
C05-1683 - (Invited) Rust Design for Corrosion Protection of Steel Exposed to Atmospheric and Marine Environments



Wednesday, 9 October 2024



1000 - 1040



Room 303A (Level 3, Hawaii Convention Center)

Abstract

Steel materials have been used in many fields as basic materials for infrastructures due to their superior strength and toughness. However, steel is significantly more susceptible to corrosion in atmospheric corrosive environments than other metals such as copper- or zinc-based materials. The large corrosion rate of steel is greatly affected by iron rust, which is a corrosion product formed on the steel surface as a result of corrosion. In general, the rust layer has poor corrosion protection properties and rather accelerates corrosion because it accelerates electrochemical reactions. To provide corrosion protection ability to the rust layer, which adversely can suppress the corrosion of steel materials, would enhance the corrosion resistance of steel in atmospheric and marine environments. The author and co-researchers have investigated the structure and electrochemical properties of the rust layer on steel and have attempted to design rust to actively increase the protectiveness of the rust layer against corrosion.

The major rust components commonly found in the atmospheric environment are iron oxyhydroxide (α -FeOOH, β -FeOOH and γ -FeOOH) and iron oxide Fe_3O_4 . β -FeOOH is structurally stabilized by the presence of Cl, so it is often found in environments with large amounts of salt such as marine environments. Among the isomers of iron oxyhydroxide, the thermodynamic stability differs, with α -FeOOH being the most stable. The author and co-researchers have elucidated that the rust layer mainly composed of the α -FeOOH structure has high corrosion protectiveness. The main reason for this is thought to be the suppression of the rust reduction reaction and therefore the reduction of the cathodic reaction rate. Since γ -FeOOH in the rust layer changes to α -FeOOH with long period of time, the mass fraction of α -FeOOH-structured rust, α/γ and α/γ^* , which are reported as the protective ability index (PAI) of the rust layer, monotonically increases over thousands of years (Fig. 1). The corrosion rate of steel with rust layer decreases as the mass fraction of α -FeOOH structural rust, PAI, increases. [Yamashita et al., Corros. Sci. 36, 283(1994); Yamashita et al., The Sumitomo Search, 57, 12(1995); Dillmann et al., Corros. Sci., 46, 1401(2004); Kamimura et al., Corros. Sci., 48, 2799(2006)]

In order to enhance the protectiveness of the rust layer, doping of nonferrous metallic elements into the rust layer would be effective. For example, it has been shown that Cr doping in α -FeOOH leads to crystal grain refinement and ion selective permeability. XAFS analysis using synchrotron radiation [Yamashita et al., Materials Science Research International, Special Technical

Publication-1, 398-401(2001); Yamashita et al., Corros. Sci., 45, 381(2003)] revealed that Cr is adsorbed on the surface of α -FeOOH crystal as CrO_x^{3-2x} [Konishi et al., Materials Transactions, 46, 337(2005)]. On the other hand, doping of Al, Ni, and Zn in the rust layer increases α -FeOOH and decreases the oxygen reduction rate, suppressing the cathodic reaction. In particular, Zn also suppresses the reduction of rust since Zn behaves as a substitutional element to Fe, which has been elucidated from anomalous dispersion behavior measurements using synchrotron radiation X-rays [Deguchi et al., SPring-8/SACLA Research Reports, Section B, 366(2023)]. In addition, doped Ni changes tetragonal crystal structure of β -FeOOH to monoclinic structure resulting formation of $\text{Fe}_{7.6}\text{Ni}_{0.4}\text{O}_{6.35}(\text{OH})_{9.65}\text{Cl}_{1.25}$ [Post and Buchwald, Am. Min. 76, 272(1991)] that increases protectiveness of the rust layer even in chloride airborne environments [Hayashida et al., Materials Transactions, 62, 781(2021)].

These facts suggest that anticorrosive rust design is possible by utilizing nonferrous metallic elements. In fact, it has been shown that when various metallic compounds that are expected to have rust design effects are added to a paint, the rust layer of a rusted steel coated with the paint is modified and corrosion resistance of the rusted steel is significantly improved (Fig. 2) [Yamashita et al., Corrosion Engineering, 66, 64(2017)]. It is hoped that further development of this rust design will improve the corrosion resistance of

steel materials and extend the service life of steel infrastructure.

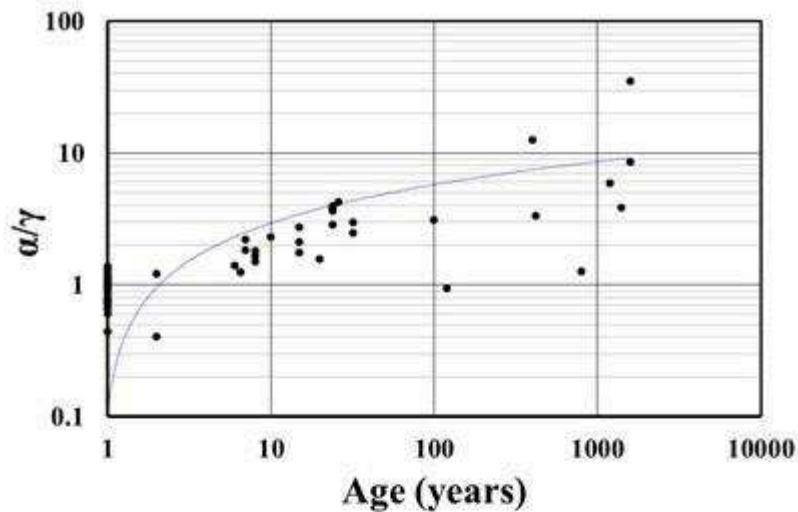


Fig. 1 Variation of α/γ of rust layers as a function of time. All data were cited from literature values.

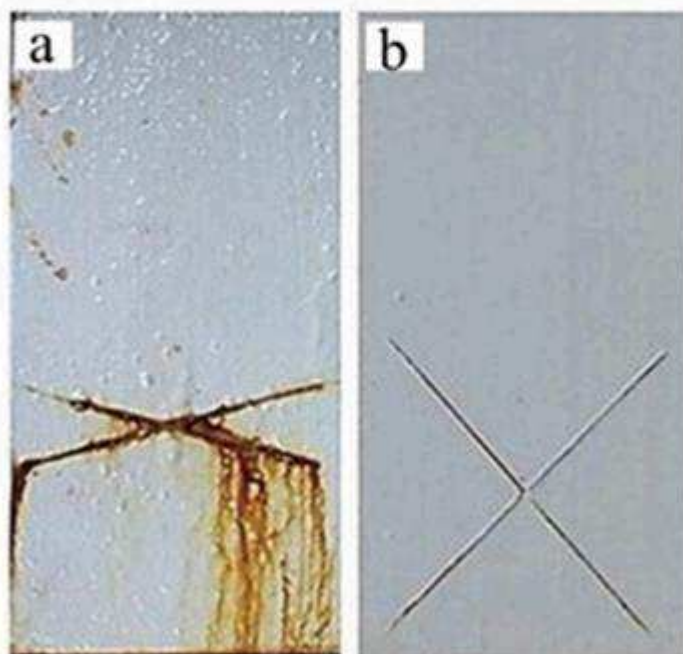


Fig. 2 Surface appearance of rusted carbon steel covered with conventional heavy-duty paint coating (a) and that covered with the rust design paint coating containing metallic compounds (b) after 720h salt spray test.

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