Solid Solution Hardening of Nickel
—Role of Transition Metal and B-subgroup Solutes—

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A systematic investigation is made on the solid solution hardening of binary nickel alloys with additions of B-subgroup and transition metal elements. The 0.2% flow stress at 77 K and the Young's modulus are measured for a variety of binary alloys to evaluate the rate of solution hardening per one atomic percent of solute \( \frac{d\sigma}{dc} \) and that of change in elastic constant \( \frac{dE}{dc} \). Together with the available data on the rate of change in lattice constant \( \frac{da}{dc} \), interpretation of the solution hardening is attempted in terms of the elastic interaction theory. It is found that \( \frac{d\sigma}{dc} \) for the additions of B-subgroup elements is linearly related with a combined parameter appropriate for the elastic interaction between solutes and edge dislocations, where the contribution of modulus misfit is minimal and atomic size misfit governs the hardening. It is also found that for the additions of transition metal elements there is an extra hardening over what is expected from the same treatment on B-subgroup elements. These findings are the same in nature as what has been observed in the solution hardening of an Ll2 intermetallic compound Ni3Al. The reason for the extra hardening by transition metal elements is discussed, and a possible contribution of electronic interaction involving d-electrons is suggested for the solution hardening by a transition metal solute in the transition metal solvent, nickel.

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I. Introduction

In the preceding paper, the solid solution hardening in Ni3Al has been investigated for ternary additions of B-subgroup and transition metal elements\(^{(1)}\). It has been found that the solution hardening in the compound cannot be interpreted for both types of alloying elements together by a single expression for the elastic interaction. Namely, it has been shown that the hardening is more intense by the additions of transition metal elements than by the additions of B-subgroup elements where the hardening is linearly related with a combined parameter for the interaction between solute atoms and edge dislocations. Then the necessity is raised to carry out the similar type of investigation on the solution hardening of nickel in order to clarify whether the anomalous hardening effect is inherent in the Ll2 crystal structure of Ni3Al or in the majority component of nickel.

Technological interest in nickel alloys has often centered on improving the heat resistant properties such as high temperature strength and creep strength by making alloys multicomponent. For this purpose, the additions of transition metals are generally accepted. Prominent examples are the modifications of commercial superalloys, in which the additions of those elements have been properly chosen utilizing regression analyses. As a more fundamental approach, the solid solution hardening has been studied in nickel binary alloys by a number of workers\(^{(2)-(9)}\), however, the alloy
additions are also in most cases restricted to the transition metals.

Our principal concern here is the more fundamental supplement of the database for alloy design of superalloys and the more immediate contribution to our basic understanding of the solid solution hardening of nickel made by the study for a wide variety of solute elements. In the present investigation, an application of Fleisher-type treatment to the solid solution hardening of nickel is attempted as an extension of the work on Ni₃Al solid solutions, in order to examine whether the anomalous hardening by transition metal elements is also observed in the present case.

II. Experimental

The alloys were prepared by arc-melting under an argon atmosphere. The purity of electrolytic nickel was 99.95% and that of alloying elements was the highest readily available. The alloying elements were added up to 8 at% within the binary solid solution range according to the compiled phase diagrams in literature. The weight loss after the melting was less than 0.1 mass% in all cases, and therefore, the nominal composition was accepted.

The ingot, being approximately 35 g, was homogenized at 1473 K for 1.8 ks, warm-rolled to a square rod with dimensions of 8×8×70 mm³, and then annealed at 1273 K for 3.6 ks in vacuum encapsulated silica tube followed by water quenching. The annealing temperature was 1373 K for alloys containing Nb or Ta because of a limited solubility at 1273 K. The grain size obtained through the above processes was ranging from 100 to 300 μm.

Compressive 0.2% flow stress measured at 77 K was used to evaluate the degree of solution hardening in each alloy. The compressive test specimen was cut from the heat treated rod to dimensions of 4×4×7 mm³, which was electropolished before the test to remove the effect of deformation on the surface. The test was carried out using an Instron-type testing machine with an approximate strain rate of 1.2×10⁻⁴/s.

Young's modulus of binary alloys was determined at room temperature through the measurement of speed of sound in the specimen. Details of the method and derivation of the value were described in the preceding paper.³

III. Results and Discussion

1. Young's modulus of binary alloys

The relation between Young's modulus vs solute concentration in binary nickel alloys is shown in Fig. 1(a) for the additions of B-subgroup elements and in Figs. 1(b) to 1(d) for those of transition metal elements. Young's modulus of nickel has been reported to be 199–210 GPa which is in good agreement with the present result. The additions of B-subgroup elements, in Fig. 1, is found always to decrease Young's modulus. It is noticeable that the relation is found almost linear in all cases.

For the additions of B-subgroup elements in noble metals, it has been shown by Köster that the change in various physical properties is expressed as a function of the valence difference between solute and solvent, ΔZ. According to his analysis, the rate of change in elastic constant per one atomic per cent of solute, dE/dc, has the following relationship;

\[
dE/dc = m(ΔZ)^2 + n\tag{1}
\]

where \( m \) and \( n \) are constants. As is shown in Fig. 2, the relation also holds in the present case for each set of elements which belong to the same period. To be noted is that \( dE/dc \) for ternary additions of B-subgroup elements in Ni₃Al is also linearly related with the \((ΔZ)^2\)³. In the figure it is found that the value of \( n \) is almost constant regardless of the period, and that the value of \( m \), being negative for any period, is larger in its absolute value for larger period.

In Fig. 2, \( dE/dc \) for indium only is shown by an open circle. This means that the value is determined by interpolation utilizing the linear relation for 4B-subgroup elements. It is because, as can be seen in Fig. 1(a), a clear relation could not be found to determine the
$dE/dc$ in the observed values of elastic constant for the addition of the element. Hereinafter, the value determined in Fig. 2 is used as $dE/dc$ for the indium addition.

2. Solid solution hardening of binary alloys

The compressive 0.2% flow stress at 77 K of binary nickel alloys is summarized as a function of solute concentration in Fig. 3(a) for the addition of B-subgroup elements and in Figs. 3(b) to 3(d) for that of transition metal elements. The most important feature in these figures is that the relation is found mostly linear for all the alloy additions within the concentration range presently examined. This is in good agreement with the theory by Nabarro(13) and also that by Suzuki(14), although the latter being developed for concentrated binary alloys. From these results we can assign the rate of flow stress increase per one atomic percent of solute as $d\sigma/dc$ for each alloying element.

3. Analytical expression of solid solution hardening

As has been discussed in the preceding paper(1) on the possible interpretations for the

\[ \text{Fig. 1 Changes in Young's modulus of binary nickel alloys with additions of (a) B-subgroup elements, (b) transition metals of 4A and 5A groups, (c) those of 6A and 7A groups and (d) those of 8A group.} \]
solution hardening, the elastic interaction between the strain field of a solute and that of a dislocation should be regarded as the major factor in many cases. Fleischer have shown that the degree of solution hardening can be well correlated with a parameter for the interaction defined as a combined effect of atomic size and shear modulus. In the elastic interaction theory, the degree of solid solution hardening, $\Delta \sigma$, is generally expressed in a form,

$$\Delta \sigma = A f_0 c^q = A' e^p c^q,$$  

where $A$, $A'$, $p$ and $q$ are constants, $c$ is the solute concentration and $f_0$ is the maximum interaction force between solute and dislocation. $e$ is termed “combined parameter” involving atomic size misfit and modulus misfit, which is regarded as proportional to $f_0$. Since Fleischer, there have been a number of efforts on the modification of the expression. The latest issue for the expression of the combined parameter is by Gypen and Deruyttere, where the modulus misfit parameter is given as

$$\epsilon_e = (\epsilon_0 + \alpha \epsilon) / (1 + |\epsilon_0 + \alpha \epsilon| / 2).$$  

In the equation $\epsilon_e$ is defined as $(1/a)(da/dc)$, $a$ being lattice constant and $\epsilon_0$ is defined as $(1/G)(dG/dc)$, $G$ being shear modulus. The constant $A$ originally appears in the expression of modulus misfit parameter proposed by Takeuchi and has been assigned as a materials constant for a particular solvent by various investigators. Then the combined parameter appropriate for the elastic interaction between solute atoms and screw dislocations is given as

$$\epsilon_s = \epsilon_e,$$

where $\epsilon$ is a constant experimentally determined. Then the combined parameter appropriate for the interaction involving edge dislocations is given as

$$\epsilon_E = 1/2(|\epsilon_0 + \alpha \epsilon_0|^{p/q} + |\epsilon_0 - \alpha \epsilon_0|^{q/p}).$$

In eq. (5), $p$ and $q$ are constants to be properly assigned, and various investigators have done the assignment to fit their theories and experimental results.

4. Analysis of the present results

Now that we have obtained $d\sigma/dc$ and $dE/dc$, application of eqs. (3) and (4) becomes possible to the solid solution hardening of nickel. The conversion from uniaxial stress, $\sigma$, to the shear stress, $\tau$, can be done by multiplying 1/2 according to the normal approximation, and that from $(1/E)(dE/dc)$ to $(1/G)(dG/dc)$ is unnecessary, provided that the concentration dependence of Poisson’s ratio is negligible. As to the value for atomic size misfit, Mishima et al. have already carried out a systematic investigation on the lattice parameter of nickel alloys, $da/dc$, and the result is directly applicable. The constant $A$ in eq. (3) is given as 3.8 for nickel by Takeuchi and the modulus misfit parameter is thereby obtained.

The present results on $d\sigma/dc$ is first related with the combined parameter of eq. (4) in Fig. 4 and with that of eq. (5) in Figs. 5 and 6. In these figures, the constant $\alpha$ in the expression of the combined parameter is by Fleischer. As shown in Figs. 3(a) to 3(d), the concentration dependence of flow stress is mostly linear and thereby $q$ can be taken as 1 in...
the present case. The choice of $p$ is somehow ambiguous, however, the range of value for $p$ assigned by various investigators falls between 1 and 2. 

It is now clear in Fig. 4 that $d\sigma/dc$ in nickel alloys has no correlation with the combined parameter of eq. (4) which is appropriate for elastic interaction between solute atoms and screw dislocations. On the other hand, in Figs. 5 and 6, a certain correlation can be found between the combined parameter and $d\sigma/dc$. In comparison of Fig. 5 with Fig. 6, the choice of parameter $p$ is found to provide no noticeable difference in such correlations. The most important feature is that with the combined parameter of eq. (5) $d\sigma/dc$ is linearly related for the additions of B-subgroup elements but not for those of transition metal elements. The

![Fig. 3 Changes in 0.2% flow stress at 77 K of binary nickel with additions of (a) B-subgroup elements, (b) transition metals of 4A and 5A groups, (c) those of 6A and 7A groups and (d) those of 8A group.](image-url)
hardening by transition metal elements is more intense and in this sense is anomalous. At any rate the solution hardening of nickel can be regarded as being governed by the elastic interaction between solute atoms and edge dislocations like in other fcc alloys. In several bcc alloys, the elastic interaction involving screw dislocation plays a major role\cite{18-22(30)}, and the use of the plateau stress above room temperature has been recommended to evaluate the solution hardening\cite{20}. It would be reasonable, because the plastic behavior of bcc crystal structure is generally controlled by the mobility of screw dislocation having a large Peierls stress\cite{34(35)}. In contrast, Yoshida et al.\cite{7} have stated that most fcc alloys show a gradual decrease in the flow stress with increasing temperature exhibiting no definite plateau stress. It is, therefore, pointed out that the solution hardening should be evaluated in those alloys by the flow stress at absolute zero temperature. This should justify the use of 0.2% flow stress measured at 77 K in the present investigation.

One of the most important conclusion drawn from Fig. 6 is that the atomic size misfit is the major factor in determining the linear correlation between the combined parameter and \(d\sigma/dc\) for B-subgroup elements. This is because the constant \(\alpha\) in the combined
parameter is 16, which means the contribution of modulus misfit in the expression is very small. Then in the situation for the additions of transition metal elements, we have to realize that there should be some extra contribution to the hardening besides the atomic size misfit, which can not be attributed to the modulus misfit.

5. Extra hardening effect by transition metal elements

There have been several reports claiming that the atomic size effect is the controlling factor for the degree of solid solution hardening in nickel. Yoshida et al.\(^7\) have shown this for the flow stress at a cryogenic temperature. Matsuo et al.\(^{36}\) and Kondo et al.\(^{37}\) have shown that it holds even for the effective stress in creep of austenitic heat resistant alloys. However, several investigators have already pointed out that there should be some extra hardening effect by transition metal elements other than atomic size misfit in nickel\(^{5\left(9\right)\left(38\right)}\), which is termed as "valence effect". Pelloux showed that there is some correlation between the degree of solution hardening and the position of transition metal elements on the periodic table\(^5\). Later, his result has been further confirmed by Philips\(^6\) for the case of additions of platinum group elements.

The origin of the valence effect is then interpreted by Decker\(^38\) to alter the stacking fault energy, while by Fleischer\(^17\) to affect the shear modulus of the solid solution. In regard to the stacking fault energy, Delehouzee and Deruyttere\(^{39}\) have shown that it increases with increasing valence of B-subgroup elements, and accordingly have assigned the apparent valence to transition metal elements. B-subgroup elements on the solution hardening is found nearly equal. Whereas that of transition metal elements is more intense by a factor of 2 in nickel. Morinaga et al.\(^{40}\) have shown that the electronic structure of Ni\(_3\)Al resembles that of nickel. This strongly suggests that the extra hardening effect in both solid solutions would be originated from the interaction between d-electrons of solute and solvent. Cottrell et al.\(^{41}\) and later Sugiyama\(^{42}\) introduced the contribution of electrical interaction to the solution hardening on the basis of static electrical field of free electrons, which, however, is concluded to be small. It is now felt that such interaction taking d-electrons into account would become significant in the present case.

6. Solid solution hardening in other solvents

In view of the above discussion, it follows that the extra hardening by transition metal elements should not be observed in fcc noble metal solvents such as copper, silver and gold but should be in fcc transition metal solvents not only nickel but also platinum and palladium. Until this work has been issued, as far as we know, the comprehensive data for the solution hardening have not been found even in nickel, much less in platinum. This does not allow us to verify this possible conclusion at present. In regard to noble metal solvents, although the solution hardening has
been extensively studied by many workers, it is not possible to prove the absence of the extra hardening because of a limited number of soluble transition metal elements most typically in copper.

In Fig. 8, a comparison is made between the maximum solid solubilities of various kinds of solute in copper and nickel. In this figure, the scale is taken as ten times the square root of concentration so as to make the small solubilities visible. Except the fcc transition metal elements forming a continuous solid solution, titanium is the only one transition metal being soluble for more than 1 at% in copper. This might be another reason why the role of transition metal elements in the solution hardening of copper has been hidden unknown. It is obvious that nickel is characterized by much larger allowances for alloying elements to be soluble than copper. This nature of nickel as a solvent, together with that of nickel based intermetallic compound Ni₃Al(43), has made it possible to yield numerous commercial alloys and has encouraged us to design new nickel based superalloys having higher performance.

There are several other attempts to correlate the solution hardening with such variables as electrical resistivity(44), solubility limit(19) or electron atom ratio(45). No rigorous theory has yet been established which enables one to predict or understand the solution hardening. To reveal the nature and origin of the solution hardening and furthermore to verify the exact cause for the extra hardening effect, the electronic interaction involving d-electrons of solute and solvent seems necessary to be evaluated as mentioned earlier. Experimentally, more fundamental properties of solid solutions, for example electrical resistivity and Hall effect, could be systematically investigated to furnish more direct information on this regard. By recent progress in electronic theory it would be possible to carry out more sophisticated approach than that done by Cottrell et al.(41) to interpret the extra hardening by this type of interaction, for which our effort is currently extended and to be published soon.

IV. Conclusion

The solid solution hardening of nickel is investigated systematically for the additions of B-subgroup and transition metal elements and the following conclusions are drawn;

(1) In applying the elastic interaction theory, the solution hardening by B-subgroup elements and that by transition metal elements can not be together interpreted by a single expression of any combined parameter.

(2) The solution hardening by B-subgroup elements can be linearly related with a combined parameter appropriate for the elastic interaction involving edge dislocations. The interaction is found mainly to come from the atomic size misfit with minimal contribution of modulus misfit.

(3) There is an extra hardening effect which can not be explained by the elastic interaction for the additions of transition metal elements. The effect is far extensive in nickel as compared with Ni₃Al.

(4) The cause of the extra hardening is considered to be some type of electronic interaction between transition metal solutes and a particular solvent also being a transition metal.

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