

Explanations of Solid Solution Hardening (Softening), Age-Hardening (Softening) and Work Hardening (Softening) Based on Chemical Bonds

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Metals and alloys are strengthened through various types of processing and treatments, but they are also weakened in other conditions. An Al-Zn alloy is hardened with a rolling but a Zn-Al alloy is softened in a similar treatment. Dislocation theory gives an explanation to the strengthening mechanism in a limited range, but it has not yet succeeded in dealing with the inequality of phenomena in those alloys. In this work, both hardening and softening mechanisms of materials have been considered, on the basis of the nature of chemical bonds in matrices. Close examinations of experimental results based on chemical bond theory revealed that strength and hardness of materials are related to the strength and types of chemical bonds established in materials. For example, solute atoms which have larger or smaller atomic bond population (ABP) than that of solvent atoms cause the solid solution hardening or softening, respectively. Thus, the bond theoretical approach gives a more comprehensive interpretation to the strengthening and softening phenomena occurring in materials.

Keywords: *solid solution softening, age-softening, work softening, ABP, AP*

1. Introduction

Pure metals are hardened when alloying element is added (solid solution hardening), age-hardenable alloys increase their hardness when aging treatment is carried out (age-hardening) and alloys are hardened, when they receive deformation due to working (work hardening). These three hardening mechanisms have been thought to exert independently with one another. Therefore, alloys have been expected to be much more hardened if processing based on these three kinds of hardening mechanisms are simultaneously carried out, compared with the case in which a single mechanism works. Moreover, it has been believed that the increase of dislocation density in metallic materials is effective to hardening of the materials.

The present authors have studied metals and alloys from the viewpoint of the chemical bonds, and obtained the results from the molecular orbital calculations [1-3]. The solid solution hardening, age-hardening and work hardening have been examined from this standpoint. As a result, it has been revealed that three fashions of hardening mechanisms are not completely independent from one another but mutually suppressed. In addition, not only hardening but also softening phenomena can occur in alloys. In this work, the authors concentrate their objective to consider how solid solution hardening (softening), age-hardening (softening), work hardening (softening) are related to each other, because all notions based on the chemical bond theory have already been described.

2. Experimental results on solid solution hardening (softening), age-hardening (softening) and work hardening (softening)

2.1 Hardening and softening

(1) It has been confirmed that solid solution hardening occurs when solute atoms are added. Contrarily, is there no solid solution softening? Answer is yes. If Ni is alloyed in Fe, the proof stress decreases from the value of pure Fe [4]. This phenomenon is called as alloy softening and reviewed

[5]. The solid solution softening is also known in the system of Cr-Re and planned to utilize this effect in commercial applications [6]

(2) When the age-hardenable alloys (Al-Cu, Al-Zn-Mg-(Cu), Al-Mg-Si, etc.) are appropriately heat-treated, these alloys are hardened. As described in the next section, however, for other type of alloys such as Zn-Al or Fe-C, etc., the highest hardness are achieved in the state quenched in water or in a work treatment and then the hardness decreases with aging treatments [1]. Thus, age-softening certainly occurs in alloys .

(3) In most cases dealing with commercial metals and alloys, the metallic substances are hardened by cold working. Therefore, it is believed that cold working hardens metals and alloys. For example, Al-Zn alloy is hardened by cold working. On the contrary, Zn-Al alloy tends to be softened simply by cold working: For Zn-5~22mass% Al alloys prepared under various conditions, a monotonous decrease of hardness was obtained with the progress of reduction in thickness of specimens. If the softened Zn-Al alloy is solution-treated, the original hardness is recovered [1, 7]. Al-1.7mass%Fe alloy is softened by preliminary treatment such as heating and hot rolling at 673K [1, 8]. Thus, it is obvious to be able to find a number of work softening alloys.

2.2 Relations among various types of hardening mechanisms and processing

Solid solution hardening, age-hardening and work hardening have been described separately, with respect to hardening behavior. However, they are mutually restricted with each other.

(1) Solid solution hardening type alloys show the maximum hardness in quenched condition. As is well known, Fe-C alloy shows a maximum hardness in the state of martensitic transformation after water-quenched treatment and the hardness decreases as the (aging) temperature increases. Moreover, as described in section 2.1, Zn-Al alloys tend to be softened when they are aged or worked. It can be thought that these alloys are softened when precipitation proceeds due to the aging or working processes[1, 7]. Solid solution hardening is exclusive to age-hardening and work hardening.

(2) As will be seen in the paper No.29, the age-hardening type alloys such as Al-4.11%Cu-0.80%Si, Al-0.46%Mg-0.92%Si or Al-5.53%Zn-2.54%Mg-1.52%Cu, hardly show the increase of hardness during their aging process after cold working of 50% reduction. In the case of Al-5.53%Zn-2.54%Mg-1.52%Cu alloy, an amount of the increase in hardness by cold working decreases with increasing aging time and becomes very small in the 2hrs-aging at 463K. The age-hardening type alloys (e.g., Al-Cu, Al-Mg-Si, Al-Zn-Mg-(Cu) alloys) show the maximum hardness in the aged condition and work hardening hardly occurs. This type of alloys is, however, softened if solution treatment is applied. Therefore, age-hardening is exclusive to work hardening and solid solution hardening.

(3) Work hardening type alloys (e.g., Al-Mn, Al-Mg, Fe-Mn alloys) show the maximum hardness in the cold worked state. They are softened when they are solution treated. The age-hardening type alloys (e.g., Al-Cu, Al-Zn-Mg-(Cu) alloys) are not age-hardened when they are worked before aging treatment. Reversely, age-hardened alloys are not work hardened. Thus, it can be concluded that work hardening is exclusive to solid solution hardening and age-hardening.

(4) The alloys are not work hardened, when solute atoms are perfectly expelled from the matrix as a second phase by furnace cooling. As shown in the paper [30], high purity (6-nine) Al is not hardened by cold working, though low purity Al shows simply work hardening. It also can be seen from the experimental results for Al-Fe alloys that Al-0.5~1.7%Fe alloys show work softening but they are simply work hardened in the case without preliminary hot-rolling. The microstructure of these work softened Al-Fe alloys shows the formation of Al₃Fe compound [1, 8].

3. Explanations based on dislocation theory and its limitation

The expressions of solid solution hardening, age-hardening and work hardening only describe the resulting phenomena. There is no feasible explanation except dislocation theory, for the reason why solid solution hardening, age-hardening and work hardening happen. The dislocation theory is

essentially established on the basis of the theory of elasticity and it explains solid solution hardening, age-hardening and work hardening in the following way.

a) Solid solution hardening is normally explained with the model that a guest atom generates strain field, due to the difference of atomic radii between solute and solvent atoms. This strain field prevents the motion of dislocations.

b) Age-hardening is based on the mechanism that strain field produced around the precipitates prevents the motion of dislocations.

c) Work hardening is interpreted by the interactions of dislocations which are introduced by plastic deformation. The strain field around other dislocations prevents the motion of dislocations.

However, it is clear that the explanations of solid solution hardening, age-hardening and work hardening by dislocation theory do not give competent understandings to the core of hardening mechanisms, as follows.

a) Solid solution hardening, age-hardening and work hardening, which the dislocation theory referring to be self-evident, are not always realized. Contrarily, solid solution softening, age-softening and work softening often happen.

b) Dislocation theory explains the strengths (hardness) of materials in terms of the existence of dislocations and their motions, but the strength (hardness) of material itself is predominant even in the materials consisting of covalent bonds or ionic bond atoms in which no dislocations exist.

c) Strain fields, which prevent the motion of dislocations, do not always exist. The solid solution is possible so that strain field does not exist. Age-hardening can occur without strain field.

In addition, pure substances (6-nine pure Al and pure gold) are hardly strengthened by cold working. These experimental results reveal that the disturbance to the motion of dislocations by strain fields is not a necessary and sufficient condition for the explanation of hardening due to plastic deformation.

The plastic deformation occurs without dislocations in amorphous alloys and it occurs by grain boundary sliding in creep phenomena. This fact means that dislocation is not always necessary for the plastic deformation. Dislocation is the specific turbulence of atomic arrangements and is based on the chemical bonds. Plastic deformation itself is possible without the motion of dislocations if the nature of chemical bond is metallic. Dislocation theory cannot explain the differences in the hardness (strength) of pure substances. These difficult and significant problems for dislocation theory can be solved from the viewpoint of chemical bond theory.

4. Explanations based on the chemical bond theory

The experimental facts on solid solubility and the facts on solid solution hardening, age-hardening, work hardening and their mutual relations, are explained from the viewpoint of the chemical bond theory as follows.

4.1 Solid solubility

Elements A and B dissolve each other if the nature of chemical bonds of both elements are similar. On the other hand, the mutual solubility decreases as the nature of chemical bonds becomes dissimilar to each other. That is, the solubility can be reduced to the consideration to similarity and dissimilarity of the chemical bonds. The formation of second phases in the age-hardened or work hardened materials may be interpreted in such a way as that solute atoms which are arranged in metallic lattice of solvent metals will be excluded from the matrix by the change of chemical bond during aging or working processes. This corresponds to the rearrangement of atoms due to the change in nature of chemical bonds; rearrangement of solute atoms having an ionic nature with solvent atoms will need time (aging process) to make compounds and that of covalent-like solute atoms with solvent atoms will need an applied power (working process) to make overlapping of bonding lobes of solute and solvent atoms which are oriented in different directions before any working treatments. In this way, the reason for the formation of the second phases in age-hardening and work hardening is clear. The

strength of chemical bonds increases when metallic bond changes to covalent nature added or ionic nature added bond and then the solubility of solute element will be decreased because the formation of compounds becomes easily due to the increase in strength of chemical bond.

4.2 Hardening mechanisms

Solid solution hardening, age-hardening and work hardening correspond to the increase of the strengths of chemical bonds between constituent atoms. The strength of chemical bonds increases when metallic bond changes to covalent or ionic bonds. This is because the unoccupied electronic state decreases in number, when the bond nature changes from metallic to covalent or ionic bonds. In metallic state, there are many unoccupied electronic states and electrons can easily occupy new electronic states during cold working process of materials; this leads to an easy transformation. When the chemical bond in metallic materials changes to much covalent-like or ionic-like nature, however, the unoccupied electronic state decreases in number and it becomes difficult for electrons to occupy new electronic states; this case corresponds to the decrease of atomic mobility. Thus the high strength (hardness) of materials could be correlated with the change in nature of chemical bonds from metallic to covalent-like or ionic-like ones.

4.3 Chemical bonds and alloy systems

As for the chemical bonds, covalent bond, metallic bond and ionic bond are primarily important in materials. They can be distinguished using the values of atomic bond population (ABP) and atomic population (AP) which can be obtained by the molecular orbital (MO) calculations, such as the extended Hückel MO method [9]. Chemical bonds would change in the direction in which energy lowers. The values of ABP and AP were calculated using the EHMO method as shown in Table 1. The calculation was carried out for an atomic cluster model which is consisted of 87, 89 and 87 atoms for fcc, bcc and hcp structures, respectively. The arrangement of atoms in the cluster model is made as spherical shape as possible, and the central atom in solvent atomic cluster was replaced with a solute atom. The structure and lattice constant reported for pure solvent element were used.

(a) Solid solution hardening type alloy is defined as an alloy in which hardening occurs only by alloying of a solute element which has a larger ABP than that of solvent atoms. From this result, the examples in this type of alloys would be estimated as Fe-C alloy, Zn-Al alloy, Mg-Al alloy, etc. As described before in Section 2.2, these alloys are softened when precipitation proceeds by aging treatments. Solid solution softening type alloy is defined as an alloy in which softening occurs only by alloying of a solute element which has a smaller ABP than that of solvent atoms.

(b) Age-hardening type alloy is defined as an alloy in which hardening does occur just after an appropriate aging treatment. Age-hardening type alloy contains the ionic bond forming elements which have a large AP. The examples are found in Al-Cu alloy, Al-Zn-Mg-(Cu) alloy, Al-Mg-Si alloy, etc. Age-softening type alloy is defined as the alloy in which softening occurs by aging treatments. The examples are the solid solution hardening type alloys (Fe-C alloy, Zn-Al alloy, Mg-Al alloy, etc.) mentioned above. In this type of alloys, hardening is associated with alloying solute atoms into matrix. Therefore, the alloy is softened if solute atoms are excluded from the matrix as precipitates and accordingly the nature of chemical bond in the matrix returns to metallic bonds. For example, aging behaviors of various Zn-Al alloys were examined by measuring the change of hardness and electric resistance during room temperature aging. Zn-5%Al, -10%Al, -20%Al and -30%Al alloys show age-softening. The electric resistance of these alloys gradually decreases and approaches to the value for 99.99%Zn in the aging time of about 40 days. This means that Al atoms are gradually excluded from Zn-Al matrix in the aging process and the composition of matrix approaches to pure Zn metal. On the other hand, Zn-90%Al alloy showed age-hardening and the

electric resistance remained almost unchanged during the aging process[1, 7]. Thus the increase in hardness of materials will be correlated with the change in bonding nature of the alloy matrix. Another example is typically seen in over-aging phenomena. When solute atoms are expelled from the matrix as a second phase region, then the strength (hardness) is lowered, because the matrix approaches to pure metallic solvent and the bond nature will return to the original metallic bond.

Table 1 Atomic bond population (ABP) and atomic population (AP) calculated by the EHMO method.

(a) Solid solution hardening type

Alloy	Element	ABP
Fe-C alloy	solvent (Fe)	0.097 < 0.102 of solute (C)
Zn-Al alloy	solvent (Zn)	0.130 < 0.150 of solute (Al)
Mg-Al alloy	solvent (Mg)	0.092 < 0.099 of solute (Al)

(b) Solid solution softening type

Alloy	Element	ABP
Cr-Re alloy	solvent(Cr)	0.154 > 0.131 of solute (Re)
Fe-Ni alloy	solvent (Fe)	0.097 > 0.054 of solute (Ni)

(c) Age-hardening type

Alloy	Element	ABP	$AP_{(solvent)} - AP_{(solute)}$
Al alloy	solvent (Al)	0.097	0
	solute (Cu)	0.055	0.033
	solute (Mg)	0.065	- 0.986
	solute (Si)	0.094	0.281
	solute (Zn)	0.085	- 0.149
	solute (Fe)	0.046	2.222

(c) Work hardening type alloy would be defined as a combination of metals which is hardened by cold working. Based on the chemical bond theory, the following situation would be expected as a mechanism in the work hardening. If the solute element has covalent-like nature of chemical bond, the distribution pattern of electrons in this atom would be asymmetrical such as bonding lobes of d-electrons and the structure would be locally different from that of solvent atoms. In this case the bonding lobes of electrons in solute and solvent atoms cannot be overlapped and the strength of the alloy would not be increased. When this alloy is deformed under cold working process, however, bonding lobes of electrons in solute and solvent atoms may be able to overlap and then the metallic nature in chemical bond of the matrix would be strengthened by the addition of covalent-like bond. Work softening alloy can be defined as a group of alloys of which bond strength is decreased by cold working. There would be two cases where the bond strength decreases by cold working. One example is found in the solid solution hardening type alloy. This type of alloys would be softened when solute atoms are excluded from the matrix due to the precipitation by cold working. Other examples, as already described in Section 2-1(3), are high pure Al of 5-, 6-nine purity and Al-1.7mass% Fe alloy.

4.4 Strengthening and softening of matrix

To understand the strength of alloys, key concept is the chemical bonds realized in matrix of alloys. This concept leads to that the strengthening of matrix is common to these strengthening mechanisms.

The strengthening of matrix is realized by strengthening the chemical bonds. The second phases formed through slow cooling such as furnace cooling are not effective for the strengthening of alloys. Age-hardening is realized only in the super-saturated solid solution obtained by quenching in water. These correlations of the procedures and results reflect that an alloy does not show age-hardening phenomena if the solute atoms are not dissolved in matrix. The strengthening of the chemical bonds by solute elements remained in the matrix is essentially important even in the age-hardening.

Softening occurs even in the age-hardening type alloys, when ionic bond becomes too strong. This is because solute element atoms are separated from the matrix, as the second phase component and the composition of matrix approaches to pure solvent. When solute atoms are excluded and the matrix becomes pure solvent, the chemical bond returns to original metallic bond, and then the strength decreases. This is over-aging (softening). When the strength of covalent bond becomes too strong under work hardening, the solute elements are gathered as a second phase and then the matrix is softened because the chemical bonds returns to original metallic bonds. This is the softening introduced by the excessive cold working.

In pure substances, work hardening does not occur. The chemical bond theory explains that the stronger chemical bond is impossible in this case because the combination of different kinds of atoms is impossible in pure substances even if the relative configuration of atoms may change by the plastic deformation. For pure substances or amorphous materials, the chemical bond theory explains the strength. The difference in the strength of the pure substances can be reduced to the difference in the strength of chemical bonds and the concept of chemical bond can effectively deal with even amorphous materials, whereas the conventional concepts of dislocation is invalid in those cases.

5. Summary

An unified explanation covering both hardening and softening of metals and alloys has been presented on the basis of the chemical bond theory.

- (1) In metals and alloys, not only hardening (solid solution hardening, age-hardening and work hardening) but also softening (solid solution softening, age-softening and work softening) occurs.
- (2) The hardening mechanisms (solid solution hardening, age-hardening and work hardening) are not completely independent. They suppress one another so as to keep the total quantity of hardness at the same level.
- (3) The interpretation based on the chemical bond is more widely applicable and consistent with experimental results than the dislocation theory. The essential part of reasons is that dislocation theory is based on the classic mechanics but the chemical bond theory has a background of quantum mechanics.

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