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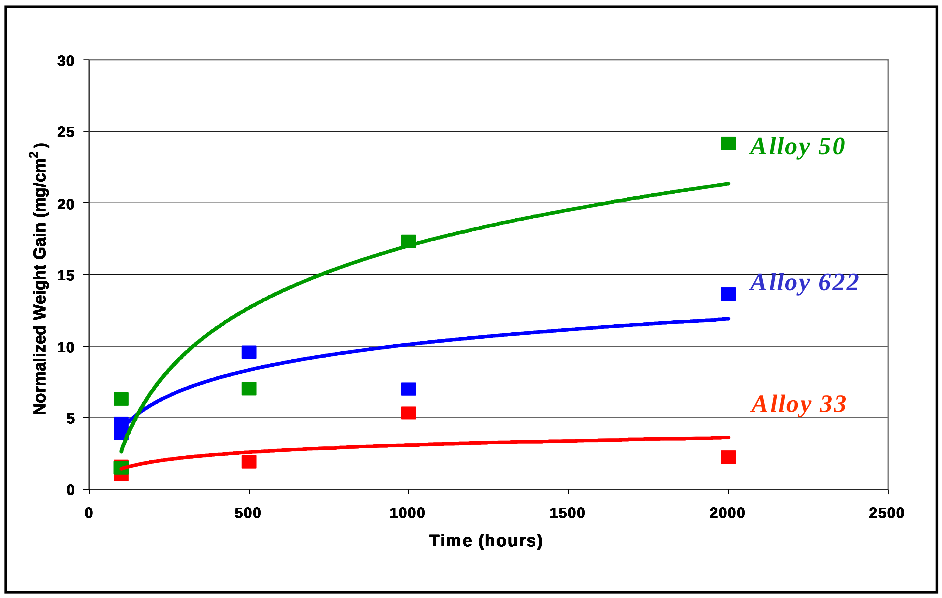
IMPROVED WELD OVERLAY COATINGS DEVELOPED FOR CORROSION CONTROL IN COAL-FIRED BOILERS

Some power generation companies are finding the need to replace waterwall tubes in their coal-fired boilers due to unusually high rates of fireside corrosion. Accelerated corrosion of waterwall tubes is caused by operating with low levels of oxygen in the combustion zone, typically in the presence of a high sulfur coal. One favored solution to this problem has been to deposit a weld overlay cladding of a more corrosion resistant alloy onto the tube. While the commonly used weld overlay cladding materials do provide more corrosion resistance than the carbon and low alloy steel alloys found in water wall tubes, they are not without their drawbacks. The weld overlay alloys used contain expensive alloying elements such as niobium and titanium, and these do not increase corrosion resistance. Additionally, due to microsegregation of some of the alloying elements occurring during solidification of the weld, these alloys are susceptible to circumferential cracking. There is a critical need in the power industry for improved corrosion resistant alloys, designed specifically for use as weld overlays in boilers operating with low NO_x firing conditions.

A Lehigh research team, led by John DuPont, has developed specifications for a new generation of weld overlay materials which are expected to provide longer-term corrosion protection at a lower cost than the alternatives. The Lehigh researchers included John Regina, Ryan Deacon, Mathew Galler, and Arnold Marder. The project was supported by Southern Company Services, Inc., Allegheny Energy Supply, Inc., Dominion Virginia Power, FirstEnergy Corp., PPL Generation LLC, Ontario Power Generation, Inc., and PITA.



Laboratory corrosion results with experimental nickel based alloys exposed to simulated low NO_x environment. Higher normalized weight gains indicate higher corrosion rates.

DuPont explains, "In an effort to reduce NO_x emissions, many coal fired power plants have implemented staged combustion practices. By delaying the mixing of fuel and oxygen, the amount of NO_x released as a by-product of combustion is reduced. The use of staged combustion has been found by many power plant operators to be one of the most cost effective methods for reducing plant emissions.

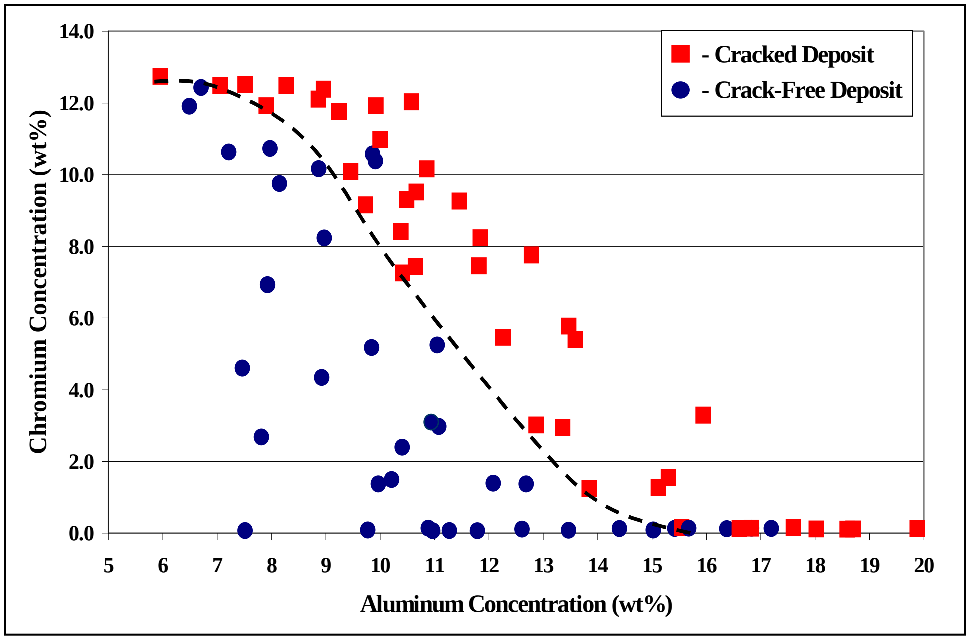
Prior to the introduction of staged combustion, most boiler atmospheres contained sufficient quantities of oxygen to allow for the formation of protective metal oxides on low alloy waterwall tubes. With staged combustion, however, the combustion zone is starved of oxygen, which creates a reducing atmosphere which prevents the formation of NO_x compounds. A consequence of creating this low-oxygen environment is the transformation of sulfur products in the coal into highly corrosive hydrogen sulfide (H_2S). Subsequent reaction of the combustion gas with the waterwall tubes leads to the formation of non-protective metal sulfides on tube surfaces and high corrosion rates. The deposition of sulfur bearing unburned coal particles on the waterwall can also lead to high corrosion rates. In the reducing atmosphere of a typical staged combustion boiler, low alloy steels experience significant corrosion and the resulting wastage rates create unacceptably short tube service lifetimes. Whereas tube lifetimes of 10-20 years are common in oxidizing environments, tube failures due to excessive wastage have occurred in less than one year in low NO_x combustion conditions.

One favored solution to this problem has been to deposit a weld overlay cladding of a more corrosion resistant alloy on to the tube. Weld overlaying is an efficient, cost effective method for producing a protective coating with a metallurgical bond to the substrate. Since the implementation of staged combustion, most power plants have utilized commercially available nickel based superalloys, such as Alloys 622 and 625, for these weld overlays. However, these alloys are expensive and are susceptible to circumferential cracking."

Several research projects at Lehigh University's Energy Research Center have evaluated the performance of both new and currently used alloys for the weld overlay application. One such project compared three new commercially available nickel based alloys, with varying amounts of chromium and molybdenum, to Alloy 622, which is the alloy currently used most widely by the utility industry. Weld overlays of all four alloys were deposited on steel substrates, and the coatings were exposed to simulated coal combustion environments. Results from a typical corrosion test demonstrate that one of the new alloys (referred to as Alloy 33 in the study) was the most corrosion resistant of the alloys studied.

DuPont's research team conducted detailed microstructural characterization of the corroded samples in order to understand differences in corrosion behavior. Elemental mapping of key alloy elements in the corrosion products showed that Alloy 33 developed an internal corrosion layer which was rich in both chromium and oxygen and acted as a diffusion barrier to prevent corrosive attack. While Alloy 50 (this is the name used for a second alloy investigated in the project) and Alloy 622 also developed thick chromium and oxygen rich corrosion layers, some regions of the scales were simultaneously enriched in molybdenum and sulfur and depleted in chromium and oxygen. During solidification of these alloys, segregation of molybdenum occurred, resulting in a non-uniform distribution of this element. This pattern was incorporated into the growing corrosion product, resulting in the formation of molybdenum and sulfur rich regions throughout the oxygen rich scale. It was found that these regions act as fast transport pathways for sulfur and other corroding species, allowing corrosive attack to continue. In contrast, Alloy 33 was able to develop a uniform, continuous chromium and oxygen rich layer without these depleted regions. Test panels of Alloy 33 weld overlays have recently been installed in several power plants and are being monitored for their field performance. Results to date show very good performance.

DuPont adds, "Iron-aluminum (FeAl) based alloys have also received considerable attention for use as weld overlays due to their low cost and excellent corrosion resistance in combustion gases with very low oxygen pressures. One of the obstacles to the commercial application of these alloys, however, is their limited weldability due to hydrogen cracking. The hydrogen cracking susceptibility increases with increasing amounts of chromium and aluminum. In contrast, the corrosion behavior improves with higher additions of chromium and aluminum. Thus, the major objective of our research on FeAl based alloys was to identify weld overlay alloys that had optimal additions of chromium and aluminum for adequate weldability and corrosion resistance. Studies using both the gas tungsten arc (GTA) and gas metal arc (GMA) welding techniques identified a range of iron-aluminum-chromium compositions which can be deposited crack free. Results from the GTA weldability study show the range of chromium and aluminum which can be added while still permitting deposition of crack-free coatings. Hydrogen embrittlement was responsible for the cracking observed at higher aluminum and chromium concentrations."



GTA weldability study of iron-aluminum-chromium alloys. Dashed line defines weldability limit due to hydrogen cracking. Data points below the dashed line correspond to a crack-free deposit.

The Lehigh researchers found that FeAl alloy compositions which fall within the weldability limit offer superior corrosion resistance to the nickel based superalloys. The improved performance of the FeAl type alloys is attributed to the development of protective oxides on the iron aluminum alloys, rather than the non-protective scales which form on the nickel based alloys. Thick, poorly adherent iron sulfides have been observed on Alloy 622 after exposure to low NO_x environments. In contrast, the iron aluminum alloys develop oxygen rich corrosion products which are very adherent to the overlay surface. The ability of these corrosion products to effectively prevent sulfur and other corrosive species from reacting with the underlying metal is the key to good corrosion resistance. Studies are currently underway to determine the precise composition of the corrosion products on these alloys and to understand the role of alloy composition in their development. Work is also in progress to improve the weldability of coatings deposited with the gas metal arc welding process, since this process is preferred by industry due to its high deposition rates. ■

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NEW PROJECT WILL EVALUATE WELD OVERLAY MATERIAL OPTIONS FOR ULTRA-LOW NO_x AND HIGH FUEL SULFUR APPLICATIONS

Recent changes in boiler operating conditions suggest that the waterwall corrosion problem may continue to become even more severe. For example, more and more plants are installing flue gas SO_2 scrubbers, which will make it possible for them to burn less expensive high sulfur coals. In addition, the regulatory limits for NO_x emissions will be reduced even further. Each of these changes is expected to lead to even more H_2S in the combustion gas and an associated increase in the corrosion rates. In addition, the application of a weld overlay coating, although generally beneficial, results in an elevated overlay metal surface temperature, because of the additional thermal resistance caused by the weld overlay. This increased surface temperature also leads to higher corrosion rates.

The Energy Research Center is initiating a new research project to investigate these effects and determine which weld overlay coating materials will be most resistant to corrosion in the face of these demanding conditions. The objective of this new research project is to determine the changes expected to the corrosion environment due to these more severe operating conditions, and then evaluate a variety of new and commercially available coatings for their resistance to corrosion. This will include an evaluation of existing commercial alloys (e.g., Alloy 622 and various stainless steels), new commercial alloys (e.g., Alloys 33 and new INCO alloys), as well as the FeAl type alloys already developed at the ERC. The results of this project will form the basis for selecting alloys for protecting against waterwall corrosion due to high sulfur coals and more demanding low NO_x firing conditions. For more information on this new project, contact John DuPont at (610) 758-3942.

RESEARCHERS' PROFILES

- ***John DuPont*** is a Professor in the Materials Science & Engineering Department and Associate Director of the Energy Research Center. His research interests are in welding, corrosion, and alloy development.
- ***Arnold Marder***, a specialist in high temperature corrosion and failure analysis, is an Emeritus Professor of Materials Science and Engineering at Lehigh.
- ***Ryan Deacon*** will graduate from Lehigh in July with a Ph.D. in Materials Science & Engineering and has accepted a position in the Materials Characterization Laboratory at Johns Hopkins University.
- ***Jonathan Regina*** obtained his Ph.D. in Materials Science & Engineering from Lehigh in 2005 and is now a Group Leader in the Materials and Fabrication Group at ExxonMobil (Houston).
- ***Mathew Galler*** earned his Masters of Science degree in Materials Science & Engineering from Lehigh in May of 2007 and is now pursuing his Ph.D. degree at the Graz Technical University in Austria.

- ***Carlos Romero*** is an Associate Director of the Energy Research Center with a Ph.D. in Mechanical Engineering. He is a specialist in combustion kinetics and emissions control.
- ***Nenad Sarunac*** has a Ph.D. in Mechanical Engineering and is an Associate Director of the Energy Research Center. His research focuses on power plant heat rate improvement, emissions control and process optimization.
- ***Harun Bilirgen*** has a Ph.D. in Mechanical Engineering and is a Senior Research Scientist in the Energy Research Center.
- ***Zheng Yao*** is a Research Scientist at the Energy Research Center and he has a MS degree from Lehigh University in Mechanical Engineering.
- ***Ricardo Moreno*** is studying for an MS degree in Mechanical Engineering at Lehigh University.