Electronic character of interdiffusion of metals in nickel

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Ni-base single crystal (SC) superalloys, which are used for turbine blades and vanes in modern aero engines, are characterized by cuboidal γ' phase precipitates coherently embedded in Ni γ matrix [1]. Substitutational alloying elements in γ matrix play an important role in creep deformation through the control of atomic interduffusions. Recently, Reed *et al.* [2, 3] have systematically investigated the interdiffusion of refractory and platinum-group metals in Ni γ matrix solid solution from the periodic table using Cameca SX50 electron microprobe analyzer (EPMA) technique. Their results demonstrated that a well established correlation was observed between interdiffusion coefficients of alloying elements and their positions in the periodic table. Elements furthest from the center of the periodic table display the largest values of interdiffusion coefficients, while elements at the center present the smallest as shown in Fig. 1a. It appears therefore that the magnitudes of interdiffusion coefficients are strongly correlated with their Goldsmith atomic radius of the interdiffusing transition metal species shown in Fig. 1b. The minima of atomic radius vs. atomic number which arise in the middle of the periodic table are the elements Rh and Ir for the 4d and 5d series, respectively. This, however, gives rise to the conclusion that the larger the atom size of an element added into Ni, the faster the interdiffusion rate of the alloying atoms. If these interdiffusion coefficients are fitted into the phenomenological Arrhenius relationship $D = D_0 \exp(-Q/kT)$, which is consistent with the vast majority of the diffusion data for metals (see [4]), then the activation energies for the interdiffusion of alloying elements in Ni are plotted in Fig. 1c. Therefore, the maximum activation energies are located at the middle of the periodic table, i.e., at Ir and Re.

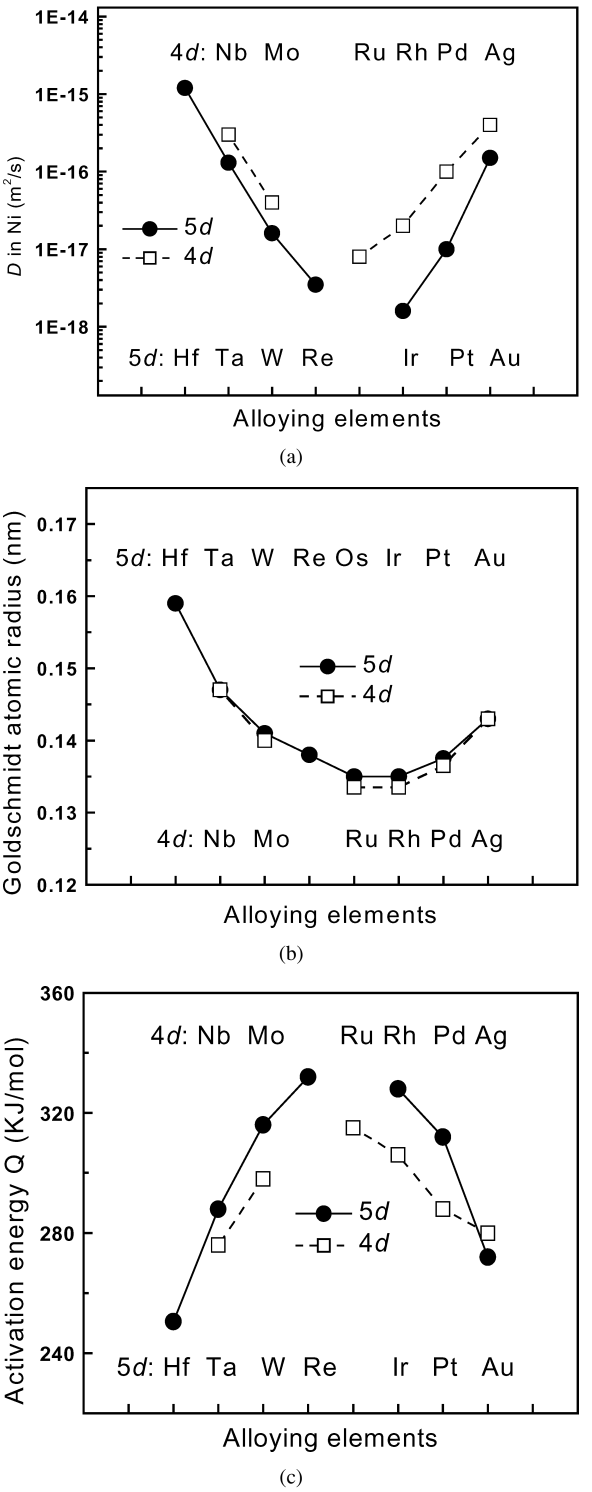
In the diffusion theory, it is known that the interdiffuion of alloying elements in Ni is via a vacancy-assisted substitutaonal diffusion mechanism [5], and that the significant lattice (atomize size) distortion always accompany this. As the radius of diffusion atoms gets larger, the diffusion coefficients in a given host should decrease. This theory is based on the fact that the local atomic interactions of the strained lattice as the vacancy and diffusing atom exchange sites, and the activation energy for interdiffusion is expected to increase with increasing misfit [6]. It is, however, opposite to the observations of Figs 1a and b. In that cases, elements lie on the middle of the period for which the misfit is smallest exhibits the lowest values of the interdiffusion coeffieients, elements towards the far west or far east of the period, such as Hf and Au, respectively, have the largest rates of interdiffusion. Moreover, it would appear that the activation energy decrease as the misfit increases.

During the interdiffisuion process, atoms will overcome the interaction bonding energy barrier between solute and solvent, and also the interaction binding energy of vacnay-solvent interaction. When solute atoms are added into the Ni solid solution, the charge transfer between Ni and solute atoms occurs. Therefore, the bond order, which represents both the bonding strength and charge transfer between solute and solvent, is a better parameter than Goldsmith atomic radius of pure elements in describing the correlation between the interdiffusion and the electrons character. In this letter, the correlation between the interdiffusion of 4d and 5d elements in Ni and their electronic character have been investigated through the calculations of the Mayer bond orders. The underlying electronic mechanism for this correlation has been analyzed.

As a molecular cluster approach, DMol3 package which is based on the density functional theory [7] was used in this study. In general, molecular cluster approach is suitable for studying electronic properties that are primarily a function of local environment [8]. The double numerical basis set are employed for Ni and alloying elements. The degree of convergence of the self-consistent iterations, measured by (r.m.s.) changes in the charge density, was set to be 10^{-5}, which allowed the energy to converge to 10^{-5} Ryd. All calculations in the present research were performed with the generalized-gradient approximation (GGA) proposed by Perdew and Wang [9]. The Mayer bond order and the total valence [10] were employed to evaluate the atomic bond strength.

The bond order in nature is the overlap of electron wave functions between atoms, which can be used to quantitatively measure the strength of atomic bonding and thus assess the interaction strengthening of solute-solvent. In this study, the Mayer bond orders are calculated [10]. The definition of Mayer bond order between atoms A and B is as follow:

$$\mathrm{BO}_{\mathrm{AB}} = 2\sum_{\mu\in \mathrm{A}}\sum_{\mu\in \mathrm{B}}[(P^{\alpha}S)_{\mu\nu}(P^{\alpha}S)_{\nu\mu} + (P^{\beta}S)_{\mu\nu}(P^{\beta}S)_{\nu\mu}] \qquad (1)$$



(a)

(b)

(c)

Figure 1 (a) The experimentally measured interdiffusion coefficients of alloying element in Ni binary solutions at 900 °C for 4d and 5d elements. (b) The Goldssmith atomic radius of 4d and 5d elements. (c) The interfussuion coefficient as expressued by Arruen sexpression for 4d and 5d elements at 900 °C [3].

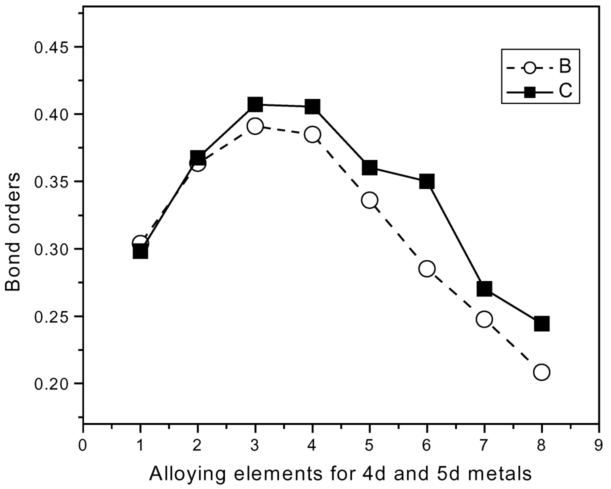


Figure 2 The calculated Mayer bond orders of 4d and 5d elements in Ni.

where P^{α}, P^{β} are the density matrices, S is the overlap matrix of the wave functions. To examine the interaction between the solute atoms (alloying atoms) and the solvent (Ni atoms), the bond orders as a result of alloying addition in Ni have been calculated. The calculation model was an fcc cluster with 63 atoms in size. The center solvent Ni atom was replaced by one solute alloying element atom, and the separation between the center alloying atom and the surface atoms is beyond the second nearest distance. This model significantly reduces the surface effect on the bond order calculations, and allows the study of the solute-solvent interactions without changing the symmetry of the cluster. The BO_{AB} values are calculated within the first nearest neighbor (FNN) B atoms around A site. The results indicate that the BO_{AB} value is small, if the separation between atoms A and B is beyond the FNN range, and thus can be neglected without altering the conclusions.

Fig. 2 shows the trend of bond orders calculated for 4d and 5d solute atoms substituted for Ni. It is similar as those in Fig. 1c for the actative energy barry. It indicates that the larger the bond order values, the higher the actative energy barry that atoms need to overcome during the interdiffusion process. By this correlation between the bond orders and the activative energy barry, the bond order could be used to partially describe the interdiffusion character. Since the bond orders describe both the interactive strength between atoms and the charge transfer of electrons between solute and solvent elements, it may be used to explain the controversy phenoma observed between Glosmist atom radius of pure elements and the interdiffusion coefficients in Fig. 1. In the interduffiuion process, the charge transfer between solute and solvent atoms occurs, and the 'atom radius' of solute atoms are closely related to the electron distribution induced by solvent. Therefore, the actual 'atom radius' of solute is usually hard to defined. Based on the character of bond orders, it is better to use bond order rather than 'atomic radius' of pure solute to correlate with interdiffusion coefficients. In addition, it was found that the peaks of bond orders are shifted to some extent in Fig. 2 for both 4d and 5d elements compared with the actative energy barriy and diffusion coefficients in Fig. 1. The reason may be that in addition to the interaction energy between solute and solvent atoms, the interaction binding energy between vacancy and solute make also contribution to the interdiffusion processing. The total diffusion activation energy essentially include the contributions from the interaction energy of vacancy and solute, and also the interaction energy between the solute and solvent atoms. *Therefore, from Fig. 1 of the measured activation energy for* 4d *and* 5d *elements in*

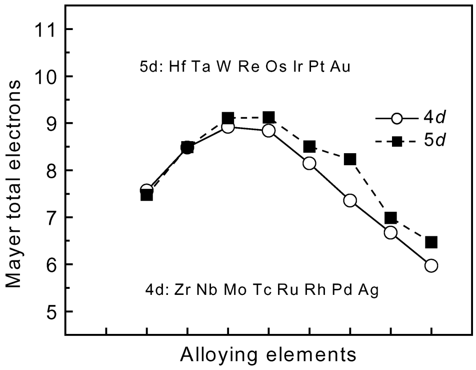


Figure 3 The calculated Mayer total valence electrons of 4d and 5d elements in Ni.

Ni, it can be anticipated that the interaction binding energy for Ru (4d) *and Ir* (5d) *will take important part in affect the trend of interdiffusion processing.*

In order to reveal the electronic mechanism underlying the interdiffusion, the total Mayer electrons of 4d and 5d elements in the Ni have been calculated as shown in Fig. 3. It is interesting to note that the total Mayer electrons of 4d and 5d elements in Ni yield the same trend as the bond orders. This indicates that the valence electrons of solute atoms dominated the bond order values, thus determine the activative energy solute-solvent part. *The interaction vacancy-solute binding energy and . . . needs further investigation. Induced by vacancy need study.*

The interdiffusion coefficient have been correlated with the bond orders of 4d and 5d metals in Ni solid solution instead of Goldsmith radios of atoms. The bond order partly describe the active energy barry that atoms will overcome in the diffusion processing. Mayer total valence electrons of alloying elements dominate the activeatve energy barry in the interdiffusion processing.

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