Solving the Insoluble: Electrolytic Tinning Lines With Insoluble Anodes

Abstract

In cooperation with Centro Sviluppo Materiali (CSM), Tenova has developed a new low-sludge tin dissolution process.

The application of Tenova insoluble anode technology minimizes the amount of sludge produced and hence the loss of tin. Other benefits are the reduction of manpower for anode handling, and therefore an increase in safety during operation, improved coating quality, better process control and elimination of phenol vapors in the working environment.

The process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor. The electrolyte is then saturated with pure oxygen.

The new tin dissolution process technology was proven on an industrial line at Ternium Siderar. The industrial campaign carried out in 2007 at Ternium Siderar confirmed that the developed tin dissolution process considerably reduces the quantity of generated sludge, and consequently the loss of tin.

This paper describes in detail the achieved improvements, as well as the satisfactory results reached, in tinplate produced with insoluble anodes.

Among the most significant results, it has been possible to optimize the anode and edge mask design, and confirm the dissolution plant efficiency and productivity. Moreover, important operational and maintenance practices have been finally defined.

A new installation, using the process with insoluble anodes, will be a 250,000 TPY electrolytic tinning line located in China.

Introduction

The Ferrostan process, as well as the other processes based on the use of soluble tin anodes, are well consolidated in electro-tinning lines. The use of soluble anodes is advantageous because the tin plated-out on the strip can be automatically produced by the dissolution of tin from the anodes. But there are disadvantages.

The most important disadvantage is the necessity to drain off the plating solution

Tenova has created a modern insoluble anode tinplating process, already proven on the industrial line at Ternium Siderar. The process is able to achieve a very low tin loss, a productivity rate of more than 30 kg/hour can be confirmed for each plating cell.

because of the different electrochemical efficiency in plating and dissolution. An increase of tin concentration in the plating solution is unavoidable with the use of tin anodes, and dilution of the solution generates overflow and discharge, with loss of expensive material and possible water pollution, unless adequately treated.

The conventional equipment used worldwide for the control of the tin concentration in the plating solution is the insoluble anode, and many producers today have one half cell equipped with insoluble anodes. However, the control of the solution is very difficult, and concerns about a rapid decrease of tin and an increase of free acid in the plating solution make the use of insoluble anodes in this way less practical. Other disadvantages in the conventional lines are the fumes exiting the plating tanks, the labor requirements for handling the tin anodes, and the low productivity.

Additionally, market demand is toward tinplate with thinner coatings; indeed, for some uses, tin coatings down to 0.2–0.4 g/m^2 are required, causing production problems.

With conventional electroplating technology, the homogeneity of tin coating thickness decreases as the coating weight decreases, due to the particular geometry of the tin anodes, which do not

Authors

Giovanni Astengo (left), research and development manager, Tenova Strip Processing, Genova, Italy (giovanni.astengo@it.tenovagroup.com), and **Thomas DeLoia** (right), sales manager, Tenova Strip Processing, Pittsburgh Pa.(thomas.deloia@us.tenovagroup.com)

Table 1

Advantages of the Insoluble Anode Process

Parameter	Benefit
Constant tin covering on strip	Less tin consumed
Better edges	Better strip quality, particularly important for thin coatings
No anode handling	Reduced labor costs, higher productivity and flexibility, safer and better working environment
No anode melting plant	Reduced labor costs
Covering on tanks	Less fumes
Electrolyte always under control	Lower electrolyte discharge, consumption and pollution
Anodes closer to strip	Reduced electricity consumption

present a continuous surface. In fact, each anode is formed by a series of vertical bars drawn against each other, so as to leave only a minimum space between the bars, which may produce a lower tin thickness.

Another cause of irregular tin coating derives from non-uniform consumption of tin bars, which in turn gives rise to preferential current distribution. For thicker coatings, such situations are alleviated, since more cells are employed in the sequence of electroplating steps, thus allowing the tin coating to grow more uniformly.

One solution to these problems is to equip the entire tinning line with insoluble anodes. They have a continuous surface, and therefore very thin tin coating layers can be produced with high thickness homogeneity.

The main advantages of tinplating with insoluble anodes are summarized in Table 1.

The main drawback is that tinplating with insoluble anodes requires a tin dissolution reactor connected to the electro-tinning line to replenish the amount of tin deposited on the strip.

Considerable research was done to dissolve tin (chemically or electrochemically) in the plating solution.[1–10] An industrial process was set up many years ago, and a few plants, mainly in Japan, are working with insoluble anodes.

The process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor. The electrolyte is then saturated with pure oxygen to accelerate the oxidation reaction of metallic tin to ionic tin.

Unfortunately, the chemical process of tin dissolution also produces a $Sn^{(IV)}$-based sludge. The critical point of the existing electro-tinning lines with insoluble anodes is the tin loss, usually higher than 10% of the dissolved tin. This is the reason why the tinplate process with insoluble anodes is not yet used worldwide.

Tenova, in strict cooperation with its connected Italian research center, CSM (Centro Sviluppo Materiali), developed an innovative process for dissolving tin. This process is able to minimize the amount of sludge and loss of Sn and has been successfully validated through extensive tests on the Ternium Siderar electrotinning line.

Insoluble Anodes

The main requirements any insoluble anode must fulfill in order to be employed in an electroplating line are as follows:

- High surface area.
- High electrical conductivity.
- Good electro-catalytic properties.
- High chemical and mechanical stability.
- Reduced problems of gas bubbles.
- Selectivity.
- Availability and low cost.

All these characteristics strongly depend on the surface chemistry and morphology of the electrodes, which for this application generally consists of a coating layer of Ru, Ir, Sn and/or Ta oxides applied on a Ti substrate. From a practical point of view, the most relevant issues are those related to lifetime, particularly the need for a high electrical conductivity and high chemical and mechanical stability.

Insoluble anodes have replaced soluble anodes on the first plating cells of the ETL of Ternium Siderar to perform the tests during the last campaign. The first plating tank equipped with insoluble anodes is shown in Figure 1.

Inert titanium-based anodes with an active precious metal coating have been used for this application. The reason is that titanium is resistant to chemical attack in acid electrolyte, such as PSA, because it has an extremely adherent and inert surface oxide film. Because of this thin-surface Ti oxide film, which is electrically non-conducting, Ti will not pass current and will therefore not act as an anode by itself. The application of the mixed metal oxide (MMO) coating to the active area of the Ti anode allows the current to flow from the Ti anode through the coated areas into the electrolyte, while the non-coated areas of the Ti anode remain inactive.

In order to optimize anode and cell design, fluid dynamic studies have been carried out to analyze the velocity distribution of the electrolyte within the cell as a consequence of the movement of the strip, as well as the effect of oxygen generation at the anode surface, where the following reaction takes place:

$$2\,H_2O \rightarrow O_2\uparrow + 4e^- + 4H^+$$

The insoluble anodes are vertically positioned in a vertical cell containing a plating solution, and spaced from a strip running through a down-pass and an up-pass (Figure 2).

The insoluble anodes are spaced from the strip by a distance of less than 50 mm, and the plating solution is blown into the gap between said anode and said strip. Due to the very high speed of the strip, the fluid dynamics of the cell tends to create a so-called Venturi effect in the region between the strip and the anode, which promotes undesired contact between the anodes and the strip and therefore marks of anodes on the strip. For this reason, anodes have been designed with a regular array of orifices, with the aim of reducing such effect. While reducing the level gap between the ascending and descending zone of the plating cell, the orifice distribution has also been conceived to maintain transverse evenness in current density distribution.

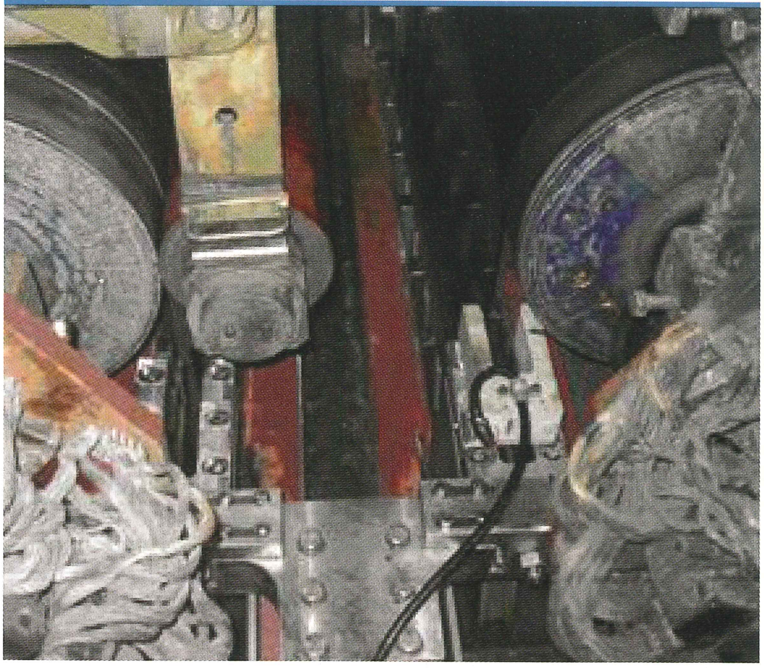
A particular design of the lower guide allows the possibility both to control the distance of the anodes from the strip, as well as to regulate the anodes' lower position in order to be equidistant to the strip after a sink roll grinding.

Numerical simulations carried out by CSM using the commercial codes Phoenics and Fluent confirmed the suitability of current anode design for the application.

No defects to the strip that could be related to the use of insoluble anodes have occurred. The optimization of the anode design has been fully confirmed to be compliant with process requirements and strip quality needs.

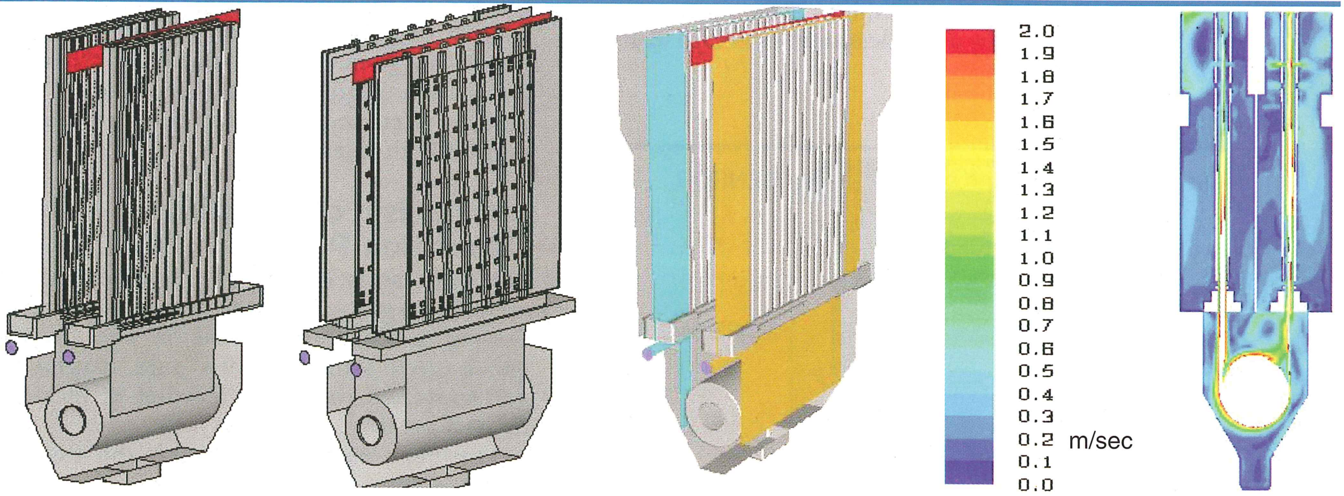
One of the most essential operating conditions stated by the manufacturer was to maintain the anodes anodically polarized at any time, as long as they were immersed in the electrolyte. The reason for this is that the PSA is a reducing acid. As long as the anode is polarized, the protective Ti oxide film will be maintained and the Ti anode will not be corroded. On the contrary, if the anodes are not kept anodically polarized, the reducing acid will attack the Ti oxide film and the anode will suffer from some corrosion. Finally, the Ti metal will dissolve, forming a thicker insulating Ti oxide film between the MMO coating and the Ti substrate. This mechanism leads to a significant increase in the operating anodic potential due to passivation by the non-conductive Ti oxide film. Eventually, the anode will be totally passivated and will cease to pass the current.

Figure 1



Insoluble anodes in first plating cell at Ternium Siderar.

Figure 2



Plating cell configurations and speed distribution within the cell.

Although no particular attention has been paid to the system, since the anodes have been often working without edge masks and without standby current, the MMO-coated titanium anodes have shown excellent behavior, and no significant increase in the operating anodic potential due to anode passivation has been observed.

After removal of the anodes from the cell and accurate flushing with water at elevated temperature to remove the sludge, no damage to the coating could be observed.

Edge Masks

Insoluble anodes are of a fixed width. In order to process strips of different widths, electrically insulating plates, so-called edge masks, are used to prevent the current from flowing between the two anodes next to the strip, thus avoiding so-called white border defects.

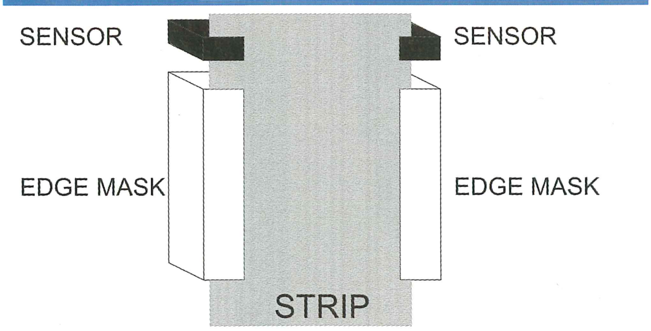
The strip edges engage in U-shaped sections arranged at the end faces of the electrically insulating plates. The degree of edge galvanization depends on the insertion depth of the strip edges into the U-shaped sections. Accordingly, it is necessary that the U-shaped sections accurately follow the strip travel.

The edge masks must follow the strip very exactly, the expected accuracy being less than 1 mm. Inductive sensors moving jointly to the masks are used to detect the strip penetration and vary the edge mask position accordingly. The working principle of the system is depicted in Figure 3.

During the last campaign at Ternium Siderar, the edge mask system was mounted on the first cell and consisted mainly of:

- Two pairs of edge masks (one at operator side, one at motor side), made of epoxy glass, each pair driven by one servo-cylinder. The masks were held from the top and guided at the bottom by the anode guides. They were supported by a stainless steel structure with slide bearings, both located outside the plating tanks for the best accessibility.
- Two servo-cylinders with linear transducers.
- Two strip edge detection sensors designed to resist at a maximum temperature of 80°C, not affected by dirt, humidity or metallic particles.

Figure 3



Edge masks.

Edge mask control was obtained by means of a local PLC communicating constantly with the PLC of the line. Communication was needed mainly to track the position of the weld, so that edge masks could open when the weld was passing through the plating cells. Edge masks also opened when the line was stopped or when the line speed was below a threshold value (30 m/minute).

Communication between the two PLCs also allowed information about strip width to be sent to the local PLC. Once the information about the strip width is known, only one strip edge sensor is needed to detect the position of the strip edge and virtually control the masks, since the position of the other edge of the strip can be easily calculated. However, the system was conceived with two edge sensors to improve system reliability. In case of failure of one of the sensors, an alarm is activated when the absolute distance of the masks is less than the strip width.

The strip edge position was monitored accurately by the inductive sensors, and edge mask drives regulated the mask position accordingly.

In comparison with the masks used in the previous test campaigns, edge mask design was significantly modified to ease inspection and access to the cell for maintenance and operational activities. Thanks to the new design, it was possible to remove all supports inside the plating tanks, at the same time permitting easy access to the edge masks and to the anodes for maintenance.

Strip edge sensors with improved design were also re-developed internally to fulfill application requirements. As expected, the position accuracy has always been around ±1 mm on both sides.

Mechanism of Dissolution Deposition Process

The process is based on the oxidation of metallic tin granules by the tinning electrolyte flowing in a dissolution reactor. The electrolyte is then saturated with pure oxygen to accelerate the oxidation reaction of metallic tin to ionic tin.

The main reactions involved in the metallic tin dissolution process are:

1. $2Sn + O_2 + 4H^+ \rightarrow 2Sn^{2+} + 2H_2O$

2. $Sn + O_2 + 4H^+ \rightarrow Sn^{4+} + 2H_2O$
3. $2Sn^{2+} + O_2 + 4H^+ \rightarrow 2Sn^{4+} + 2H_2O$
4. $Sn^{2+} + 2PSA \rightarrow Sn(PSA)_2$
5. $Sn + Sn^{4+} \rightarrow 2Sn^{2+}$

Oxygen is necessary to enhance the reaction rate of the oxidation of tin by the acidity of the bath formed at the insoluble anode.

The electrochemical reactions occurring at the electroplating site with insoluble anodes are:

6. $2Sn^{2+} + 4e^- \rightarrow 2Sn$ (cathode)
7. $2H_2O \rightarrow O_2 + 4e^- + 4H^+$ (anode)

The four moles of hydrogen ions formed at the anode (reaction 7) restore as many moles of hydrogen ions consumed in the dissolution reactor to dissolve two moles of metallic tin (reaction 1), which, in turn, restore the two moles of tin deposited on the strip (reaction 6). Thus the mass balance is assured.

Pilot Dissolution Plant at Ternium Siderar

An industrial-scale reactor was realized to feed the first insoluble anodes electrolytic cell of the electro-tinning line of Ternium Siderar in San Nicolas, Argentina (Figure 4). The plant was designed for a dissolution capacity of 30 kg/hour, although higher capacity (>35 kg/hour) could be achieved.

The plant consists mainly of a chemical reactor, a pressurizing pump, oxygen feeders with improved design, and a tank for the preparation and storage of the solution.

The reactor is a vertical, cylindrical vessel divided in two parts. The upper part has a large diameter to prevent small tin particles from escaping the reactor. The total volume is about 1 m^3.

The plating solution is fed from the bottom into the reactor through a distributor that supports the metallic tin particles and distributes the solution. Before entering the reactor, the solution is enriched in dissolved oxygen.

A good recirculation of the electrolyte with the plating solution of the line was obtained by installing two pumps, so that a recirculation flow of approximately 15 m^3/hour could be achieved. A suitable heat exchanger was installed in the circuit in order to maintain the plating solution at a constant temperature.

The tin dissolution rate of the plant is controlled by the flowrate of the oxygen. The plant can automatically calculate the oxygen flowrate needed to dissolve the tin that has been plated in the cells, depending on the current provided by the rectifiers, thus maintaining a constant tin concentration in the plating solution.

Figure 4

Tin dissolving plant at Ternium Siderar.

Results of Plating Test

An investigation was carried out on the tinplated strip produced with the insoluble anodes. Scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) were employed to analyze surface morphology during the previous campaigns. According to the SEM/EDS analyses performed in comparison with tinplated strip obtained with soluble anodes, no difference in crystal shape or degree of coverage was detected (Figure 5).

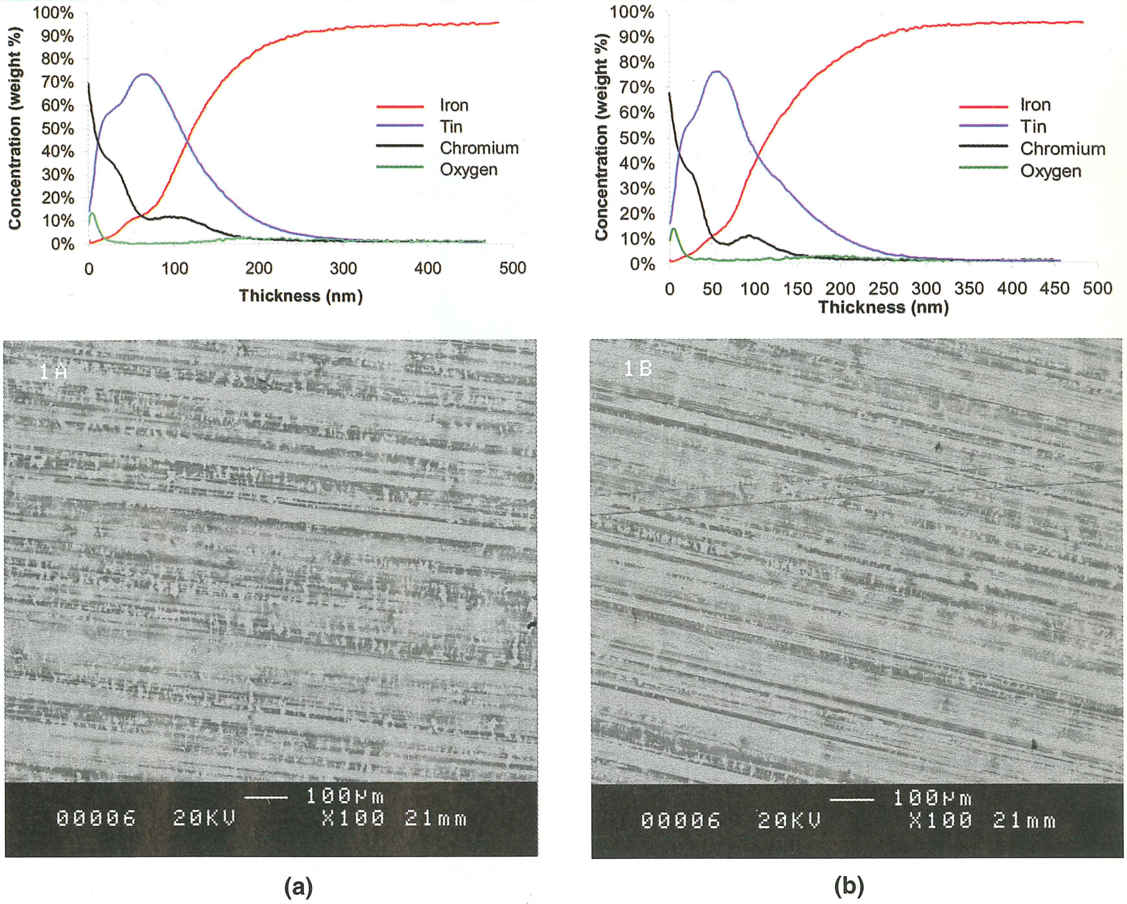
Visual checks during the last campaign confirmed good quality of the tinplate in terms of brightness and homogeneity of tin coating thickness.

Conclusions

The new tin dissolution process technology was proven on a plant connected to the industrial electrolytic tinning line at Ternium Siderar. The last industrial campaign confirmed that the developed tin dissolution process considerably reduces the quantity of generated sludge and consequently the loss of tin.

Since the dissolution plant has been operated continuously during a 9-month period, important confirmations and results have been obtained for an improved design and operation of a tinning line fully equipped with insoluble anodes. In particular:

Figure 5



SEM micrographs and element profiles of tinplate obtained with soluble (a) and insoluble (b) anodes.

- Insoluble Anodes: Optimization of the anode design fully confirmed. Material selected has shown good behavior, although no particular attention has been paid to the system.
- Edge Masks: The sensors and the control system are fully compliant with the required specifications. The system has shown a very stable behavior, as well as a very accurate positioning (position accuracy < 1 mm).
- Dissolution Plant: The results of the previous years, such as oxygen efficiency (> 90%) and productivity (> 30 kg/hour), have been fully confirmed.
- Electrolyte: The electrolyte produced with the dissolution plant has been demonstrated to be fully compliant with the requirements of the tinning line. This has been confirmed by replacing all electrolyte with new electrolyte produced in the dissolution plant.
- Operation: Final definition of operational and maintenance practices.

According to Ternium Siderar, the most promising aspects of the system of insoluble anodes are:

- Improved strip quality related to the elimination of chronic defects, such as white edges and marks of anodes.
- Elimination of anode handling.
- More flexible campaigns in terms of strip width programming, since the edge masks can adapt to all strip widths.
- Moreover, the dissolution plant allows controlling the tin concentration in the electrolytic solution of the line.

All the tested improvements will be installed on the future 250,000 TPY electrolytic tinning line located in China. The tinplate process with insoluble anodes is ready for full industrialization, bringing with it all the advantages connected to the use of insoluble anodes.

Conversion of the ETL line at Ternium Siderar has been contemplated as a future investment.

Tenova was awarded a contract from Jiangsu Sunshine Group Co., China, for a 250,000 TPY tinning line with a process speed of 550 m/minute, equipped with insoluble anodes and edge masks with associated tin dissolution plant. The plant will have features tested at Ternium Siderar.

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This paper was presented at AISTech 2008 — The Iron & Steel Technology Conference and Exposition, Pittsburgh, Pa., and published in the Conference Proceedings.

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