A New Method of Alloy Design Using a Genetic Algorithm and Molecular Dynamics Simulation and Its Application to Nickel-Based Superalloys

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A new method of alloy design was proposed using a genetic algorithm and molecular dynamics simulations. In this method, evaluations of physical quantities using molecular dynamics simulations and an efficient global search using a genetic algorithm allow optimization of an equilibrium composition for a multi-component alloy satisfying a given design rule. The alloy design method was used to design nickel-based superalloys in the elemental systems simulating those of TMS-63 and CMSX-2. The obtained atom fractions in the γ phase and γ' phase, and atom fractions in the Ni and Al sublattices of the γ' phase were compared with the experimental values. The comparisons showed that the global features of TMS-63 and CMSX-2 were reproduced well. Furthermore negative lattice misfits were of about 1% and positive elastic misfits for c_{11} and c_{12} were of about 10% for both alloys. Finally sources of the inaccuracies for the obtained atom fractions and possible improvements for the design method were discussed.

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I. Introduction

Considerable expectations have been placed on computer simulations as aids in developing new alloys. Physical properties invaluable in developing new alloys are calculated by computer simulations for a given alloy structure and composition. Molecular dynamics simulation method is the most suitable to calculate mechanical properties among various computer simulation methods. Alloy design is essentially an optimization problem to search for an alloy's structure and composition in order to satisfy a given design rule. In this sense, an alloy design is recognized as a kind of inverse problem. It is, however, impossible to optimize a composition for a multi-component alloy by a round robin approach using molecular dynamics simulations, because of the great computational demand.

A new method of alloy design was proposed by combining a genetic algorithm and molecular dynamics simulations⁽¹⁾. The genetic algorithm is a biologically inspired optimization method mimicking the evolution of life⁽²⁾⁻⁽⁴⁾. Living things have optimized properties under a given environment based on their self-organization and evolution. Evolution can also be recognized as a kind of inverse problem. If the living thing and its environment are replaced by an alloy and a design rule respectively, it seems possible that alloy design could be accomplished by a method similar to biological self-organization and evolution. During evolution, natural selection occurs according to each living thing's properties. In the case of alloy design, its properties are calculated by molecular dynamics simulations. Self-organization is effectively taken

into account by assuming a specific form of an alloy gene in the genetic algorithm. The proposed method provides optimization of a composition for a multi-component alloy under a given design rule by evaluating physical quantities using molecular dynamics simulations and making an efficient global search using the genetic algorithm.

This paper describes the new method of alloy design using the genetic algorithm and molecular dynamics simulations. Design of several nickel-based superalloys is done to demonstrate the method's usefulness and results are reported here.

II. Methodology

First, various conventional methods to design nickel-based superalloy are briefly reviewed and their features and faults are discussed. Then the basic algorithm of the new alloy design method and each computation step of the algorithm are described in detail.

1. Conventional alloy design methods

(1) Multiple regression analysis⁽⁵⁾⁽⁶⁾

In nickel-based superalloys the γ' phase precipitates coherently in the γ phase solid solution so that its high temperature strength and resistance to creep deformation are improved for the alloys. It is important to investigate the dependencies of compositions and a volume ratio of the γ phase and γ' phase on the bulk alloy composition. Many experimental data on nickel-based multi-element alloys have been accumulated in the last decades. These experimental data were interpolated by the multiple regression analysis in order to optimize properties of the alloy.

The multiple regression analysis is practical and reli-

able as long as an optimized composition is found within the composition space where there are many experimental data, i.e. an interpolation regime. When an optimized composition is found outside such a composition space, i.e. an extrapolation regime, its accuracy drops. In that case, further experiments to obtain data on the volume ratio, alloy composition of each phase and modification of the regression formulae are required.

(2) PHACOMP method⁽⁷⁾

Although Fe-based, Ni-based, and Co-based alloys were used equally in early heat resistant superalloys, Ni-based superalloy became more important after the precipitation hardening mechanism of the γ' phase was identified. In the 1960's high-temperature strength was further improved by increasing the volume of the γ' phase which could be done by adding strengthening elements, such as Al and Ti. On the other hand, it was also found that unfavorable phases, such as the σ phase, were precipitated for some alloy compositions. The PHACOMP (phase computation) method was developed to predict the conditions for σ phase precipitation. The PHACOMP method uses the electron vacancy density of the metal element iN_i^v , defined as the number of states of d -electrons above the Fermi level per single atom. The electron vacancy density of the element iN_i^v is used to define the electron vacancy density of an alloy $\bar{N}^v$,

$$\bar{N}^v = \sum_i N_i^v \cdot \Delta n_i \quad (1)$$

$$N_i^v = 10.66 - (e/a)_i \quad (2)$$

where Δn_i is the concentration of element i in the alloy and $(e/a)_i$ is the number of valence electrons per single atom. The PHACOMP method predicts that precipitation of the σ phase does not take place when $\bar{N}^v$ remains below a critical value.

It is, however, questionable that a validity of the assumption that the electron vacancy density of an alloy is equal to a mean value of electron vacancy density of a metal element. Further the PHACOMP method can not predict an optimized alloy composition.

(3) d -Electron alloy design method⁽⁸⁾⁻⁽¹¹⁾

In this method, parameters of the electronic states of transition metal elements in an alloy are calculated using the DV-X α molecular orbital method⁽¹²⁾⁽¹³⁾. The d -electron density $\bar{M}^d$ and the bond order $\overline{BO}$ of an alloy are evaluated for the model cluster of the γ' phase in which an Al atom located at the center of the model cluster is replaced by a 3d transition metal element (Ti, V, Cr, Mn, Fe, Co, Ni, or Cu), or a 4d transition metal element (Zr, Nb, or Mo), or a 5d transition metal element (Hf, Ta, or W),

$$\bar{M}^d = \sum_i M_i^d \cdot \Delta n_i \quad (3)$$

$$\overline{BO} = \sum_i BO_i \cdot \Delta n_i \quad (4)$$

where Δn_i is the concentration of element i in the alloy. The d -electron density $\bar{M}^d$ of an alloy is much more reli-

able for design than $\bar{N}^v$ of the PHACOMP method. Both the d -electron density $\bar{M}^d$ and the bond order $\overline{BO}$ of the alloy are good indicators for selecting elements to be used in the alloy. Only the addition of a single transition atom element to the Al sublattice of the γ' phase is considered, addition to the Ni sublattice and any correlation due to multiple addition of transition atoms are ignored in this method. Furthermore the d -electron alloy design method can not predict an optimized alloy composition.

(4) Cluster variational method⁽¹⁴⁾⁻⁽¹⁸⁾

This method predicts equilibrium compositions of the γ' phase and the γ phase, the γ'/γ volume ratio, lattice misfit, and atom fraction in the sublattice of the γ' phase at a tetrahedral cluster with interaction via the Lennard-Jones potential. The lattice misfit δ_a is determined as a difference of lattice constants between the γ' and γ phases,

$$\delta_a = \frac{a^{\gamma'} - a^{\gamma}}{a^{\gamma}} \quad (5)$$

An equilibrium concentration is obtained so that the tie-line principle is satisfied. Comparisons between the calculated values using the cluster variational method and the experimental values using the atom probe method show good agreement for various commercial and experimental alloys⁽¹⁹⁾.

It is, however, important to take into account the difference of elastic constants between the γ' phase and the γ phase so as to increase high-temperature strength further, because superalloys are used under tensile stress⁽²⁰⁾. For this reason, attention should be paid not only to the lattice misfit δ_a , but also to the elastic misfits $\delta_{c_{ij}}$ defined as

$$\delta_{c_{ij}} = \frac{c_{ij}^{\gamma'} - c_{ij}^{\gamma}}{c_{ij}^{\gamma}} \quad (6)$$

where $ij=11, 12$, or 44 . The elastic misfits are not taken into account in the cluster variational method. Although high-temperature strength is affected by the γ'/γ volume ratio, the precipitation of the σ phase is problematic. Thus an examination is probably needed using the PHACOMP method or other more rigorous methods for the equilibrium composition obtained in the cluster variational method.

2. New alloy design method

It is desirable that the alloy design be based on the calculated values of the chemical potential μ , lattice misfit δ_a , elastic misfits $\delta_{c_{ij}}$, electron vacancy density $\bar{N}^v$, and d -electron density $\bar{M}^d$ without using experimental values of the equilibrium composition and the γ'/γ volume ratio. These physical quantities are calculated at a finite temperature using the first-principle molecular dynamics simulations for a given equilibrium composition. It is, however, impossible to optimize an equilibrium composition for a multi-component alloy by a round robin approach using molecular dynamics simulations, because of the huge computational demand. This problem prohibits re-

searcher from designing alloys using solely molecular dynamics simulations.

A new method of alloy design is proposed to solve this problem by combining molecular dynamics simulations and a genetic algorithm. A genetic algorithm is a biologically inspired mathematical method to solve complex optimization problems. In the proposed method, evaluations of physical quantities using molecular dynamics simulations and an efficient global search using a genetic algorithm allows an optimization of the equilibrium composition for a multi-component alloy with a given design rule. The basic algorithm of the proposed method is described briefly. Each step is treated in sub-sections II.2.(1) to II.2.(11). Figure 1 summarizes the design method.

(1) Input data –step (a)

Several input parameters have to be read in step (a). They are N_g , $k_{\max}$, Δn , P_{co} , P_{mut} , and c_{ls} . N_g is the number of genes. $k_{\max}$ is the number of generations to be calculated and is hence equal to the number of iterations from steps (d) to (j). Δn is an increment of density used in calculations of chemical potentials of each element. P_{co} and P_{mut} are probabilities of a cross-over and a mutation, respectively. P_{co} and P_{mut} are normalized for a pair of gene and for each bits of gene, respectively. c_{ls} is a parameter for linear scaling in the calculation of the fitness value.

Fig. 1 A new method of alloy design is proposed to solve this problem by combining molecular dynamics simulations and a genetic algorithm. In this method, evaluations of physical quantities using molecular dynamics simulations and an efficient global search using the genetic algorithm allows an optimization of an equilibrium composition for a multi-component alloy satisfying a given design rule.

(2) Initialization of physical quantity database –step (b)

The physical quantity database is initialized in step (b). The parameters of the database related to the γ phase are a lattice constant a^{Ni} , elastic constants c_{11}^{Ni} , c_{12}^{Ni} , cohesive energy E^{Ni} of nickel, and a slope of the lattice constant $da^{\gamma}/dp_i^{\gamma}$, slopes of the elastic constants $dc_{11}^{\gamma}/dp_i^{\gamma}$, $dc_{12}^{\gamma}/dp_i^{\gamma}$, a slope of the cohesive energy $dE^{\gamma}/dp_i^{\gamma}$ when the element i is added to the γ phase. The parameters of the database related to the γ' phase are lattice constant $a^{\text{Ni}_3\text{Al}}$, elastic constants $c_{11}^{\text{Ni}_3\text{Al}}$, $c_{12}^{\text{Ni}_3\text{Al}}$, cohesive energy $E^{\text{Ni}_3\text{Al}}$ of Ni_3Al intermetallic compound, and a slope of the lattice constant $da^{\gamma'(\text{Ni})}/dp_i^{\gamma'(\text{Ni})}$, slopes of the elastic constants $dc_{11}^{\gamma'(\text{Ni})}/dp_i^{\gamma'(\text{Ni})}$, $dc_{12}^{\gamma'(\text{Ni})}/dp_i^{\gamma'(\text{Ni})}$, a slope of the cohesive energy $dE^{\gamma'(\text{Ni})}/dp_i^{\gamma'(\text{Ni})}$ when the element i is added to the nickel sublattice of the γ' phase and a slope of the lattice constant $da^{\gamma'(\text{Al})}/dp_i^{\gamma'(\text{Al})}$, slopes of the elastic constants $dc_{11}^{\gamma'(\text{Al})}/dp_i^{\gamma'(\text{Al})}$, $dc_{12}^{\gamma'(\text{Al})}/dp_i^{\gamma'(\text{Al})}$, a slope of the cohesive energy $dE^{\gamma'(\text{Al})}/dp_i^{\gamma'(\text{Al})}$ when the element i is added to the aluminum sublattice of the γ' phase. These parameters are obtained by molecular dynamics simulations for various alloys and intermetallic compounds.

(3) Generation of initial alloy gene –step (c)

Compositions of alloys are written in alloy genes. Each alloy gene represents an alloy with a specific composition. Initial compositions are generated using a random number so that each alloy has a random composition. The composition is written as a geno-type as described below. As a result, initial alloy compositions are distributed over the entire alloy composition space. Such a distribution allows a global search to be made among all possible alloy compositions. Structure of the alloy gene is described in Section II.3 in detail.

(4) Conversion of geno-type to pheno-type –step (d)

A binary expression of the alloy gene is called the geno-type and it is needed for a cross-over and a mutation. On the other hand, a decimal expression of the alloy gene is called the pheno-type. The geno-type is converted to the pheno-type in this step.

(5) Calculation of physical quantity –step (e)

For the obtained alloy composition, a lattice constant, elastic constants, free energy, and chemic potentials are calculated using the physical quantity database. Effects of multi-additive elements are assumed as linear superpositions of each additive element. Details are described in Section II.4.

(6) Fitness –step (f)

Fitness indicates the degree of satisfaction for a given design rule. The minimal design rule for a nickel-based superalloy is that the tie-line principle has to be satisfied for each additive element. The fitness function is determined so as to be equal to unity when the tie-line principle is satisfied exactly. The functional form of the fitness is discussed in Section II.5.

(7) Discrimination –step (g)

The alloy gene with the maximum fitness value is selected from all alloy genes. If the selected value is larger than $f_{\max}$, then the alloy composition search is finished and the process goes to step (k). Otherwise the search is continued by proceeding to step (h).

(8) Linear scaling –step (h)

An optimization using the genetic algorithm is very efficient as long as the fitness value is small. The efficiency, however, goes down for larger fitness values so that a large number of searching steps is needed to reach the optimum fitness value. To prevent an inefficient search, fitness values are scaled using the linear scaling method. The scaled fitness value f' is obtained by scaling the raw fitness value f as below:

$$f' = a_{ls}f + b_{ls} \quad (7)$$

where coefficients a_{ls} and b_{ls} are evaluated by two conditions: (i) the average value of the scaled fitness f'_{av} is equal to the average value of the raw fitness f_{av} ; (ii) the maximum value of the scaled fitness $f'_{\max}$ is c_{ls} times of the average value of the raw fitness f_{av} .

$$a_{ls} = (c_{ls} - 1) \frac{f_{av}}{f_{\max} - f_{av}} \quad (8)$$

$$b_{ls} = (1 - a_{ls})f_{av} \quad (9)$$

When a fitness value scaled by the linear scaling method becomes negative, the negative fitness value is replaced by a null value.

(9) Selection –step (i)

N_g genes with large fitness values are selected from N_g genes by the roulette method. First, a fan-shaped piece on a roulette wheel is assigned where its area is proportional to the fitness value of each gene. Then the wheel is spun and a gene is selected according to the fan-shaped piece where the ball steps. N_g genes are selected by repeating N_g spins of the roulette wheel.

(10) Cross-over and mutation –step (j)

Cross-overs are generated in the selected N_g genes with a probability P_{co} . A pair of geno-types G_i and G_j are cut at an arbitrary point to get four fragments G_i^a , G_i^b , G_j^a , and G_j^b . Then G_i^a is linked to G_j^b and G_j^a is linked to G_i^b . Afterwards mutations are generated for each gene. A mutation is defined as reversing a bit of a geno-type with a probability P_{mut} .

(11) Output data –step (k)

Bulk composition, composition of the γ phase, composition of the γ' phase, composition of the Ni sublattice in the γ' phase, and composition of the Al sublattice in the γ' phase are obtained as a result of the alloy design. Lattice constant of the γ phase a^γ , lattice constant of the γ' phase $a^{\gamma'}$, elastic constants of the γ phase c_{ij}^γ , elastic constants of the γ' phase $c_{ij}^{\gamma'}$, lattice misfit δ_a , and elastic misfits $\delta_{c_{ij}}$ are also obtained.

3. Alloy gene

Various properties of alloys originate in a macroscopic structure, an atomistic structure, and an alloy composition. Nickel-based superalloys have a precipitation hardening structure in which the γ phase matrix surrounds the γ' phase precipitates. The γ phase is nickel-based solid-solution and the γ' phase is based on an Ni_3Al intermetallic compound with the L1_2 structure. Once elements used in the nickel-based superalloy are specified, the rest of freedoms of alloy designs are alloy compositions. Thus the alloy composition is encoded in the alloy gene. Compositions of each alloy are expressed by a binary number on the alloy gene. The alloy gene expressed by a binary number is defined as the geno-type gene. There are two ways to express alloy compositions, i.e. fraction of each element or the number of each element. For the alloy gene expressed by atomic fractions, there is a problem that a sum of each alloy fractions differ from 100% in the case of crossover or mutation. The alloy gene, expressed by the number of each element, is used in this paper.

The structure of an alloy gene of nickel-based superalloy is shown in Fig. 2. The alloy gene consists of three parts, i.e. the γ phase part, Ni sublattice of the γ' phase part, and Al sublattice of the γ' phase part. In each part, the number of Al, Ti, V, Cr, Co, Ni, Nb, Mo, Hf, Ta, W, and Re in the corresponding phase or sublattice is written. Two numbers under the element symbols in Fig. 2 indicate the data length and offsets used in translating a binary expression to a decimal expression. An alloy gene expressed as a decimal number is called the pheno-type gene. The data lengths of Ni in the γ phase, Ni in the γ' phase, and Al in the γ' phase are each 22 bits. Other elements have a 20 bits length. Offsets of Ni in the γ phase, Ni in the γ' phase, Al in the γ' phase are $2^{20}=1,048,576$ and offsets of other elements are $2^0=1$. Transforming the geno-type to the pheno-type is accomplished by translating gene's binary expression to decimal expression and adding the offset value for each element.

Fig. 2 The structure of an alloy gene of nickel-based superalloy is shown. Two numbers under the element symbols indicate the data length and offsets used in translating a binary expression to a decimal expression.

4. Evaluations of physical quantities

In a previous paper, molecular dynamics simulations were used to analyze lattice constant a , cohesive energy E_0 , and elastic constants c_{11} and c_{12} of nickel-based superalloys for Al, Ti, V, Cr, Co, Ni, Nb, Mo, Hf, Ta, W, and Re additions⁽²¹⁾. It was clarified that changes of all physical quantities evaluated were proportional to the changes of the concentration of additive elements. These results were fitted by the linear least square method and the obtained parameters are saved as a database is given below. A set of data which contains these parameters is called the physical quantities database.

(1) Lattice constant a^{Ni} , elastic constants c_{11}^{Ni} , c_{12}^{Ni} , and cohesive energy E^{Ni} for Ni

(2) Lattice constant $a^{\text{Ni}_3\text{Al}}$, elastic constants $c_{11}^{\text{Ni}_3\text{Al}}$, $c_{12}^{\text{Ni}_3\text{Al}}$ and cohesive energy $E^{\text{Ni}_3\text{Al}}$ for Ni_3Al intermetallic compound

(3) Slope parameter of lattice constant $da^\gamma/d\rho_i^\gamma$, slope parameters of elastic constants $dc_{11}^\gamma/d\rho_i^\gamma$, $dc_{12}^\gamma/d\rho_i^\gamma$, and slope parameter of cohesive energy $dE^\gamma/d\rho_i^\gamma$ for an addition of element i to Ni

(4) Slope parameter of lattice constant $da^{\gamma(\text{Ni})}/d\rho_i^{\gamma(\text{Ni})}$, slope parameters of elastic constants $dc_{11}^{\gamma(\text{Ni})}/d\rho_i^{\gamma(\text{Ni})}$, $dc_{12}^{\gamma(\text{Ni})}/d\rho_i^{\gamma(\text{Ni})}$, and slope parameter of cohesive energy $dE^{\gamma(\text{Ni})}/d\rho_i^{\gamma(\text{Ni})}$ for an addition of element i to the Ni sublattice of Ni_3Al

(5) Slope parameter of lattice constant $da^{\gamma(\text{Al})}/d\rho_i^{\gamma(\text{Al})}$, slope parameters of elastic constants $dc_{11}^{\gamma(\text{Al})}/d\rho_i^{\gamma(\text{Al})}$, $dc_{12}^{\gamma(\text{Al})}/d\rho_i^{\gamma(\text{Al})}$, and slope parameter of cohesive energy $dE^{\gamma(\text{Al})}/d\rho_i^{\gamma(\text{Al})}$ for an addition of element i to the Al sublattice of Ni_3Al

Suppose that elements including Ni and Al among 12 elements shown above are chosen and a single crystal nickel-based superalloy is cast consisting of these elements. Lattice constant a , cohesive energy E_0 , and elastic constants c_{11} and c_{12} for such a nickel-based superalloy are calculated with the physical quantities database using the following equations:

$$a^\gamma = a^{\text{Ni}} + \sum_i \frac{da^\gamma}{d\rho_i^\gamma} \rho_i^\gamma \quad (10)$$

$$c_{11}^\gamma = c_{11}^{\text{Ni}} + \sum_i \frac{dc_{11}^\gamma}{d\rho_i^\gamma} \rho_i^\gamma \quad (11)$$

$$c_{12}^\gamma = c_{12}^{\text{Ni}} + \sum_i \frac{dc_{12}^\gamma}{d\rho_i^\gamma} \rho_i^\gamma \quad (12)$$

$$E^\gamma = E^{\text{Ni}} + \sum_i \frac{dE^\gamma}{d\rho_i^\gamma} \rho_i^\gamma \quad (13)$$

$$a^{\gamma'} = a^{\text{Ni}_3\text{Al}} + \sum_i \frac{da^{\gamma'(\text{Ni})}}{d\rho_i^{\gamma'(\text{Ni})}} \rho_i^{\gamma'(\text{Ni})} + \sum_i \frac{da^{\gamma'(\text{Al})}}{d\rho_i^{\gamma'(\text{Al})}} \rho_i^{\gamma'(\text{Al})} \quad (14)$$

$$c_{11}^{\gamma'} = c_{11}^{\text{Ni}_3\text{Al}} + \sum_i \frac{dc_{11}^{\gamma'(\text{Ni})}}{d\rho_i^{\gamma'(\text{Ni})}} \rho_i^{\gamma'(\text{Ni})} + \sum_i \frac{dc_{11}^{\gamma'(\text{Al})}}{d\rho_i^{\gamma'(\text{Al})}} \rho_i^{\gamma'(\text{Al})} \quad (15)$$

$$c_{12}^{\gamma'} = c_{12}^{\text{Ni}_3\text{Al}} + \sum_i \frac{dc_{12}^{\gamma'(\text{Ni})}}{d\rho_i^{\gamma'(\text{Ni})}} \rho_i^{\gamma'(\text{Ni})} + \sum_i \frac{dc_{12}^{\gamma'(\text{Al})}}{d\rho_i^{\gamma'(\text{Al})}} \rho_i^{\gamma'(\text{Al})} \quad (16)$$

$$E^{\gamma'} = E^{\text{Ni}_3\text{Al}} + \sum_i \frac{dE^{\gamma'(\text{Ni})}}{d\rho_i^{\gamma'(\text{Ni})}} \rho_i^{\gamma'(\text{Ni})} + \sum_i \frac{dE^{\gamma'(\text{Al})}}{d\rho_i^{\gamma'(\text{Al})}} \rho_i^{\gamma'(\text{Al})} \quad (17)$$

Here ρ_i^γ , $\rho_i^{\gamma'(\text{Ni})}$, and $\rho_i^{\gamma'(\text{Al})}$ are the concentrations of the additive element i in the γ phase, Ni sublattice of the γ' phase, and Al sublattice of the γ' phase, respectively. These concentrations are normalized by the total number of atoms of the γ phase, Ni sublattice of the γ' phase, and Al sublattice of the γ' phase, respectively. The summations in eqs. (10) to (13) are made for all additive elements except Ni. In eqs. (14) to (17), the first summation terms are made for all additive elements except Ni, and the second summation terms are made for all additive elements except Al. It should be noted that all slope parameters defined for each element are obtained by adding a single element to the Ni or Ni_3Al matrix. Thus it is not rigorous to use eqs. (14) to (17) in the case of multiple element additions. However, it may be a good approximation as long as the concentration of additive element is low and they may give a fair approximation, even if the concentration of additive elements is high, because the main concern is relative differences of physical quantities between the γ and γ' phases.

Furthermore Heilmholtz free energy F of the superalloy is calculated using a cohesive energy E .

$$F^\gamma = -\frac{N^\gamma}{2} E^\gamma - TS^\gamma \quad (18)$$

$$F^{\gamma'} = -\frac{N^{\gamma'} + N^{\gamma'(\text{Al})}}{2} E^{\gamma'} - TS^{\gamma'} \quad (19)$$

where T , S , N^γ , $N^{\gamma'(\text{Ni})}$, and $N^{\gamma'(\text{Al})}$ are temperature, entropy, the total number of atoms in the γ phase, the total number of Ni sublattices in the γ' phase, and the total number of Al sublattices in the γ' phase, respectively. For each alloy gene, the total number of atoms in the γ phase N^γ , the total number of Ni sublattices in the γ' phase $N^{\gamma'(\text{Ni})}$, and the total number of Al sublattices in the γ' phase $N^{\gamma'(\text{Al})}$ are varied within a range determined by bit length and offset value of the alloy gene. Thus before calculating free energy F these numbers have to be normalized so that the ratios $N^{\gamma'(\text{Ni})}:N^{\gamma'(\text{Al})}=3:1$ and $N^\gamma:N^{\gamma'(\text{Ni})}+N^{\gamma'(\text{Al})}=1:1$ are kept.

Entropy S is calculated by counting the number of states of atomic configurations for additive elements as follows

$$S^\gamma = k_B \ln (N^\gamma C_{n_1}^\gamma \cdot N^{\gamma'} C_{n_1}^{\gamma'} \cdot \dots \cdot C_{n_f}^{\gamma'}) \quad (20)$$

$$S^{\gamma'} = k_B \ln \left(\frac{N^{\gamma'(\text{Ni})} C_{n_1}^{\gamma'(\text{Ni})} \cdot N^{\gamma'(\text{Al})} C_{n_1}^{\gamma'(\text{Al})} \cdot \dots \cdot C_{n_f}^{\gamma'(\text{Al})}}{N^{\gamma'(\text{Al})} C_{n_1}^{\gamma'(\text{Al})} \cdot N^{\gamma'(\text{Al})} C_{n_2}^{\gamma'(\text{Al})} \cdot \dots \cdot C_{n_f}^{\gamma'(\text{Al})}} \right) \quad (21)$$

where k_B , n_i^γ , $n_i^{\gamma'(\text{Ni})}$, $n_i^{\gamma'(\text{Al})}$, $n C_m$, and f are the Boltzmann constant, the number of atoms of the additive element i in the γ phase, the number of atoms of the additive element i in the Ni sublattice of the γ' phase, the number of atoms of the additive element i in the Al sublattice of the γ' phase, the number of combinations choosing n atoms among m atoms, and the number of elements in the superalloy, respectively.

When the total number of atoms is variable, a thermodynamically equilibrium state is given as the mini-

mum point of grand potential Ω

$$\Omega^\gamma = F^\gamma - \sum_i \mu_i^\gamma n_i^\gamma \quad (22)$$

$$\Omega^{\gamma'} = F^{\gamma'} - \sum_i \mu_i^{\gamma'} (n_i^{\gamma'(\text{Ni})} + n_i^{\gamma'(\text{Al})}) \quad (23)$$

where μ_i^γ and $\mu_i^{\gamma'}$ are chemical potentials of the element i in the γ phase and the γ' phase, respectively. Then chemical potential of the element i μ_i is calculated using the following equations:

$$\mu_i^\gamma = \frac{\partial F^\gamma}{\partial n_i^\gamma} \equiv \frac{F^\gamma(n_i^\gamma + \Delta n_i^\gamma) - F^\gamma(n_i^\gamma)}{\Delta n_i^\gamma} \quad (24)$$

$$\begin{aligned} \mu_i^{\gamma'} &= \frac{\partial F^{\gamma'}}{\partial (n_i^{\gamma'(\text{Ni})} + n_i^{\gamma'(\text{Al})})} \\ &\equiv \frac{F^{\gamma'}(n_i^{\gamma'(\text{Ni})} + n_i^{\gamma'(\text{Al})} + \Delta n_i^{\gamma'}) - F^{\gamma'}(n_i^{\gamma'(\text{Ni})} + n_i^{\gamma'(\text{Al})})}{\Delta n_i^{\gamma'}} \end{aligned} \quad (25)$$

where Δn_i is increment of the number of atoms of element i , and the number of atoms of all other elements is kept constant.

5. Design rule and fitness

For an alloy consisting of many elements, concentration of each element at an equilibrium state is determined by the tie-line principle so that chemical potential of each element is balanced in each phase. The design rule for nickel-based superalloy is determined so that the tie-line principle is satisfied in the γ and γ' phases, as shown in Fig. 3.

First, a tangent line is drawn using free energy of the γ phase F^γ and its slope s_i^γ at $\rho_i = \rho_i^\gamma$, toward to the γ' phase in order to obtain an estimated free energy of the γ' phase $\tilde{F}^{\gamma'}$ at $\rho_i = \rho_i^\gamma$:

$$\tilde{F}^{\gamma'}(\rho_i^\gamma) = s_i^\gamma(\rho_i^{\gamma'} - \rho_i^\gamma) + F^\gamma(\rho_i^\gamma) \quad (26)$$

where the slope s_i^γ is given by chemical potential of the γ phase

$$\rho_i^{\gamma'} = N^{\gamma'} \mu_i^\gamma. \quad (27)$$

Next, another tangent line is drawn using free energy of the γ' phase $F^{\gamma'}$ and its slope $s_i^{\gamma'}$ at $\rho_i = \rho_i^{\gamma'}$, toward to the γ phase in order to obtain an estimated free energy of the γ phase $\tilde{F}^\gamma$ at $\rho_i = \rho_i^{\gamma'}$:

$$\tilde{F}^\gamma(\rho_i^{\gamma'}) = s_i^{\gamma'}(\rho_i^\gamma - \rho_i^{\gamma'}) + F^{\gamma'}(\rho_i^{\gamma'}) \quad (28)$$

where the slope $s_i^{\gamma'}$ is given by chemical potential of the γ' phase

$$s_i^{\gamma'} = (N^{\gamma'(\text{Ni})} + N^{\gamma'(\text{Al})}) \mu_i^{\gamma'}. \quad (29)$$

The tie line of the element i is obtained when both the difference between the estimated free energy of the γ phase $\tilde{F}^\gamma$ and the free energy of the γ phase F^γ at $\rho_i = \rho_i^\gamma$, and the difference between the estimated free energy of the γ' phase $\tilde{F}^{\gamma'}$ and the free energy of the γ' phase $F^{\gamma'}$ are minimized. Thus a fitness f is determined as the quantity to indicate the degree of satisfaction of the design rule.

Fig. 3 For an alloy consisting of many elements, concentration of each elements at an equilibrium state is determined by the tie-line principle so that a chemical potential of each element is balanced in each phase. The design rule for nickel-based superalloy is determined so that the tie-line principle is satisfied in the γ and γ' phases.

$$\begin{aligned} f = & \left[1 + \frac{1}{M-1} \sum_i \left| \frac{\tilde{F}^\gamma(\rho_i^{\gamma'}) - F^\gamma(\rho_i^{\gamma'})}{F^\gamma(\rho_i^{\gamma'})} \times 100 \right| \right. \\ & \left. + \frac{1}{M-1} \sum_i \left| \frac{\tilde{F}^{\gamma'}(\rho_i^\gamma) - F^{\gamma'}(\rho_i^\gamma)}{F^{\gamma'}(\rho_i^\gamma)} \times 100 \right| \right]^{-1} \end{aligned} \quad (30)$$

where M is the number of elements in the alloy, and the summation is made for all elements except nickel.

III. Alloy Design

Atom fractions of the γ and γ' phases were measured for several nickel-based superalloys, i.e. TMS-63 alloy⁽²²⁾ and CMSX-2⁽²³⁾. For equivalent systems of these alloys, alloy designs were made using the proposed design method.

1. Systems to be designed

TMS-63 is a 5-component alloy consisting of Ni, Al, Cr, Mo, and Ta. Its is known as one of the highest performance heat-resistant superalloys. CMSX-2 is an 8-component alloy consisting of Ni, Al, Co, Cr, Mo, W, Ti, and Ta and it has been applied in many gas-turbine systems. Although Mo is used in CMSX-2, the fraction is 0.3% which is so small as to be negligible. Alloy designs were made for the element systems in which combinations of elements were identical to the above mentioned two superalloys, i.e. the Ni-Al-Cr-Mo-Ta element system, which is equivalent to TMS-63 superalloy, and the Ni-Al-Cr-Co-W-Ti-Ta element system, which is equivalent to CMSX-2 superalloy, in order to investigate performances of the proposed alloy design method. The temperature appearing in eqs. (18) and (19) was determined to be 1273 K which is typical for gas-turbine blade materials in operation.

2. Input parameters

Input parameters, N_g , $k_{\max}$, Δn , P_{co} , P_{mut} , and c_{ls} are listed in Table 1 for Ni-Al-Cr-Mo-Ta and Ni-Al-Co-Cr-W-Ta-Ta systems. The number of alloy genes was 100 for both systems. Typical values were chosen for P_{co} and P_{mut} ; the former is chosen to be close to unity and the latter is often chosen to be equal to the reciprocal of the total number of bits of each gene in order to generate a single mutation for each gene on average. Efficiencies of optimization of alloy composition are strongly dependent on the values of these parameters. The most efficient values of P_{co} and P_{mut} were searched for around the typical values, as explained in the next section.

IV. Results and Discussion

Nickel-based superalloys were designed in the elements systems simulating TMS-63 and CMSX-2.

1. Optimization

Dependencies of fitness values on P_{co} and P_{mut} were surveyed for Ni-Al-Cr-Mo-Ta systems. The fitness values were averaged between 80 to 100 generations. Dependency of the averaged fitness values on P_{co} is shown in Fig. 4(a), where P_{mut} was fixed at 3.0×10^{-3} . Dependency of the averaged fitness values on P_{mut} is shown in Fig. 4(b), where P_{co} was fixed at 0.9. Although there are two peaks at P_{mut} equaling 3.0×10^{-3} and 6.0×10^{-3} in Fig. 4(b), the obtained alloy compositions are very close to each other and are recognized as an identical composition. On the other hand the reciprocal of the total number of bits of each gene is 3.0×10^{-3} . P_{co} equaling 0.9 and P_{mut} equaling 3.0×10^{-3} are obtained as the most efficient parameter values. For the Ni-Al-Cr-Mo-Ta element system, optimization is successful and the obtained maximum raw fitness and the maximum scaled fitness among 100 genes after 5000 generations are 0.7181 and 1.356, respectively. Fitness values are shown for the first 100 generations in Fig. 4(c).

Dependencies of fitness values on P_{co} and P_{mut} were surveyed for the Ni-Al-Cr-Co-W-Ti-Ta element system next. The fitness values were averaged between 80 to 100 generations. Dependency of the averaged fitness values on P_{co} is shown in Fig. 5(a), where P_{mut} was fixed at 3.0×10^{-3} . Dependency of the averaged fitness values on P_{mut} is shown in Fig. 5(b), where P_{co} was fixed at 0.9. P_{co} equaling 0.9 and P_{mut} equaling 3.0×10^{-3} are obtained as the most efficient parameter values. For the Ni-Al-Cr-

Fig. 4 For the Ni-Al-Cr-Mo-Ta element system, optimization was successful. (a) Dependency of the averaged fitness values on P_{co} , where P_{mut} was fixed at 3.0×10^{-3} , (b) dependency of the averaged fitness values on P_{mut} , where P_{co} was fixed at 0.9, and (c) fitness values for the first 100 generations.

Co-W-Ti-Ta element system, optimization is successful and the obtained maximum raw fitness and the maximum scaled fitness among 100 genes after 5000 generations are 0.8548 and 1.540, respectively. Fitness values are shown for the first 100 generations in Fig. 5(c).

2. Atom fractions and misfits

The experimental and calculated atom fractions and fractions in sublattices for the Ni-Al-Cr-Mo-Ta element system obtained after 5000 generations are shown in Fig. 6. Figure 7 presents the analogous data for the Ni-Al-Cr-Co-W-Ti-Ta element system. Both figures indicate that the obtained alloy compositions and atom fractions in both sublattice of the γ' phase reproduce the global features of the measured values well. The compositions however are not in very good agreement with the measured values for some additive elements. The deviations are large, especially for the additive elements with small fractions.

The designed values of lattice constant, elastic constants, and their misfits obtained for the Ni-Al-Cr-Mo-Ta and Ni-Al-Cr-Co-W-Ti-Ta systems are shown in Tables 2 and 3, respectively. The designed alloys have two common features (1) Negative lattice misfit of about 1% is observed. (2) Positive elastic misfits for c_{11} and c_{12} of about 10% are observed. It is well known that nickel-

Table 1 Input parameters.

Parameters	Ni-Al-Cr-Mo-Ta system	Ni-Al-Co-Cr-W-Ti-Ta system
N_g	100	100
$k_{\max}$	5000	5000
Δn	1.0×10^{-2}	1.0×10^{-2}
P_{co}	0.90	0.90
P_{mut}	3.0×10^{-3}	3.0×10^{-3}
c_{ls}	2.0	2.0

Fig. 5 For the Ni-Al-Cr-Co-W-Ti-Ta element system, optimization was successful. (a) Dependency of the averaged fitness values on P_{co} , where P_{mut} was fixed at 3.0×10^{-3} , (b) dependency of the averaged fitness values on P_{mut} , where P_{co} was fixed at 0.9, and (c) fitness values for the first 100 generations.

based superalloy possesses a large mechanical strength in the high temperature regime due to precipitation hardening structure and its mechanical strength there is strongly dependent on the shape of the precipitant, although the mechanism is not well understood. Furthermore the shape of the precipitant is determined by the values of the lattice misfit. On the other hand, the elastic misfits are related to elastic deformation, but not to a plastic deformation directly. There might, however, be a correlation between the early stage of plastic deformation and the elastic misfits. Thus lattice and elastic misfits might be good quantities for indicating the degree of precipitation hardening. The features mentioned above for lattice and elastic misfits seem essential to understanding the high mechanical strength in the high temperature regime.

3. Sources of inaccuracies and possible improvements

There are several sources for the inaccuracies of the results described in the previous section. The first is the method to calculate internal energy. It should be noted that the internal energy E of the alloy with multi-additive elements is approximated by linear superposition of the alloy with a single additive element in eqs. (10) to (17). This approximation might cause an inaccuracy in energy evaluation for multi component alloys. The most straight-

Fig. 6 Experimental and calculated atom fractions and fractions in sublattices for the Ni-Al-Cr-Mo-Ta element system obtained after 5000 generations. The obtained atom fractions in both the γ and γ' phases reproduced the global features of the experimental values.

Fig. 7 Experimental and calculated atom fractions and fractions in sublattices for the Ni-Al-Cr-Co-W-Ti-Ta element system obtained after 5000 generations. The obtained atom fractions in both the γ and γ' phases reproduced the global features of the experimental values.

Table 2 Physical quantities of the Ni-Al-Cr-Mo-Ta system.

	γ phase	γ' phase	Misfit
Lattice constant, $a/10^{-1}$ nm	3.773	3.741	-0.852%
Elastic constant, $c_{11}/10^{11}$ Pa	1.677	1.934	15.3%
Elastic constant, $c_{12}/10^{11}$ Pa	0.8654	1.074	24.1%

Table 3 Physical quantities of the Ni-Al-Co-Cr-W-Ti-Ta system.

	γ phase	γ' phase	Misfit
Lattice constant, $a/10^{-1}$ nm	3.790	3.666	-3.28%
Elastic constant, $c_{11}/10^{11}$ Pa	1.535	2.038	32.8%
Elastic constant, $c_{12}/10^{11}$ Pa	0.8247	1.276	52.4%

forward improvement is to make molecular dynamics simulations directly in the alloy design algorithm without using the physical quantity database or the approximation of eqs. (10) to (17). The next source is the potential parameters between different elements used in the molecular dynamics simulations. Although an arithmetic mean is used to obtain the parameters, this is obviously a crude approximation. It is difficult to obtain these parameters using experimental data. To obtain better potential parameters, the first principle electronic structure calculation can be used. The third source is the design rule. Although only the tie-line principle is used in this paper, it is not clear whether such a basis for the design rule for TMS-63 and CMSX-2 is valid. A possible change is to add the lattice and elastic misfits to the tie-line based design rule. The fourth source is the calculation of entropy. Only a configurational entropy is included in the free energy calculation. A vibrational contribution to entropy is however probably important for the Ni_3Al intermetallic compound⁽²⁴⁾. The last source of inaccuracies is the optimization algorithm. In this paper the simple genetic algorithm is used, which has weaknesses in accuracy and efficiency. A possible improvement is to use a more elaborate genetic algorithm.

V. Conclusion

Molecular dynamics simulations are the most suitable way to calculate mechanical properties among computer simulation methods. It was however impossible to optimize an equilibrium composition for a multi-component alloy by a round robin approach using molecular dynamics simulations, because of the huge computational demand. This problem has prohibited researchers from designing alloys using solely molecular dynamics simulations. A new method of materials design was proposed using a genetic algorithm and molecular dynamics simulations. In this method evaluations of physical quantities using molecular dynamics simulations and an efficient global search using the genetic algorithm provide an optimization of an equilibrium composition for a multi-component alloy satisfying a given design rule. The de-

sign rule used in this paper was the tie-line principle. The alloy design method was used to design nickel-based superalloys in element systems simulating TMS-63 and CMSX-2. The optimum values for input parameters such as P_{co} and P_{mut} were determined by systematic parameter surveys. The obtained atom fractions in the γ and γ' phases, and atom fractions in the Ni and Al sublattices of the γ' phase were compared with experiments. The comparisons showed that the global features of TMS-63 and CMSX-2 were reproduced well. The obtained compositions however were not in very good agreement with the measured values for some additive elements. The deviations were large especially for additive elements at small fractions. Furthermore negative lattice misfit of about 1% and positive elastic misfits for c_{11} and c_{12} of about 10% were obtained for both alloys. Finally sources of inaccuracies and possible improvements for the proposed alloy design method were discussed. With these improvements and estimations for phase stability, the proposed alloy design method should provide a new computational tool for materials science.

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