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New Theoretical Approach to Properties of Aluminum Alloys Based on Chemical Bond Nature of Constituent Atoms

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The major framework of physical metallurgy has been built up until 1960s. A large amount of knowledge and experimental results have been accumulated, based on the concepts established in the physical metallurgy so far. Nevertheless, some concepts have provided only phenomenological interpretations to alloys and related materials, which hold for a limited research field. The present authors intend to make a theoretical approach, which can be applied to get wider prospects to the behavior and characteristics of alloys, on the basis of concepts drawn from chemical bond theory and quantum chemistry. At the starting point of the present discussion, the authors consider the solid solubility in alloys and propose a guideline to understand solid solubility in alloys. The second subject considered in this study is the definition and classification of the hardening types of alloys such as solid-solution hardening, precipitation hardening and deformation hardening alloys.

Keywords: Al alloys, Solid solubility, Hardening mechanisms, Chemical bonds, Population analysis

1. Background

In 20th century, science and technologies based on quantum theory have been extensively developed, and Schroedinger's equation is recognized as a general formula ruling all aspects of substances [1,2]. Mulliken made an invaluable contribution to the foundation of the molecular orbital (MO) theory in quantum chemistry, and also introduced the concepts of the so-called "population analysis" which are found nowadays in a lot of university textbooks of the quantum chemistry and research papers in materials science. Recently, such scrutinized studies based on the quantum chemistry have increasingly gained ahead in materials design.The central idea of the present study is that quantum theoretical rules and behavior of electrons dominate most fundamental properties of alloys, including the solid solubility, hardening mechanisms which have been interpreted by classical concepts so far [3-5]. The present study would stress the importance of the viewpoint based on chemical bond theory and the effective combination of Schroedinger's equation and Mulliken's parameters, especially atomic bond population (ABP) and atomic population (AP) [6-8].

2. Solid solubility and trends of chemical compound formation in alloys

A normal alloy comprises two (or more) metallic element atoms, and at least one element is metallic. Empirical examinations revealed that solubility is much dependent on alloying elements, and properties of alloy are sensitive to the combinations of atoms. Thus, the solubility is a fundamental but one of the most important roperties of alloy. In spite of the importance, the general scheme of the alloy solubility has not been fully understood yet. Hume-Rothery, and slightly later Engel and Bruwer showed some empirical rules partly hold for the explanation. Although Hume-Rothery proposed an empirical "size-factor" rule, close examinations of the experimental data revealed that not small number of exceptions have been found in alloys.

Employing notions of quantum chemistry, the present study lead to a conclusion that the dissolution of solute atoms possibly occurs if the chemical bond natures of solvent and solute atoms are similar to each other, from the qualitative point of view. On the contrary, solute component is immiscible in solvent if the bond nature of the solute significantly differs from that of solvent. This tendency can be related to spatial distribution of electron probabilities. Mulliken's two parameters; ABP and AP are available for the quantitative estimation of the tendency. With respect to the quantitative consideration, the other important aspect can also be drawn from energetic calculations based on the MO theory. That is, the cohesive energy shows no extreme change and the energy is expressed as a nearly straight line with the chemical composition in the model calculations if a solute can dissolve in a solvent, whereas an insoluble element forms chemical compounds if dissolution of solute accompanies a large increase at a certain composition, in terms of the cohesive energy. Contrarily, the solute element introducing a large decrease in the cohesive energy will be insoluble.

Thus, the criteria of soluble, insoluble and compound formation can be fixed from the viewpoint of chemical bond theory. As far as the periodic table and electronic structures of atoms are concerned, all of the elements listed in the table are divided into s-d electron block (transition elements), s-p electron block (typical elements) and s-f electron block (rare earth elements). If an alloy comprising two elements categorized in a common block, the dissolution can easily occur to each other. But it is difficult to expect that two elements dissolve mutually if constituent atoms are categorized in different systems. Two elements belonging to the s-d electron block easily make an alloy of metallic bond and s-p electron and s-f electron blocks are tend to form the chemical compound of covalent and ionic bond respectively.

3. The definition of concepts and criteria of classification of the alloy types

To understand main characters of alloys, we must prepare the categories and define the characters of them. Since we build up the categories based on the concepts established in chemical bond theory, we refer it important to consider the interactions between solvent and solute atoms. As is found in chemical bond, however, there are often cases that the interactions between solute and solvent atoms are mixed. In this study, we present next six ideal types of characters, to discuss from the viewpoint of chemical bonds:

(1) solid solution hardening type, (2) age (precipitation)-hardening type,
(3) work-hardening type, (4) anti-corrosion type,
(5) heat-resistant type, (6) casting type.

Remarks on the nature of chemical bonds and electronic structures relevant to the characters are successively given. It should be noted that definitions of the characters are not always same to those that are conventionally prevailed.

3.1.Solid solution hardening type

(Definition) Solid solution hardening is defined as the hardening introduced only by dissolving the solute atoms in atomic scale in matrix.

The solid solution hardening means the hardening only by the dissolution of solute atoms. The other hardening originated from heat treatment or cold working is excluded from this definition. What kind of chemical bond causes the solid solution hardening thus defined? And how is the electronic structure of bonds? To answer these questions, we should return to the chemical bond theory. The chemical bond strengthening due to dissolution of atoms results in the increase of hardness as solute–dissolved state. The metallic bonds can be referred to the electron-deficient covalent bonds and associate the overlapping atomic orbitals. Therefore, the hardening may appear as the increase in ABP (Atomic Bond Population). In other words, an alloying element which causes solid solution hardening is an element introducing the effect that makes ABP larger in the material than pure solvent atoms. The element inducing the effect decreasing ABP from that of pure solvent, does not cause the solid solution hardening. The quantum state unoccupied by electrons (the so-called "electron-deficient state") decreases, when ABP becomes larger, compared with that of the pure solvent and the nature of chemical bond changes from metallic to covalent bonds. The strength (hardness) of the substance should increase, because the electrons are refrained from fluctuating, therefore atoms lose diffusivity at that time. After all, the solid solution hardening type will be judged from the following criterion.

(Criterion) Solute atoms that make ABP larger than solvent atoms can effectively work as element atoms in a solid solution hardening alloy.

3.2. Age (Precipitation)-hardening type

(Definition) Age(Precipitation)-hardening alloy is defined as an alloy which is hardened by precipitation (due to phase decomposition). Age(Precipitation)-hardening is privileged to occur when dissolved solute atoms are re-arranged in an alloy categorized in this type.

The precipitation-hardening means that the hardening is promoted only by heat treatment. Other hardening due to solid solution hardening or cold working after heat treatment is excluded in this definition. What kind of chemical bond is related to the precipitation-hardening thus defined? And how are the electronic structures built up in this type of alloy? In a precipitation-hardening alloy, it is not possible to expect a case that ABP of alloying element is larger than that of the pure solvent atoms like solid solution hardening. Why does the hardening occur in a case that two elements of alloy have a small ABP? An alternative mechnism of strengthening can be originated from ionic bonds working between the constituent atoms. In case of the alloy with some extent of an ionic bond nature, ABP of alloying elements is smaller than that of the pure solvent. Then, the stable ionic bond is not formed only by the dissolution of alloying element. The stabilization of ionic bonds requires not only the electronic transfer induced by the difference in the electro-negativity between solvent and solute atoms, but also the stabilization of the Coulomb interaction. Ions with the same electric polarity never occupy the neighboring positions, and the re-arrangement of ions consequently happens, so that the Coulomb energy becomes minimum as a whole. Therefore, the dissolution of the solute atoms is insufficient to form a stable state for the entity of ionic bonds. The re-configuration of ionic atoms during the aging is indispensable so that the Coulomb energy become lowest. If an ionic bond is formed, the quantum state unoccupied by electrons surely decreases. Thus, ionic bonds refrain atoms from motions and the strength (hardness) of the material is increased. Summarizing the above discussion, we can judge whether the precipitation-hardening can be expected or not in a concerned alloy, using the following criterion.

(Criterion) Ionic bond is formed and stabilized in an age(precipitation)-hardening alloy. Age-hardening machanism can be expected, if a blend of metals fulfils the conditions that ABP of alloying element is smaller than that of the pure solvent atom, and AP of alloying element largely changes from that of the neutral solvent atom.

3.3. Work hardening type

(Definition) Work hardening means a part of the hardening which is introduced directly from the cold working. Even if the hardening is superposed by solid solution hardening and precipitation hardening, they are disregarded in this definition. The part of hardening only induced by the deformation of atomic arrangement due to cold working is considered.

What kind of chemical bond caueses the work hardening of this definition? And how can we relate the work-herdening to electronic states in materials? The work hardening is originated from a scheme based on neither solid solution hardening nor precipitation-hardening. Therefore, ABP of alloying element is not altered to a large extent, compared with that of the pure solvent. In addition, AP of alloying element should not change much from the pure solute, so that it is impossible to form ionic bond, either. How does the solute atom make material hardened? Suppose that the solute and solvent atoms individually compose different crystal structures in solids. In this case, the spatial symmetry of the bonding electrons of solute atoms significantly differs from that of solvent atom in an alloy. This situation compels the solute atoms to be unstable, when the solute atoms occupy the crystallographic atom positions of the solvent. Therefore, it is difficult to expect that the overlap of bonding orbitals positively works only by replacing solvent atoms with solute atoms in the crystal. To get a more stable state for the bonding orbitals with different symmetry, the original arrangement of solvent atoms in crystal must be destroyed and compromised. One of the most easiest and effective ways is cold working, because the plastic deformation introduces the destruction of bonds in a crystal. The local lattice imperfection in the crystal can accommodate the guest atoms with electrons in spatial distributions differing from solvent atoms. Thus, the formation of a new covalent bond results in a new scheme of strengthening, which is different from those mentioned above. After covalent bond is locally formed, electron-deficient states are reduced and the material is hardened. Hereafter, new judgment criterion is given as follows.

(Criterion) Solute atoms composing a crystal structure different from that of solvent atoms and having a strong tendency to form covalent bond is suitable for work hardening.

3.4. Anti-corrosion type

(Definition) Corrosion resistance is defined as the property which are difficult to be corroded under the global environment.

Water and oxygen are main corrosive substances in the global environment. There are acids, alkalis and halide ions as special corrosive substances. The corrosion by such substances ultimately reaches ionic reactions and charge- transfer reactions. Namely, the corrosion resistance means the capability that suppresses the ionic and charge-transfer reactions. For enhancement of the anti-corrosion property, the following condition is necessarily achieved; the electrons are difficult to be removed by water, oxygen, acids, alkalis and halide ions. Namely, a large electro-negativity is necessary. For example, substances with a tendency to form covalent bonds have a strong resistance and strong covalent bond films also protect water corrosions. When such protective films are required, Cr, Si, Al, rare earth elements etc. are included in allloys as additives. Neither ionic bond nor metallic bond can be positively used, but covalent bond is necessary to suppress the corrosion by the ionic reaction and charge-transfer reaction. The electron-deficient state decreases and the energy fluctuation become small, when the covalent bond is dominant. Therefore, the corrosion reaction is suppressed.

(Criterion) When an element with a large electro-negativity is added as a solute and the covalent bond nature increases, the energy fluctuation decreases and the corrosion with ionic reaction or charge-transfer reaction are suppressed.

3.5. Heat-resistant type

(Definition) Heat-resistance is defined as the property integrating high strength, oxidation resistance and corrosion resistance at high temperatures.

This definition is sufficient when the terminology of the heat-resistant alloy is used in the meaning: (1) materials strength is large at high temperatures, (including creep strength etc. which resist to deteriorate with time), (2) material is not oxidized in the atmosphere at high temperatures, (3) the corrosion resistance is maintained even at high temperatures.

The conventional criterion has requested the materials belonging to this group to have high melting points. However, this criterion does not assure that both oxidation resistance and corrosion resistance are simultaneously kept at high temperatures in the material with a high melting point. For example, tangusten has the highest melting point among the elements listed in the periodic table, but is well-known the fact that this element poorly resists oxidation and corrosion. Thus, the melting point is not sufficient to be placed to an essential condition for considering whether or not corrosion resistance is kept at high temperatures. Namely, only strength and oxidation resistance remain in the conventional definition. What kind of the evaluation can be avalable for the classification? It may be necessary to return to the definition of stability in order to get an answer to this question. The guidelines of the stability are (1) a large cohesive energy and (2) a small energy fluctuation. What kind of chemical bond satisfies these conditions of the stability simultaneously ? A metallic element with a high melting point like W satisfies the first condition that the cohesive energy is large because there is good correlation between melting point and cohesive energy. However, this element lacks oxidation and corrosion resistances. The second condition of small energy fluctuation is necessary in order to satisfy oxidation resistance and corrosion resistance simultaneously. For example, Pt and Pd are excellent in oxidation and corrosion resistances, if one does not pursue the extreme of the first condition. The chemical bond must not be metallic bond but the covalent or ionic bond is preferrable, in order to increase the resistances. The electron-defficient states decrease in this case. Thus, we can consider the property, taking the results obtained by the MO calculation into accounts. The information is critically important, whether or not (1) cohesive energy of solvent atom is large, (2) ABP of alloying element is larger than that of solvent metal (covalent bond) or AP of alloying element changes largely from that of solvent metal (ionic bond). After all, the criterion for the heat-resistance is as follows:

(Criterion) Large cohesive energy, small energy fluctuation and strong covalent or ionic bond should be satisfied in the alloy.

3.6. Casting type

(Definition) Casting alloy is defined as an alloy which has a low melting point, good fluidity and no casting defects.

The name of casting alloy is conventionally used for an alloy of which is used for casting. However, only the metallic material which has an excellent castability is called with this term in our study. What kind of chemical bond causes the castability thus defined ? To begin with, it may be worthwhile to point out that two crutial conditions; low melting point and good fluidity, can be evaluated by the cohesive energy of pure substance. Practical problems due to gases can be solved by melting under the vacuum or inert gas atmosphere. Low melting point alloys, e.g., Mg-, Zn-, Sn-, and Pb-base alloys, can be casted in such a way. However, when the cohesive energy of the solvent metal is high as is often seen in Fe alloys etc., it is achieved by the addition of an element with a tendency to form strong covalent bond. When the element with strong covalent bonds such as C, Si exists, the clustering occurs around such element atoms. The atoms are strongly bound to each other inside each cluster. However, the binding force is weakened between the clusters due to the electron transfer to accomplish the saturation of covalent bonds. Therefore, each cluster obtains freedom to move, and accordingly the melting point decreases and fluidity increases. In addition to the two effects, the gaseous atoms are not absorbed in the material when the saturation of covalent bond is established. The suppression of casting defects is finally resulted. The mechanism above described is, for example, expected to occur in an alloy system of which the phase diagram appears the eutectic type.

(Criterion) Cohesive energy of solvent metal is small, or the elements belonging to IVb column of the periodic table with a strong covalent bond nature are contained in the casting alloy when the cohesive energy of the solvent metal is large.

4. Conclusions

The present paper described an alternative way to understand the solid solubility, hardening mechanisms, anti-corrosion, heat-resistance and casting property, on the basis of chemical bond theory and quantum chemistry. The authors would stress that the new approach is available for all types of materials and provides a compass to understand and forecast the properties. In addition, one can quantitatively discuss the phenomena including even macroscopic properties such as strengths, if some essential values are collected by quantum physics/chemistry calculations.

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