Development of the Next Generation of Bath Hardware Materials

The galvanizing of steel sheet by continuous hot dipping in a molten bath of zinc containing various amounts of aluminum is the most efficient and economical method of providing corrosion protection to most steel compositions. However, the performance of galvanizing molten metal bath hardware can strongly influence both the downtime experienced by a line and the coating quality. Typical galvanizing lines operate for an average of two weeks prior to required downtime for hardware maintenance. In 1996 and 2001, the International Lead Zinc Research Organization (ILZRO) in Research Triangle Park, N.C., conducted two surveys among worldwide continuous hot dip production lines. The surveys' results show that, for most companies, the most frequent cause of line stoppage is pot hardware problems that are related to one or more of the following three issues:

- Performance of bearings supporting rotating components, such as the sink roll, stabilizer roll and deflector roll.
- Corrosion of pot hardware in molten zinc, including corrosion of materials subjected to sliding contact.
- Nucleation and growth of dross (intermetallic particles) on pot hardware, especially roll surfaces causing cosmetic defects in strip coating.

The ILZRO surveys, which included hot dip production lines around the world, also summarized the state of the art in materials technology for molten metal bath hardware. The rolls, including sink rolls and stabilizer rolls, are made primarily of stainless steel 316L, which is a low-carbon version of 17Cr-12Ni austenitic grade. Stainless steel 316L is also used for snout tips. Roll bearings are generally made of a cobalt-based superalloy, commercially trademarked as Stellite. In some cases, WC-Co coatings are applied to the roll surface for improved resistance to wear and corrosion.

Many research efforts on various aspects of continuous hot operation have been reported

A frequent cause of line stoppage on galvanizing lines is pot hardware problems. A cooperative program to improve pot hardware materials and designs has led to significant cost savings for companies that operate galvanizing lines, along with many of their suppliers.

from Europe, Australia and China in past years. Some examples are studies on the circulation patterns of molten metal in the zinc molten metal bath of a continuous strip galvanizing line. Surface segregation of minor elements, including C, Si, Mn, P, S, Cr, Ni, Al, Cu and Ca, affecting the quality of hot dip coating has also been reported. Steel companies in Japan conducted research on the development of molten metal bath hardware. Kobe Steel has attempted the development of HVOF (high-speed oxygen flame) sprayed WC-Co coating for sink rolls in a galvanizing bath. Hitachi Ltd. has investigated the feasibility of using ceramics or ceramic-coated steels for the molten metal bath hardware in hot dip conditions.

Since 2001, a more fundamental approach to the improvement of pot hardware materials and designs, aimed at creating entirely new classes of pot hardware materials, has been under way in a cooperative program co-funded by the U.S. Department of Energy with a

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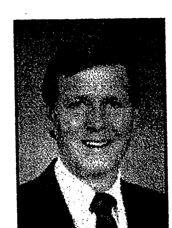

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total budget of $4.6 million. The goal of this program is to increase the lifetime of pot hardware components. Along with improving quality, such hardware improvements would have a significant impact on costs; a typical annual cost for line downtime for a North America galvanizing line is about $800,000 per year. Thus, for the 57 hot dip galvanizing lines operating in the U.S., this figure would be calculated as $45.6 million per year. Cooperating in this program are 19 sponsors, listed in Table 1. These include U.S. steel companies that operate galvanizing lines, along with many of their pot hardware and coating suppliers.

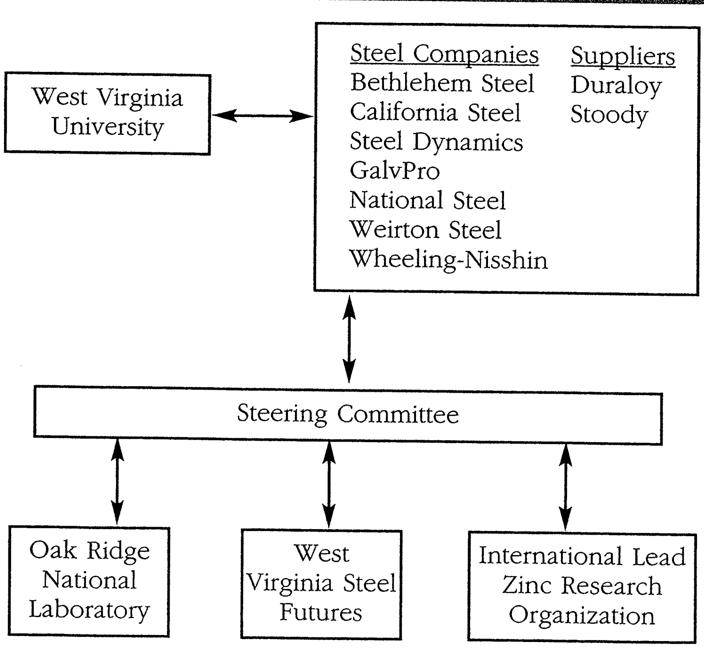
The research team includes West Virginia University (WVU), Oak Ridge National Laboratory (ORNL) and the International Lead Zinc Research Organization (ILZRO). A steering committee will manage all aspects of the project. The national laboratory, university research organization and industry participants will carry out the technical aspects of the project. Figure 1 illustrates the project management and coordination plan.

Table 1

Co-sponsors of the "Improved Materials for Pot Hardware" Program

Company	Location
AK Steel Corp.	Middletown, Ohio
ASB Industries	Barberton, Ohio
Bethlehem Steel Corp. (now ISG)	Bethlehem, Pa.
California Steel Industries	Fontana, Calif.
Deloro Stellite	St. Louis, Mo.
Duraloy Electroalloys	Scottdale, Pa.
Ellison Surface Technologies	Hebron, Ky.
Fontaine Engineering	Bridgeport, W.Va.
ILZRO	Research Triangle Park, N.C.
Metaullics Systems	Solon, Ohio
National Steel Corp. (now U. S. Steel)	Mishawaka, Ind.
Praxair	New Castle, Pa.
Steel Dynamics	Butler, Ind.
Stoody Thermadyne	Bowling Green, Ky.
Teck COMINCO	Toronto, Ont., Canada
Vesuvius	Beaver Falls, Pa.
Weirton Steel (now ISG Weirton)	Weirton, W.Va.
West Virginia Steel Futures	Weirton, W.Va.
Wheeling-Nisshin	Follansbee, W.Va.

Figure 1



Organizational plan for project coordination and management.

Project Priorities and Work Plan

This program focuses on three topics, each related to a specific galvanizing bath composition. Bearing wear is being considered mainly in galvanizing baths, with minor work also being done in galvanneal baths. Bearing materials include both monolithic materials, such as metal alloys and ceramics, and coated materials using plasma spray and other processes. The second topic is dross buildup, largely focusing on galvanneal baths with a minor emphasis on galvanizing baths. Here the mechanisms of dross buildup are being studied along with optimization of coatings for roll surfaces that can minimize dross buildup. The third topic, being given less emphasis than the other two, is dross formation in the Galvalume bath. Here, phase relations are of importance, as well as the interaction of roll surfaces with Galvalume dross to minimize Galvalume line stoppages.

To address these priorities, a total of six tasks are under way, as listed in Table 2. Tasks 1, 4 and 6 are led by West Virginia University, while tasks 2 and 3 are led by Oak Ridge National Laboratory. West Virginia University is also cooperating with six steel mills on Task 5, involving in-plant testing and trials of new materials. Figure 2 shows the work breakdown structure of the program.

As seen in the breakdown, there are three rounds of testing being conducted, with each round lasting about six months. The first round of testing focuses on the current commercial available materials and sets up the baseline of the materials development, while

Table 2

Tasks of the Research Program, "Improved Materials for Pot Hardware"

Task No.	Title	Investigator
1	Failure analysis and materials characterization	West Virginia University
2	Materials and process modeling	Oak Ridge National Laboratory
3	Materials development	Oak Ridge National Laboratory
4	Materials testing and analysis	West Virginia University
5	In-plant testing and trials	Joint with sponsors
6	Meetings and reports	West Virginia University

the second and third rounds of testing focus on the newly developed materials.

Failure Analysis and Materials Characterization

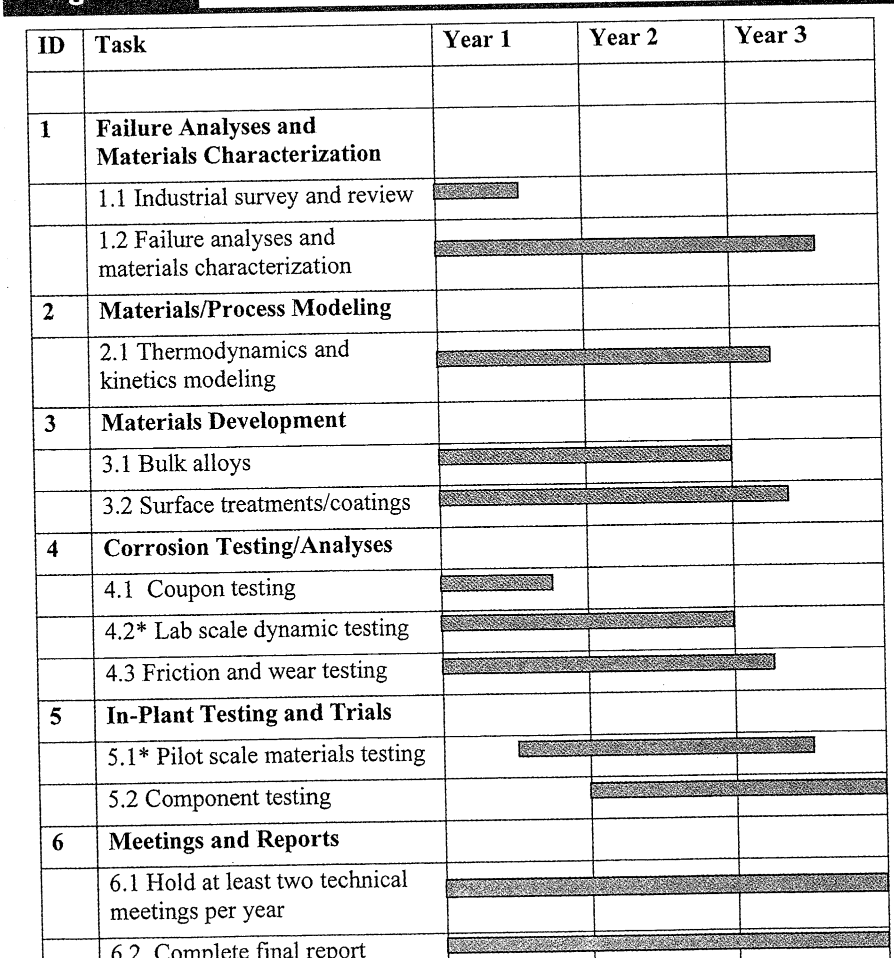
Several program sponsors generously donated to this program a number of used pot hardware materials for study. Early in the examination of pot roll materials, it became clear that dross buildup occurred in areas where the pot roll surface does not touch the strip. Even small areas of noncontact between strip and roll surface become locations where dross buildup occurs. When buildup first occurs, the dross particles are isolated from each other by the surrounding liquid zinc. With time, additional dross particles build up and the roll surface changes to an area with increasingly less liquid zinc fraction. As dross particles build up on each other, the liquid fraction moves progressively outward to the new contacting surface. Thus, cross-sections of dross buildup on rolls that have been in service for a time show a completely solid layer of built-up dross at the roll/dross interface.

Moving outward toward the built-up surface, the liquid fraction becomes increasingly higher, out to the roll surface where a dilute mixture of interconnected dross particles are mixed with the galvanizing alloy. This is the surface condition that steel strip sees when it passes over the pot rolls in areas of buildup. The dross particles in the semisolid pot roll surface layer can occasionally break off and adhere to the strip surface, or compact and be more massive, depending on local equilibrium conditions. This is illustrated in Figure 3, where bottom dross on both the sink and stabilizer rolls is apparent. A similar mechanism of dross buildup on Galvalume rolls can also be found.

Materials Testing and Analysis

There are four groups in the research team conducting testing and analysis of materials for pot hardware application. The lab scale liquid metal corrosion test is carried out by Oak Ridge National Laboratory, while the in-plant

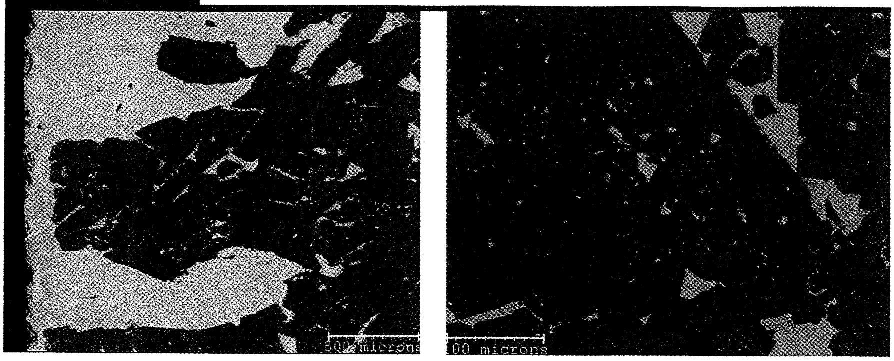
Figure 2



Note: * (decision points: go/no go)

Work breakdown structure.

Figure 3

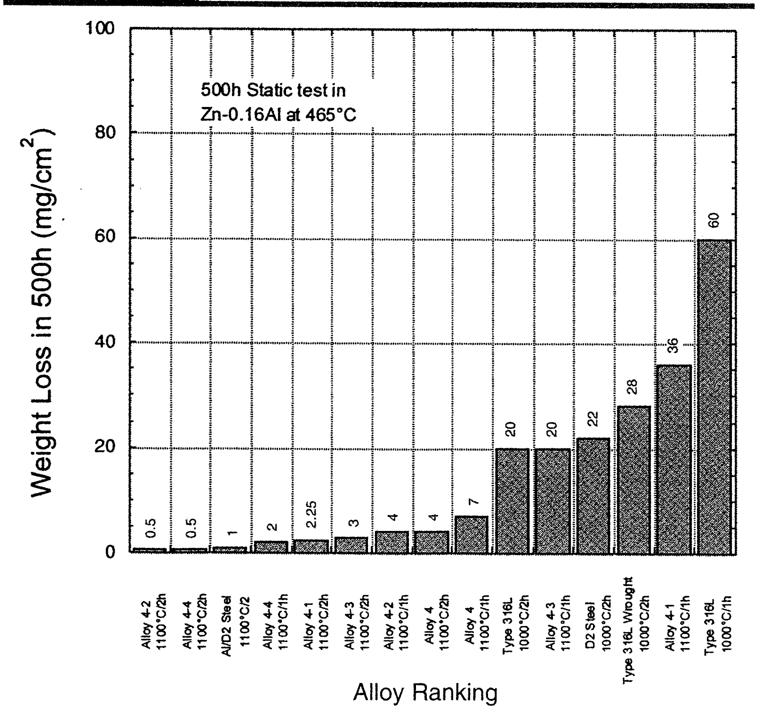


(a) (b)

Dross buildup in GI bath: (a) Zn bath side and (b) roll face side.

corrosion test is conducted by WVU. In addition, two sets of bearing and pot roll surface testing apparatus have been developed by WVU. One of the bearing testers, originally constructed by Duraloy Technologies to conduct immersion testing on real-scale bearing samples in a 500-pound zinc pot, was donated to WVU at the beginning of the project. It was modified to allow roll surfaces to oppose each other in the zinc bath, thus modeling dross buildup conditions. Another small lab-scale bearing tester was constructed for screening experiments at WVU. This consists of a ball of test material that is pressed against a socket of a second material, all immersed in liquid zinc. Wear between the ball and socket and the friction coefficient will be measured in order to screen and evaluate the pot hardware materials. The results of the first round of tests are reported and summarized as follows.

Figure 4



Alloy ranking after ORNL lab-scale static corrosion test, preoxidation treatment condition.

Lab-scale Liquid Metal Corrosion Test — Commercially available materials, along with a wide range of initial candidate materials, were investigated using static corrosion testing in liquid zinc at Oak Ridge National Laboratory. Rankings of all materials tested with a preoxidation treatment are shown in Figure 4. Their superior performance compared to the as-machined specimens can be seen by comparing Figure 4 to 5. Of note is alloy Tribocor 532N, an alloy consisting of 50% Nb-30% Ti and 20% W, as well as Alloy 4, containing 20% Cr-6.5% Al-0.5% Ti, with the balance being Fe, along with small additions of Si, Mn, C and Y. Both of these alloys were developed at Oak Ridge National Laboratory. The other compositions shown in Figure 5 are commercially available. To meet the goal of the program, which was significant improvement in pot hardware performance, it was deemed necessary that the testing materials have significant improvement over the performance of stainless steel 316L in the static corrosion tests, at least for screening purposes. This means that the material would need to have a corrosion rate of around 10 mg/m^2 in 500 hours. Seven materials from the static tests have been found to achieve this: Tribocor with a nitrided surface, the ACD ceramic, Tribaloy T800, a tungsten-20% molybdenum weld overlay, the Metaullics 2012 and 2020 alloys, and a tungsten weld overlay. If a preoxidation treatment is given, then nine additional materials also meet this target, and all are variants of Oak Ridge National Laboratory's Alloy 4 with oxidation treatments at 1,100°C between one and two hours. Such treatments are compatible with preheats given by line operators to pot hardware rigs before they are brought into service.

In-plant Liquid Metal Corrosion Test — The first round of candidate materials were chosen for testing. These included four substrate alloys and three hardfacing alloys. Initial trials at the six cooperative galvanizing lines of this study were conducted with these test materials. The initial substrate alloys were chosen as:

- CF-3M, the cast variant of stainless steel 316L, which is a baseline roll material for testing in the program.
- Stellite 6, a cobalt-based superalloy that serves as the baseline material for bearing materials.

- Oak Ridge Alloy 4.
- Metaullics Alloy MSA 2012.

The three hardfacing alloys are:

- Laser-clad tungsten carbide.
- Spray-coated tungsten carbide.
- SiAlON ceramic.

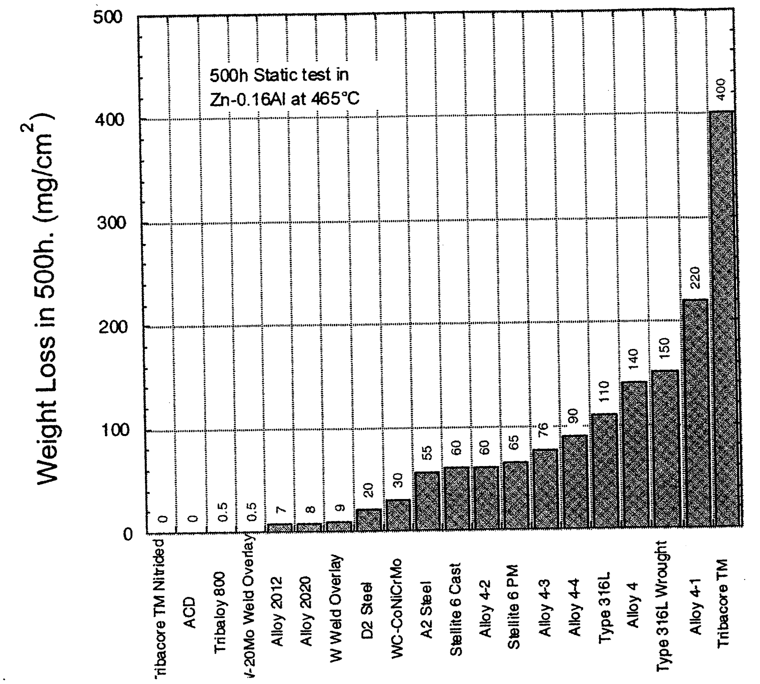
These materials are first being tested by static immersion at the cooperating galvanizing lines. California Steel Industries and Weirton Steel are operating galvanizing lines, National Steel and AK Steel are operating galvannealing lines and Wheeling-Nisshin and Bethlehem Steel are operating Galvalume lines. The samples are long, thin strips of either the substrate material, CF3M spray coated or laser coated with the tungsten carbide coating, or Oak Ridge Alloy 4 spray coated with the tungsten carbide coating. Results from these tests are as follows:

- **Corrosion in the GI/GA Bath.** The corrosion rates of the alloys were calculated based on the data at 1 inch from the bottom of the specimens. Figure 6 illustrates the corrosion rates of the base alloys and coating in the GI/GA bath. There is no measurable thickness change for Stellite 6 and MSA 2012 specimens immersed up to four weeks in different baths. In the meantime, the corrosion rate of CF-3M alloys is around 3.5×10^{-3} inches/week for all four GI/GA baths in this investigation. The corrosion rate of Spray-WC coating is around 1.9×10^{-4} inches/week, which is about $^{1}/_{18}$ of the corrosion rate of CF-3M.

- **Corrosion in the GL Bath.** The corrosion rates of the alloys in the Galvalume bath are shown in Figure 7. Although Stellite 6 and MSA 2012 behave very well in GI/GA bath, the corrosion rates of MSA 2012 is the fastest among the four alloys listed in the figure, which is around 1.5×10^{-2} inches/week. After 12 weeks of immersion in the GL bath, the lower 3 inches of MSA 2012 have disappeared. The corrosion rate of Stellite 6 is about 75 percent of CF3M, and the rate of ORNL-4 is about 1.4 times that of CF-3M.

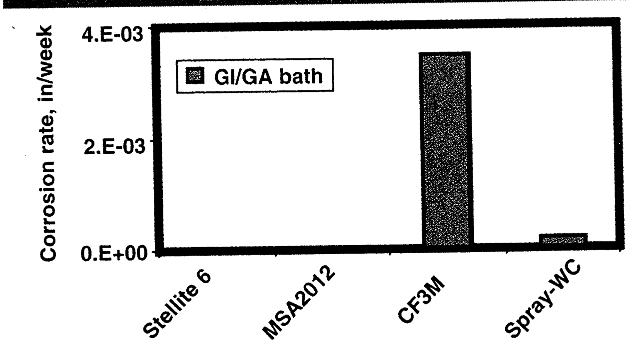
- **Uniform Dissolution Versus Selective Corrosion.** In general, a weight loss method is often used to evaluate the pot hardware materials' corrosion resistance, since it is simple and easy to conduct. This method assumes that the corrosion is a uniform dissolution process and that the less material that is lost, the better corrosion resistance it offers. However, the results from this investigation show that there are two kinds of corrosion. The

Figure 5



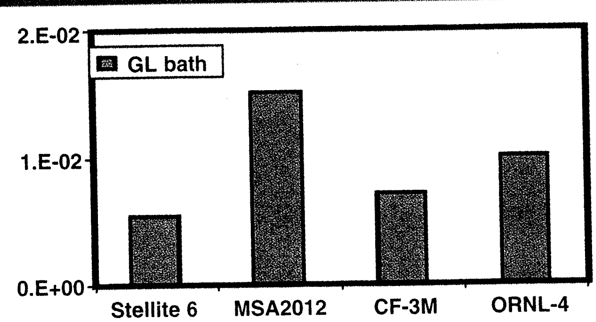
Alloy ranking after ORNL lab-scale static corrosion test, as-machined condition.

Figure 6



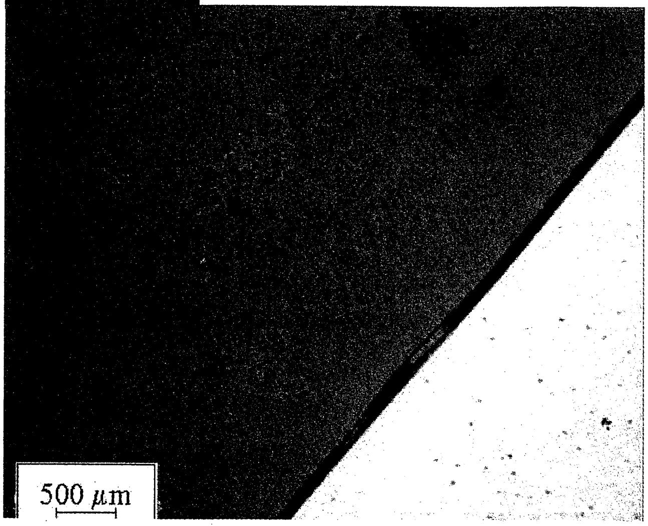
Corrosion rates of the alloys in GI/GA bath.

Figure 7



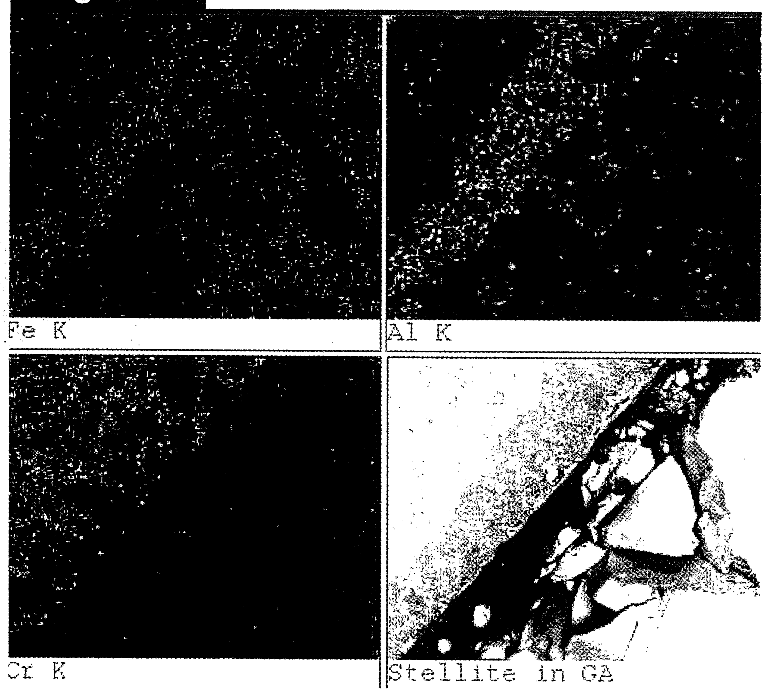
Corrosion rates of the alloys in GL bath.

Figure 8



Stellite 6 in a GL bath for four weeks (SEM/BSI).

Figure 9



Elemental map of Stellite 6 in a GA bath.

SEM/BSI picture of Stellite 6 after immerging in a GL bath for four weeks is shown in Figure 8. The bottom right corner is Stellite 6 alloy, and the freezing bath is on the left. There is only one intermetallic layer between the bath and the alloy, which indicates that the corrosion of Stellite 6 in a GL bath is a uniform dissolution process. However, contrary to the alloy in a GL bath, the corrosion of Stellite 6 in a GI/GA bath is a selective corrosion reaction. Fe and Al in the bath will segregate toward the alloy and react with the matrix to form an intermetallic compound. Cr and Co in the alloy will diffuse out of the alloy and react with the molten metal (Figure 9). Therefore, the weight loss method is not a valid corrosion measurement method under these conditions, because the procedure is not a uniform dissolution process.

Lab-scale Wear Testing — Screening of candidate materials was conducted using the WVU small-scale zinc pot bearing materials tester. The materials were tested for wear and coefficient of friction. The testing was done while the materials were submerged in a 860°F galvanize bath. Figure 10 illustrates a comparison of the wear rates of various material pairs tested. All tests were performed at a contact pressure of 200 psi and a contact velocity of 10.4 inches/second. The test duration for most trails was 24 hours. Figure 11 shows the coefficient of friction between the two materials found using the lab-scale tester. It can be seen from a comparison of friction coefficient and wear rate that like materials produce high friction and low wear, whereas unlike materials have high wear and low friction.

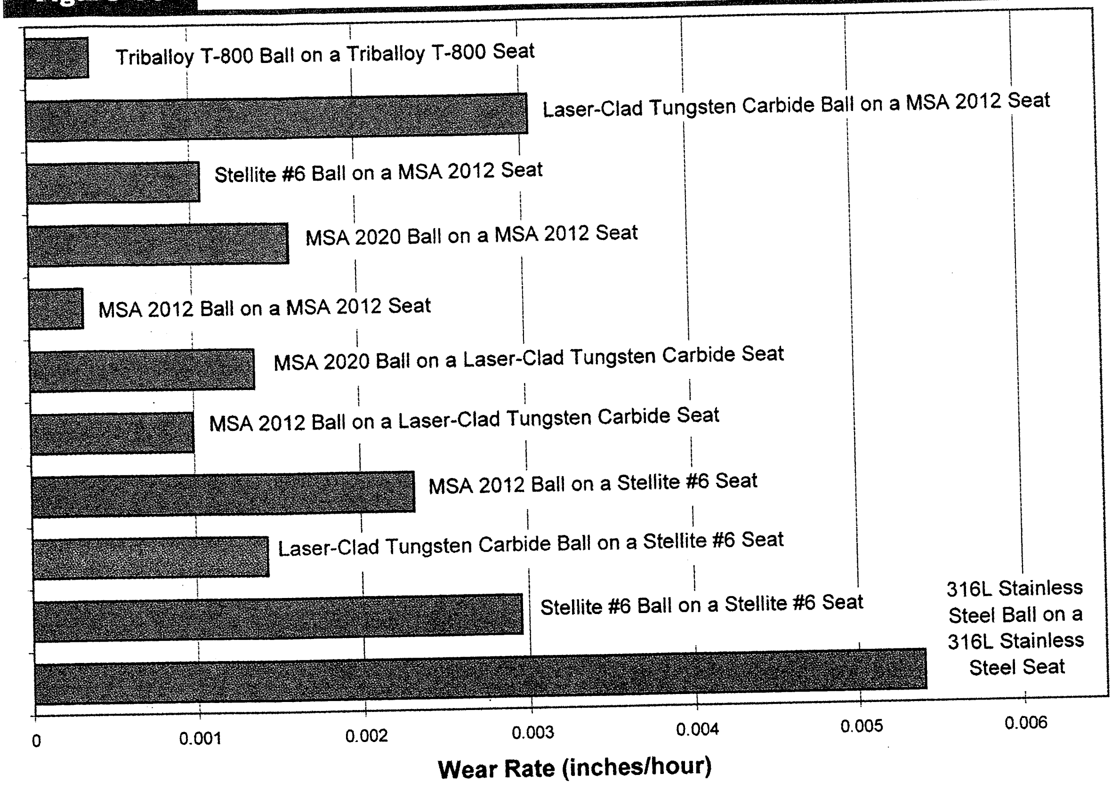
Summary

Reliable performance of galvanizing pot hardware is essential to the productivity of a hot dip galvanizing line and the quality of coatings produced. The most frequent cause of galvanizing line stoppage is pot hardware problems. In order to increase the lifetime of pot hardware components by an order of magnitude, since 2001 a cooperative program was co-funded by the U.S. Department of Energy and the galvanizing-related industries in the U.S., with a total budget of $4.6 million. In this paper, the program was briefly introduced, along with a summary of the first round of test results.

Three topics are being focused on in this program: liquid metal corrosion, bearing wear and dross buildup. In the first round of tests, static corrosion tests of CF3M (casting version of 316L), Stellite 6 and MSA 2012 in industrial galvanizing (GI), galvanneal (GA) and Galvalume (GL) baths were carried out, and the samples were investigated by optical microscope and SEM/EDAX. It was found that there are two types of corrosion behaviors: dissolution and diffusion-controlled intermetallic compound formation.

The wear of bearing materials was studied by two unique test facilities specifically designed for this project. One is a small-scale multifunctional wearing tester, which can test wear rate and friction coefficient of the materials in a short period of time. Another is a 500-pound zinc bath to conduct a long-term bearing wear test. In the first round, the wear of several commercially available bearing materials was tested, and the microstructure

Figure 10

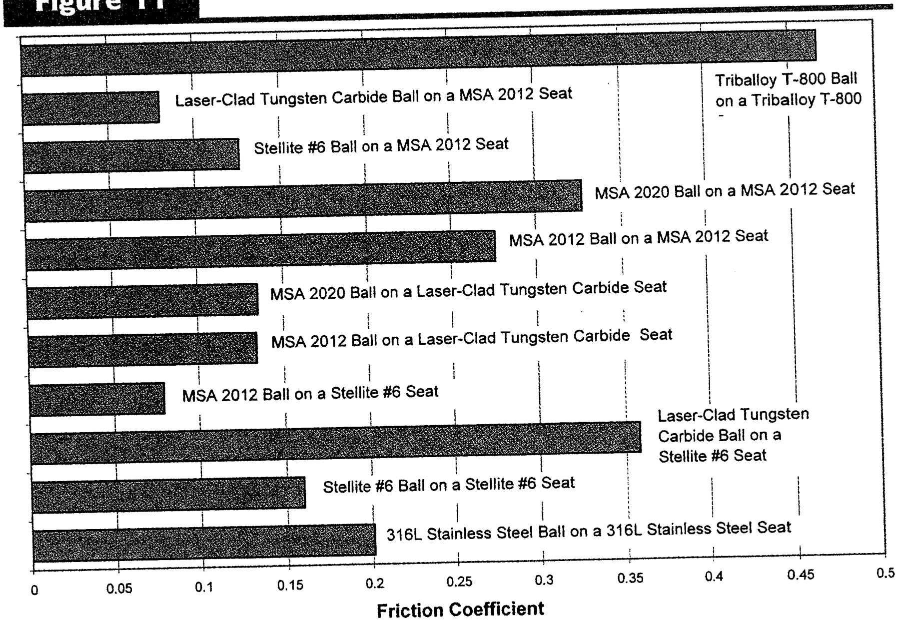


Material wear rates using the WVU small-scale tester.

and wearing surface of the materials after the test were studied by optical microscope and SEM. A unique dross buildup setup that consists of two sleeves counter-rotating against each other was used to simulate the dross buildup in the production line.

Through collaboration with the U.S. Department of Energy, the U.S. steel industry and its suppliers have opened the possibility of creating an entirely new class of pot hardware materials that have the potential to provide significant performance improvements over existing materials. The multipronged attack being taken by Oak Ridge National Laboratory and West Virginia University, with additional technical support from Teck Cominco, has the potential of meeting these goals, as already shown by a number of materials in initial screening tests. Readers are invited to view the current status of the project at: http://iofwv.nrcce.wvu.edu/index-steel.cfm. ✦

Figure 11



Material coefficient of friction using the WVU small-scale tester.

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