

IMPROVEMENT OF WATERSIDE CORROSION RESISTANCE AND PROBLEMS IN FIELD APPLICATION OF ALUMINUM RADIATOR TUBES

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ABSTRACT The influences of the chemical compositions and thickness of a sacrificial inner layer on the corrosion resistance of Al-alloy automobile radiator tube stocks were examined by the elevating temperature glassware corrosion tests using OY water. By providing a thick inner anode clad containing sufficient Zn, excellent waterside corrosion resistance was obtained. However, protection against pit perforation seemed to become incomplete when alkaline cooling water was kept hot for a long duration. The sacrificial anodic effect of the inner clad could be lost under such conditions.

Keywords: aluminum, automobile radiator, cooling water, corrosion

1. INTRODUCTION

In order to gauge down the aluminum alloy tube for use in automotive radiators, it is important to maintain good corrosion resistance. Many studies have been carried out regarding the waterside corrosion of an Al-alloy radiator tube and its protection¹⁾⁻⁴⁾. However, these results have been quite different based on the testing conditions, and the essential method to prevent waterside corrosion has not been clarified. In this paper, the influence of the chemical compositions and thickness of the sacrificial inner layer on waterside corrosion resistance of Al-alloy radiator tube stocks were examined using the glassware corrosion tests with OY water widely used in fabricators. Based upon these results and corrosion potential measurements, the alloy design of the tube stock that provides good waterside corrosion resistance was discussed. Some recent studies have indicated that the sacrificial inner layer could not protect the core alloy under certain conditions⁵⁾⁻⁶⁾, which were distinct from the tests using OY water. Therefore the influences of pH and temperature on the corrosion resistance of tube stocks were also examined by corrosion tests and electrochemical measurements using coolants while considering the service environment.

2. EXPERIMENTAL

2.1 Materials

Six tube stocks for non-corrosive flux brazing consisting of core, A4045 outer filler clad and inner anodic clad which contained Zn were prepared. Chemical analyses and clad thickness of these materials are shown in Table 1.

2.2 TEST PROCEDURES

2.2.1 Waterside corrosion test

The waterside corrosion tests were carried out following ASTM D1384 elevating temperature glassware testing methods with OY water (solution A in Table 2). Test coupons, 50mm by 80mm, were

cut from brazed tube stocks and the external surface and edge masked using silicone resin. Every 24 hours the solutions were maintained at 361K for 8hr and then cooled to room temperature for 16hr.

Table 1 Chemical composition and structure of the specimens

No.	Filler		Core				Inner anode				Total thickness (um)
	Alloy	Thickness (um)	Composition(mass%)				Composition(mass%)				
			Si	Fe	Cu	Mn	Si	Fe	Mg	Zn	
1	A4045 9.67Si 0.12Fe	25	0.50	0.17	0.47	1.16	0.35	0.20	1.26	0.97	25
2											40
3											54
4							25				
5							40				
6							54				

Table 2 Composition and characteristics of corrosion test solution

Solution	Composition of solution(ppm)				pH	EC(ms/cm)
	Cl ⁻	SO ₄ ²⁻	Cu ²⁺	Fe ³⁺		
A	195	60	1	30	3.0	1.1
B			-	-		

2.2.2 Elemental distribution analysis of cross section

The redistribution of elements such as Cu, Zn, Si, Mg, Mn and Al through the material which was the result of diffusion during brazing, was monitored by electron probe microanalysis (EPMA) line scanning in the tube thickness direction.

2.2.3 Measurement of corrosion potential change through thickness

The inner surface of the brazed tube stock coupons was carefully polished using emery paper to eliminate a certain thickness such as approximately 20, 30, 40, 50 and 100um. After masking all but the polished surface with resin, the corrosion potential of these specimens was measured in reference to a saturated calomel electrode in stirred B solution as listed in Table 2, that was employed to avoid the depositing of metal ions in OY solution at room temperature for 24hr. By plotting the results, which were the average of the measured data during 24hr for each specimen, versus the polished off thickness, the corrosion potential change with thickness for each tube stock was obtained.

3. RESULTS AND DISCUSSION

3.1 Influence of inner clad thickness and alloying elements on corrosion behavior

Figure 1 shows the maximum pit depth for specimens after every testing duration in OY solution. Figure 2 shows the relationship between the maximum pit depth and inner clad thickness after 2810hr of testing. Figure 3 shows the cross sections of the maximum pit depth after 1880hr of testing. These results indicated that the inner clad thickness had the greatest effect on the corrosion resistance and the decrease in maximum pit depth as the inner clad was thickened. In case of the thin inner clad of 25um, the maximum pit depth was found to vary proportionately with the testing duration and created perforations after 2980hr of testing. On the specimen with a thicker inner clad over 40um, the maximum pit depth was independent to the testing duration and was well controlled. Especially, No.6 specimen having a thickness of 54um and high Zn inner clad showed good corrosion resistance and the pit depth was controlled within the inner clad.

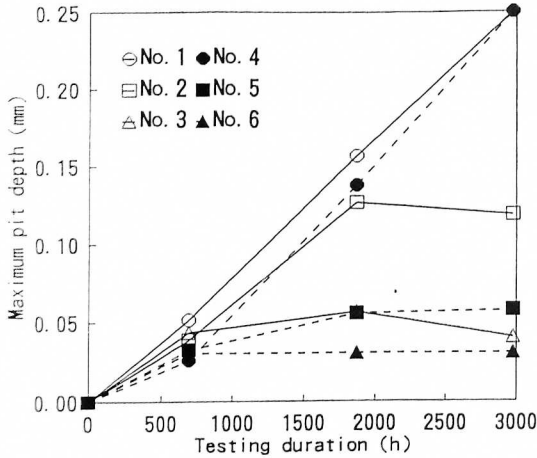


Fig. 1 Results of corrosion test in A solution.

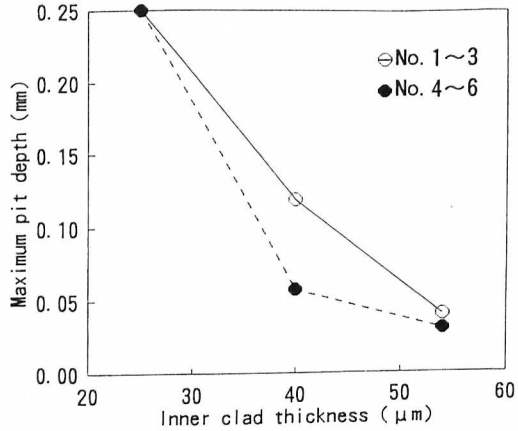


Fig. 2 Relation between maximum pit depth after 2980 corrosion test in A solution and inner clad thickness.

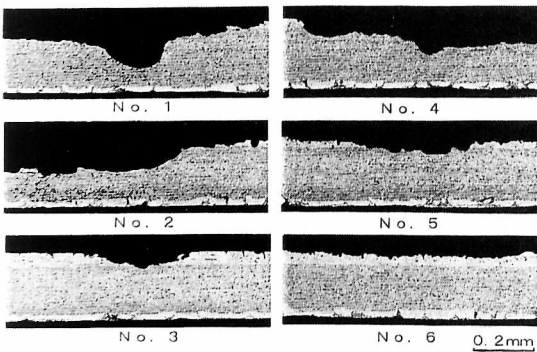


Fig. 3 Cross sections of pit for typical specimens after 1880h corrosion test in A solution.

The redistribution of elements through the material of typical brazed tubes is shown in Figure 4-a and b. Zn contained in the inner clad diffused into the core and Cu in the core diffused into the inner clad during brazing. When the inner clad was as thin as 25μm (Fig. 4-a), the concentration of Zn at the inner surface was reduced to half or less than before brazing and Cu in the core approached the inner surface. On the other hand, when inner clad was as thick as 54μm (Fig. 4-b), almost 3/4 of the Zn remained in the inner surface and Cu in the core did not approach the inner surface. Good corrosion resistance of the tubes with a thick inner clad seems to be dependent on this

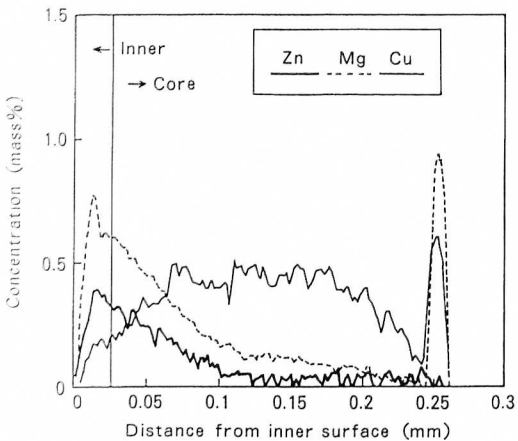


Fig. 4-a Results of EPMA line scan of Zn, Mg, and Cu across the brazed specimen No. 1.

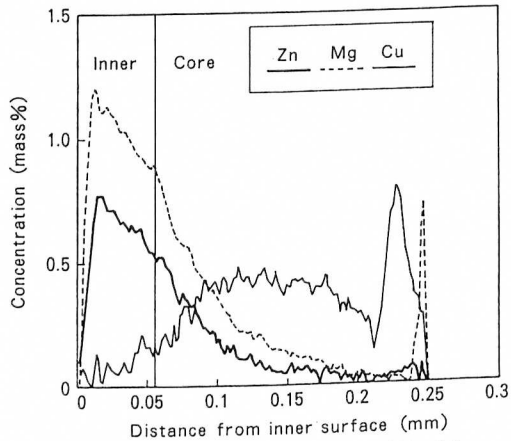


Fig. 4-b Results of EPMA line scan of Zn, Mg, and Cu across the brazed specimen No. 3.

redistribution of Zn and Cu, which might promote an active corrosion potential at the inner surface enough to protect the core. The corrosion potential changes through the thickness in B solution are shown in Figure 5. The potential for the inner clad surface was the most anodic and it gradually changed to cathodic with the distance from the inner surface for every tube. The potential difference between the inner surface and middle of the core increased with inner clad thickness and Zn content.

According to these results, it has been considered that the potential difference between the inner clad layer as a sacrificial anode and the core as a cathode is required to protect the core from water side corrosion. The potential difference between the inner surface and the bottom of the pit formed after the maximum duration of the corrosion test, which is determined from Figure 5, is shown Table 3. The specimens on that pit that were well controlled (No.3, 5 and 6) had a potential difference of more than 60mV between the inner surface and bottom of the pit formed after the long corrosion test. If there was a potential difference of more than 60mV in the inner clad, the pit depth would be controlled within the inner clad like No.6. In the case of specimen No.2 on which the pit depth was controlled after reaching to

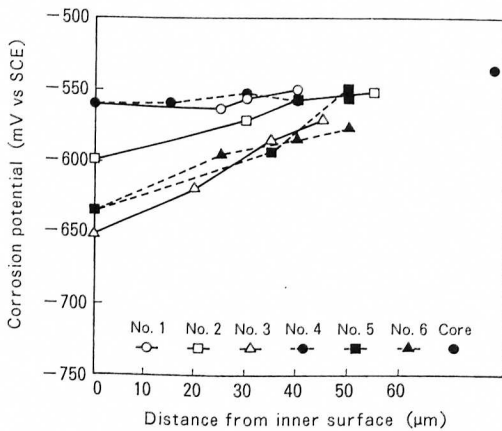


Fig.5 Results of corrosion potential distribution measurement in B solution.

the core, it is considered that the same potential difference was obtained after the pit penetrates the middle of the core. Perforation of specimen No.1 and 4 seems to be the result of no potential difference. The obtained value of the effective potential difference to protect a pit was similar to the results of studies¹⁾⁻⁴⁾ in similar tests with dilute solutions. However, it must be understood that the value will be changed with the characteristics of the cooling water such as electric conductivity, Cl⁻ ion content and so on. A well designed sacrificial inner layer will be effective to protect against pit perforation when using water containing corrosive reagents such as Cl⁻.

Table 3 Corrosion depth and potential difference between the inner clad surface and the pit bottom

No.	Corrosion depth* ₁ (μm)	E _{corr} at inner surface (mv vs SCE)	E _{corr} at pit bottom (mv vs SCE)	Potential difference (mV)
1	>250	560	(535)* ₂	25
2	120	600	(535)* ₂	65
3	50	635	570	65
4	>250	560	(535)* ₂	25
5	60	635	550	85
6	30	650	590	60

*1 : after 2980hr immersion test in A solution, *2 : () indicates E_{corr} of core

3.2 Problems in service environment

The present study shows the good effect of the sacrificial anode of the inner clad in cooling water containing corrosive ions. However, recent studies have indicated that the inner layer can not provide sacrificial protection of the core alloy under certain conditions⁵⁾⁻⁶⁾. Tests were carried out

		pH			
		7.5	8.0	9.0	10.0
Temperature (K)	363				
	377				
	388				

Fig.6 Film formation after immersion tests.

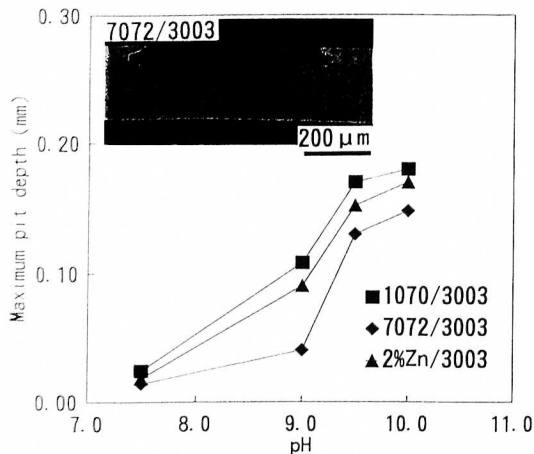
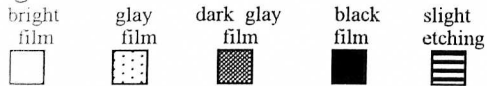


Fig.7 Relation between maximum pit depth after 1440h corrosion test in the coolants and pH of the coolants.

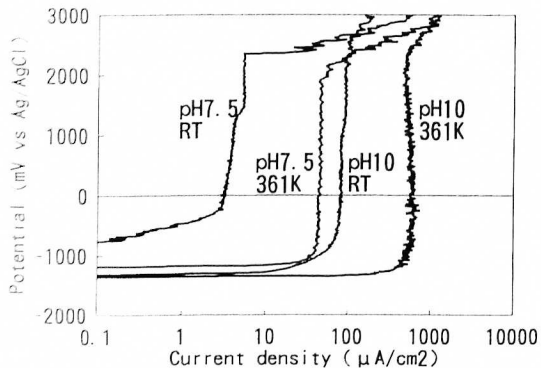


Fig.8 Results of anodic polarization measurement in the coolants of pH7.5 and 10 at room temperature for A7072.

using ASTM water (100ppmCl⁻, 100ppmSO₄²⁻ and 100ppmHCO₃⁻) or its modifications that promoted alkaline, and they were kept at a temperature above 361K for longer term than low temperature. As it has not been clarified in a past study, the influences of pH and temperature on corrosion resistance were also examined for some typical radiator tube stocks having A3003 (Al-1.2%Mn-0.15%Cu), A1050 (pure Al), A7072 (Al-1%Zn) and Al-2%Zn on the waterside. Since it is well known that a film forms on an Al surface boiled in hot, weakly alkaline solutions and the same film formation is reported in these studies, film formation behavior was investigated using an immersion test at 363K to 388K for one hour in the 30% service coolants and controlling these pH from 7.5 to 10.0 using NaOH. The results are shown in Figure 6. A thick black film was formed at temperatures of 377K to 388K and about pH 9.0. When the pH or temperature was higher than the values, the inner surface changed with a slight alkaline etching. On the other hand, when the pH or temperature was lower than these values, bright surface film was formed. These results have been consistent with the results predicted from the potential-pH diagram. The glassware corrosion test almost the same as already described was carried out using the coolants with various pHs. The inner surface after the tests corresponded with the results of the short immersion tests. In the neutral coolants, a bright film formed and no pits were observed. In the weakly alkaline coolants of pH 8.0 to 10.0, a black film formed and corrosion pits were observed. Figure 7 shows the maximum pit depth after 1440hr of the glassware tests and cross sections of the maximum pit depth on the specimen having an A7072 inner clad after 2160hr testing in the coolant of pH10. The maximum pit depth increased as the pH increased. Also, there was no difference in the maximum pit depth, which penetrated into the core, among these specimens. As shown in Figure 7, in the

solution with a pH greater than 9.0, the effect of the sacrificial anode seemed to be negligible. This was similar to the other specimens. Anodic polarization was measured in the coolants of pH 7.5 and 10 at 361K and room temperature. The result for A7072 is shown in Figure 8. It was also similar to the other specimens. It is well known that above the pitting potential, the current will immediately increase during anodic polarization, the protective surface film on Al will break down and pitting corrosion will take place. Cathodic protection of Al is achieved by controlling the corrosion potential to the passive state below the pitting potential. At that time, the corrosion rate will be restricted to the current in the passive state. Since the current in the passive state is quite large and the polarization curve indicates that the corrosion rate is under anodic control for any Al alloy, as shown in Figure 8, a sacrificial anodic effect can not be expected in hot alkaline coolants. Figure 8 also indicates that the corrosion potential seems to be located below the pitting potential and the pitting mechanism in alkaline coolants may be different from common cool neutral solutions containing Cl⁻. The deep pits in hot alkaline coolants seemed to be the result of focusing of corrosion current from surrounding local wide cathode to the defects where preferential dissolution takes place to produce the black surface film on the surrounding area. Therefore, it is also important that an Al radiator tube be protected by the sufficient coolants.

4. CONCLUSIONS

The influences of chemical compositions and the thickness of the sacrificial inner layer on the corrosion resistance of Al-alloy automobile radiator tube stocks were examined by elevating the temperature of glassware corrosion tests using OY water. It is important to have both a sufficient inner thickness for preventing the approach of Cu diffused from the core to the inner surface during brazing and sufficient Zn content in the inner clad for having a potential difference greater than 60 mV between the inner surface and core. With the sacrificial inner clad satisfying these conditions, the corrosion depth of the inside of the tube was controlled less than the inner clad thickness for the long term. A well designed sacrificial inner layer will be effective to protect pit perforation in using water containing corrosive reagents such as Cl⁻.

The influences of pH and temperature on the corrosion resistance were also examined using corrosion tests and electrochemical measurements with pH controlled service coolants. In the coolants of pH 9.0 to 10.0, the black film formed on the inner surface and pits approached the core. It is considered that the pits were the result of preferential dissolution at the defects of the formed porous surface film and the effect of the sacrificial anode was lost because of increasing of current in the passive state in alkaline coolants. Therefore, it is also important that an Al radiator tube must be protected by the sufficient coolants.

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