Metallurgical Approaches for Controlling Solid Surface Reaction

Yoshitaka NISHIYAMA* Tomohiko OMURA

Abstract
Adsorption of various molecules is dissociated on metal surface, resulting in some corrosion. Alloying elements promoting the non-dissociative adsorption suppress the surface reaction with the molecules, e.g. CO gas at high temperature, H₂ gas at high pressure, H⁺ in aqueous solution. In addition, the effective alloying elements are evidently associated with their surface energy.

1. Introduction
Metal that is exposed to gas or liquid (aqueous solution) usually corrodes. Corrosion can be referred to as oxidation, carburization, nitridization, hydrogen penetration, atmospheric corrosion, or molten salt corrosion depending on the types of gas and solution involved in the phenomenon. Knowledge of thermodynamics constitutes the first step in understanding corrosion. In other words, thermodynamic parameters in external environments are used to examine free energy to form chemical compounds (e.g., corrosion products), thereby assessing the stability. Thermodynamic parameters are very important information in terms of engineering. Not only do they allow for the estimation of corrosion behavior of a metal material that is used, but they also serve as design guidelines for the development of a new material.

When an external substance reacts with metal, it penetrates into the inside through the surface of the solid-state metal. Therefore, it is important to understand the microscopic reactions on the surface of solids. The atoms on the surface of a solid are at the dangling bond level as they have no binding partners. In other words, the surface energy is higher than that inside the solid metal. Various molecules are absorbed and dissociated in order to lower the surface energy (surface tension) equivalent to the excessive energy per unit area. These processes can be explained using the electronic state theory. For example, Blyholder suggested in 1964 a dissociative adsorption reaction mechanism in which electrons are transferred between CO molecules and metal. Details of the surface reactions based on the electronic state theory will be discussed in another report later in this issue. In this paper, we describe the interpretation of surface reactions based on the experiment results and the direction that alloy metallurgy going forward can take in order to control solid surfaces.

2. Concept of Dissociative Adsorption and Its Relationship with Alloy Elements

Figure 1 shows a schematic view of the potential energy of a molecule that is approaching the surface of solid metal. The horizontal axis denotes the reaction coordinate on any scale. The molecule is closer to the solid surface as the coordinate is closer to the farthest to the left. Three potential energy curves based on the Lennard-Jones potential compose the entire curve in the schematic diagram. When the molecule approaches the solid surface (on the right side in Fig. 1), (a) physical adsorption on which the van der Waals force is acting occurs. This is weak binding energy. When the molecule further comes closer to the surface, (b) molecular chemisorption in which the bond becomes stronger occurs. The activation energy (ΔE*) barrier between (a) and (b) is the barrier between physical adsorption and chemisorption. In addition, when electrons taken out from the metal’s Fermi level enter the antibonding orbital of the molecule, the bond of the molecule becomes weaker and (c)

Fig. 1 Schematic potential energy diagrams of H₂ molecule approaching to a metal surface

* General Manager, Head of Div., Dr. Eng., Hydrogen & Energy Materials Research Lab., Steel Research Laboratories 1-8 Fuso-cho, Amagasaki, Hyogo Pref. 660-0891
the dissociative adsorption in which the molecule breaks into two atoms occurs. The activation energy ($\Delta E^*$) barrier between (b) and (c) is the barrier between chemisorption and dissociation. Then, the dissociated atoms (d) dissolve into the solid metal.

The important phenomenon here is (c) dissociative adsorption. Control of the dissociative adsorption allows for the suppression of reactions. For example, in an experiment using pure metal and CO molecules Cu is effective for suppressing dissociative adsorption. When a CO molecule comes closer to the surface of the bcc-Fe(100) plane, hybridization occurs between the $2\sigma^*$ antibonding orbital of the CO molecule and the $d$ orbital of the Fe. In other words, electrons are back donated from the $d$ orbital to the $2\sigma^*$ orbital. As a result, the C-O bond becomes weaker and the CO molecule is dissociatively adsorbed. On the other hand, even when a CO molecule comes closer to the surface of the fcc-Cu(100) plane, back donation of electrons is less likely to occur, therefore the C-O binding is maintained. This behavior closely relates to the state of the electrons in the metal's $d$ orbital. The higher the Fermi level is, the less likely the back donation of electrons occurs.

As described in the Introduction, the state of the dangling bond level on the surface of solid metal is related to the surface energy. Figure 2 shows the surface tension data of Keene\textsuperscript{11} plotted against the corresponding International Union of Pure and Applied Chemistry (IUPAC) numbers. These numbers are equivalent to the number of valence electrons for the 3d, 4d, and 5d groups. In addition, the surface tension is a force per unit length (mN/m\textsuperscript{-1}). The surface tension tends to be convexed, peaking around seven as the number of d electrons. According to Fig. 2, the steel materials that we handled were those of surface-active with high surface energy. This means that, when these materials are used as products, the surface reactions to reduce the surface tension decreases and dissociative adsorption reactions are also reduced. A metallurgical method that uses such surface-active elements has the potential to change the surface reactions to suppress corrosion.

Here, we describe the stability of chemical compounds as described in the Introduction. Figure 3 shows free energy of carbide formation in 3d-transition metal at 650°C plotted against IUPAC numbers on the horizontal axis. The free energy of the formation of chemical compounds becomes larger as the number of valence electrons increases, which means that the stability decreases. This energy correlates to some extent with electronegativity at which perfect covalent binding starts to have ion binding properties, likely to form stable chemical compounds with elements for which electronegativity is smaller (i.e., the group number is smaller) than that of carbon belonging to group 14 of IUPAC. The surfaces of chemical compounds also have dangling bonds. It has been reported that the state of surface electrons was observed through angle-resolved photoemission spectroscopy (ARPES) in a paper.\textsuperscript{19}

In the next chapter, we describe actual cases of reactions between solid metal and gas, and between solid metal and aqueous solution.

3. Reaction between Solid-state Metal and Gas
3.1 Reaction between CO molecules and metal

We investigated reactions between metal and CO gas at high temperature. In a simulated 60%CO-26%H\textsubscript{2}-11.5%CO\textsubscript{2}−2.5%H\textsubscript{2}O (in vol%) synthesis gas, the atmosphere carburized due to the CO gas where carburization and metal dusting corrosion occur and carbon accumulates on the surface.\textsuperscript{9,11} We used fcc-Ni as a representative from group 10 of the 3d-transition metal. We added elements that belong to groups 11, 14, and 15 to the Ni and evaluated the Ni-X binary alloys.\textsuperscript{9,11} Figure 4 shows the amounts of deposited carbon accumulated on such binary alloys after they were heated in the above simulated synthesis gas at 650°C for 100 hours plotted against the amounts of the additive elements X on the horizontal axis.\textsuperscript{10} Compared to the amount of carbon deposited on pure Ni (broken line in the figure), adding the elements of groups 11, 14, and 15 reduced the amounts of carbon deposited. This indicates that adding these elements suppresses dissociative adsorption of CO gas onto the Ni surface. The estimated effective amount of Ge, Sn, and Pb to be added to suppress the amount of carbon deposited to the level not exceeding 1g·m\textsuperscript{-2} is approximately 2 at%, 3 at%, and 0.1 at%, respectively. The effective amounts of these elements to be added are obviously less than the effective amount of Cu (20 at% or more) for Ni-Cu binary alloys (Fig. 4(a)).

Adding P, Sb, and Bi (group 15 elements) remarkably reduces carbon deposition caused by CO dissociative adsorption. The effective amounts of P, Sb, and Bi to be added to reduce the amount of carbon deposited to the level not exceeding 1g·m\textsuperscript{-2} are 0.02, 0.15, and 0.003 at%, respectively. Comparing these effective amounts to those of the group 14 elements, the group 15 elements worked better even when the amounts to be added were smaller than the group 14 elements. Figure 5 shows the microstructures of the cross sections of the after-the-test materials to which Sn was added as a representative element from group 14. When the amounts of Sn added are
0.25 at% and 0.49 at%, the surface is very coarse. This is attributable to a reduction in the thickness of the metal caused by metal dusting corrosion. Adding 2.51 at% Sn reduces roughness of the surface. At 4.83 at% Sn, almost no corrosion is seen. The corrosion behavior viewed from the form of the surface aligns well with the amounts of carbon resulting from the deposition behavior as shown in Fig. 4. As described above, adding Cu of group 11 and the other elements of groups 14 and 15, the Fermi levels of which are higher (surface energy is smaller) than that of Ni (group 10) to Ni to form an alloy, suppresses dissociative adsorption of CO molecules, thereby reducing corrosion.

The effects of the amounts to be added based on the group numbers are larger than the surface tension values projected from Fig. 2. The surface segregation involves this. Tanaka, et al.\(^{13}\) projected the surface physical properties of molten alloys and mixed molten salts based on thermodynamics on the surfaces. The physical properties of solid-state metal can be considered in a similar way in terms of thermodynamics. Butler\(^{14}\) derived the relationship between the chemical potential of the surface \(\mu_{\text{surf}}\) and the inner chemical potential \(\mu_{\text{bulk}}\), defining the outermost surface (single atomic layer) is the surface, as equation (1),

\[
\mu_{\text{surf}} = \mu_{\text{bulk}} + \sigma \cdot A_i
\]

where \(\sigma\) is the surface tension, \(A_i\) is the molar surface area of component \(i\), and \(\sigma \cdot A_i\) is the excessive energy on the surface. The result of thermodynamic calculation shows that when the curve of activity of a binary alloy is biased to positives, the surface segregation of the solute elements becomes large from the low-concentration area. Furthermore, when the activity is biased to negatives, surface segregation appears in the high-concentration area. For example, the activity of Cu in a Ni-Cu binary alloy is biased to positives.\(^{12}\)

To confirm that surface segregation occurs in the Ni-X binary alloys at 650°C, the Ni-X binary alloys (X = Cu, Sn, Sb) were heated at 650°C in a vacuum atmosphere. Then the surface was measured through ARPES. For quantitatively evaluating the surface segregation of each alloy from the measurement results, a hierarchical model was used.\(^{15}\) Figure 6 shows the obtained results with the horizontal axis denoting the amounts of X added and as the vertical axis representing the surface segregation concentration.\(^{12}\) This diagram shows that the concentrations of all the added elements are higher on the surface than those inside the solid metal; also, the surface concentration of Cu (group 11) is the highest, followed by Sn (group 14), and then Sb (group 15). When the surface segregation concentrations for 20 at% Cu, 3 at% Sn, and 0.15 at% Sb, which are the effective amounts of the solute elements to be added to suppress carbon deposition as obtained in the experiment, are estimated based on Fig. 6, these will be approximately 65 at% Cu, 50 at% Sn, and 30 at% Sb.

### 3.2 Reaction between \(H_2\) molecules and metal

The reaction between \(H_2\) molecules and metal is important to understand the hydrogen penetration into a metal material in the hydrogen gas environment and the hydrogen embrittlement caused by such penetration. To start with the conclusion, various types of metal show the same tendency in terms of the likelihood of dissociative adsorption of CO molecules described in the previous chapter, as well as the likelihood of dissociative adsorption of \(H_2\) molecules and following hydrogen penetration. In other words, a covalent bond or orbital is formed between the H-1s orbital and the d orbital of the transition metal with high surface energy, stabilizing the dissociation of a transition metal molecule to an H atom. On the other hand, for simple metal without d orbitals in the valence band (e.g., Al) and for metal for which d orbitals are not extensive (e.g., Cu, Ag, Au, Zn, and Cd), a covalent bond or chemical bond with an H atom is un-
The following is a sample of verification for the above theory using three Fe-Cr-Ni alloys (stainless steel) and an Al alloy. These alloys were exposed to high-pressure hydrogen gas at 45 MPa and 85°C for 100 hours. Figure 7 shows the concentrations of hydrogen absorbed in the alloys after the exposure. The materials used in the test specifically were austenitic stainless steel (SUS316L), stainless steel with 4% of Al, ferritic stainless steel (SUS430) (these three had been solution heat treated), and aluminum alloy (A6061) (thermal aged after solution heat treatment). Regarding the test pieces of the three stainless steel materials, in order to consider the influence of an oxide film formed on the surface, we used those on which an oxide film had been formed through various treatments in advance, in addition to those the surfaces of which had been polished. The test pieces taken from the passivated stainless steel material (316L) and materials with an oxide film formed through heat treatment in a dew-point controlled atmosphere (4Al-SS, 430) absorbed hydrogen much less than those taken from the polished stainless steel materials. On the surface of 4Al-SS that was heat treated under the dew-point controlled condition, 200-μm-thick Al₂O₃ was formed; and on the surface of 430 that was subjected to the same treatment, 150-μm-thick Cr₂O₃ was formed. Furthermore, the amount of hydrogen absorbed in the polished A6061 was much smaller than the other polished materials.

To investigate the influence of the oxides on the surface, tensile plastic deformation was caused to tensile test piece plates in the hydrogen gas environment described above. The process was halted, and the test pieces were retained for 100 hours. Figure 8 shows the concentrations of hydrogen that the test pieces absorbed. When plastic deformation was caused to the passivated 316L material and the 4Al-SS with Al₂O₃, the amounts of absorbed hydrogen sharply increased, coming close to the values of the polished materials shown in Fig. 7. It was confirmed through surface observation that the oxide film on the surface was broken by plastic deformation by 10% or more. In other words, an oxide film on the surface works to prevent hydrogen from getting in the metal. However, if such oxide is broken due to deformation and the metal under the oxide comes into contact with hydrogen gas, hydrogen easily enters the metal. On the other hand, when plastic deformation was caused to A6061, hydrogen absorption was not brought forward. This shows that the reason why the amount of hydrogen that the A6061 absorbed was small was resulted from the effect of the metal elements themselves, not from the function of the oxide film (Al₂O₃) on the surface.

The effect for suppressing hydrogen penetration of Al alloys was considered based on first-principles molecular orbital calculations. It has been demonstrated that when adiabatic potential curves under the condition in which H₂ molecules are brought near the (100) planes of Al and Fe are calculated, strong Pauli repulsion occurs in the Al and there is a high energy barrier before the dissociation state. However, in Fe that has an unoccupied d band, the state reaches that of the chemisorption of H₂ molecules without an activation process. This dissociation process is explained in terms of the electron theory from the Blyholder mechanism as is the case with the CO molecule dissociation mechanism of the metal dusting phenomenon described above. It is thought that oxides also have a similar suppression effect on the dissociation reactions of H₂ molecules.

Fe-base alloys thus encourage the dissociative adsorption of H₂. However, when the temperature is equal to or lower than a specified temperature, such effect is unlikely to work as shown in the dependence of the amount of hydrogen absorption on temperature (in hydrogen at 80 MPa) in Fig. 9. The critical temperature is 50°C for low-alloy steel (0.2%C-1%Mn steel), 80°C for SUS420 (0.2%C-12%Cr steel), and 150°C for SUS316L (18%Cr-8%Ni-2%Mo steel), depending on the amount of Cr. However, it has been confirmed that even when the temperature is equal to or lower than such critical temperatures (~40°C to room temperature), if plastic deformation is caused, hydrogen absorption is sharply accelerated as is the case with Fig. 8. In view of the dependence of the critical temperature on the amount of Cr and the effect of plastic deformation to bring forward hydrogen absorption, at low temperature, an oxide film that has been formed in advance even on the surface of a polished material works to suppress hydrogen penetration.
4. Reaction between Solid-state Metal and Aqueous Solution

The following is the reaction between H⁺ in aqueous solution and metal, and its influence on hydrogen penetration. The tendency that each type of metal has of H atom adsorption in aqueous solution and following hydrogen penetration is completely opposite to that in an environment with gas molecules as described later.

The reactions in which the surface of metal absorbs H atoms in aqueous solution is advanced as indicated by the combination of the Volmer mechanism and the Tafel mechanism or the combination of the Volmer mechanism and the Heyrovsky mechanism as follows.

Part of the H atoms (Had) absorbed by the metal surface enter the metal material.

\[
\text{Volmer mechanism} \quad H^+ + e^- \rightarrow H_2 (2)
\]
\[
\text{Tafel mechanism} \quad H_2 + H^+ \rightarrow H_3 (3)
\]
\[
\text{Heyrovsky mechanism} \quad H_2 + H^+ + e^- \rightarrow H_3 (4)
\]

Elements in groups 12 to 16 (e.g., P, S, As, and Pb) and chemical compounds that include such elements (e.g., hydrogen sulfide [H₂S] and thiocyanate ion [CNS⁻]) encourage hydrogen penetration from aqueous solution.²⁰ It is thought that such action mechanism prevents H atoms from recombining to return H₂, molecules shown in equations (3) and (4) and stabilizes the state of H₂. Figure 10 shows the exchange current density (hydrogen overvoltage)²¹ of the hydrogen production reactions of various elements organized using IUPAC numbers. It shows the periodicity similar to Fig. 2. The hydrogen production exchange current density of the elements in groups 12 and above is small (hydrogen overvoltage is large). This reflects the fact that the reactions in which H atoms recombine to be H₂ molecules as shown by equations (3) and (4) are slow. On the other hand, the hydrogen production exchange current density of the elements in groups 7 to 10 is large (hydrogen overvoltage is small). Therefore, these elements are expected to have the effect of suppressing hydrogen penetration on the contrary.

We had low-alloy steel (0.2%-1Mn steel) contain various elements and then immersed in pH 3.5 acetie acid solution. Figure 11 shows the amounts of hydrogen penetrated at that time (hydrogen permeation coefficients calculated based on hydrogen permeation test results).²² Ni (group 10) makes the spontaneous potential higher (reduces hydrogen overvoltage) and suppresses hydrogen penetration. Cu (group 11) and Mo (group 6) have similar effects. On the other hand, even a very small amount of S (group 14) makes the spontaneous potential lower (increases hydrogen overvoltage) and intensely accelerates hydrogen penetration. S exists as Mn sulfide in steel and chemically dissolves in aqueous solution, which produces H₂S²³ exerting large influence even when it is a very small amount.

The reason that the action of the elements in hydrogen gas is completely opposite to that in aqueous solution is explained as follows using Fig. 1. Elements with high surface energy work to lower activation energy (ΔE**) from (b) to (c). Therefore, such elements promptly dissociate H₂ molecules absorbed in the hydrogen gas environment to H atoms that are easily absorbed inside the solid metal. On the other hand, such elements in aqueous solution make H atoms absorbed on the surface of the metal promptly bond to be H₂ molecules and discharge them. Elements in which ΔE** is low and thus the activation energy for recombination from (c) to (b) is low can be easily discharged. This means that when designing the components of a material, it should be noted that the hydrogen penetration action is completely opposite depending on the state of hydrogen (molecules or atoms) in the environment.

5. Conclusion

In this paper, we explained that the dangling bond level on the surface of solid metal affects the dissociative adsorption of molecules of gas/aqueous solution that the surface contacts, determining the surface reaction. Solid surfaces are actively investigated in the field of catalysts using the electronic state theory and various surface analysis methods. Applying the rules and principles obtained through these studies to the steelmaking field can allow for expert design of steel products, metallurgically using surfactant elements. This idea can also be applied to interfaces, not only the surfaces. For example, new metallurgical control may be allowed for the adherence of an interface between solids (e.g., oxide scale and metal) and grain boundary bonding in a solid.

References

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