 8) and the known features of the ternary phase diagram, We later studied 4- and 5-element systems, concentrating on the interaction between the different alloying additions and how that affects the phase structure of the alloy. The 5-element (Ni-22.56Al-9.47Ti-33.5Cr-1.95Cu) alloy shown in Fig. 10 is a good example of the type of information that is easily available with this technique: the numerical simulation using BFS for calculating the energy shows that Ti and Cr retain their individual behavior (Heusler and α-Cr precipitate formation, respectively) with the addition of Cu segregation to the NiAl/Cr interface, as well as the formation of a new Ni-Al-Ti ordered phase in the NiAl/Cr interface. Other issues are apparent from the simulation, including the clustering of Ti atoms in the presence of antistructure Ni atoms in the NiAl matrix.

Progress in the BFS application to superalloys

We are currently in the initial stages of using a similar approach to the study of fcc-based superalloys. The main ingredient of the method - the parameterization of the BFS equations - is being implemented for up to 9 elements (Ni,Co,Cr,Al,Ti,Mo,Ta,W and Nb). Once the parameterization is completed, we plan to individually test the ternary, quaternary and then higher order additions to the base alloy and perform a similar analysis to that previously described for NiAl-

based alloys. By comparing the BFS predictions for the ternary cases with available - although scarce - experimental data, we expect to develop the necessary confidence on the first-principles determined BFS parameters which will be the basis for the high-order calculations. Moreover, also in a similar fashion to the NiAl project, we will supplement our analytical BFS calculations with large-scale Monte Carlo/BFS computer simulations, concentrating on the temperature effects and simulated annealing, and its influence on the resulting microstructure.

In addition, previous work using BFS for the analysis of fcc Ni-based superalloys has been extensive and it provides a solid foundation to the upcoming research. Following the methodology described above (i.e. building a set of possible atomic configurations and calculating the energetics and properties with BFS), we completed the process of determining a specific set of physical properties (compressibility, density and energy of formation) to the experimental validation of the theoretical predictions. A Ni-25Al-12.5Cu-25Au alloy was specified from a set of 200+ alloys, and later processed and analyzed in the laboratory (Figs. 11-12).

The first step for our current program consists in the determination of the BFS parameters. These quantities (two for each pair of elements) as well as the necessary parameters for each individual atomic species (another four parameters) are determined using first-principles calculations. These parameters, unlike competing techniques, are determined once only and they are used, unchanged, in any other application involving these elements. The transferrability of the BFS parameters is a powerful advantage of BFS, as it allows for immediate application to other systems as soon as the initial work in determining them is completed. We are in the process of determining the necessary parameters for the 9 elements of interest (Ni,Al, Co,Cr,Ti,Mo,Ta,W and Nb) and the BFS parameters for every combination of them (Ni-Al, Ni-Co,...). Once this phase of the program is completed, we will proceed to analyze the behavior of each one of the alloying additions (Co, Ti, ...) in the Ni-Al-Cr base alloy, their solubility limit, the site preference scheme, etc. , and later examine higher-order combinations. In doing so, we expect to gain understanding on the observed and expected behavior of the final alloys, based on our knowledge on the individual effects and how each new element added modifies the behavior of the previous ones.

Conclusions

The BFS technique is capable of:

1) Determine the energetics, lattice parameter and other properties of complex alloys. 2) Provide the calculational basis for large-scale computer simulations of the alloy formation process therefore introducing substantial time and cost savings by assisting in the alloy design process. 3) Model complex systems: previous work dealt with up to 5-component, 3-phase systems which exhibit interfacial segregation. 4)With additional computational modules, it can be extended to calculate mechanical properties as well as improved modeling of the heat treatment and its relation to the microstructure of the alloy.

References

1. Bozzolo, G., Ferrante, J. and Kobistek, R., J. Computer-Aided Mater. Design **1** (1993) 305; Bozzolo, G. and Ferrante, J., J. Computer-Aided Mater. Design **2** (1995) 113.

2. Bozzolo, G., Noebe, R.D., Ferrante, J. and Amador, C., Scripta Metall. Mater. **33** (1995)1907.

OBJECTIVE

- To apply a recently developed computational modeling technique (the BFS method for alloys) to assist in the determination of superalloy properties.

- To introduce a new methodology in alloy design focusing on time, cost and hardware savings.

Fig. 1

THE BFS METHOD FOR ALLOYS

GENERAL CONCEPT

- Calculates the energy of formation of a predetermined atomic configuration for a given bulk composition.
- By comparing the energy of different configurations, it is then possible to determine the ground state structure by finding the minimum energy configuration.
- The calculation provides the energy of formation, lattice parameter and bulk modulus for each configuration. By adding other modules, other physical and mechanical properties could also be predicted.

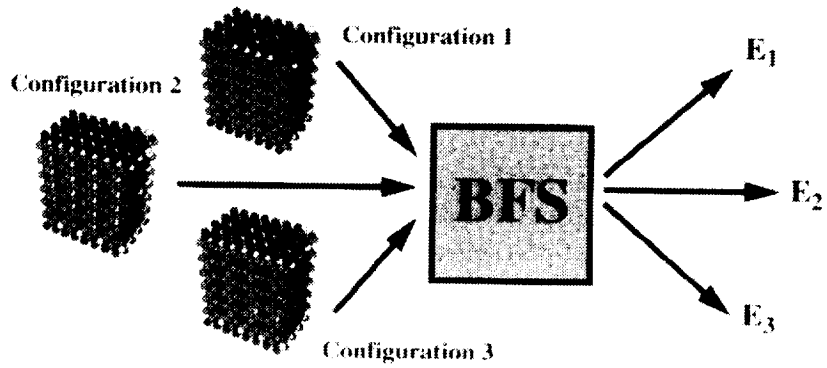


Fig. 2

THE BFS METHOD

- The energy of formation of an arbitrary alloy structure is the sum of individual atomic contributions in the alloy

$$\Delta H = \sum_i \varepsilon_i$$

- The energy of each atom consists of a strain energy (structural effects) and a chemical energy (compositional effects) contribution, linked by a coupling factor g

$$\varepsilon_i = \varepsilon_i^{strain} + g_i \varepsilon_i^{chem}$$

- The three quantities are determined by using methodology derived from Equivalent Crystal Theory, which is based on quantum perturbation theory.

- This involves solving transcendental equations for each term, for each atom, where the parameters used are determined only once, via first-principles calculations.
  - The parameterization is universal and does not change with each specific application.
  - The parameterization does not rely on experimental input.

Fig. 3

THE BFS METHOD : PROCEDURE

ANALYTICAL CALCULATIONS

1. Construct an arbitrary distribution of N atoms of different species in arbitrary sites.
2. Compute the energy of formation of such a structure:
   - For each atom, compute the contribution to the energy of formation by solving the BFS equations.
   - Add the contributions.
   - Compare the result with that of other distributions to determine the configuration with minimum energy.

THE QUALITY OF THE RESULTS DEPENDS ON THE NUMBER AND TYPE OF CONFIGURATIONS CONSIDERED

Output: Information on the ground state structure as well as metastable states.
Trends and behavior of properties (i.e. , lattice parameter dependence on composition).

NUMERICAL CALCULATIONS

Monte Carlo algorithms for simulating the heat processing of the sample.

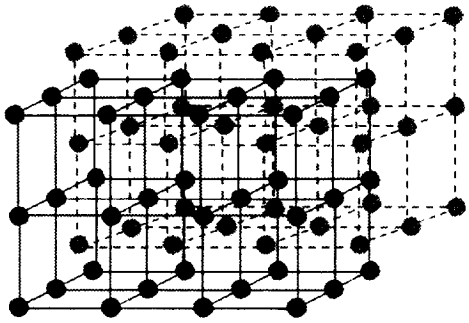
Output: Details on the microstructure; influence of temperature.

Fig. 4

DETERMINATION OF THE DEFECT STRUCTURE OF BINARY NiAl ALLOYS

B2 structure

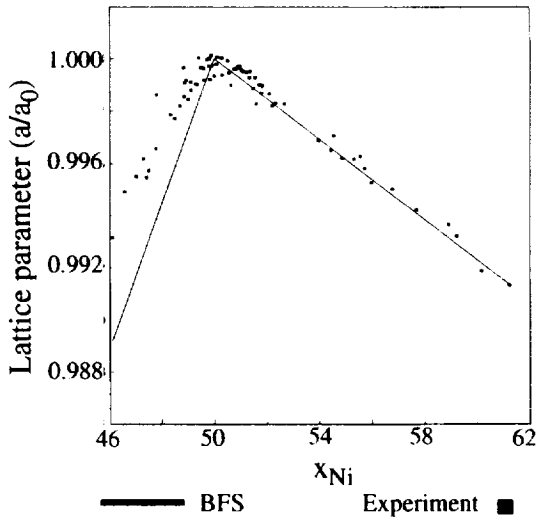
72-atom cell typically used for calculations



Different configurations are created by locating atoms and vacancies in different sites.

A large set of configurations can be created with possible distributions of atoms and vacancies.

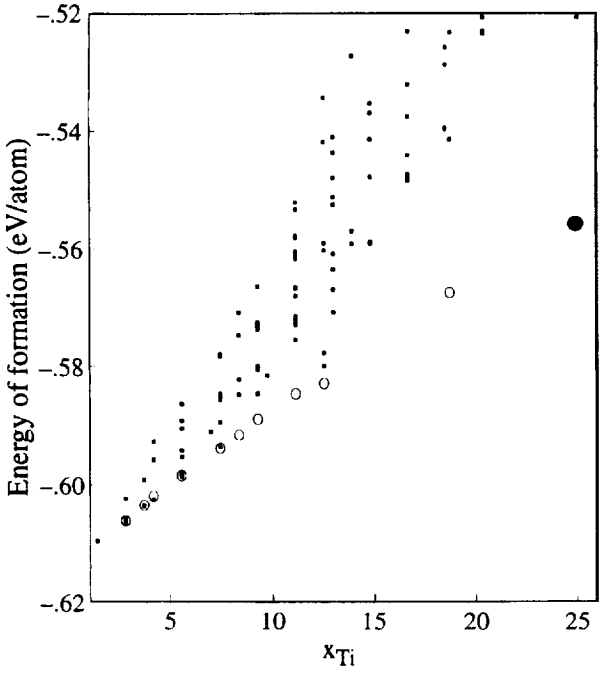
The energy is then computed with BFS for each configuration in the set.



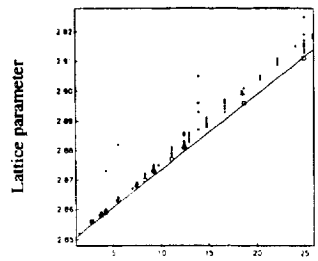
BFS results: obtained from the minimum energy structure at each concentration, from a 200+ set of possible distributions.

Fig. 5

ENERGY OF FORMATION OF 150 Ni_{50} $(Al,Ti)_{50}$ CONFIGURATIONS



- Below 5 at. % Ti, the energy for disordered solid solutions is less than that for Heusler ordering.
- Above 5 at. % Ti, the energy for Ti in Heusler ordered arrangements is less than that for random solid solution configurations.
- From this analysis the solubility for Ti can be estimated at 5 at. % Ti.
- Lattice paramter of the constituent phase can also be determined.



○ Heusler ordering ● Ni_2AlTi -Heusler phase ■ Disordered structures

Fig. 6

MONTE CARLO/BFS SIMULATIONS OF THREE Ni-Al-Ti ALLOYS

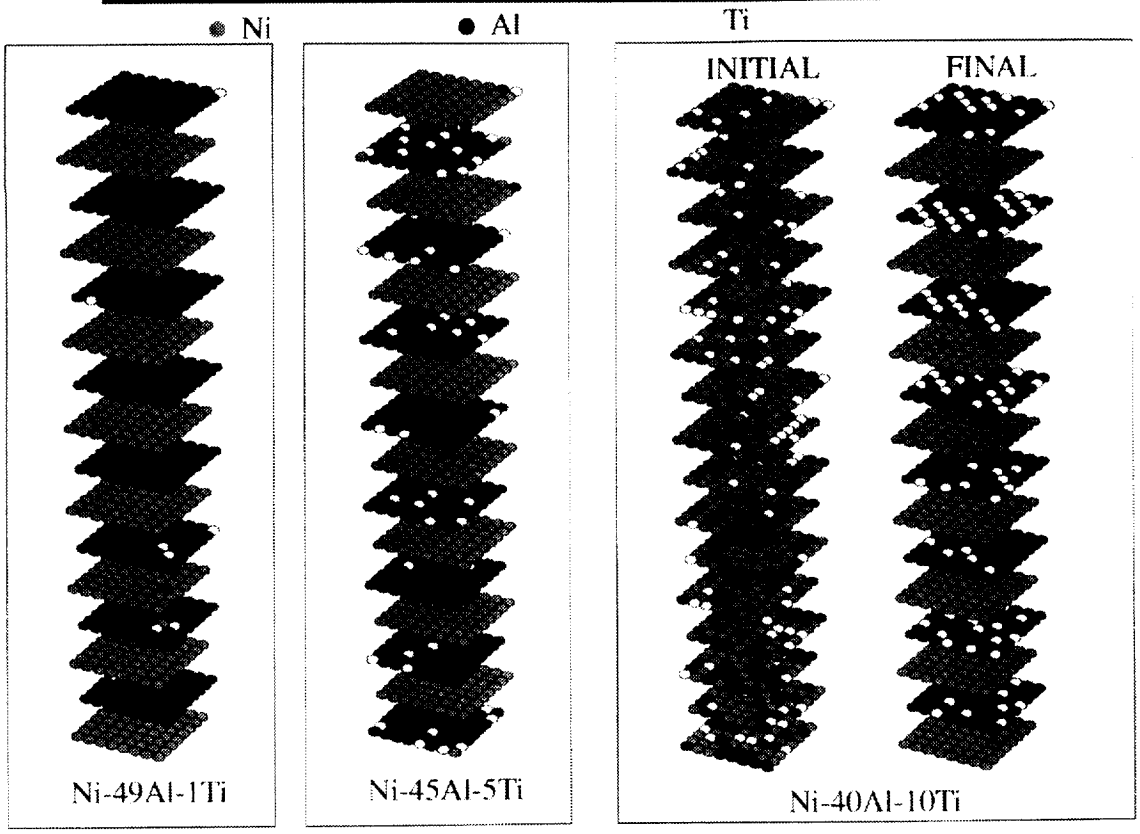


Fig. 7

Microstructure of $Ni_{50}(Al,Ti)_{50}$ Alloys

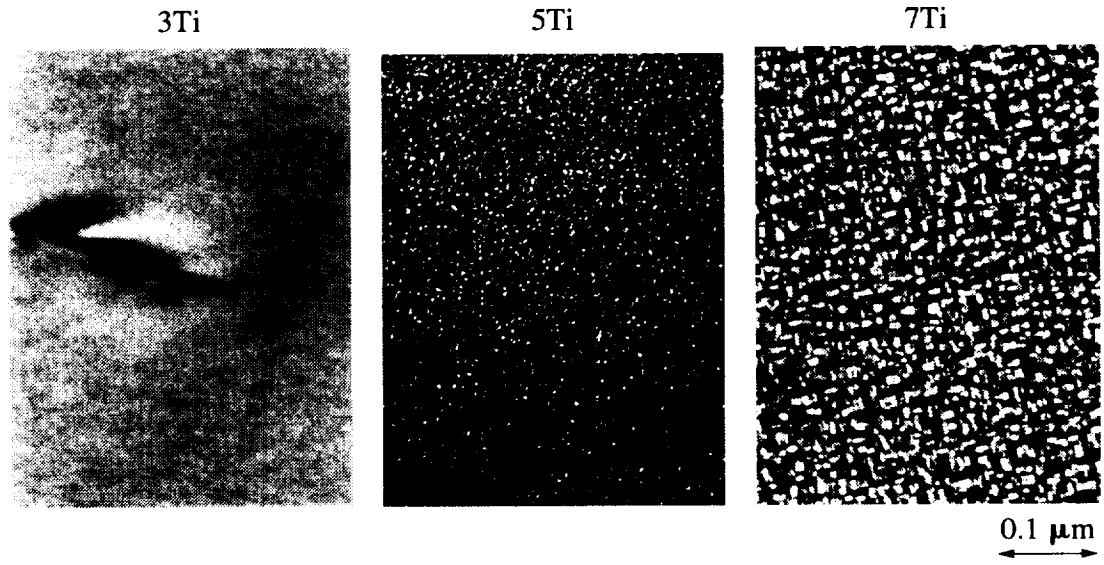


Fig. 8

Monte Carlo/BFS simulations for two Ni-Al-Cr alloys

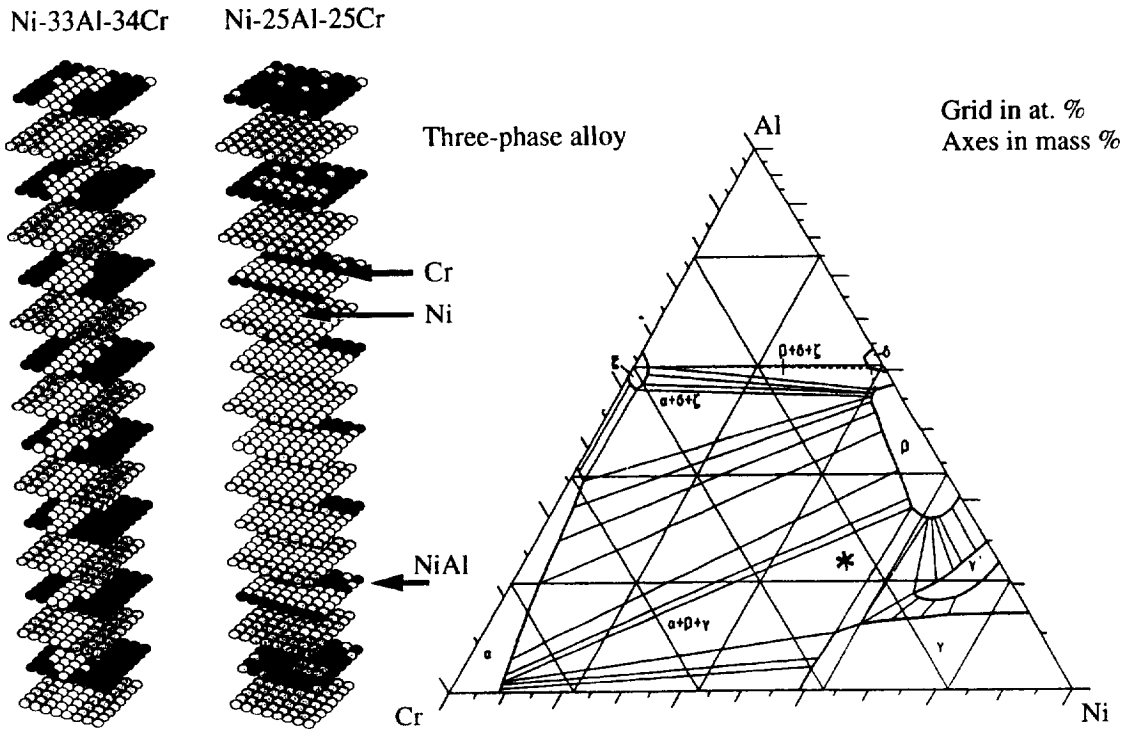


Fig. 9

PENTALLOY

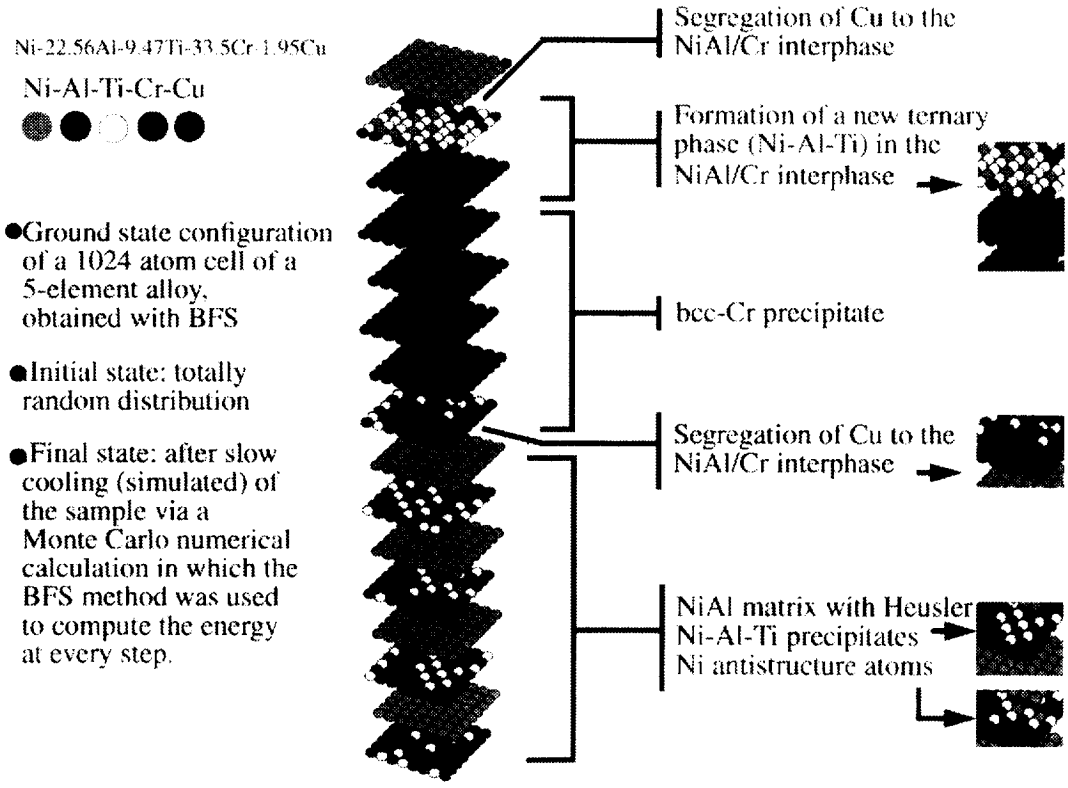


Fig. 10

FCC ALLOYS

BFS WAS PREVIOUSLY APPLIED TO THE DETERMINATION OF PHYSICAL PROPERTIES OF FCC-BASED QUATERNARY ALLOYS:

- A set of 350+ (Ni-Al-Cu-Au) alloys was defined and studied.
- Classified according to their density, compressibility and energy of formation.
- These alloys were later made and analyzed to confirm theoretical predictions.
- Methodology will be applied to the study of up to 9 component superalloys.

Fig. 11

MONTE CARLO/BFS SIMULATION OF A Ni-25Al-12.5Cu-25Au ALLOY

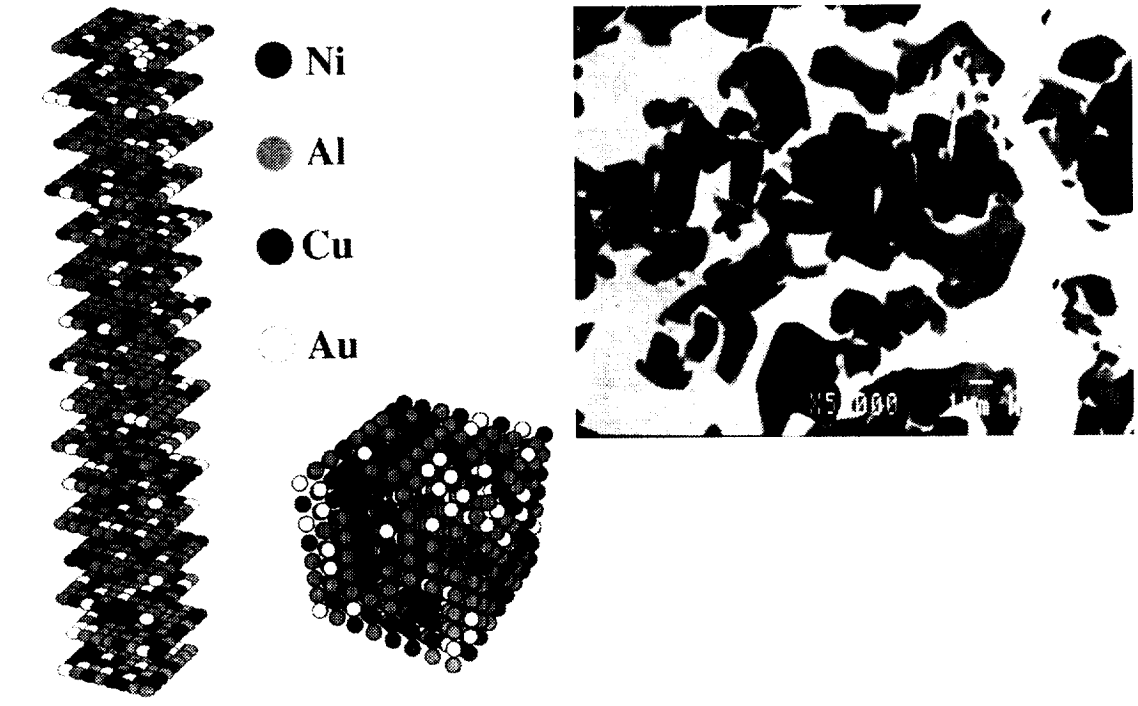


Fig. 12

APPLICATION OF BFS TO SUPERALLOYS

FOLLOWING A SIMILAR PROCEDURE TO THAT USED FOR NiAl ALLOYS, THE BFS METHOD WILL BE USED TO:

- INVESTIGATE THE BASIC PROPERTIES OF Ni-Al-Cr FCC-BASED ALLOYS
- INVESTIGATE THE BEHAVIOR OF ALLOYING ADDITIONS TO THE BASE ALLOY
  - INDIVIDUALLY, STUDYING ALL POSSIBLE QUATERNARY SYSTEMS.
  - SIMULTANEOUSLY INCREASING THE NUMBER OF ADDITIONS, STUDYING THE INTERACTION BETWEEN THEM AND THE RESULTING BEHAVIOR.
  - STUDYING THE FUNDAMENTAL PROPERTIES OF THE RESULTING ALLOYS.

Fig. 13

SUMMARY

- The BFS method has been used to determine the structure of NiAl alloys of increasing complexity, ranging from the binary B2 NiAl alloy to a 5-element alloy.
- The methodology was used to first determine, theoretically, specific properties of a 4-element fcc alloy, then verified experimentally.
- BFS parameters were determined for 9 alloy components (Ni, Al, Cr, Co, Ti, Mo, Ta, W and Nb) for application in superalloys.

Fig. 14

CONCLUSIONS

- Computer modeling using BFS provides the same description of NiAl, NiAl+Ti and NiAl+Cr properties that experiment does but also provides much needed additional information on atomistic effects.

- BFS efficiently assists in alloy design, providing detailed information concerning, for example

  - alloy energetics
  - site occupancy
  - lattice parameter
  - precipitate structure
  - solubility limits
  - lattice misfit
  - temperature effects

- The flexibility of BFS can be extended to any arbitrary system, with any number of components and crystallographic structures. The methodlogy will be applied to the study of 9-component superalloys.

- At minimal cost, time, and personnel requirements, provides valuable support for alloy development programs.

Fig. 15

FUTURE WORK

•BFS INPUT:

Determine BFS parameters for Ni, Al, Cr, Co, Ti, Mo,Ta,W, and Nb.

Determine BFS parameters for all the binary combinations.

•ANALYTICAL BFS CALCULATIONS

Determine properties of ternary, quaternary, etc. alloys

•MONTE CARLO/BFS SIMULATIONS

Determine partitioning ratios γ/γ'.

Fig. 16