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Mechanism of Adhesion of Epoxy Resin to Steel Surface

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Abstract:

To clarify the mechanism of adhesion of epoxy resins to cold-rolled steel (CR), galvanized steel (GI), and galvannealed steel (GA), macroscopic adhesive joint failure tests and molecular-level model experiments were conducted. When adhesive joints of CR, GI, and GA sheets were tested for loss of strength in a humid environment, it was found that the GI adhesive joints were inferior to the CR and GA adhesive joints in durability, and that the failure mode was adhesive failure for the CR and GA adhesive joints, whereas it was a mixture of cohesive failure and adhesive failure for the GI adhesive joints. When the type of bond at the interface between zinc oxide or iron oxide and epoxy compounds was studied by the temperature-programmed desorption (TPD) method under a ultrahigh vacuum, it was found that the epoxy compounds were dissociated between phenoxy oxygen and aliphatic carbon and chemically adsorbed on both zinc oxide and iron oxide, and that when water was coadsorbed (dissociatively adsorbed), the bonding of epoxy was destroyed only on zinc oxide. According to these findings, it was concluded that the formation of interfacial chemical bonds contributes to the adhesion of epoxy resins to CR, GI, and GA sheets. The entry of water into the interface breaks the chemical bonds for the GI adhesive joints, but not for the CR and GA adhesive joints. This is the reason why the GI adhesive joints are less durable than CR and GA adhesive joints.

1. Introduction

1.1 Steel products and epoxy resins

There are many products in which ferrous materials are used as bonded by epoxy resins. For example, galvanized steel sheets for automotive bodies are coated with epoxy-base cathodic electrodeposition primers, and automobile door hems are coated with epoxy-base structural adhesives. Epoxy paints are commonly used as primers for precoated steel sheets that are used in large amounts for household electric appliances. With polypropylene-coated steel pipes and sheet piles used as heavily protected materials in offshore structures, the first primer layer is often of epoxy resin. The required adhesion between epoxy resins and steel surfaces varies with specific applications. Modified resin systems and steel surface treatment methods that are empirically considered optimum are selected. The mechanism of adhesion at the adhesive-

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adherent interface, basic to the technologies involved, is not fully understood yet, however.

1.2 Past studies and recent moves concerning mechanism of adhesion

The phenomenon of adhesion at the interface between an organic compound, such as a paint or an adhesive, and an adherent, such as a metal, plastic, wood or ceramic, has been actively studied since the last years of the 18th century. These research efforts may be classifed into two main approaches. One approach starts with theory and tries to understand and predict the phenomenon of adhesion. The other involves the observation of fracture surface conditions after an adhesive failure and estimation of the original interfacial bond. Among the former approach are the theories of interfacial chemistry, such as wetting theory[1-5] starting with Young's equation[6] and theory ascribing interfacial bonding to the acid-base interaction[7,8]. Surface and fracture surface analyses in the latter category are often applied to metal adhesion. For example, the research by Venables et al.[9] of the topography of anodized aluminum surfaces is famous. Recently, a new approach has appeared as an adhesion research method. It analyzes a more simplified model in place of an actual adhesive structure by using surface analysis instruments. Either a model having a thin metal film vapor deposited on a polymer[10] or a model having a metal spin coated with a thin polymer film[11,12] is used. These models are used because ordinary surface analysis can directly yield information on the interface. In other words, a very thin film of metallic or organic material is prepared, and signals are detected as they are transmitted from the interface through the film. This technique can obtain molecular-level information on the bonding of the adhesive interface that has been difficult to analyze in the past.

1.3 Purposes of study

This study is intended to clarify the mechanism of interfacial adhesion on a molecular level focusing on the mechanism of adhesion between the epoxy resin and ferrous material as described at the beginning. In a preliminary step, the strength and loss of strength under wetting were investigated for epoxy-adhesive joints of cold rolled steel sheets and galvanized steel sheets, respectively. Then, the difference of bond strength between the two types of adhesive joints was correlated to the difference of the failure mode examined by fractography. Next, to model the surface structure of the cold-rolled steel sheet and galvanized steel sheet, ferrous oxide (FeO) and zinc oxide (ZnO) were vapor deposited on a gold substrate under ultra high vacuum, and epoxy resin model compounds were adsorbed to a few molecular layers on the vapor-deposited coating. The form and energy of bonding at the interface were clarified from the type of fragments disbonded from the interface and the temperature of disbonding. When water was coadsorbed on the surface of the specimen, whether or not the epoxy bonds would be replaced was investigated and compared with the strength loss of the adhesive joints under wetting.

2. Strength loss and failure mode of adhesive joints in humid environment[13]

The adhesive bonding of cold-rolled steel and galvanized steel by epoxy adhesives is highlighted as a joining process that provides better rigidity and fatigue strength than conventional spot welding. There still remains the problem of reliability in long-term use that is common to all adhesive structures. Galvanized steel has an additional problem of coat peeling during static failure, which, however, is not dealt with here because the authors have already published a report on this issue[14]. There are many causes of decrease in adhesive strength with time. The universal and gravest factor is moisture in the atmosphere. Adhesive joints of cold-rolled steel and galvanized steel were prepared and investigated for change with time in strength in a humid environment. To interpret the difference in wet durability between different adherends, the surfaces of the adherents after failure were analyzed, and the difference in microscopic failure modes were examined.

2.1 Experimental methods

2.1.1 Materials

A commercial one-component thermosetting amine-cured epoxy structural adhesive was used to bond three types of steel sheets listed in **Table 1.**

2.1.2 Adhesive joint fabricating conditions

The adherends were alkaline degreased, bonded on coated surfaces by the epoxy adhesive into a single lap joint according to JIS K 6850, as illustrated in **Fig. 1**, and cured at 170°C for 30 min. Two 0.1 mm diameter copper wires were installed in the lap to keep the adhesive layer thickness constant. The single lap joint was treated with zinc phosphate and cathodically electroprimed to prevent corrosion from occurring at portions other than the lap of the joint in the wet test and from affecting the bond strength of the joint.

2.1.3 Adhesive durability test

Two types of humid environments were prepared: (1) a humidity cabinet at 49°C and 95% RH; and (2) warm water immersion at 50°C. Adhesive joints of galvanized steel (GI) and galvannealed steel (GA) sheets were exposed to the environment (1), and adhesive joints of cold-rolled steel (CR) sheets were exposed to the severer environment (2). Three specimens each were removed at 2-week intervals and tensile shear tested for breaking strength.

The tensile shear test was conducted at room temperature and a crosshead speed of 10 mm/min on an Instron tensile testing machine. Adhesive joints not exposed to humid environment were also tensile shear tested as control specimens.

2.1.4 Analysis of adhesive fracture surfaces

Specimens were machined from the overlap ends of GI and GA adhesive joints the failure of which was initiated by stress concentrations in the tensile shear test and were analyzed for surface elements by X-ray photoelectron spectroscopy (XPS).

Table 1 Sheet steels used as adherents

Type of steel	Sheet thickness (mm)	Coating composition	Coating weight (g/m^2)
Galvanized steel (GI)	0.8	100% Zn	90
Galvannealed steel (GA)	0.8	85% Zn, 15% Fe	45
Cold-rolled steel (CR)	0.8	(100% Fe)	—

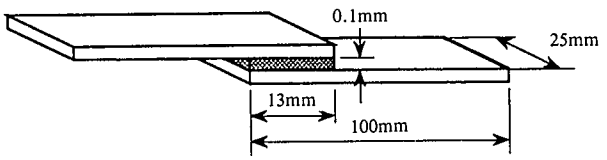


Fig. 1 Single lap joint (JIS K 6850)

Whether the mode of microscopic failure was adhesive or cohesive failure was determined according to the XPS results.

2.2 Results and discussion

2.2.1 Change in tensile shear strength of adhesive joints

Fig. 2 shows the change with time in the tensile shear strength of the GI, GA, and CR adhesive joints. The tensile shear strength decreases with increasing exposure time in the humid environment for each type of adherent, but the rate of the decrease is higher for GI than for CR and GA. In other words, the galvanized steel (GI) is inferior in epoxy resin adhesive durability to the galvannealed steel (GA) and the cold-rolled steel (CR). This is also routinely experienced with paint systems. Since the galvanized steel is lower in paint adhesion, long-term paint durability in particular, than the cold-rolled steel, it is chromated or zinc phosphated in preparation for painting.

2.2.2 Elemental analysis of adhesive fracture surface by XPS

Whether or not the adhesive joints would differ in the mode of failure (adhesive or cohesive failure) was investigated to clarify the reason for the difference in adhesive durability among the GA, CR, and GI adhesive joints. **Table 2** gives the elemental analysis results by XPS of the adhesive fracture surfaces and adherent surfaces of the GA and GI adhesive joints. The XPS surface analysis detects only those elements that are present in several tens of Ängstroms of the surface, so that carbon, oxygen, and nitrogen derived from organic compounds and other impurities adsorbed on the surface from the atmosphere are high in proportion. Oxygen also originates in zinc oxide on the surface. **Table 2** inditates that there are 20 to 30% carbon, about 50% oxygen, and about 20% zinc on the surface of both types of adherents before adhesion. The surface composition of adherents after failure was studied paying particular attention to the zinc and carbon contents by reference to these values.

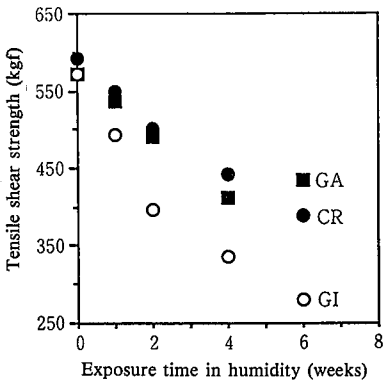


Fig. 2 Decrease in breaking strength of adhesive joints of three types of adherents in humid environment

Table 2 Results of XPS elemental analysis of adhesive joint fracture surfaces and adherent surfaces

Analyzed surface	Surface composition (%)			
	C	O	N	Zn
1. Galvannealed steel sheet (GA)				
a) Adherent surface before adhesion	32.6	49.7	0.1	17.2
b) Adhesive joint fracture surface: without exposure to humidity	71.1	25.7	1.8	1.3
c) Adhesive joint fracture surface: 10 weeks of exposure to humidity	58.7	32.3	3.3	5.1
2. Galvanized steel sheet (GI)				
a) Adherent surface before adhesion	20.1	56.3	1.1	21.9
b) Adhesive joint fracture surface: Without exposure to humidity	36.4	46.8	3.6	13.1
c) Adhesive joint fracture surface: 10 weeks of exposure to humidity	35.7	51.2	3.1	9.8

When the GA adhesive joint was broken without exposure to humidity, the carbon content more than doubled, but the zinc content was lower by one order of magnitude. This is because the adhesive still remains on the fracture surface covering the zinc coating. In other words, the failure mode is cohesive failure. When the GA adhesive joint was broken in 10 weeks of exposure to humidity, the carbon content was still higher than that on GA before adhesion. The zinc content was lower, but the difference was smaller than when tested without exposure to humidity. This suggests that the failure mode is cohesive failure on the whole, but an adhesive failure region also begins to appear locally. It is reasonable to think that this corresponds to the start of transition to an adhesive failure near the edge that is most susceptible to the weaking of interfacial bonding strength by water penetration into the coating-adhesive interface.

The fracture surface composition of the GI adhesive joints is practically the same irrespective of whether or not they were tested in the humid environment. There are much more adhesive failure regions than observed with the GA adhesive joints. Coupled with the finding that the loss of adhesion in the GI adhesive joints under a humid environment was more pronounced than the CR and GI adhesive joints, the interfacial bond strength between GI and the adhesive is not only essentially weak but is weakened further by the infiltration of water into the interface.

According to the above results, the change in the failure mode of joints with exposure to humidity is schematically illustrated in **Fig. 3**. This finding suggests that the interfacial bond strength between the epoxy adhesive and the steel sheet and the resistance of the interfacial bond to the penetration of water vary with the type of metal or oxide present on the steel sheet surface. It is not advisable to discuss the interfacial molecular structure from such macroscopic test results alone. For example, similar results may be obtained from the difference of surface roughness between GI and GA. A detailed study of the interfacial adhesion mechanism will be described in the next chapter.

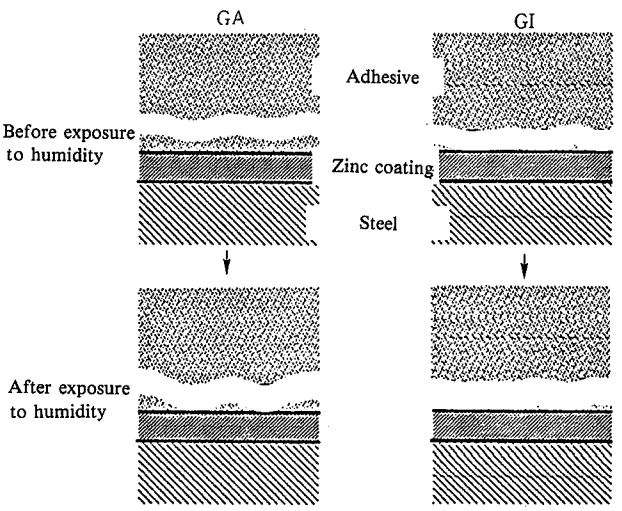


Fig. 3 Schematic illustration of change in failure mode of adhesive joint through exposure to humidity

2.3 Conclusions

Adhesive joints of cold-rolled steel (CR), galvanized steel (GI), and galvannealed steel (GA) sheets were prepared and tested for change with time in bond strength in a humid environment. The surfaces of adherents after failure were analyzed, and the adhesive joints were investigated for difference in the macroscopic mode of failure. The following conclusions were derived:

(1) The GI adhesive joints suffered a greater loss of strength in the humid environment than the CR and GA adhesive joints.

(2) The mode of failure was mainly adhesive failure for the GI adhesive joints, irrespective of whether or not the test was made in a humid environment. The GA adhesive joints suffered cohesive failure when tested in a dry environment and increased in adhesive failure when tested in a humid environment.

3. Molecular-Level Study of Adhesion Mechanism[15-17]

A famous report by Glazer[18] deals with interfacial bonding with epoxy resins. He measured the surface pressure of monomolecular films of various epoxy resins formed on the water surface using a Langmuir surface balance, and found that the bond strength of the epoxy resin to the water surface depends on its hydroxy group content but not on its epoxy group or hydrocarbon content. From these findings, he surmised that hydrogen bond is the basis for the adhesion of adherents to surface hydroxy groups, like wood and metals, to epoxy resins, and proposed the interfacial bond model presented in **Fig. 4**.

The previous chapter suggested the possibility that a surface comprising zinc oxide and one on which iron oxide is present may differ in the mechanism of interfacial adhesion to epoxy resins and the mechanism of degradation by water. The above adhesion mechanism cannot satisfactorily explain the fact that bond strength and wet durability vary from metal to metal. (Hydrogen bond will be replaced by water, irrespective of the type of metal.) When attention is turned to organic compounds, the above adhesion mechanism cannot explain the fact that epoxy resins have better bond strength than other organic polymer compounds having hydroxy groups. To study the adhesion mechanism of epoxy resins in detail at the molecular level, epoxy resin model compounds were investigated for adsorption and desorption behavior on clean zinc oxide and iron oxide formed in a ultrahigh vacuum (UHV) chamber, and the form and intensity of interfacial bonding were clarified. Whether or not this bond would be

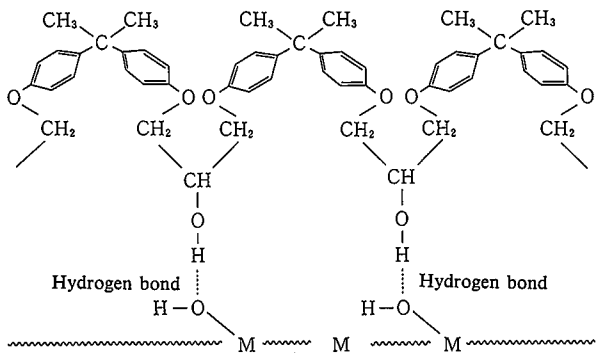


Fig. 4 Mechanism of adhesion between epoxy resin and metal surface as proposed by Glazer[18]

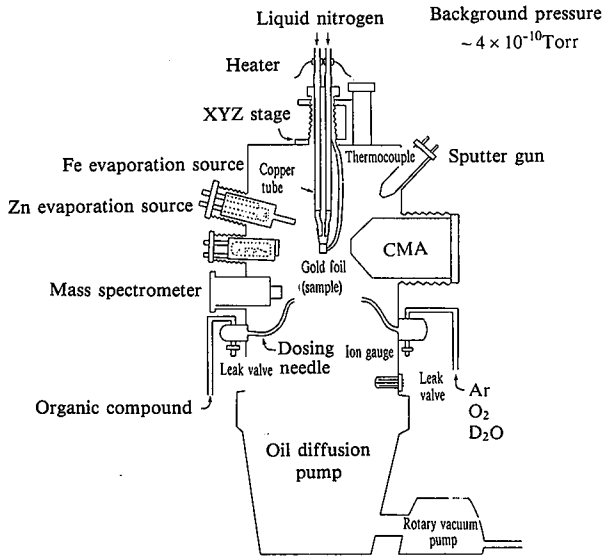


Fig 5 Ultrahigh-vacuum surface analyzer

replaced by coadsorption of water was also studied, and its correlation with the wet durability of adhesive joints was examined.

3.1 Experimental methods

3.1.1 Ultrahigh vacuum chamber

The configuration of the ultrahigh vacuum chamber used in the experiment is shown in **Fig. 5**. An oil diffusion pump was used in the exhaust system, and the ultimate vacuum was 4×10^{-10} Torr. The components of the system are described according to the experimental procedure.

(1) Argon sputter gun: Cleans the sample surface.

(2) Zinc and iron evaporation sources: Form zinc and iron films by heating zinc and iron wires.

(3) CMA: Checks the film composition by Auger spectroscopy.

(4) Sample holder: Heats and cools the sample (100-700 K).

(5) Dosing needle: Introduces organic materials and gases (argon and oxygen).

(6) Mass spectrometer: Detects molecular species desorbed from the sample.

3.1.2 Formation of thin films of zinc oxide and iron oxide

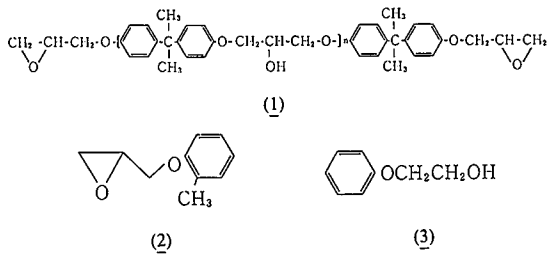
Gold foil, measuring 25 μm in thickness and 1 cm^2 in surface area, was mounted on the sample holder. The system was evacuated to a ultrahigh vacuum. The gold foil was heated to 773 K and cleaned by argon sputtering. The iron or zinc evaporation source was heated, and a thin film of iron or zinc was formed on the sample surface. The sample was annealed for about 1 h at an oxygen partial pressure of 10^{-6} to 10^{-7} Torr and sample temperature of 473 to 623 K to oxidize the metal film. The respective films were composed of iron oxide (FeO) and zinc oxide (ZnO) and 5 to 10 molecular layers thick.

3.1.3 Introduction of organic compounds

The sample was cooled to 100 K, and an organic compound was introduced through the dosing needle and adsorbed on the surface of the sample. The organic compounds introduced are epoxy model compounds A(2) and B(3) having the partial structure of bis phenol A epoxy resin (1), as shown in **Fig. 6**.

3.1.4 Analysis of interfacial bond form and energy by temperature programmed desorption (TPD)

The sample was heated at 10 K/min to 700 K, and the organic molecular species being desorbed were detected by mass spec-



(1)

(2)

(3)

Fig. 6 Structures of epoxy resin (1) and model compounds (2 and 3)

trometry. More specifically, the mass number of the detector was fixed at a certain value, and temperature programmed desorption (TPD) spectra where the temperature is plotted along the horizontal axis against the detection intensity of the molecular species having the mass number were recorded. In many cases, multiple spectra were obtained as the dosage of the organic compound. The adsorption energy of the epoxy model compound on iron oxide and zinc oxide was obtained, on the basis of the fact that the equation of Readhead[19] holds between the peak temperature T_p of the spectrum and the adsorption energy E_1 of the molecular species. Carbon sometimes remains on the sample surface after the end of the measurement. To remove residual carbon, the sample was annealed again under the oxygen partial pressure.

3.1.5 Coadsorption with water

In the experiment on coadsorption, water and the organic compound were separately and sequentially adsorbed on the sample surface using the two dosing needles.

3.2 Results and discussion

3.2.1 Adhesion mechanism of epoxy resins[16]

The adhesion mechanism of epoxy resins was determined according to the results of many adsorption experiments conducted using not only the epoxy model compounds A and B, but also simple substituted benzenes having the partial structures of the epoxy model compounds A and B. Here are introduced only representative data for a lack in space availability. For details, refer to the literature[15,16]. **Figs. 7** and **8** show TPD spectra of the epoxy model A on zinc oxide and iron oxide, respectively. The spectra are arranged by mass number (m/e) and presented in increasing order of dosage in mL (millilangmuir) from bottom to top. When the dosage is about 10 mL, the oxide surface is considered to be completely covered with a monolayer of organic compound.

The mass number 164 is equal to the molecular weight of the model compounds, but the change in the dosage in the corresponding TPD spectra (a) varies with zinc oxide and iron oxide. For zinc oxide, the desorption peaks shift to the low end of the temperature range with increasing dosage. This is the so-called second order desorption type and is characteristically observed when interfacial bonding with an oxide is effected through the benzene ring[15]. For iron oxide (**Fig. 8(a)**) in contrast, the first peak appears at 390 K at low dosage and grows in the same position with increasing dosage, and the second peak eventually appears at 280 K. This is a characteristic observed when dissociative adsorption occurs through the side chain. Given the stability of the intermediate, bond disassociation is predicted to occur between oxygen adjacent to the benzene ring, or phenoxy oxygen, and carbon adjacent to phenoxy oxygen. In fact, the spectrum

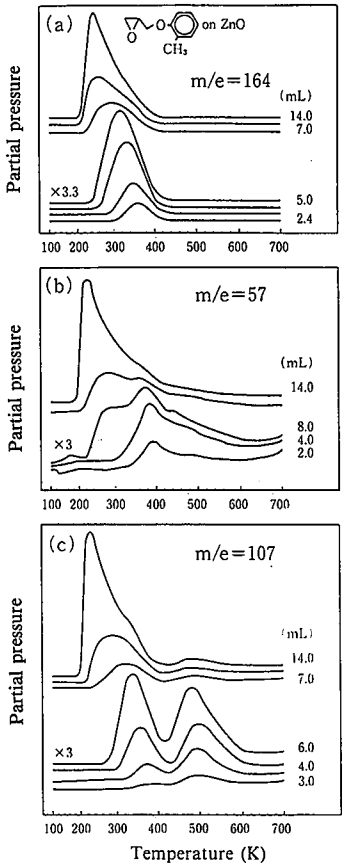


Fig. 7 TPD spectra of epoxy model A on ZnO

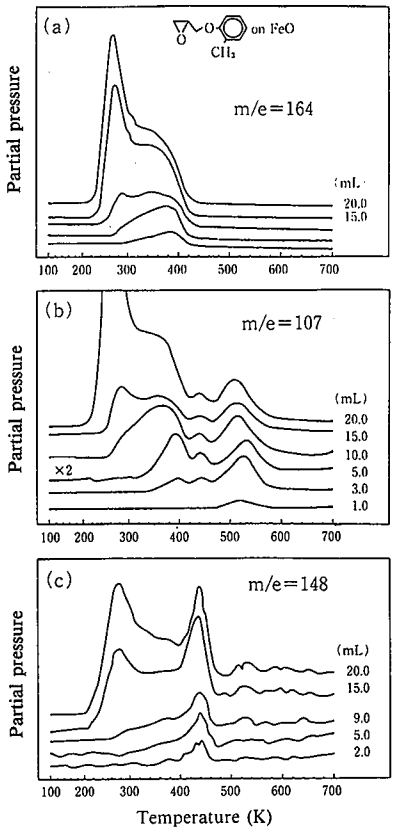


Fig. 8 TPD spectra of epoxy model A on FeO

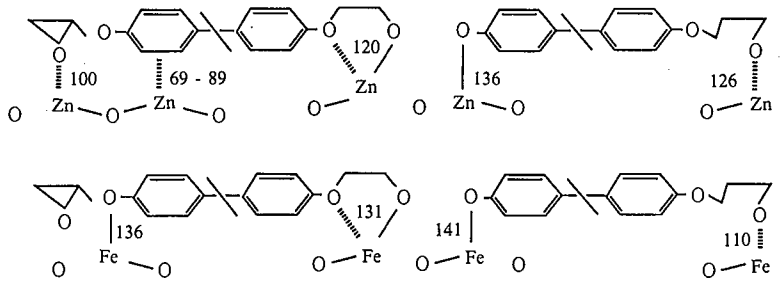


Fig. 9 Adhesion mechanism of epoxy resin on iron oxide and zinc oxide
Numbers indicate binding energy (kJ/mol).

of **Fig. 8(b)** detected at the mass number 107 corresponding to the fragment produced by this bond dissociation reveals the two peaks at the high end of the temperature range that are not observed in the spectrum of **Fig. 8(a)**. The 520 K peak appears in the same position as the phenol peak where dissociative adsorption is known to occur between phenoxy oxygen and carbon[15]. To summarize the above results, the epoxy model A is considered to be bonded to the surface of zinc oxide by molecular adsorption through the benzene ring and to the surface of iron oxide by dissociative adsorption through bond dissociation between phenoxy oxygen and carbon. **Fig. 7(c)** suggests that similar dissociative adsorption partly occurs on the zinc oxide surface as well.

A similar study was conducted also on the epoxy model B. **Fig. 9** shows the adhesion mechanism of epoxy resins studied from these results. This mechanism is considered more reasonable than Glazer's model because the phenoxy group, a characteristic structure of epoxy resins, is directly involved in interfacial bonding and because the bond form and energy vary with the type of oxide present.

3.2.2 Substitution of water for adsorbed organic compound

A metal surface in air is an oxide surface and is covered with chemically and/or physically adsorbed water. In this sense, the metal surface in air is different from a thin oxide film formed in a ultrahigh vacuum. Whether or not the adhesion mechanism of **Fig. 9** also holds in air can be verified by coadsorbing water on the metal surface and examining the TPD spectrum of the water-coadsorbed metal surface. The coadsorption of the organic compound and water is also helpful in elucidating the mechanism of strength loss in adhesive joints in a humid environment. Several organic compounds, including the epoxy model compounds A and B, were coadsorbed with water on zinc oxide and iron oxide and were investigated for the change in adsorption energy as compared with the case in which water was not coadsorbed.

The results are summarized in **Table 3**. The values of adsorption energy are obtained from the peak positions of the TPD spectra. First, the adsorption of water is examined. Water was adsorbed on each oxide in two states, and the peak of lower energy was a main peak. In other words, water was dissociatively adsorbed on the oxide surface in the ultrahigh vacuum to a very slight degree. Next, the desorption energy of the organic compounds is compared in the presence and absence of water. The adsorption energy of trifluorotoluene and benzene on zinc oxide was reduced by the coadsorption of water, but water had no effect on other combinations.

Table 3 Adsorption energy of organic compounds on zinc oxide and iron oxide

(kJ/mol)

	Trifluoro-toluene	Benzene	Epoxy model A	Epoxy model B	Water (D_2O)
On ZnO surface					
1. Adsorbed singly	62	75	140	140	89: Coordinative adsorption 152: Dissociative adsorption
2. Coadsorbed with water	58	59	140	140	—
On FeO surface					
1. Adsorbed singly	65	57	127	130	55: Physisorption 105: Dissociative adsorption
2. Coadsorbed with water	65	57	127	130	—

The above results can be easily interpreted if compared with **Table 3**. Namely, if an organic compound is lower in adsorption energy than water, it is replaced by water and loses its adsorption energy when coadsorbed with water. In contrast, if it has an adsorption energy higher than that of water, it is not replaced and affected by water when coadsorbed with water. The adsorption energy of water is based on coordinative adsorption or physical adsorption. The adhesion mechanism illustrated in **Fig. 9** is thus found to hold even when the oxide surface is covered with physically or coordinatively adsorbed water molecules.

One half to two-thirds of adsorbed water molecules on metal surfaces in air are reported to be dissociatively adsobred[20]. Therefore, when estimating the mechanism of adhesion in air or the mechanism of adhesion deterioration by water from the results of **Table 3**, the adsorption energy of dissociatively adsorbed water should be used as a reference. If so, it is suggested that all the organic compounds listed in Table, including the epoxy model compounds, are replaced by water on zinc oxide and that the replacement of epoxy by water does not take place on iron oxide. This agrees well with the durability tendency of adhesive joints of cold-rolled steel and galvannealed steel sheets described in the preceding chapter. Namely, the epoxy resin adheres by the mechanism of **Fig. 9** to the surface on which iron oxide is present and is not easily replaced by water. The adhesive joint is thus high in wet durability. When the surface is composed only of zinc oxide, the epoxy resin is replaced from the surface by dissociatively adsorbed water, so that the adhesive joint is inferior in wet durability.

4. Conclusions

For the purpose of clarifying the mechanism of adhesion between steel sheet surfaces and epoxy resins, cold-rolled steel, galvanized steel, and galvannealed steel sheets were bonded by epoxy resins, and the resultant adhesive joints were examined for such macroscopic phenomena as bond strength, and bond strength loss and change in the mode of failure through exposure to humidity. Then, epoxy model compounds were adsorbed on zinc oxide and iron oxide surfaces, and resultant interfacial bonding was studied at the molecular level. The following conclusions were obtained:

(1) Adhesive joints of galvanized steel sheets suffer adhesive failure between the zinc coating and the adhesive and are poor in wet durability. Adhesive joints of galvannealed steel sheets and cold-rolled steel sheets undergo cohesive failure and is superior in wet durability. This suggests that a surface composed of zinc oxide alone and a surface containing iron oxide in addition to zinc oxide are different in the mechanism of adhesion with epoxy resins and the mechanism of deterioration in adhesion through exposure to humidity.

(2) Organic compounds having the partial structure of epoxy resins are adsorbed on iron oxide and zinc oxide by bond dissociation between phenoxy oxygen and carbon. This experimental finding overturns the conventional theory that epoxy resins adhere to metal oxide by hydrogen bonding. Iron oxide and zinc oxide delicately differ from each other in the adhesion mechanism and bond energy with epoxy model compounds.

(3) The above interfacial bond with the epoxy model compound would be broken by the dissociative adsorption of water on zinc oxide, but not on iron oxide. This explains the tendency of (1) above at the molecular level, and indicates that the adhesion mechanism of (2) above is valid not only for the epoxy resin model compounds, but also for actual steel sheets bonded or painted with epoxy resins.

Acknowledgment

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