

Praxair Surface Technologies, Inc.

Cost-Efficient and Environmentally Friendly Coating Process

Ceramic coatings are among the most durable materials, underlying the performance and extending the service life of equipment parts that must operate reliably in harsh environments, including aircraft landing gear, tractors, oilfield pumps, and gun tubes. However, in the mid-1990s, processes that could apply wear-resistant coatings and that were environmentally friendly had not been developed.

In 1995, Praxair Surface Technologies, Inc., and Surface Solutions, Inc., partnered to develop, test, and evaluate a promising, but experimental, coating technology invented by Surface Solutions. Early work with Surface Solutions' linear magnetron sputtering (LMS) process indicated that it had the potential to apply uniform, high-quality ceramic coatings to the internal surfaces of steel cylinders, but the innovative technology had been demonstrated only on a very small scale. If technical barriers were overcome, ceramic coatings could be applied as cheaply as hard-chrome plate, without generating the hazardous wastes associated with electroplating. The market opportunity, the potential for spillover benefits into other industries, the enabling nature of the technology, and Praxair's unique approach led the Advanced Technology Program (ATP) to award \$793,000 in cost-shared funding to the company in 1995. When the project concluded in 1998, Praxair had made significant progress but had not achieved its technical goals. While the company is still interested in the technology, its current financial state prevents any further research and development activities.

COMPOSITE PERFORMANCE SCORE

(based on a four star rating)

No Stars

Research and data for Status Report 95-07-0006 were collected during October - December 2001.

Existing Technologies Produce Environmentally Hazardous Waste

Applying metal alloy, refractory metal, and ceramic coatings onto metal and non-metal substrates is an essential step in manufacturing many equipment components. Coatings may reduce costs by enabling simplified fabrication processes, increased product quality, lengthened equipment life, and reduced manufacturing and maintenance costs. In many cases, the coatings provide the only practical way to repair or refurbish equipment. Ceramic-coated surfaces substantially, and sometimes dramatically, increase the mechanical components' ability to resist wear, corrosion, and thermal extremes. Coatings are used extensively by many industries.

For example, a modern aircraft gas turbine engine can have more than 800 coated areas on 450 components in order to resist hostile environments, provide sealed surfaces, and reduce the need for lubrication.

Traditionally, technologies used to coat the inside of cylinders, such as chrome electroplating and high-temperature chemical vapor deposition (CVD), produce high-performance coatings, but rely on environmentally harmful processes. Wear-resistant, corrosion-resistant, and environmentally friendly inside-diameter (ID) coatings had not been developed. Surface Solutions, Inc.'s linear magnetron sputtering (LMS) technology had the potential to fill this need.

Cylinder IDs Pose Challenge to Traditional Ceramic Coatings

Manufactured components have different coating requirements. For example, a component may need high surface hardness and abrasion resistance with bulk toughness (i.e., resistance to brittle crack propagation) or, alternatively, it may need an extremely high-temperature-, corrosion- and abrasion-resistant surface with bulk strength. The challenge is to identify or develop a coating that provides the desired functional properties and then to develop the process for applying it effectively to the substrate material. Cylinder ID coatings represent a case where potential higher quality coatings have been identified, but are not used because there is no process to apply them.

Neural networks and complex materials processing were both emerging technologies, and the combination of these two in a single venture increased the risk of the project.

Praxair's research showed that two ceramic hard coatings, titanium nitride (TiN) and chromium nitride (CrN), exhibit excellent wear characteristics compared to hard-chrome plate, without the environmental problems. However, the ability of existing coating processes to coat cylinder ID surfaces was limited to cylinder length-to-diameter ratios of less than one. The LMS process had the potential to apply an ID coating on cylinders with length-to-diameter ratios greater than 30 to 1.

Advantages of LMS Technology

The original LMS concept was developed and patented by Surface Solutions. The sputtering technology deposits particles onto the substrate in a uniform and even manner. LMS-applied coatings, if successfully deposited on the inside surfaces of cylinders, would address a longstanding need that could only be met by electroplating or high-temperature CVD.

Both of these processes create environmental problems and cannot deposit coatings such as TiN and CrN that provide superior wear and corrosion resistance. Thus, the use of the LMS process would not only help solve a serious environmental problem, it would also improve

(by factors of 5 to 10) the performance of components that previously had to rely on chrome plate for surface treatment. Further, the coatings applied by the LMS process would not only reduce the cost of maintaining many types of equipment, it could also lengthen the operational time of equipment, which is often of much greater value. However, Surface Solutions, a five-person company in 1995, did not have the resources needed to develop the technology to the point of being commercially useful.

Wide Range of Potential Applications

Potential applications for the LMS technology were broad. For example, the lifespan of the hydraulic cylinders on heavy construction and mining equipment can be a critical factor in determining operating costs and sometimes in maintaining the safety of the equipment. Extending the life can lengthen the operating time between overhauls, which would benefit the operator and would also enhance the equipment's marketability for the manufacturer through its ability to offer longer warranties. This is important in the competitive heavy equipment industry where Japanese and other foreign competitors challenge U.S. manufacturers. Other potential applications include extruder and injection equipment, heat exchanger tubes, and gun barrels.

The LMS technology held promise for the production of tubular filters with tremendous improvements in environmental safety over the present state-of-the-art filtration systems. The LMS technology could be used in the generation of anti-coking coatings used in the chemicals and plastics industry, with the potential for significant cost savings. Thus, the knowledge gained from this project might also be of substantial value in developing other uses for coatings applied by the LMS process.

ATP Funds Development of LMS for Heavy Equipment Applications

The promise of using the LMS technology to apply coatings to longer cylinders (up to the industry standard of two meters) was the catalyst that brought together Praxair and Surface Solutions. Praxair partnered with subcontractor Surface Solutions to further develop LMS technology in order to coat cylinders of much greater length-to-diameter ratios than currently possible.

Praxair negotiated an exclusive license with Surface Solutions to use the patented LMS technology in applying coatings to cylindrical components for widespread commercial use. LMS technology would provide an innovative approach to an industry-wide problem in coatings that would also benefit numerous other industries. Praxair had a clear plan to bring to market this technology that could effectively compete with foreign companies. Therefore, in 1995, ATP awarded the company \$793,000 in cost-shared funds for a three-year initiative. The overall objective of the ATP-funded project was to improve the durability of heavy equipment by replacing chrome plating with ceramic hard coatings on the inner diameter of cylindrical components. For example, hydraulic cylinders for off-road vehicles operate in dirty environments where components need to be coated to reduce the effects of abrasion and to increase corrosion resistance in order to extend the operating life of the component. The coating materials selected to replace electroplated chrome were CrN and TiN. These coating materials, deposited via the LMS technique onto tubular steel substrates, were expected to improve component service life by at least a factor of four and, at the same time, eliminate the environmental concerns associated with chrome plating. The ATP-funded project's specific objectives were to 1) establish the technical viability of a laboratory prototype LMS system for producing uniform, defect-free, wear-resistant coatings on the inner diameter of cylindrical components two meters long or with length-to-diameter ratios of 30 to 1; and 2) define the performance enhancements attainable by replacing chrome plating with TiN or CrN on hydraulic cylinders and oilfield slurry pumps.

Ultimately, the commercial application of LMS technology would provide several industries with significant broad-based economic benefits, such as increases in efficiency, reductions in cost, and alternatives to chrome electroplating. Praxair hoped to commercialize the technology through three customers with whom it had initiated discussions: General Electric, Halliburton, and Caterpillar.

Delays in Prototyping the System Lead to Limited Results

Design problems with the LMS prototype system plagued the early stages of development. The first

problem was the instability of the hollow cathode, and the second was the inability of the chamber-cooling system to tolerate the sustained high-temperature operating conditions necessary for optimum deposition. These problems led to unexpected delays, which shortened the time that was available to spend on optimizing coating conditions, a key part of the technical plan. Coupled with organizational changes within Praxair's upper management and the project management team, the project fell behind schedule.

A second LMS prototype system was designed to overcome the aforementioned technical problems and was capable of applying TiN on cylinders up to 1 meter in length and 152.4mm in diameter. This new system, however, could not coat the inner diameters of longer cylinders (up to two meters) with a uniform thickness, a necessary prerequisite for broad commercialization; nor could it coat cylinders with length-to-diameter ratios of up to 30 to 1. Finally, only limited progress was made on applying CrN coatings to cylinders. Solving these problems proved to be even more difficult than expected, and Praxair's two project objectives were not achieved.

Technical Delays and Financial Problems Halt Cylinder ID Project

At the completion of the ATP-funded project, Praxair's research activities for coating the inner diameter of cylinders with TiN and CrN ceased. A combination of factors led to the decision to stop the development of the technology. Primarily, development had not progressed to a point where Praxair could see clear opportunities worthy of further internal funding. The company acknowledged that the experience from previously unsuccessful R&D projects influenced its decision to cease funding. Secondly, the departure of Praxair's project manager, who had tremendous expertise, left an unfilled void. Finally, the worsening financial condition of Praxair's Surface Technologies division resulted in reduced R&D budgets.

Conclusion

The research and development conducted during this project advanced the coating industry's understanding of the newest form of physical vapor deposition (linear magnetron sputtering). However, the anticipated

advantages of LMS technology to improve wear and corrosion properties were not fully realized.

In spite of setbacks in prototype system development, Praxair was able to attain adequate TiN coatings on inner diameters up to 1 meter in length and 152.4mm in diameter, but the project goals of coating the inside of cylinders 2 meters long or with length-to-diameter ratios of 30 to 1 were not realized. Nor were acceptable CrN coatings produced. At the project's completion, further R&D and commercialization of the technology were not pursued.

PROJECT HIGHLIGHTS

Praxair Surface Technologies, Inc.

Project Title: Cost-Efficient and Environmentally Friendly Coating Process (Ceramic Coating Technology for the Internal Surfaces of Tubular/Cylindrical Components)

Project: To improve the durability of heavy equipment by replacing the chrome plating on the inner surfaces of cylindrical components with ceramic hard coatings such as CrN and TiN.

Duration: 9/1/1995-8/31/1998

ATP Number: 95-07-0006

Funding (in thousands):**

ATP Final Cost	\$ 793	66%
Participant Final Cost	<u>400</u>	34%
Total	\$ 1,193	

Accomplishments: During this ATP project, Praxair successfully utilized the linear magnetron sputtering (LMS) technology to deposit a titanium nitride coating with uniform color and thickness at a rate of 0.04 microns/minute for cylinders up to 1 meter in length and 152.4mm in diameter.

Commercialization Status: There are no plans to commercialize this technology. Limited technical success and current financial conditions have forestalled the company's ability to pursue further development of the technology necessary for commercial introduction. Praxair remains interested in the commercial potential of using LMS for coating the internal surfaces of tubular and cylindrical components in the heavy equipment industry.

Outlook: The outlook for this technology is poor due to Praxair's current financial condition.

Composite Performance Score: No stars

Focused Program: Materials Processing for Heavy Manufacturing, 1995

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** As of December 9, 1997, large single applicant firms are required to pay 60% of all ATP project costs. Prior to this date, single applicant firms, regardless of size, were required to pay indirect costs.