Argonne National Laboratory Develops Alloys to Resist Metal Dusting

Degradation of structural components made from iron- and nickel-based alloys by metal dusting occurs in a variety of high temperature, high carbon activity processes which are in widespread use in the chemical and petrochemical industries. Metal dusting is a corrosion phenomenon that occurs in these alloys and is characterized by pitting and mass wastage when exposed to strongly carburizing gas atmospheres in the temperature range of 400 to 800°C. The development of new R&D 100 Award winning alloys at the Argonne National Laboratory (ANL) will have positive impacts on a number of industries and enable significant energy savings. This technology was recently selected by the independent judging panel and editors of *R&D Magazine* as one of the 100 most technologically significant products introduced into the marketplace in 2006.

Figure 1. An alloy tube from a syngas plant that has been severely damaged by metal dusting.

To avoid metal dusting problems industry is often forced to design lower temperature processes that are less energy efficient, waste more materials, and have lower yields. Historically, the hot gases in the process systems have to be quenched from 800 to 400°C to circumvent the metal dusting attack. For example, in reformer plants, high temperature gases have to be quenched by water, which loses high quality heat.

Research on metal dusting has been conducted for over 50 years, but suitable alloys for resisting metal dusting had not yet been developed. The industry as a whole had significant uncertainty about the mechanism that leads to metal dusting, and had not been able to develop an approach to combat this attack. Prior research demonstrated that the materials can undergo metal dusting in the laboratory at atmospheric pressure. However, the simulation of actual process environments was difficult and was not attempted, primarily because the processes operate at high pressures.

A breakthrough in the understanding of the mechanisms for the initiation and propagation of metal dusting at ANL has lead to the development of new metal dusting-resistant alloys. A study conducted at ANL (under the temperature, pressure and gas composition conditions found in the reformer environment) has clearly established the role of carbon deposition in the mechanism leading to initiation and propagation of metal dusting attack.

ANL researchers found that the interaction between carbon and the oxide scales that form on metal components is the key to preventing metal dusting. The Argonne study found that chromium oxide (Cr_2O_3) and chrome-iron spinel form on commercial alloys exposed to the reformer environment. Raman Spectroscopy determined that Cr_2O_3 was the most protective type of scale, and that chromium-rich spinels were more resistant to metal dusting than more iron rich spinels, which could be reduced by carbon. The researchers were then able to develop alloys that form Cr_2O_3 scale that have proven resistant to metal dusting.

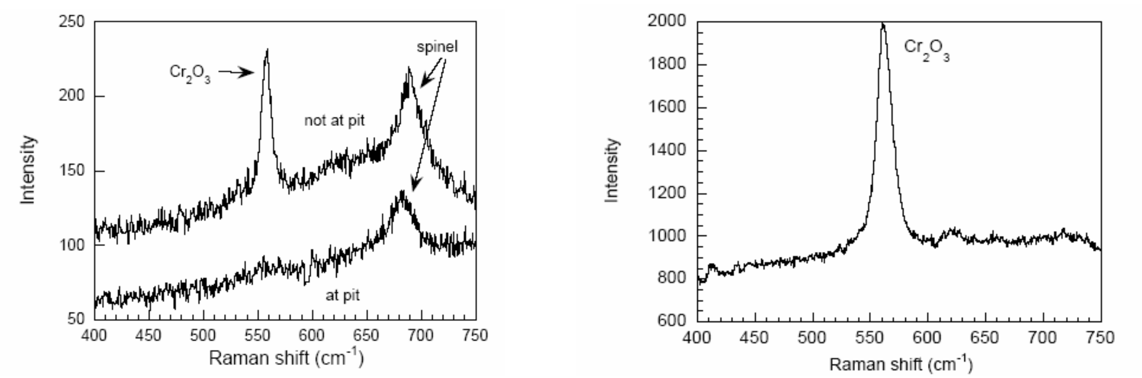

Figure 2. Raman spectra of (left) Type 310 stainless steel at pit and non-pit locations and (right) ANL-developed alloys after 1,100-h exposure in a metal dusting environment at 210 psi and 593°C. The degradation resistant ANL alloy and unpitted areas of the commercial alloy, exhibit high chromium oxide.

Laboratory tests demonstrated that large pits were observed on commercial alloys after exposure to the metal dusting environment. However, the surface of the ANL-developed alloy was still smooth (and without pits) after exposure to the same environment for 5,700 hours. The lifetimes of ANL-developed alloys in the metal dusting environment are greatly extended by minimal formation of spinel phase on the alloy surface.

The initial application of the ANL-developed alloys is in plants involved in hydrogen and synthesis gas production. ANL-developed alloys can also be used for components (such as waste heat boilers and gas bypass lines) exposed to metal dusting environments in methanol and ammonia reformer plants. The ANL-developed alloys also can be very effective in gas-to-liquid plants, in which natural gas is being converted into liquid fuels. Metal dusting is also observed at high temperatures in oxidizing-carburizing environments that are prevalent in the heat-treatment industry. The problem also occurs in direct reduction processes in the production of iron. Besides solving these problems, the ANL alloys could be used in chemical/petrochemical/petroleum refining processes where high concentrations of hydrocarbon and elevated temperatures are present.

By eliminating or minimizing the metal dusting attack with these alloys, the reformer processes can recover the heat at 800°C, and the equivalent of 4.6 million J/m^3 of hydrogen would be saved. This translates to 107 million standard m^3/day (475 billion Btu/day) of hydrogen production. This is equivalent to a saving of 13 million standard m^3/day of natural gas. An estimated $220-290 million can be saved annually in the hydrogen industry alone. Several alloy manufacturers are interested in producing larger quantities of our alloy for further evaluation in reformer plant environments.

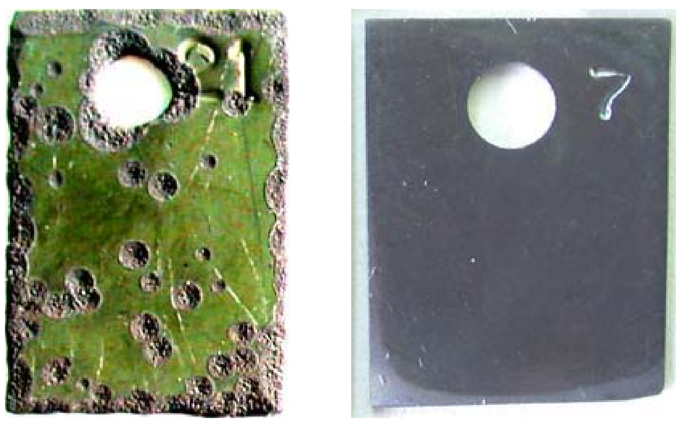

Figure 3. Photograph of commercial Ni-base Alloy 600 and ANL-developed alloy after 5,700-h exposure to the same metal dusting environment at 593°C.

For more information see:
http://www.anl.gov/techtransfer/Awards/rd100_short.html#dusting

For a Fact Sheet on the Project:
http://www.eere.doe.gov/industry/imf/pdfs/16944_metal_dusting.pdf

Or contact:
For technical Information, Krishnamurti (Ken) Natesan, Argonne National Laboratory, 630-252-5103, natesan@anl.gov
For licensing information, Terry Maynard Office of Technology Transfer, Argonne National Laboratory, 630-252-9771, maynard@anl.gov.