

Corrosion Behavior of Zn - 5 mass% Al Alloy

by

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The corrosion resistance of hot dip Zn-Al alloy coated steel sheet is shown to be improved through changing a cooling rate after hot dipping. The Zn-5 mass% Al alloy and Zn-5 mass% Al - Mischmetal alloy which were melted and cooled to room temperature with five different methods were corrosion-tested in stagnant 2% HCl and 3% NaCl aqueous solution at 308 K.

In 2% HCl solution, the corrosion behavior of Zn - 5 mass% Al alloy strongly depended on a cooling rate, while that of Zn - 5 mass% Al - Mischmetal alloy was almost independent of the cooling rate. The mischmetal addition makes the cooling rate dependence of the corrosion behavior of Zn - 5 mass% Al alloy less pronounced. In 3% NaCl solution, the corrosion behaviors of Zn - 5 mass% Al alloy and Zn - 5 mass% Al- Mischmetal alloy depended on the cooling rate complicatedly. A white product was formed on each sample after corrosion- testing in 3% NaCl solution. By adding mischmetal to the Zn - 5 mass% Al alloy, a pitting corrosion in 3% NaCl solution tended to be suppressed.

1. Introduction

For the sake of protecting a steel sheet used under severe corrosion environment, several types of Zn - Al alloys were developed recently for hot dip galvanizing bath¹⁾⁻³⁾. These alloys are dual phase alloys composed of α -phase and β -phase at room temperature⁴⁾⁵⁾. The corrosion behavior of α -phase must be different from that of β -phase, so that the corrosion behavior of Zn - Al alloy is anticipated to depend on a microstructure with different fractions and configurations of α -phase and β -phase. The corrosion behavior of steel coated with each of these alloys, therefore, is also anticipated to depend on a microstructure of coating, namely on a cooling rate after hot dipping. In this context, the authors investigated the effect of Al-content and cooling rate on the corrosion behavior of Zn - Al alloy and clarified that the corrosion

rate of Zn-Al alloy depended on the Al-content and that the corrosion rate of Zn - 50 mass% Al and Zn - 60 mass% Al alloys depended on the cooling rate⁶⁾⁷⁾. A Zn - 5 mass% Al - Mischmetal alloy, which have been used as hot dip galvanizing bath replacing pure molten zinc bath⁸⁾⁹⁾, is innately a Zn - Al alloy. The cooling rate dependence of the corrosion behavior remains obscure in the case of Zn - 5 mass% Al - Mischmetal alloy. The mischmetal addition to a Zn-5 mass% Al alloy is reported to suppress the occurrence of bare spot during hot dipping³⁾, while the effect of mischmetal addition on the corrosion behavior of alloy coating has not yet been investigated.

In the present paper, Zn - 5 mass% Al alloy and Zn - 5 mass% Al - Mischmetal alloy which were melted and cooled to room temperature at five different cooling rates were corrosion-tested in

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stagnant 2 % HCl and 3 % NaCl aqueous solutions, and the corrosion behavior of these alloys were elucidated on the basis of the cooling rate.

2. Experimental procedure

The Zn-5 mass% Al alloy (Z alloy) was prepared by weighing and melting zinc (99.9%) and aluminium (99.99%) in a graphite crucible. The Zn - 5 mass% Al -Mischmetal alloy (M alloy) was commercial one. Each alloy of ca. 500 g was remelted at 923 K in a graphite crucible, held at 723 K for 7.2 ks and cooled from this temperature to room temperature with five different methods. The five cooling methods used for each alloy were a water quenching (TR1), an air cooling (TR2), a furnace cooling (TR3) and a cooling at a constant rate of 2.41 K.s⁻¹ (TR4) and 1.21 K.s⁻¹ (TR5), in an order of cooling rate. After being cooled, these ten materials were cut into 3mm × 15mm × 10mm plate such as schematically illustrated in Figure 1 (a), and embedded in an epoxy. The corrosion test plane of 3mm × 15mm (shaded plane in Figure 1) was polished with a successive grade of SiC paper and a buff with a diamond paste before corrosion-testing. Each specimen was immersed in stagnant 2 % HCl and 3% NaCl aqueous solutions at 308 K and a mass of specimen was traced for a corrosion period. Dissolved oxygen in the solutions was not removed and was about $7 \times 10^{-3} \text{ g} \cdot \text{l}^{-1}$ before corrosion-testing.

3. Results and Discussion

3. 1 Appearance of corrosion test plane

Figure 2 shows the microstructure of Z-TR1 (Z alloy prepared by TR1) specimen before corrosion-testing. The structures of Z alloy and M alloy prepared by TR1 were similar to each other. The structures of TR1 specimens were composed of a zinc-rich primary crystal (white dendritic region) besides an eutectic (zinc-rich + aluminum-rich) phase. A zinc-rich phase is a β -phase and an aluminum-rich phase is a α -phase³⁾. A zinc-rich primary crystal was also found in TR2 specimens. The structures of the other specimens were composed of the eutectic phase only. The eutectic structure became rough as the cooling rate decreased from TR1 to TR3 and then levelled off.

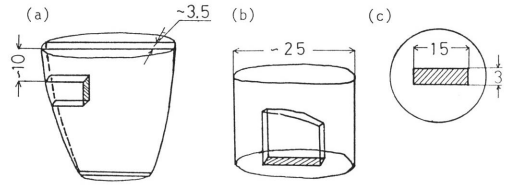


Fig. 1 Cutting procedure (a), mounting (b) and specimen size (c) in mm.

Figure 3 shows the surface appearances of specimens corroded in 2% HCl solution for 90 ks. The whole surface was attacked in every specimen. Z-TR1 specimen was attacked evenly, while M-TR1 specimen was attacked unevenly. In the other specimens, no difference in the surface appearance was found between Z alloy and M alloy. Each grain was attacked distinguishably. Each dimple corresponds to each grain.

A detail observation on the surface of specimen corroded in 2% HCl solution revealed a lamellar striation. Figure 4 shows across section of lamellar striation and a distribution of aluminum and zinc in M-TR1 specimen corroded in 2% HCl solution for 92 ks. The lamellar striation became a skeleton. The skeleton included as much aluminum as an aluminum-rich phase of matrix eutectic. This fact implies that the β -phase was attacked preferentially to the α -phase. Figure 5 shows the cooling rate dependence of the thickness of aluminum-rich skeleton found on the specimen

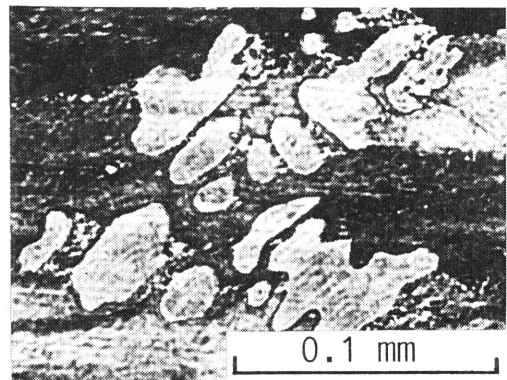


Fig. 2 Microstructure of water-quenched Zn-5 mass% Al alloy before corrosion-testing.

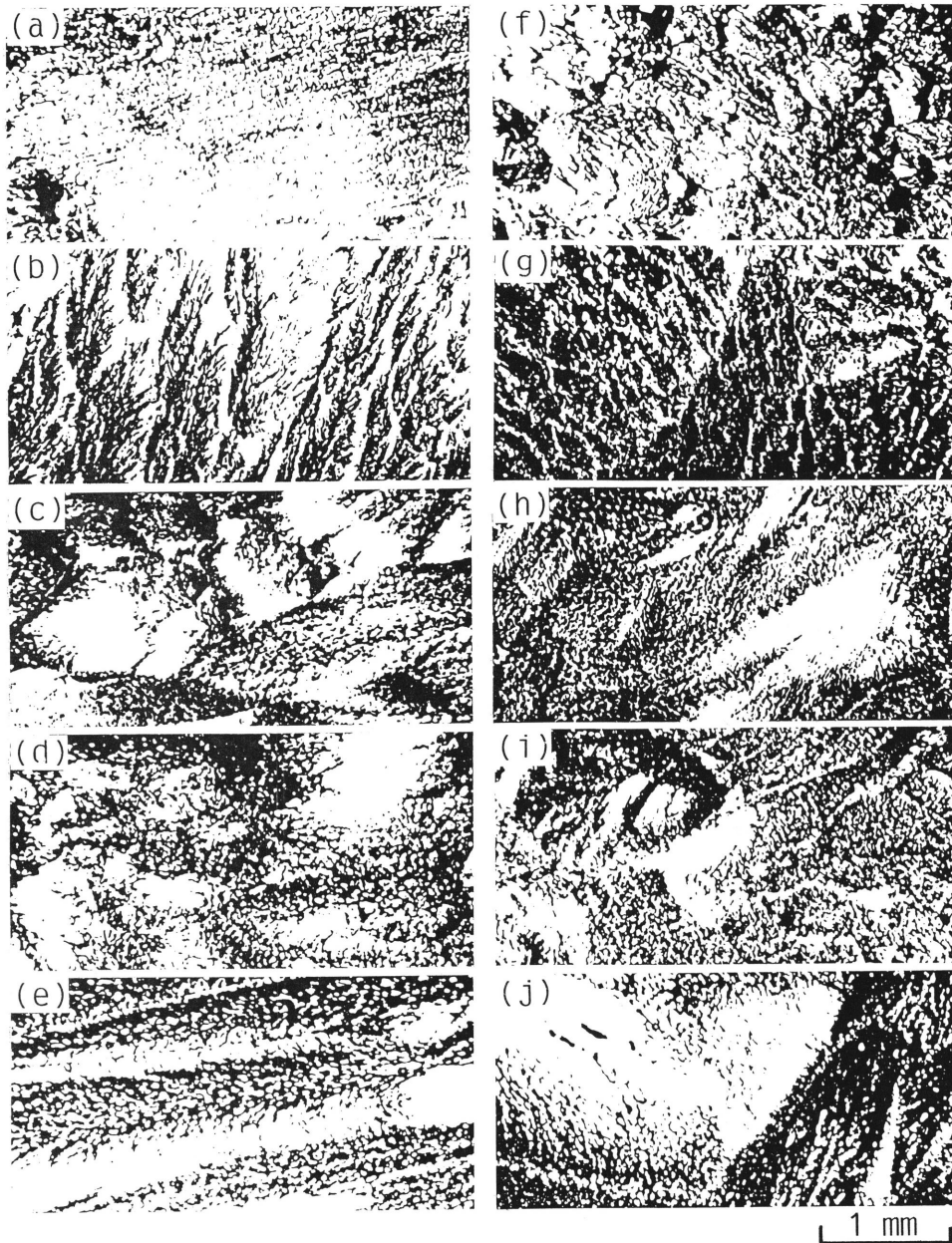


Fig. 3 Surface appearances of Zn-5mass%Al ((a)–(e)) and Zn-5mass%Al-Mischmetal ((f)–(j)) alloys after corrosion-testing in 2% HCl solution.

(a), (f) : TR1, (b), (g) : TR2, (c), (h) : TR3, (d), (i) : TR4, (e), (j) : TR5

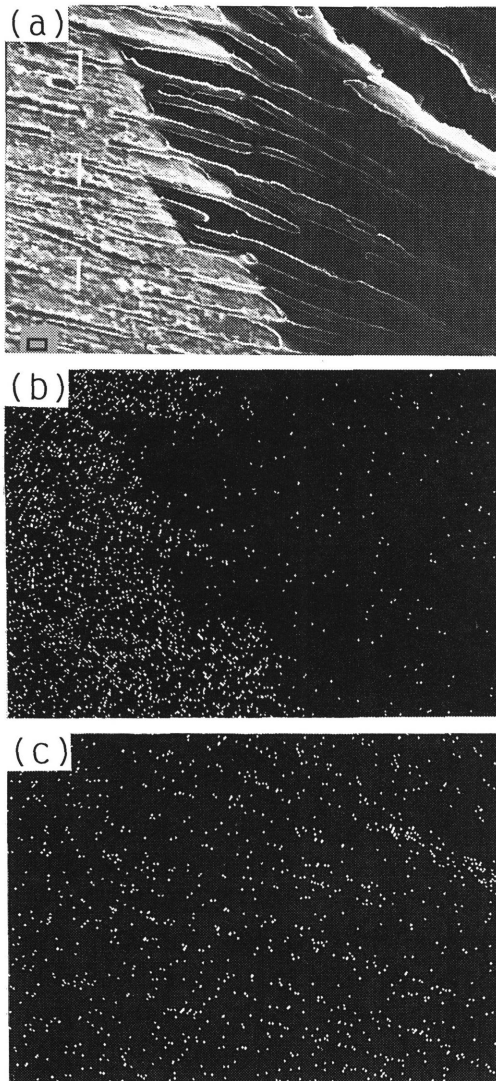


Fig. 4 Cross section (a) and X-ray plane images of Zn (b) and Al (c).

croded in 2 % HCl solution for 92.0 ks. Although the β -phase was attacked preferentially to the α -phase, the corrosion rate of the β -phase was about the same order as that of the α -phase in the case of TR1 specimen, and the α -phase of a thickness from a few μm to 10 μm remained as the skeleton. On the other hand, the difference in corrosion rate between these two phases increased as the cooling rate became slow down, and the α -phase of over 50 μm in thickness remained in the case of TR4 and TR5 specimens. This fact means that the

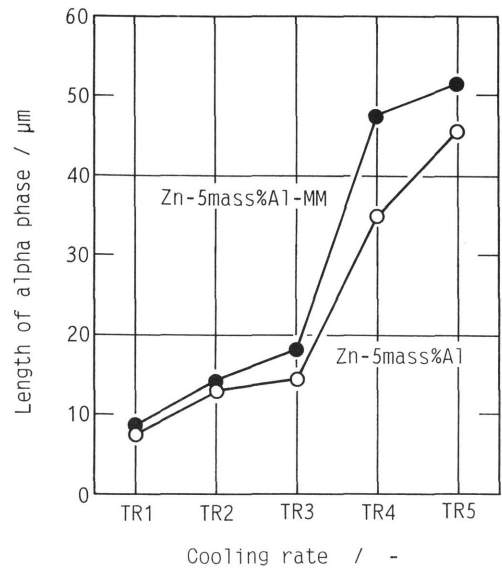


Fig. 5 Cooling rate dependence of the thickness of α -phase skeleton.

α -phase with the equilibrium composition possesses a good corrosion resistance against 2% HCl solution. The β primary crystal was attacked at a rate equal to or slightly slower than the corrosion rate of eutectic.

Figure 6 shows the surface appearances of TR2 specimens corroded in 3 % NaCl solution for 720 ks. Both alloys started to be attacked at a local spot and this spot grew larger in area with increasing corrosion period. A white product was formed and covered the whole test plane. In later corrosion period, pits were found in the case of Z-TR1, M-TR1 and Z-TR2 specimens. Therefore, to obtain an information about an in-depth corrosion behavior, the corrosion product covered the plane was removed by a slight polishing. Figure 7 illustrated that the Z alloy was locally attacked, forming pits, while the M alloy was attacked generally.

In a salt spray test, the β primary crystal is reported to affect corrosion behavior of Zn-Al alloy containing ca. 5mass% Al and an α -phase/ β -phase interface to be attacked preferentially¹⁰⁾. In the present study, these were not confirmed.

Being independent of mischmetal addition, a white corrosion product indicated X-ray diffraction

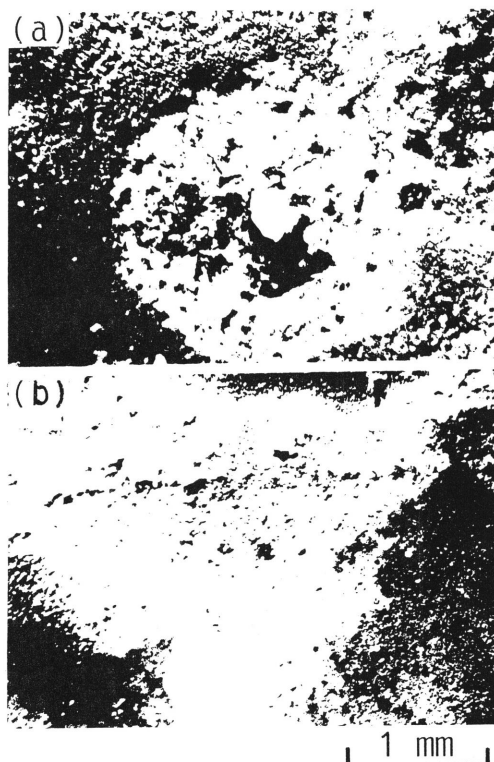


Fig. 6 Surface appearances of furnace-cooled Zn-5mass%Al (a) and Zn-5mass% Al-Mischmetal (b) alloys after corrosion-testing in 3% NaCl solution at 308 K for 720 ks.

peaks that were different from those of ZnO , $Zn(OH)_2$, Al_2O_3 , and $Al(OH)_3$.

3. 2 Mass change during the corrosion test

Figure 8 shows the mass change of Z alloy during corrosion-testing in 2% HCl solution. Figure 9 shows the influence of mischmetal addition to the Z alloy on the mass change during corrosion-testing in 2% HCl solution. The mass of each specimen decreased as the corrosion period increased. In the case of Z alloy, the mass loss was greater in an order of TR5, TR4, TR3, and TR2 and TR1, namely the cooling rate affected the corrosion behavior of this alloy pronouncedly. On the contrary, the mass losses of M alloys did not depend significantly on the cooling rate and their values were comparable

to those of Z-TR4 and Z-TR5 specimens. Figure 10 plots the mass change of Z alloy during corrosion-testing in 3% NaCl solution. Figure 11 shows the influence of mischmetal addition to the Z alloy on the mass change during corrosion-testing in 3% NaCl solution. The mass change of Z alloy increased as the corrosion period increased. The mass change of M alloy complicatedly depended on the cooling rate. The corrosion behavior of Z alloy in 2% HCl solution described above coincided with that of Zn-50 mass% Al alloy or Zn - 60 mass% Al alloy whose mass loss also depended on the cooling rate and the mass loss of water quenched specimen (TR1 specimen) was greatest^{6,7)}.

The difference in the corrosion behavior may be caused by the difference in microstructures of Z alloy and M alloy. Moreover, in the case of corrosion-testing in 3% NaCl solution, the corrosion product remained on the surface of each specimen, and also remained in the pits in the case of Z alloy specimen. This may also account the difference in the corrosion behavior between these alloys.

As described above, the corrosion behavior of α -phase is distinguishable from that of β -phase against 2% HCl solution. This difference in the corrosion behavior must be the case against 3% NaCl solution. To account the difference in corrosion behavior of Z alloy and M alloy, namely to clarify the effect of mischmetal addition on the corrosion behavior of Z alloy, we attempted to examine where mischmetal added existed in the structure or in the corrosion product by use of X-ray microanalysis and ion microanalysis (IMA). This attempt was failed because of small amount of mischmetal. But, IMA demonstrated that the Al-content of corrosion product of Z alloy was different from that of M alloy. The IMA intensity ratio of aluminum and zinc is summarized in Table 1, which means that the mischmetal addition to the Z alloy suppressed the corrosion of zinc-rich portion of this alloy, or enhanced the corrosion resistance of aluminum-rich one in 3% NaCl solution.

Judging from the pit formation of Z alloy and the general corrosion of M alloy, the addition of mischmetal suppressed the corrosion of zinc-rich portion of Z alloy and made the surface of this alloy more

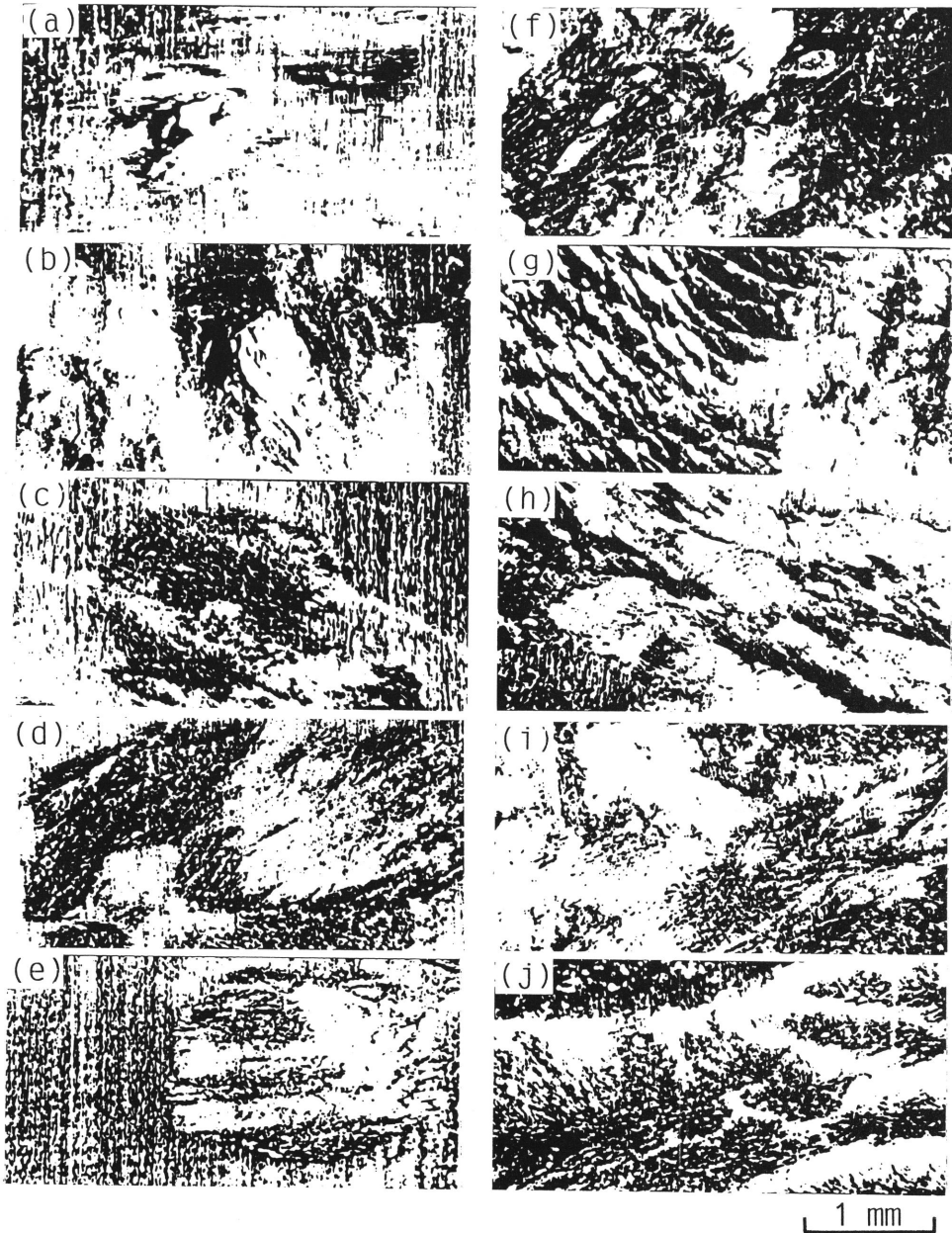


Fig. 7 Surface appearances of Zn-5mass%Al ((a)–(e)) and Zn-5mass%Al-Mischmetal ((f)–(j)) alloys after corrosion-testing in 3% NaCl solution at 308 K for 720 ks. Corrosion product was removed by a slight polishing.

(a),(f) : TR1, (b),(g) : TR2, (c),(h) : TR3, (d),(i) : TR4, (e),(j) : TR5

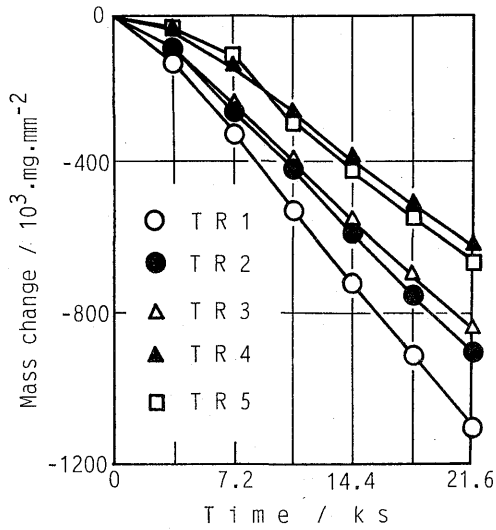


Fig. 8 Cooling rate dependence of the mass change of Zn-5mass%Al alloy by corrosion in 2% HCl solution.

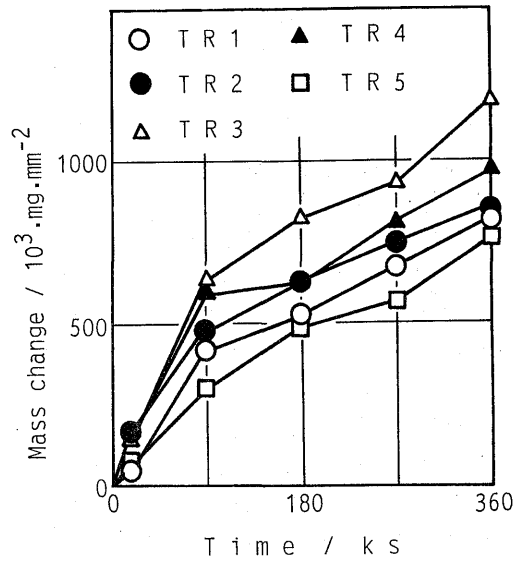


Fig. 10 Cooling rate dependence of the mass change of Zn-5mass%Al alloy by corrosion in 3% NaCl solution.

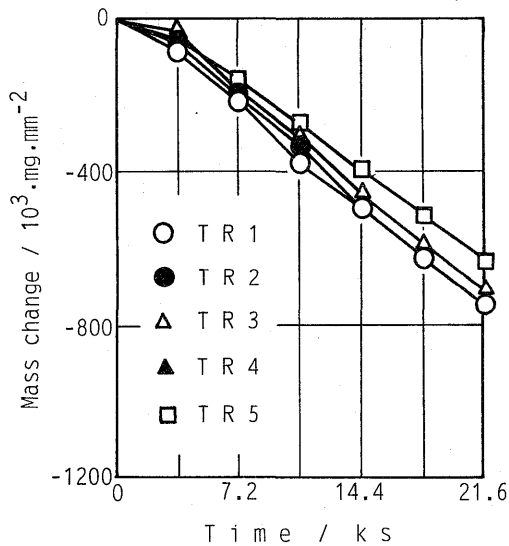


Fig. 9 Cooling rate dependence of the mass change of Zn-5mass%Al-Mischmetal alloy by corrosion in 2% HCl solution.

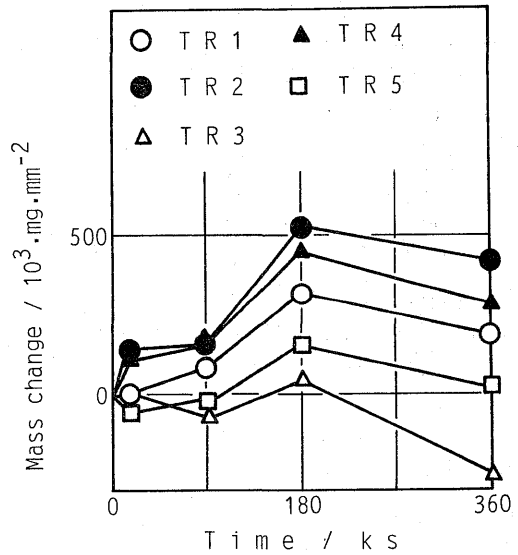


Fig. 11 Cooling rate dependence of the mass change of Zn-5mass%Al-Mischmetal alloy by corrosion in 3% NaCl solution.

homogeneous against corrosion in 3% NaCl solution.

IMA also revealed the existence of O^- ion, trace Cl^- ion and no OH^- ion. This suggests that the corrosion product must be mainly composed of

ZnO. Suzuki et al. investigated the corrosion behavior of Zn - 22 mass% Al alloy and those of melt sprayed Zn - 15 mass% Al and Zn - 22 mass% Al alloys in NaCl aqueous solution and found the corrosion products composed of $ZnCl_2$ and Al

Table 1 Zn⁶⁴/Al²⁷ ratios.

sample		Zn ⁶⁴ /Al ²⁷ × 100
raw material	Zn-5mass%Al	0.3639
	Zn-5mass%Al-MM	0.4880
corrosion product	Zn-5mass%Al	31.67
	Zn-5mass%Al-MM	14.70

(OH)₃¹¹⁾¹²⁾. Our X-ray diffraction analysis has not reveal the existence of these compounds as well as ZnO.

4. Conclusion

Zn - 5 mass% Al alloy and Zn - 5 mass% Al - Mischmetal alloy with different microstructures were corrosion-tested in stagnant 2% HCl and 3% NaCl aqueous solutions at 308 K, and the effects of microstructure and mischmetal addition on the corrosion behavior were investigated.

In 2% HCl solution, the mass change of both alloys decreased as the corrosion period increased. The corrosion behavior of Zn - 5 mass% Al alloy depended on the cooling rate and the mischmetal addition made the cooling rate dependence of the corrosion behavior of Zn - 5 mass% Al alloy less pronounced. The β -phase was attacked preferentially to leave the α -phase undissolved as a skeleton.

In 3% NaCl solution, the corrosion behavior of Zn - 5 mass% Al alloy as well as that of Zn - 5 mass% Al - Mischmetal alloy depended on the cooling rate complicatedly. A white product, which indicated X-ray diffraction peaks which were different from those of ZnO, Zn (OH)₂, Al₂O₃ and Al (OH)₃, was formed on each corroded specimen. The mischmetal addition to the Zn - 5 mass% Al alloy changed its corrosion style from a pitting corrosion to a general corrosion.

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