

Atmospheric Corrosion of Zinc and Zinc Alloy Using In-situ Raman Spectroscopy

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Introduction

Zinc-coated steel has been widely used as a high corrosion-resistive material for vehicle body panels and construction. Zinc coating containing Ni and Al is expected to be more protective than that without Ni and Al. In our previous study using Raman spectroscopy, the formation sequence to $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4$ (zinc hydroxy chloride or simonkollite) was examined by corrosion of zinc under atmospheric condition in the presence of sodium chloride particles. The zinc hydroxy chloride was found under the condition at relative humidity (RH) higher than 80 %. At the lower RH, zinc oxide, ZnO , was only detected. In this paper, we present the effect of Ni and Al which individually are contained in the zinc coating layer on the formation sequence of the corrosion products in the presence of NaCl by using “in-situ” Raman spectroscopy.

Experimental

Three steel specimens which were coated by pure Zn, Zn-12% Ni alloy or Zn-5% Al alloy were employed. The samples were cut to $1 \times 2 \times 0.1$ cm. The samples were ultrasonically degreased in acetone. A Raman corrosion cell was made of cylindrical glass, in which a laser light (514.5 nm wavelength) of an argon ion laser was incident to the zinc plate from the bottom in the cell and Raman scattering light from the surface of the specimen plate was collected in the direction normal to the incident light. Before the corrosion experiment, NaCl particles were precipitated by dropping 10 μl of 3% NaCl aqueous solution on the specimens and drying in a vacuum desiccator. The specimen was fixed in the corrosion cell for Raman spectroscopic measurement and then the humidified air at RH 84 or 75 % was introduced into the cell. Surface analysis by XPS was also done.

Results and Discussion

During the exposure in humidified air, it was formed from the sequent change of Raman spectra that aqueous ZnCl_2 layer was initially formed and then $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4$ appeared for the all specimens. We focused formation time of the aqueous ZnCl_2 and the $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4$. The Raman peak intensity is shown in

Figure 1 as a function of the exposure time for the specimen of pure Zn, Zn-12% Ni, and Zn-5% Al. In this figure, the Raman peak intensity at wavenumber of 290 cm^{-1} is plotted for aqueous ZnCl_2 layer, and the intensity at 390 cm^{-1} for solid zinc hydroxy-chloride. It is seen that during the exposure in humidified air at RH 84 %, aqueous ZnCl_2 layer was initially formed and then $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4$ appeared after a few hours for the all specimens.

The coating containing Ni or Al, required longer exposure time than pure Zn coating until the Raman peak of aqueous ZnCl_2 layer was appreciable. The XPS analysis found that NiO existed for the initial surface on Zn-12% Ni coating and AlOOH for Zn-5% Al coating. Ni and Al oxide and/or hydroxide on the initial surface before the exposure may delay the appearance of aqueous ZnCl_2 layer and zinc hydroxy-chloride. It was assumed that NiO or AlOOH existed before the exposure suppresses the dissolution of Zn and keep the concentration of ZnCl_2 low in the surface solution layer for the longer time. From the delay time until appearance of Raman peaks of aqueous ZnCl_2 layer, it is conceivable that the corrosion rate is the order of pure Zn > Zn-12% Ni > Zn-5% Al.

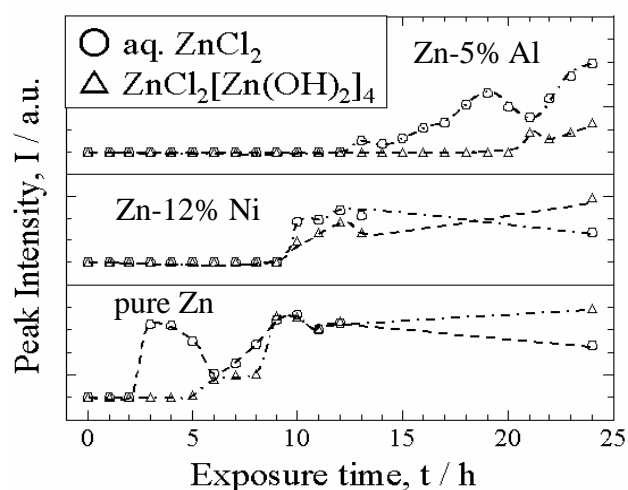


Fig. 1 Transient of peak intensity of aqueous ZnCl_2 and simonkollite formed on Zn-coated steel exposed to humid air at 84% RH.