

Sacrificial Corrosion Protection Ability of Aluminum Alloys for Automobile Heat Exchangers

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ABSTRACT Aluminum is widely used in automobile heat exchangers in order to decrease their weight and improve efficiency. Normally aluminum corrodes by pitting, and this can cause leakage, which is fatal to the heat exchanger. Mechanisms of sacrificial corrosion are therefore used to suppress pitting in heat exchangers made of aluminum. The ability scope of such sacrificial materials in suppressing corrosion is investigated using scanning electrodes, and the results of the evaluation are reported.

1. INTRODUCTION

Automobiles are equipped with a variety of heat exchangers for such systems as radiators and air conditioners, and aluminum alloys are often used making them light in weight. Typical heat exchangers include radiator, condenser, evaporator, and heater, and they tend to have a potential problem of corrosion when aluminum is used. These products have heat exchanging medium (long life coolant) flowing inside and their outside is exposed to, depending on the position of attachment, different environments such as anti-freezing mixture and dew condensation. In the case of heat exchangers for air conditioners where the contained medium like chlorofluorocarbon is non-corrosive, the corrosive environment inside can be neglected. Generally, however, materials for heat exchangers should be provided with anti-corrosion measures, both inside and outside, to assure the life of the products.

It is characteristic of aluminum materials that they often suffer from corrosion pitting in the depth direction. If pitting proceeds in a heat exchanger and penetrates its medium path, the exchanger falls out of use due to leakage of the medium. As a means to protect pitting in aluminum, it is normal practice to adopt sacrificial corrosion protection, whereby a material that is electrochemically less noble than the medium path material is provided for in order to protect the medium path by feeding electrons. The outer surface of products are usually protected, in the case of heat exchangers using butt seam welded tubes, by making the radiating fin material less noble than the tube material to effect sacrificial protection. In the case of extruded tubes, because it is difficult to form a solder layer onto the tubing, the fin material is clad with solder, while the outer

surface of the tube is covered with a sacrifice layer formed by Zn thermal spraying or the like. In both cases, the inner surface, being always in contact with a cooling medium, is covered with a cladding layer which is less noble than the tube core material.

As mentioned, sacrificial protection based on potential difference is extensively utilized in aluminum heat exchangers and accordingly, at the time of product design, it is very important to optimize the ability of protection as well as to understand quantitatively the extent of protection. The authors evaluated the extent of sacrificial corrosion protection by using the scanning electrode method and investigated its correspondence with the corrosion test. The results will be presented in this report.

2. EVALUATION OF SACRIFICIAL PROTECTION ABILITY

Since sacrificial protection makes use of material's potential difference to suppress corrosion, surface analyses at the time of design such as potential distribution¹⁾⁻²⁾ and corrosion current distribution would be very efficient to realize a material development with a reduced cycle time. Analysis methods include scanning vibration electrode method, Kelvin probe method, and scanning electrode method and others, each having characteristics of its own as described below.

2.1 Scanning Vibration Electrode Method³⁾⁻⁴⁾ (Figure 1)

A micro electrode made of Pt or such is driven to vibrate mechanically in a test solution, electrode potentials at amplitude peaks are measured, and electrode potential differences corresponding to vibration amplitude are calculated. The current flowing in the direction of vibration is then determined by using the electrode potential differ-

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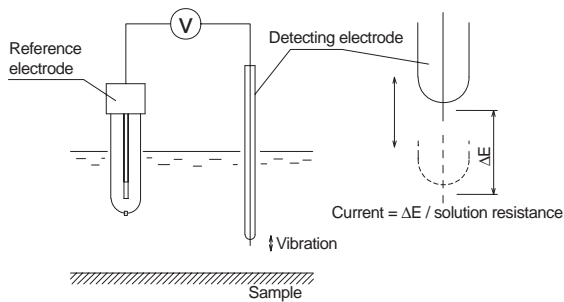


Figure 1 Schematic view of scanning vibration electrode

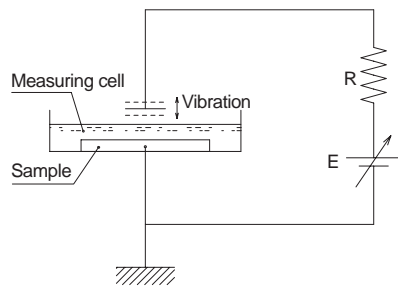


Figure 2 Schematic view of Kelvin probe

ence thus obtained together with the solution resistance. This method is capable of directly determining the amount and distribution of effective current that is working for sacrificial protection, since it measures the current that flows into or out of the portion of interest.

2.2 Kelvin Probe Method⁵⁾ (Figure 2)

A non-contact electrode is positioned above a sample constituting a capacitor with it. As the electrode is made to vibrate, the capacitance changes accordingly inducing electrical charges to flow, the amount of which is measured to represent the surface potential of the region under observation. Since the measured potential is not a potential in thermodynamic equilibrium, calibration is required using a reference electrode.

When this method is applied to corrosion analysis, it should be noted, it is sometimes influenced by the changes of the capacitor caused by geometrical changes of the surface as well as by deposition of corrosion products, which may take place during corrosion analysis.

2.3 Scanning Electrode Method⁶⁾ (Figure 3)

The probing electrode consists of a reference electrode and the Loggin capillary connected with salt bridge and

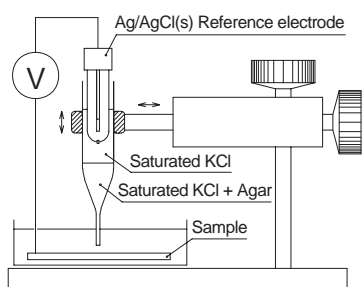


Figure 3 Schematic view of scanning electrode

saturated KCl solution. The pointed end is used as a probe to directly measure the potential of a spot on the sample which enables, because its space resolution is fine, measurements of surface potential distribution by moving the probe over the sample.

Occasionally, however, thermal compensation is needed since its reference electrode belongs to external electrodes. Furthermore, at measurements in diluted solutions and from time to time, KCl dissolves from agar that comprises the salt bridge at the capillary and influences the sample surface to induce pitting.

2.4 Corrosion Test Method

This is a method most commonly used, in which test samples modeling the actual products are prepared and they are subjected to corrosion tests in corrosive environments. Typical test methods include salt spray test, CASS test and others, and they specify their respective evaluation criteria for each product. Although corrosion test method is indispensable for final evaluation of products, the method takes a considerably long time to complete making it difficult to apply for all materials at the time of material design.

3. EXPERIMENTAL METHOD

In this study, the surface potential distribution of samples each comprised of a sacrifice material and a tube core material bonded together was measured in an OY water using a scanning electrode, and the results were compared with those of corrosion tests.

The scanning electrode used in the measurements consisted of a glass tube having a pointed end of 100 μm in diameter which contained a salt bridge made up of saturated KCl and agar, together with a Ag / AgCl(s) reference electrode jointed by saturated KCl solution. The probe was mounted on a fixture that incorporated a micrometer, thereby enabling scanning parallel to as well as perpendicular to the sample surface.

Test pieces were of the alloys having compositions shown in Table 1. They were soaked at 520°C for 4 hr after

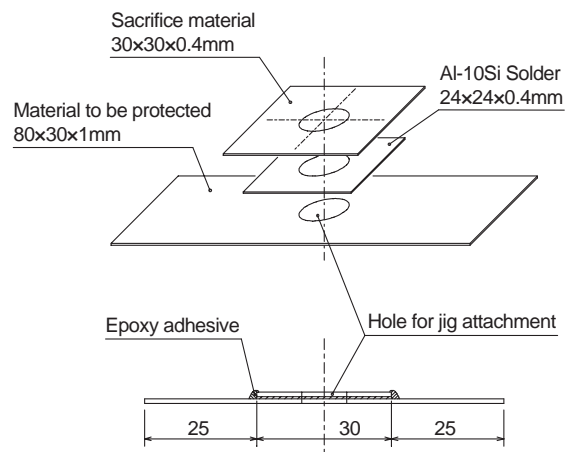


Figure 4 Corrosion test sample

	Si	Fe	Cu	Mn	Zn
Core material 1	0.2	0.3	0.15	1.1	—
Core material 2	0.3	0.2	0.5	1.1	—
Sacrifice material 1	0.1	0.2	—	—	1.0
Sacrifice material 2	0.1	0.2	—	—	4.0

(wt%)

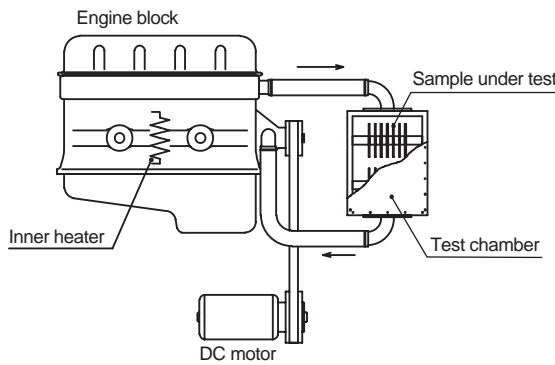


Figure 5 Schematic view of circulating corrosion test equipment

casting, hot rolled to 3 mm thick, intermediately annealed at 400°C for 2 hr, and finally cold rolled to 0.4 mm thick to make test pieces. Subsequently, they were assembled as shown in Figure 4 and brazed at 600°C for 3 min in air. Since a small amount of solder with solder flux was seen to leak out of the bonded area, the area was etched by 10 % NaOH for 30 sec at 50°C, desmatted by 1:1 HNO₃ for 30 sec, and its periphery was sealed with epoxy adhesive so that solder leakage might not influence the measurement.

Two types of samples were prepared and tested: samples having an ordinary sacrificial ability consisting of core material 1 / sacrifice material 1 (hereafter called Sample 1); and samples having an enhanced sacrificial ability consisting of core material 2 / sacrifice material 2 (hereafter called Sample 2).

Samples were kept in a circulating OY water environment for one week, using a circulating corrosion test equipment illustrated in Figure 5⁷⁾, and were transferred from the circulating corrosion test equipment to a still OY water environment after corrosion turned into a steady state. OY water, the composition of which is shown in Table 2, was ladled out of the test equipment and was used in the still OY water environment test.

Surface potential was measured by the scanning electrode held 100 μm above the sample surface. Sample potential was picked up by an aluminum stick, 3 mm in diameter with its entire surface insulated excluding its end face, pressed against the sacrifice material to make electrical contact. Furthermore, the mixed potential of the system was determined with the scanning electrode fixed to a position that is 10 mm apart from the edge of the test sample.

	Concentration
Cl ⁻	195
SO ₄ ²⁻	60
Fe ³⁺	30
Cu ²⁺	1

(ppm)

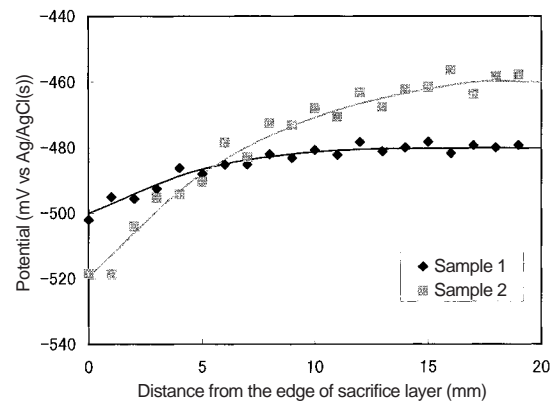
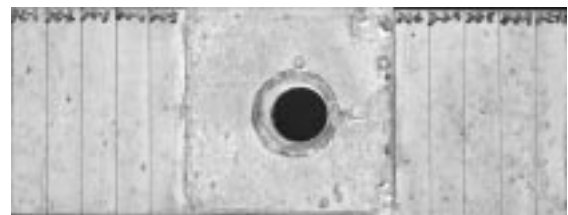
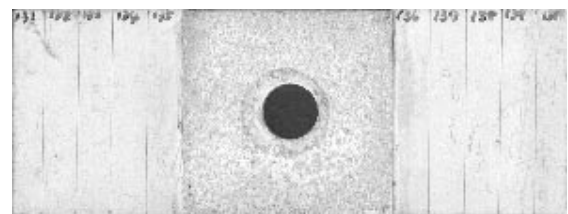


Figure 6 Surface potential distribution



Sample 1



Sample 2

Photo 1 Appearance of samples after cleaning

4. RESULTS

Figure 6 shows the results of surface potential distribution measurements beginning from the edge of the sacrifice material. Since the test sample consists of core material and sacrifice material soldered together, the potential changes gradually from a less noble state at the sacrifice material edge to a noble state at a distance, reaching an equilibrium potential that depends on the property of each sample. Equilibrium potentials at a distance for Sample 1 and Sample 2 are, since they have different core materi-

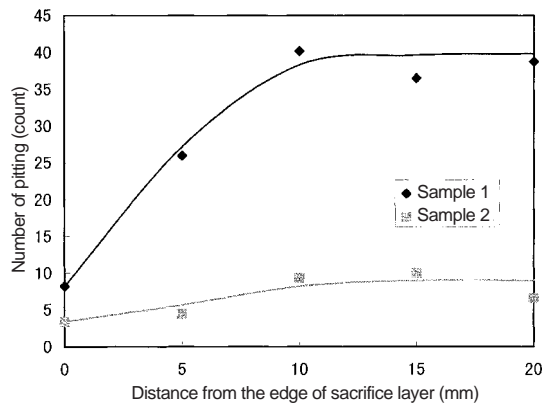


Figure 7 Distribution of pitting frequency

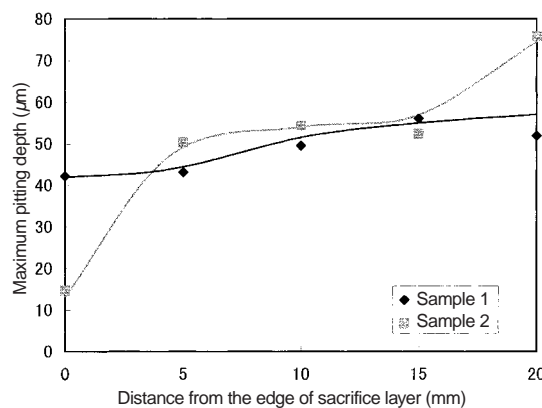


Figure 8 Maximum pitting depth in the 5 mm range

als, approximately -480 mV and -460 mV respectively.

Photo 1 shows the appearance of samples after they underwent circulation corrosion tests with their corrosion products removed. Both samples show larger numbers of pitting on the sacrifice material but smaller numbers on the core material. A more detailed observation on the sacrifice material indicates that Sample 1 has a localized distribution of pitting leaving some surface areas undamaged as rolled, while Sample 2 has a uniform distribution over the entire surface. Pitting frequency on the core material is seen to be small near the sacrifice material and increases at a distance. Statistics of the number of pitting counted every 5 mm beginning from the sacrifice material edge is shown in Figure 7, where the number of counts for a range from 0 mm to less than 5 mm is marked on the 0 mm position. Figure 8 shows, in a similar manner, the results of measurements for the maximum pitting depth in the range.

The number of pitting increases as the distance from the sacrifice material increases, reaching a value almost constant at a position 10 to 15 mm away. When Sample 1 and Sample 2 are compared, the former has more counts generally.

In common with the pitting count, maximum pitting depth for ranges partitioned every 5 mm is shallower than the average for the 5 mm range where the distance from the sacrifice material is 0 to 10 mm, but reaches a constant

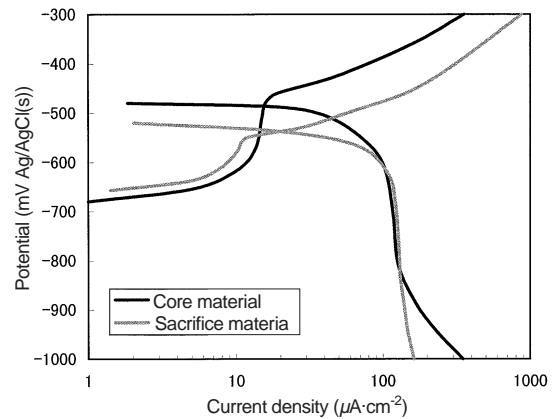


Figure 9 Polarization curve of Sample 1 in OY water

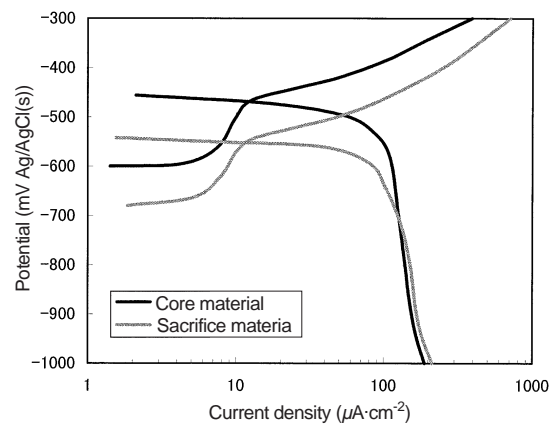


Figure 10 Polarization curve of Sample 2 in OY water

value farther on. With Sample 2, a tendency is seen in which the depth is shallow for the 0 mm range, becoming deeper for the 20 mm range where the distance from the sacrifice material is 20 mm or more.

5. DISCUSSION

Due to protection by sacrifice material, pitting in its neighborhood is suppressed not only in its occurrence number but also in its maximum depth. Electrochemical states of these samples were estimated by measuring their polarization curves at 25°C in an OY water that is the same as used in the experiments. Core material and sacrifice material of each sample were etched by 10 % NaOH for 30 sec at 50°C, and desmatted by 1:1 HNO₃ for 30 sec before measurement. Assembled samples were entirely masked with epoxy adhesive excluding 1 cm², and their polarization curves were measured at a scanning speed of 20 mV/min. The potential was measured in terms of the equilibrium potential of each material, beginning at a time 30 min after N₂ deaeration for the anode side, and also 30 min after aeration to atmosphere for the cathode side. A reference electrode of saturated Ag / AgCl was used. From the results shown in Figure 9 and Figure 10, electrochemical behaviors of the core and sacrifice materials in the state of sacrificial corrosion protection can be read respec-

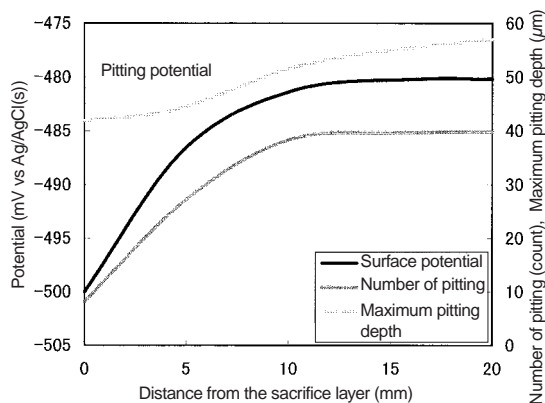


Figure 11 Relationship between pitting and surface potential distribution of Sample 1

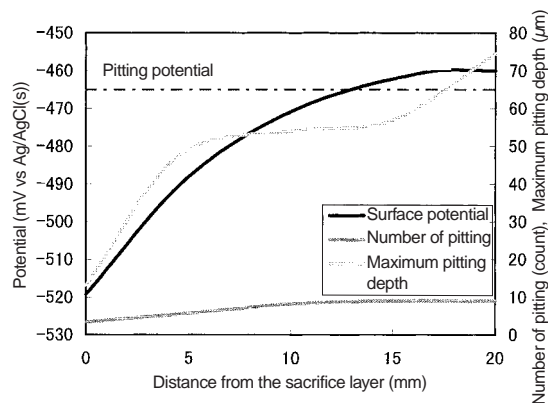


Figure 12 Relationship between pitting and surface potential distribution of Sample 2

tively, since the figures represent both materials of each sample together in a sheet.

Pitting possibility depends on the surface potential and its anodic polarization curve. Thus, the relationship between pitting and surface potential distribution was studied for the two samples, and the results are shown in Figure 11 and Figure 12.

The state of electrochemical corrosion protection for Sample 1 is estimated as follows. The surface potential of the core material near the sacrifice material is maintained at around -500 mV, which is less noble than the corrosion potential of core material 1 in OY water (-480 mV) by 20 mV. As the distance from the sacrifice material increases, the surface potential approaches the corrosion potential of core material 1, reaching quite near the pitting potential of core material 1. With Sample 2, on the other hand, the surface potential of the core material near the sacrifice material is around -520 mV, which is less noble than the corrosion potential of core material 2 (-456 mV) by 64 mV, providing a larger potential difference than Sample 1.

Pitting occurrence declines when the surface potential of core material becomes less noble than the corrosion potential or the pitting potential. With the materials of present study, in which the corrosion and pitting potentials of core material are almost equal, creation of corrosion nuclei is supposed to be suppressed due to the surface potential kept less noble than the pitting potential. The nearer to the sacrifice material, the less noble the surface potential of the core material is kept, thereby increasing the difference with respect to the pitting potential. Pitting occurrence decreases as the difference between the surface potential and the pitting potential increases, and in the case of Sample 1, minimizing to one fifth of that at a position 20 mm or farther from the sacrifice material where sacrificial corrosion protection is no longer effective. The tendency is similar in the case of Sample 2, although pitting occurrence is smaller in number than Sample 1 at a position 20 mm or farther. This suggests that the pitting potential of a material influences not only the potential at which pitting begins to grow, but also the occurrence frequency of pitting nucleus.

Maximum pitting depth is seen to become shallower when the surface potential of core material is less noble

than the corrosion potential by 10 mV or more. This fact is supposed to be the result of suppression of pitting growth, similar to suppression of pitting occurrence, which is caused by a surface potential that is less noble than the pitting potential. The effect of depth suppression becomes distinct with the larger potential difference: while maximum pitting depth of Sample 1, which has a maximum potential difference of about 20 mV between the core and sacrifice materials, is 42 μm at a position closest to the sacrifice layer, that of Sample 2 having a difference of 60 mV is 12 μm .

In terms of sacrificial corrosion protection, the ability of Sample 1 is effective to suppress pitting occurrence considerably but is insufficient to stop efficiently the growth of pitting that has once occurred. Its pitting depths become shallower near the sacrifice material than at a distance, but their absolute values are larger than those of Sample 2. With Sample 2 in contrast, as shown in Figure 7 and Figure 8, core material 2 has a lower pitting occurrence than core material 1, but pitting that has once occurred there has a possibility of growing to the same depth. However, as indicated by the polarization curves in Figure 9 and Figure 10, the difference between the corrosion potentials of the core and sacrifice materials is larger, resulting in an augmented protection ability of the sacrifice material than Sample 1 to make pitting near the sacrifice material much shallower.

6. CONCLUSIONS

We have studied the surface corrosion potentials of corrosion samples that are modeling combinations of sacrifice material / core material in OY water utilizing a scanning electrode. The following conclusions have been drawn.

- 1) Pitting occurrence of core materials can be efficiently suppressed by incorporating sacrifice materials, making the surface potential of core material less noble than the corrosion potential. The larger the potential difference with respect to the corrosion potential, the greater the suppression effect becomes.
- 2) To suppress pitting growth, it is necessary to make the potential less noble than the corrosion potential of core material by 10 mV or larger. The larger the poten-

tial difference, the greater the suppression effect becomes.

- 3) Sacrifice protection can be analyzed by the use of scanning electrode. By using this method, the extent of effective sacrificial protection is clarified.

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