TECH**BRIEF**

Improved Corrosion-Resistant Steel for Highway Bridge Construction Knowledge-Based Design

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Introduction

The use of weathering steels for construction of new highway bridges has recently increased significantly. These steels provide construction cost savings of more than 10 percent because there is no need to paint the steel, as unpainted steel is easier to install and handle. In addition, the life-cycle cost savings are more than 30 percent because weathering steels require less maintenance and are more durable than common construction steels. Also, use of weathering steels provides significant environmental benefits because there are no volatile organic compounds (VOC) from paints, and there is no need for removal or disposal of contaminated blast debris over the life span of the structure. However, the current weathering steels are not considered adequate for marine and other high saline environments. The objective of this project was to point out new directions for the development of low-cost steels with much better weathering characteristics than those of currently used weathering steels.

Approach

This project did not involve experimental laboratory or field tests of weathering steels. Instead, it focused on an extensive analysis of available data regarding the weathering performance of steels in different environments, effects of different conventional and nonconventional alloying elements on weathering of steels, and mechanisms leading to the reduced corrosion rates of those steels with the goal of suggesting ways to improve the weathering characteristics of modified existing steels. Prior design of weathering steels was purely empirical, and the steel design focus was on a small number of conventional elements such as manganese (Mn), silicon (Si), chromium (Cr), nickel (Ni), copper (Cu), molybdenum (Mo), and phosphorus (P) in a narrow concentration range. Since the effects of these elements on corrosion properties of steels were well known for many decades, only marginal improvement in weathering performance of steels could be achieved by adjusting the concentrations of these elements.

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With the increased use of thermodynamics (i.e. Pourbaix diagrams), electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD), and Mössbauer spectroscopy in the corrosion field, it became obvious that there might be several different mechanisms for imparting corrosion resistance to weathering steels depending on the nature of the alloying element and on the environment. Thus, better understanding the corrosion mechanisms led to a significant extension of the list of possible alloying elements that improve the weatherability of steel. Discussion below suggests that more significant increases in weathering performance of steels could be achieved by using less common alloying elements such as tungsten (W), titanium (Ti), aluminum (Al), rare earths (RE), etc., than by using traditional alloying elements. These suggestions are based on the laboratory-performed accelerated weathering tests as well as on studies of the effects of these elements on thermodynamic, kinetic, electrochemical, crystallographic, and other properties of native oxide layers on steels.

Results

Since the corrosion process is electrochemical by nature, the electrical potential of the system and pH of the environment are very important factors in the weathering of steels. Pourbaix diagrams, also known as potential/pH diagrams, map out possible stable equilibrium phases of an aqueous electrochemical system.[1] Weathering of steel depends on the formation of a hard passive surface film (oxide or salt) that inhibits further corrosion. The Pourbaix diagram indicates that pure iron is passive at pH values from 9 to 12.5 (iron hydroxide forms in this pH range).[1] Below or above this pH range, iron corrodes freely. Pourbaix diagrams for binary systems (iron-other elements) or ternary (iron-two other elements) calculated at Northwestern University and other research groups showed the following:

- When Ni is added, it prevents the corrosion of iron (Fe) at a pH higher than 12.5 by the formation of a stable oxide. In addition, Ni extends the passive region down to pH 7.[2] Formation of the spinel double oxide ($NiFe_2O_4$) on the steel during weathering provides an additional measure of protection from further corrosion.

- When Cr is added to Fe, the passive region is extended further than in case of Ni down to pH equal to 4.5, and no ions are formed at high values of pH. Thus, Cr is more effective in corrosion protection of Fe than Ni.

- When W is added to Fe, the anion $(WO_4)^{-2}$ is formed at pH as low as 5.[3] This anion, when combined with the Fe cation during early stages of weathering, forms a salt that concentrates in the pores of the rust and acts as a corrosion inhibitor. No ions are formed at high pH values in Fe-W systems. Thus, this alloy is also passive at high pHs.

- When Al is added to Fe, a stable $FeAl_2O_4$ protective oxide forms in a wide pH region (from 4 to 14).[3]

Since no information on corrosion kinetics could be deduced from Pourbaix diagrams, further analysis of the effects of these elements on morphology and electrical (impedance) resistance of the films formed on the surfaces of steels that have been performed by other analytical techniques were reviewed to ascertain whether the addition of these elements improved the weatherability of steel.

The rust on steel is a semiconductor; therefore, the direct measurement of electrical resistance of it is not possible. Instead, EIS has been successfully applied to the study of corrosion systems for many decades and has been proven to be a powerful and accurate method for measuring corrosion rates. For example, when EIS was used to determine the resistivity of the oxides on the surface of binary alloys, the highest resistance of the rust was observed when 1 percent of W was added to Fe.[4] The resistance of the rust formed on Fe with 1 percent W was one order of magnitude higher than that of the rusts formed on Fe with an addition of 3 percent cobalt (Co), 0.1 percent P, or 0.8 percent Al. In addition, the resistance was a few times higher than that of rust formed on steel containing 0.8 percent Mo or 3 percent Ni. According to the American Society for Testing and Materials (ASTM)'s Volume 03.02, *Wear and Erosion: Metal Testing*, Co, P, Mo, and Ni are very potent in making steel weatherable.[5] Thus, on the basis of EIS results, it could be anticipated that W would be an even more potent element than others in the weathering of steels.

Another recent research of the steels containing Al confirmed the conclusions made from Pourbaix diagram analysis.[6] The addition of 0.8 percent Al to steel almost doubled the impedance of the rust compared to similar steel without Al. This further suggests that Al could significantly improve the weatherability of steels.

The addition of another element, Ti, to the steel leads to a modification of the rust morphology (as found by transmission electron microscopy (TEM) and characterized by XRD, nitrogen (N_2) absorption, and Mössbauer spectroscopy).[7] Ti-enriched ultrafine α-FeOOH particles plug the pores in the rust film formed on the steel surface, which significantly increases the passivation ability of the rust. Another benefit of small Ti addition is its ability to suppress the formation of pearlite in steel, improving the weatherability of steel.[8] Steel that contains pearlite has significantly lower weatherability than steel of the same composition but with the C in solution in the ferrite.[9]

It was found that very small additions of RE elements to steel significantly improve its weatherability. In one investigation, it was found that after 2,250 days of outdoor exposure, the corrosion rate of steel that contained a very small addition of RE elements (0.029 percent) was two times less than that of the steel without these elements.[10] The addition of these elements moved the corrosion potential of the steel in a positive direction as well as significantly increased the electrical resistance of the rust layer. These results showed that the addition of REs of proper proportion may significantly diminish corrosion tendency and promote the formation of the steady and compact rust layer.

While corrosion resistance is an important performance factor for steels, other factors need to be considered in the design of improved weathering steels. These factors include mechanical properties such as strength, ductility, and high fracture resistance at low temperatures; the ability of steel companies to produce steel through steel-making processes; the ease of steel structure fabrication such as weldability and machinability; the absence of adverse health effects during steel production and structure fabrication; reasonable cost; etc. For example, P is very effective in increasing the weatherability of steel; however, in amounts exceeding 0.1 percent, it significantly imbrittles the steel. Elements Cr and Mn are very effective for weatherability, but steels containing these elements release carcinogenic fumes during welding. As a result, the concentration of these elements in steel needs to be kept to a minimum. However, the element Mo is very expensive and should be avoided if possible.

As demonstrated before, less common alloying elements in steel (Al, Ti, W, and REs) can significantly affect the steel weatherability. The addition of any of these elements or their combination would not significantly affect the price of steel because these elements are inexpensive when added in small amounts. The mechanical properties of steel were shown to be improved by the addition of some of these elements. For example, the addition of REs to steel refined the microstructure, increased the strength, and increased fracture toughness. Furthermore, the use of Al in steel increased its strength and did not affect the toughness. Meanwhile, the use of Ti refined the microstructure, eliminated pearlite, and dramatically increased fracture toughness at cryogenic temperatures.

Based on these findings, an experimental approach is suggested to design a more effective weathering steel based on an ASTM A710 Grade B steel developed at Northwestern University.[11,12] This 70-ksi yield steel has excellent ductility, fracture toughness, weldability, machinability, and weatherability that is superior to the properties of other weathering steels presently used for bridges. The following elements are proposed to be added to the steel separately: Al in 0.2–0.8 percent, Ti in 0.1–1.0 percent, RE elements in 0.01–0.05 percent, and W in 0.3–1.0 percent. The mechanical and fracture properties should be tested. If they conform to bridge steel requirements, the weatherability of steel should be investigated in accelerated tests. Additional steel compositions that include the combination of two or more of these elements could be designed after the preliminary mechanical, fracture, and corrosion tests are performed, and the beneficial effects of these elements on steel properties are ascertained.

Conclusions

Based on research performed by different groups and on work performed at Northwestern University, it is found that many of the less used elements in steel such as Al, Ti, W, and REs could significantly improve the weatherability of steel.

Weathering steel could not be designed solely on its weathering characteristics. The composition should be optimized in respect to weathering characteristics, strength, ductility and fracture properties, ease of processing and fabrication, cost, and adverse health effects.

Further experimental work is recommended. For example, an improved corrosion-resistant steel could be designed by modification of ASTM A710 Grade B steel composition by the addition of Ti, Al, P, W, RE elements, and other elements not usually found in steels.

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