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Extra contribution of transition-metal solutes to the solid-solution hardening of nickel

Tetumori Shinoda*
Research Laboratory of Precision Machinery and Electronics, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Kin-ichi Masuda-Jindo
Department of Materials Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Yoshinao Mishima and Tomoo Suzuki
Research Laboratory of Precision Machinery and Electronics, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

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Experimental results on the solid-solution hardening of nickel alloys show that there is an anomalous hardening induced by transition-metal elements compared to the hardening induced by the *B* subgroup (*sp* valence) elements, which cannot be understood within the framework of the classical linear elasticity theory. It is demonstrated that this extra solution hardening by the transition-metal solute atoms can be correlated with the "chemical interaction" between the solutes and edge dislocations (band-structure-energy contribution to the solute-dislocation interaction). For this purpose, calculations of the chemical interaction energies, δE_{chem} have been carried out for fifteen kinds of transition metals and eight kinds of *B*-subgroup solute atoms using a tight-binding-type electronic theory of *s*-, *p*-, and *d*-basis orbitals.

I. INTRODUCTION

There have been many experimental efforts on the solid-solution hardening on various solvents, such as Fe and Nb with bcc crystal structure and Cu, Ag, Au, Al, and Pb with fcc crystal structures.[1-5] It is generally accepted that the solid-solution hardening can be described well in terms of the "elastic" interactions between solute atoms and dislocations, which has been proposed by Fleischer.[5,6] In the solid solution of nickel, however, it has often been observed that the linear and single-valued relationship does not hold between the increase in yield stress and an elastic interaction parameter.[7,8] Recently, two of the present authors and their co-workers have demonstrated quite clearly such an extra solution hardening in binary nickel alloys.[9] The results are reproduced in Fig. 1. Obviously, the plots of the increase in 0.2% flow stress per 1 at. % of the solute, $d\sigma/dc$, versus the size misfit parameter, $|\varepsilon_a|$, are split into two correlation curves, one for transition-metal elements and the other for *B*-subgroup elements. The values of $d\sigma/dc$ for transition-metal elements are anomalously larger than those for *B*-subgroup elements. The similar anomaly of the solution hardening by transition-metal elements has also been observed in a nickel-based $L1_2$ intermetallic compound Ni_3Al.[10-12]

These results indicate that the solution hardening of these systems can not be interpreted solely within the framework of the Fleischer-type elasticity theory. In order to understand the anomalous solution hardening of nickel as well as Ni_3Al, it is felt that a more fundamental theoretical approach, such as the microscopic electronic theories, are required. The semiclassical Thomas-Fermi approach,[13,14] however, is unsatisfactory for the determination of the interaction energy between two kinds of defects, i.e., a solute and a dislocation, in transition-metal-based alloys, where *d*-band energy plays a central

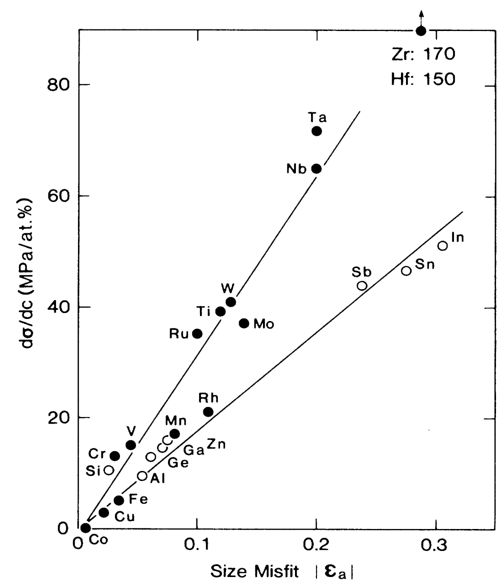

FIG. 1. Relation between the increase in yield stress of nickel at 77 K per 1 at. % of solute, $d\sigma/dc$, and the size-misfit parameter $|\varepsilon_a|$. The size-misfit parameter is defined by the absolute value of $(1/a)(da/dc)$, where a is the lattice parameter of nickel and da/dc the change in lattice parameter per 1 at. % of solute.

role. The estimation of such electronic interaction energy, hereafter referred to as "chemical" interaction energy, should be achieved by more appropriate electronic theory. However, the first-principles electronic theory[15] is too complicated to be applied to the interpretation of the energy associated with such lattice defects.

In the present paper, the "chemical" interaction energy between a solute (both transition-metal and *B*-subgroup elements) and an edge dislocation in nickel is derived for use in tight-binding-type electronic theory.[16,17] It is well known that in fcc metals the solution hardening is controlled by the motion of edge dislocations.[3–5] This is true even in nickel.[9] In accord with the experimental observation, the calculated result shows that the contribution of the chemical interaction to the solid-solution hardening in nickel is quite strong for transition-metal solutes and is almost absent for *B*-subgroup solutes. It will be presented that the chemical interaction energy is attributed to the characteristic *d*-electron hopping interactions, i.e., the *d*-*d* two-center integrals, between host nickel and a transition-metal solute.

II. PRINCIPLE OF CALCULATION

The chemical interaction energy δE_{chem} between a substitutional solute atom and an edge dislocation is defined by

$$\delta E_{\text{chem}} = \delta E_{\text{disl-sol}} - \delta E_{\text{disl}} - \delta E_{\text{sol}} \ , \tag{1}$$

where δE_{sol}, δE_{disl}, and $\delta E_{\text{disl-sol}}$ are the changes in the band-structure energies due to introduction of an isolated solute atom, an edge dislocation, and both a solute atom and an edge dislocation simultaneously into a pure and perfect crystal, respectively.

The change in the band-structure energies, δE_{sol}, δE_{disl}, and $\delta E_{\text{disl-sol}}$, can be calculated quite efficiently by using the second-moment approximation and Gaussian local density of states.[16–18] It is known that this type of tight-binding scheme leads to the essentially correct results for the interpretation of a wide variety of lattice defects in transition metals.[19–22] Within the self-consistent Hartree approximation,[16–18] the change in the band-structure energy due to any kind of lattice defect δE can be written as

$$\delta E = 2\sum_i \sum_\lambda \int_{-\infty}^{E_F} E[\rho_i^\lambda(E) - \rho_0^\lambda(E)]dE - \alpha_i^\lambda \int_{-\infty}^{E_F} \rho_0^\lambda(E)dE - (\alpha_i^\lambda/2) \int_{-\infty}^{E_F} [\rho_i^\lambda(E) - \rho_0^\lambda(E)]dE \tag{2a}$$

$$= 2\sum_i \sum_\lambda (2/\sqrt{2}\pi)\exp(-(E_F)^2/2\mu_2^\lambda)\{[(\mu_{2i}^\lambda)']^{1/2} - (\mu_2^\lambda)^{1/2}\} \ , \tag{2b}$$

where $\rho_0^\lambda(E)$ and $\rho_i^\lambda(E)$ are the local density of states for the perfect lattice and for the imperfect lattice having a certain kind of defect at atomic site *i*. The superscript λ stands for nine valence orbitals, i.e., *s*, p_x, p_y, p_z, *xy*, *yz*, *zx*, x^2-y^2, and $3z^2$-r^2 atomic wave functions. α_i^λ denotes the diagonal matrix elements of the defect perturbing potential for a λ orbital at atomic site *i*, and E_F is the Fermi energy of the system. The factor of 2 and the last two terms in the square brackets of Eq. (2a) are for the spin degeneracy and for the criterion of double counting of the electron-electron interaction energy.

In Eq. (2b), μ_2^λ is the second moment in the perfect lattice and $(\mu_{2i}^\lambda)'$ is the reduced second moment for the λ orbital at atomic site *i* in the imperfect lattice. This equation is derived under the condition that each atom is electrically neutral.[18,23] Noteworthy is that the present theory allows us to treat both transition-metal and *B*-subgroup impurities on the same basis. Summing up all the *s*-, *p*-, and *d*-electron hopping processes among atoms within the cutoff distance of 1.3 times the nearest-neighbor distance of the perfect fcc crystal, the reduced second moment $(\mu_{2i}^\lambda)'$ is given by

$$(\mu_{2i}^\lambda)' = \mu_{2i}^\lambda - (\mu_{1i}^\lambda)^2 = \sum_{i\,(\neq j)} \sum_{\lambda'} V_{ij}^{\lambda\lambda'} V_{ji}^{\lambda'\lambda} \ , \tag{3}$$

where $V_{ij}^{\lambda\lambda'}$ denotes the hopping integral between the λ orbital at atomic site *i* and the λ' orbital at atomic site *j*. μ_{1i}^λ is the first moment for the imperfect lattice equal to α_i^λ in Eq. (2a), and is determined by using the assumption of local charge neutrality.

The explicit expressions of the second moment μ_{2i}^λ are given for the perfect fcc crystal,[24] in terms of the two-center integrals among *s*, *p*, and *d* orbitals; that is, $ss\sigma$, $sp\sigma$, $pd\pi$, $sd\sigma$, $dd\delta$, etc.[25] The magnitude and the distance dependence of the two-center integrals, derived in Harrison's universal tight-binding theory,[26] are employed.

The *d*-*d*—coupling two-center integrals are given by

$$((dd\sigma), (dd\pi), (dd\delta)) = (-16.2,\ 8.75,\ -1.62)\hbar^2(r_d r_d')^{3/2}/mR_{ij}^5 \ , \tag{4}$$

where *m* and $\hbar$ are the electron mass and Planck's constant. r_d and r_d' are the *d*-state radius of each atom at atomic sites *i* and *j*, and R_{ij} is the distance between the atomic sites *i* and *j*. In the present calculation, the coefficient $(dd\delta)$ is assumed to be one tenth of $(dd\sigma)$. In Table I the *d*-state radius r_d for transition-metal solutes taken from Ref. 26 is summarized. The *s*-*d*— and *p*-*d*—coupling two-center integrals are given by

$$((sd\sigma), (pd\pi), (pd\sigma)) = (-3.16,\ 1.36,\ -2.95)\hbar^2 r_d^{3/2}/R_{ij}^{7/2} \ , \tag{5}$$

and the *s*-*s*—, *p*-*p*—, and *p*-*p*—coupling two-center integrals are given by

$$((ss\sigma), (sp\sigma), (pp\pi), (pp\sigma)) = (-1.40,\ 1.84,\ -0.81,\ 3.24)\hbar^2/mR_{ij}^2 \ . \tag{6}$$

For the perfect crystal, *s*-, *p*-, and *d*-atomic levels, E_s,

TABLE I. Number of s, p, and d electrons, N_s^{imp}, N_p^{imp}, and N_d^{imp}, and the d-state radius r_d (in nm). Also given are s-, p-, and d-band contributions to δE_{chem}: δE_s, δE_p, and δE_d (in eV). (N_s^{imp}, etc. are taken from Ref. 27 and r_d is from Ref. 26.)

Solute	N_s^{imp}	N_p^{imp}	N_d^{imp}	r_d	δE_s	δE_p	δE_d
Ti	0.685	0.722	2.539	10.8	−0.066	−0.040	−1.375
Zr	0.715	0.659	2.536	14.1	−0.131	−0.024	−2.714
Hf	0.818	0.768	2.324	14.4	−0.162	−0.123	−2.763
V	0.637	0.393	3.650	9.8	−0.034	−0.003	−1.224
Nb	0.657	0.649	3.579	12.8	−0.089	0.001	−2.422
Ta	0.770	0.776	3.332	13.4	−0.133	−0.117	−2.640
Cr	0.624	0.776	4.518	9.0	−0.017	−0.065	−1.018
Mo	0.649	0.795	4.407	10.4	−0.047	−0.095	−1.666
W	0.760	0.937	4.138	12.7	−0.119	−0.234	−2.450
Mn	0.646	0.785	5.489	8.6	−0.019	−0.067	−0.883
Fe	0.633	0.751	6.528	8.0	−0.006	−0.034	−0.613
Ru	0.641	0.788	6.400	10.5	−0.046	−0.091	−1.481
Co	0.644	0.740	7.533	7.6	−0.005	−0.021	−0.349
Rh	0.631	0.746	7.464	9.9	−0.033	−0.050	−1.143
(Ni)	0.651	0.721	8.551	7.1	0.000	0.000	0.000
Cu	0.699	0.733	9.505	6.7	0.004	0.002	−0.219

E_p, and E_d are determined so as to fit the numbers of s-, p-, and d-band electrons, N_s, N_p, and N_d, taken from linear muffin-tin orbital—atomic-spheres-approximation (LMTO-ASA) band-structure calculations.[27] For a transition-metal impurity, the numbers of s, p, and d electrons, N_s^{imp}, N_p^{imp}, and N_d^{imp}, are simply taken to be equal to those for the corresponding pure and perfect crystals composed of each impurity element.[27] These values are summarized in the first three columns of Table I. This assumption seems to be reasonable in view of the fact that the numbers of subband electrons do not depend strongly on the local atomic environment.[28] Furthermore, the values of N_s^{imp}, N_p^{imp}, and N_d^{imp} are quite similar to those determined[29] from the atomic energy levels E_s^{imp}, E_p^{imp}, and E_d^{imp} of the atomic-structure calculations by Herman and Skillman.[30]

For a B-subgroup solute impurity, the numbers of s and p electrons, N_s^{imp} and N_p^{imp}, are determined by using the atomic energy levels E_s^{imp} and E_p^{imp} taken from Ref. 30 and by assuming that $E_d^{\text{imp}} \rightarrow +\infty$, i.e., $N_d^{\text{imp}}=0$. The calculated values are presented in Table II, together with the values of $E_p^{\text{imp}}-E_s^{\text{imp}}$ and the electronic state of free atoms.

For the calculations of δE_{disl} and $\delta E_{\text{disl-sol}}$, we only take into account the interaction between an impurity atom and one of partial edge dislocations, since an edge dislocation is usually split into two partials in nickel. The atomic configuration around the partial edge dislocation is determined, for simplicity, from the analytical solution based on the isotropic linear elasticity theory.[31] The dissociation of the edge dislocation in this case is of the Schockley type according to $(a/2)[\bar{1}10] \rightarrow (a/6)[\bar{2}11] + (a/6)[12\bar{1}]$ on the (111) slip plane, where a is the lattice constant in nickel, 35.238 nm.[32] The width of the Schockley partial dislocation is taken to be $8|\mathbf{b}|$, where $|\mathbf{b}|$ is the Burgers vector of the edge dislocation, defined as $|\mathbf{b}|=(a/2)[\bar{1}10]$. The factor of 8 is taken based on the fact that the stacking-fault energy for nickel is ~ 160 mJ/m^2.[33]

The values of δE_{chem} vary with the distance of the impurity atom from the line of the partial dislocation of interest, since the magnitude of $\delta E_{\text{disl-sol}}$ itself does so in Eq. (1). In the present study, only the maximum absolute values of δE_{chem} are presented.

III. RESULTS AND DISCUSSIONS

A. General trend of δE_{chem}

In Fig. 2 are shown the calculated values of δE_{chem}, as a function of the size-misfit parameter $|\varepsilon_a|$ obtained by

TABLE II. Number of s and p electrons, N_s^{imp} and N_p^{im}, the difference in p and s energy levels, $E_p^{\text{imp}}-E_s^{\text{imp}}$ (in eV), and free-atom state of B-subgroup elements. The values of $E_p^{\text{imp}}-E_s^{\text{imp}}$ with and without asterisks are taken from Refs. 26 and 30, respectively.

Solute	N_s^{imp}	N_p^{imp}	$E_p^{\text{imp}}-E_s^{\text{imp}}$	Free-atom state
Zn	0.7699	1.2301	5.02*	$(4s^2)$
Al	1.0641	1.9359	5.254	$(3s)^2(3p)^1$
Ga	1.1348	1.8652	6.47*	$(4s)^2(4p)^1$
In	1.0749	1.9252	5.439	$(5s)^2(5p)^1$
Si	1.4080	2.5920	7.035	$(3s)^2(3p)^2$
Ge	1.4600	2.5400	8.02*	$(4s)^2(4p)^2$
Sn	1.3822	2.6178	6.558	$(5s)^2(5p)^2$
Sb	1.6425	3.3675	7.563	$(5s)^2(5p)^3$

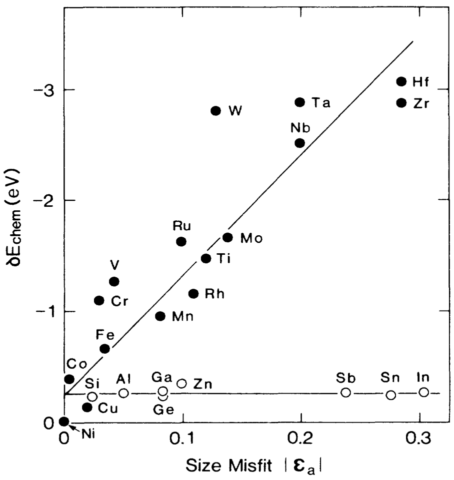

FIG. 2. Calculated chemical interaction energy δE_{chem} as a function of the size-misfit parameter $|\varepsilon_a|$, experimentally determined.

the experiment.[9] It can be seen that $\delta E^{\text{TM}}_{\text{chem}}$ for transition-metal solutes increases roughly in proportion to $|\varepsilon_a|$. In contrast, $\delta E^{B}_{\text{chem}}$ for B-subgroup solutes changes very slightly irrespective of the magnitude of $|\varepsilon_a|$. These are rather expected results, since the size-misfit effect of the solute atom is not taken into account in the present calculation of δE_{chem}.

The last three columns in Table I summarize the values of δE_s, δE_p, and δE_d, i.e., the contributions of s, p, and d bands to $\delta E^{\text{TM}}_{\text{chem}}$ for transition-metal solutes. It can be seen that δE_{chem} comes mostly from the d-band contribution, δE_d. Table I also shows that the solute atom with a larger d-state radius r_d, and hence with larger d-d hopping matrix elements, has stronger binding energy with edge dislocations. This can be naturally understood because the stronger impurity potential leads to the larger difference in r_d between host atom and impurity atom and vice versa. The effect of the d-d hopping interactions can be seen more clearly by assuming a fixed value of r_d equal to that of nickel. The calculated values of $\delta E_{\text{chem}}(r_d=7.1)$ are presented in Fig. 3. It is seen that $\delta E_{\text{chem}}(r_d=7.1)$ shows the maximum, where the number of d electrons is about five. This trend is often observed in the relation between the cohesive energy of transition metals and the number of d electrons. Notable is that $\delta E_{\text{chem}}(r_d=7.1)$ is strongly reduced in magnitude, compared to the value of δE_{chem}, shown in Fig. 2.

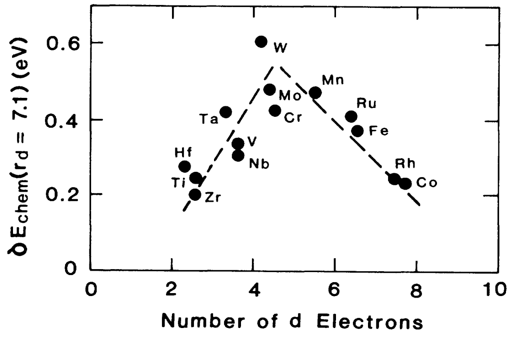

FIG. 3. Chemical interaction energy $\delta E_{\text{chem}}(r_d=7.1)$ calculated by assuming the fixed value of $r_d=7.1$ nm for transition-metal solutes in nickel, as a function of the number of d electrons.

Furthermore, for transition-metal solutes it is found that the d-state radius r_d depends sensitively on the size-misfit parameter $|\varepsilon_a|$, as shown in Fig. 4. Now, the remarkable correlation between $\delta E^{\text{TM}}_{\text{chem}}$ and $|\varepsilon_a|$, found in Fig. 2, could be interpreted through the strong dependence of δE_{chem} on r_d. On the other hand, for B-subgroup solute elements the values of $\delta E^{B}_{\text{chem}}$ are much smaller and insensitive to the $|\varepsilon_a|$ shown in Fig. 2. This trend can be also interpreted by the fact that there is no effective d-d hopping interactions between the host nickel and B-subgroup solute atoms. This is because the d-state radius is effectively zero and hence the d-atomic level is sufficiently high for B-subgroup solutes.

Summarizing the general trends of δE_{chem} for transition-metal and B-subgroup elements, it is concluded that an extra interaction of edge dislocation exists only for transition-metal solutes. It is obvious that the extra interaction energy for transition-metal solutes arises from the characteristic d-d hopping matrix elements, which are proportional to the product of the d-state radius, $(r_d r_d')^{3/2}$.[34] Also obvious is that this effect is effectively absent for B-subgroup elements.

B. Comparison with experiments

In order to make more direct comparison, the experimental value of $d\sigma/dc$ is plotted against the calculated value for transition metals, $\delta E^{\text{TM}}_{\text{chem}}$ for transition-metal solutes, in Fig. 5. A rather good correlation between them indicates that the chemical interaction energy δE_{chem} plays a central role in the solution hardening of nickel with transition-metal solutes. Note that the data for W, Zr, and Hf deviate significantly from the correlation, the reasons for which are unknown at present. However, it is suggested by Chen *et al.*[35] that Zr and Hf atoms tend to form a pairwise cluster in the nickel crystal. As for W,

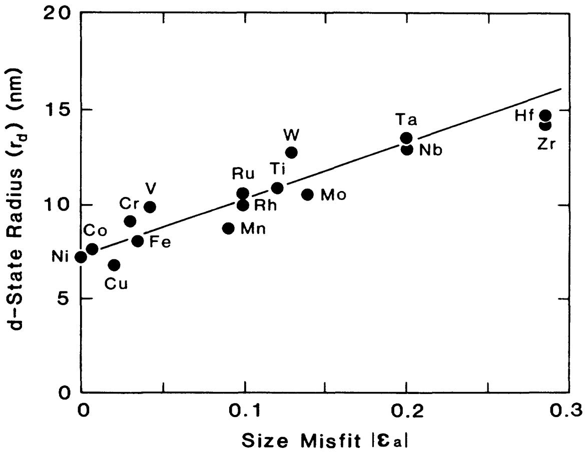

FIG. 4. Relation between the d-state radius of solutes, r_d, and the size-misfit parameter $|\varepsilon_a|$.

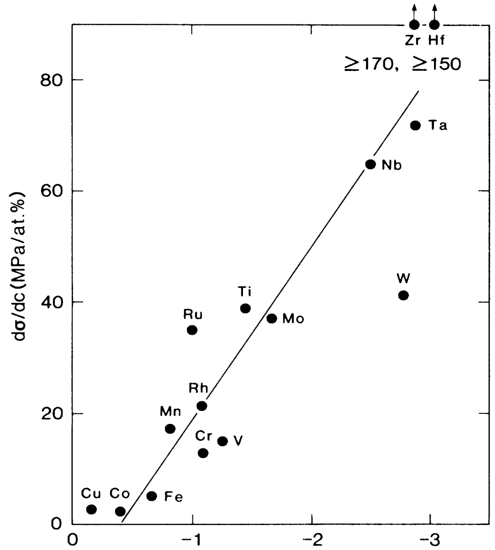

FIG. 5. Relation between the observed value, $d\sigma/dc$, and the calculated value of the chemical interaction energy for transition-metal solutes, $\delta E_{\mathrm{chem}}^{\mathrm{TM}}$, in nickel.

the deviation would be responsible for the relatively larger value of r_d, which is possibly overestimated by Harrison *et al.*,[26] as evidenced by the relation in Fig. 4.

C. Relative importance of chemical and elastic interaction energies

The present calculations of the solute-dislocation interaction energies are incomplete in a sense that the lattice relaxations around the solute atoms are not taken into account. According to the isotropic linear elasticity theory, the size-misfit (SM) elastic interaction energy δE_{SM} between a substitutional solute and an edge dislocation is given by

$$\delta E_{\mathrm{SM}} \cong -\Omega \frac{\mu b}{\pi r_0} \frac{1+\nu}{1-\nu} \,|\, \varepsilon_a \,| \;, \tag{7}$$

where Ω is the atomic volume, r_0 the atomic radius, μ the shear modulus, and ν Poisson's ratio of nickel. Using Eq. (7) with typical values of $r_0 = 12.46$ nm, $b = 24.92$ nm, $\mu = 79.96$ GPa (Ref. 36), and $\nu = 0.31$ (Ref. 36) for nickel, we can obtain $\delta E_{\mathrm{SM}} \cong -4.89 \,|\, \varepsilon_a \,|$ eV.

The modulus-misfit (MM) interaction energy between a substitutional solute and an edge dislocation, δE_{MM}, can be estimated by using the equivalent inclusion theory by Eshelby.[37] This leads to

$$\delta E_{\mathrm{MM}} \cong \frac{\Omega}{8} \frac{b^2}{\pi^2 r_0^2} \frac{1-2\nu}{(1-\nu)(1-\nu^2)} \frac{dE}{dc} \;, \tag{8}$$

where dE/dc represents the change in the Young's modulus of the host metal due to the addition of a solute element. From Eq. (8), δE_{MM} is estimated to be of the order of $(\frac{1}{4} - \frac{1}{20})\delta E_{\mathrm{SM}}$. Among the elastic interaction energies δE_{el}, therefore, the modulus-misfit interaction is less important than the size-misfit interaction for the solution hardening of nickel alloys, as has been pointed out previously.[9]

At present, the theory for the solid-solution hardening is not complete and is controversial.[38] As a first approximation, however, it can be assumed that the experimental value of $d\sigma/dc$ is proportional to the whole solute-dislocation interaction energy, represented by $\delta E_{\mathrm{el}} + \delta E_{\mathrm{ex}}$. Here, the extra interaction energy δE_{ex} is defined as $\delta E_{\mathrm{ex}} = \delta E_{\mathrm{chem}}^{\mathrm{TM}} - \delta E_{\mathrm{chem}}^{B}$, where $\delta E_{\mathrm{chem}}^{B}$ is taken as an average value. This definition of the extra interaction energy is based on the fact that the solution hardening for *B*-subgroup elements can be described mainly by the size-misfit interaction and the contribution of δE_{chem} is absolutely small. Therefore, the solution hardening of nickel can be expressed as

$$\frac{d\sigma}{dc} \cong \begin{cases} AK_{\mathrm{el}} \,|\, \varepsilon_a \,| & \text{for } B\text{-subgroup solutes,} \\ A(K_{\mathrm{el}} + K_{\mathrm{ex}}) \,|\, \varepsilon_a \,| & \text{for transition-metal solutes ,} \end{cases} \tag{9}$$

where A, K_{el}, and K_{ex} are proportional coefficients; $AK_{\mathrm{el}} \,|\, \varepsilon_a \,|$ and $AK_{\mathrm{ex}} \,|\, \varepsilon_a \,|$ denote the elastic interaction energy and the extra interaction energy, respectively.

Using Eq. (9) and the experimental data of $d\sigma/dc$, the best-fitted ratio of the proportional coefficients $\alpha = K_{\mathrm{ex}}/K_{\mathrm{el}} \simeq 0.8$ can be obtained, and the excellent correlation between the value of $d\sigma/dc$ and the properly scaled size-misfit parameter $(1+\alpha) \,|\, \varepsilon_a \,|$ is shown in Fig. 6. The result indicates that the size-misfit interaction energy and the chemical interaction energy are of the same order of magnitude and have equal importance for transition-metal solutes.

From the values of δE_{chem} in Fig. 2, a linear relationship is obtained between δE_{ex} and $|\, \varepsilon_a \,|$, as $\delta E_{\mathrm{ex}} \cong -9.83 \,|\, \varepsilon_a \,|$ eV for transition-metal solutes in nickel. Thus, by comparing the magnitudes of the size-misfit and chemical interaction energies, the theoretical

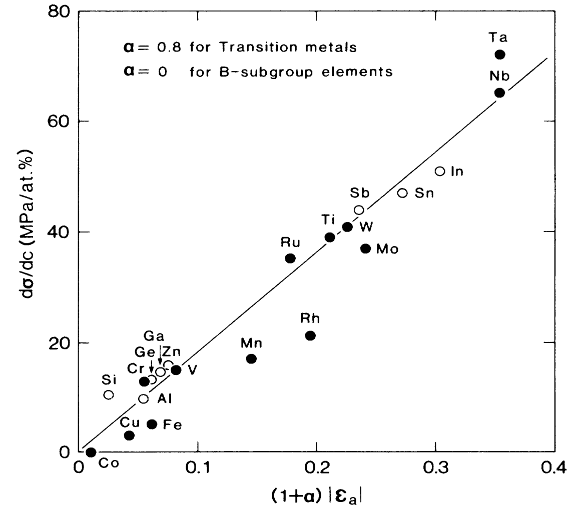

FIG. 6. Relation between the increase in yield stress of nickel per 1 at. %, $d\sigma/dc$, and modified size-misfit parameter $(1+\alpha) \,|\, \varepsilon_a \,|$, where α is chosen to be 0.8 for transition-metal and zero for *B*-subgroup elements.

ratio of K_{ex} to K_{el} is obtained as $\alpha_{\mathrm{th}}=K_{\mathrm{ex}}/K_{\mathrm{el}}\cong 2.0$. This theoretical value of α_{th} can be favorably compared to the experimental value of 0.8. Here, it can be emphasized that a part of the chemical interaction energy derived here certainly corresponds to the extra solution hardening of nickel with transition-metal solutes.

IV. CONCLUSIONS

To understand the physical origin of the anomalous solid-solution hardening of nickel alloys, the chemical interaction energies between a solute atom and an edge dislocation, δE_{chem} are calculated using a tight-binding-type electronic theory. It is demonstrated that in nickel there exists an essential difference in the solute-dislocation interaction energy between transition-metal and *B*-subgroup solutes, in agreement with the experimental results on the solution hardening. The chemical interaction energy δE_{chem} arises mainly from the characteristic *d*-*d* hopping interactions between the host nickel and transition-metal solutes, which are essentially absent for the *B*-subgroup elements having only *sp* valence.

Though the present calculations of δE_{chem} are based on a number of assumptions for simplicity, i.e., the lowest-order moment approximation as well as neglect of lattice relaxation and charge transfer around the solute atoms, they are essentially acceptable and significant for the understanding of the solid solution hardening of nickel. In this respect, the extra solid-solution hardening may also be expected in other transition-metal solvents. The procedure presented here would be applicable to account for the similar anomaly in solution hardening of the nickel-based intermetallic compound $\mathrm{Ni_3Al}$ having ordered fcc crystal structure, and the study is now going on. Finally, it should be recognized that the anomalous, extra solution hardening has not been observed clearly until very recently. The reasons are the following: (1) The experiments on solid-solution hardening have focused mainly on the noble-metal solvents or *B*-subgroup solvents, in which a limited number of solutes are soluble. (2) The systematic experimental study on the solution hardening for transition-metal solvents with both transition-metal and *B*-subgroup solutes has not been performed.

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[*] On leave from Hitachi Research Laboratory, Hitachi Ltd., Saiwai-Cho, Hitachi, Ibaraki 317, Japan.

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$$\mu_2^s=12(ss\sigma)^2+12(sp\sigma)^2+12(sd\sigma)^2\ ,$$

$$\begin{aligned}\mu_2^{p_x}&=\mu_2^{p_y}\\&=\mu_2^{p_z}=4[(pp\sigma)^2+2(pp\pi)]^2+(sp\sigma)^2\\&\qquad+(pd\sigma)^2+2(pd\pi)^2]\ ,\end{aligned}$$

$$\begin{aligned}\mu_2^{xy}=\mu_2^{yz}=\mu_2^{zx}&=3(dd\sigma)^2+4(dd\pi)^2+5(dd\delta)^2\\&\qquad+3(sd\sigma)^2+3(pd\sigma)^2+4(pd\pi)^2\ ,\end{aligned}$$

$$\begin{aligned}\mu_2^{x^2\text{-}y^2}&=\mu_2^{3z^2-r^2}\\&=\tfrac{3}{2}[(dd\sigma)^2+4(dd\pi)^2\\&\qquad+3(dd\delta)^2+(sd\sigma)^2+(pd\sigma)^2+4(pd\pi)^2]\ .\end{aligned}$$

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