OmegaBond™ Advanced Tubing Technology

In chemical processing applications, many challenges exist where the current tubing materials in process equipment like heat exchangers are not robust enough to withstand the corrosive service environment of the process. In the design of some equipment, it may be advantageous to incorporate the use of multiple or dissimilar materials in the same component. The use of dissimilar materials within a component often allows engineers to economically design for optimum performance. However, joining such materials is often problematic due to fusion welding limitations resulting in a joint that is susceptible to corrosion or mechanical failure.

ATI Wah Chang and Snamprogetti have jointly developed a robust, advanced tubing design for use in corrosive chemical processes and other applications. These products incorporate new enabling materials and materials-joining technologies. The new tubing will enable the application of multiple and/or dissimilar metals in a single tube. The design, performance, features and benefits of this new technology are discussed.

In addition, the application of the new tubing to Urea Plants, particularly Snamprogetti’s process, will be discussed. The advantages of this new material technology will be presented as a solution to corrosion and erosion issues that may have been observed in some components in certain plants.

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In 2004, ATI Wah Chang and Snamprogetti, S.p.A began working together to jointly bring to market a new series of advanced tubings solutions for urea plants using Snamprogetti's process technology. Snamprogetti, S.p.A. is a leading engineering firm engaged in the design and licensing of urea manufacturing technology. The result of this collaboration was OmegaBond™ advanced tubing solution that will allow both urea and other chemical processing manufacturers to realize numerous benefits. Recognized benefits include: a reduction in corrosion-related down time, reduced maintenance-related costs, potential energy savings and finally, the technology should allow for more aggressive operating conditions with higher process yields.

The urea process is an ideal environment for OmegaBond™ technology and provides several good examples of corrosive problems commonly found in the chemical processing industry.

History of the Urea Process

The urea production process involves chemicals and conditions that corrode and/or erode most ordinary materials of construction. Plant designers and operators have been working for years to
minimize unplanned downtime and maintenance. Such optimization has occurred by varying operating parameters and construction materials. While significant progress has been made, some urea plants continue to experience unplanned maintenance and downtime due to materials-related equipment malfunctions or failures.

Selection criteria for materials of construction in urea plants are dictated by localized process operating parameters. Materials of construction have changed as the urea manufacturing process has evolved and materials technology has improved. Stainless steel has historically been regarded as the baseline material of construction for corrosion resistance in many different applications, including urea plants. Conditions in portions of urea strippers have proven problematic for stainless steel. Even with tight temperature and chemistry controls, it is always necessary to add some level of passivation to protect stainless steels used in urea strippers to prevent premature failure by corrosion.

Reactive metals (titanium and, in particular, zirconium) have proven themselves to be very corrosion resistant to the chemical environment encountered in a urea plant. These materials, when properly designed and fabricated, withstand the most severe conditions. Titanium has been used extensively in the urea process and was one of the original materials of construction in urea strippers. While titanium is successfully used in the urea process, materials limitations and related cost have driven engineers to look at other material options. Much current interest focuses on zirconium due to the metal’s unsurpassed performance in severe chemical processes. Zirconium components have not been retro-fitted widely into existing urea process equipment because of the cost and technology associated with physically connecting new zirconium parts with the existing non-zirconium parts. Zirconium’s properties make joining it to other metals difficult, and standard joining methods typically will not produce a joint with properties adequate for service in severe environments. The perceived difficulty fabricating zirconium has been a contributing factor for limited adoption, causing designers to specify other metals to avoid the difficulty of the joint.

ATI Wah Chang and Snamprogetti have collaborated on a new innovative technology for joining corrosion resistant metals. This technology has distinct, advantageous applications in urea production and may have the same advantages in other chemical processing applications. Zirconium can now be used in the most aggressive parts of a urea plant without replacing an entire process component, thus avoiding some difficulties that are currently encountered with some methodologies.

**Common Urea Processing Conditions**

Industrial urea production is accomplished at very high pressures and temperatures. In a typical urea process, carbon dioxide (CO₂) and ammonia (NH₃) are reacted under the conditions of 180°C and 150 bar to produce ammonium carbamate (H₂NCOONH₄) as an intermediate product.

Snamprogetti utilizes the ammonia stripping process, depicted below. In the Snamprogetti process, excess NH₃ is used to strip NH₃ and CO₂ from the decomposition of unconverted ammonium carbamate. This process usually occurs in a “stripper”, a vertical falling film heat exchanger, at a temperature of approximately 205°C and pressure of about 150 bar. The insides of the tubes in the stripper are generally considered to have the worst corrosion issues.

Ammonium carbamate is the primary corrosive species in this environment. Very few materials can withstand ammonium carbamate in these conditions.
Reactive Metals in Urea Production

Titanium and zirconium are both used extensively in the chemical process industry and have similar properties in many corrosive environments. They both tend to form adherent passive oxide layers that protect the bulk metal from further corrosion. This layer renders them highly corrosion resistant in most chemical media.

Another characteristic they share is that both are non-toxic and biocompatible. Their corrosion products are generally simple non-toxic oxides. This attribute is a distinct advantage when the product is sold to the agriculture industry. In a typical 2500 TPD urea plant, the total stripper surface area of the stainless steel tubes is approximately 870 m². According to Dr. T.L. Yau, a corrosion rate of 50µm/y (2mpy) corresponds to over 0.87 kg (almost 2 lbs) of metal dissolving from stainless tubes each day (Ref. 1). This fact deserves serious consideration since many other common materials of construction contain metals, such as chromium and nickel, which would be undesirable contaminants in the urea process because the end product is used in fertilizer. It can be expected that maximum limits on metallic impurities contained in urea-based fertilizer products will continue to be lowered by both customer and legislative mandate.
Titanium

Titanium has been used extensively in the urea industry and has many attributes that allow it to provide good service life. Although titanium does resist direct corrosion by ammonium carbamate, its oxide layer is prone to erosion. This leads to localized erosion where high fluid velocities abrade the protective layer. This phenomenon causes the tubes to wear at predictable rates. While titanium is not very sensitive to the urea chemical environment, the erosion leads to a limited lifetime in service. Some plant operators have extended titanium stripper life by retubing the stripper after several years of service.

In order to use titanium in a urea stripper, the titanium tubes must be welded to a suitable substrate. Titanium cannot be successfully welded directly to ferrous alloys. A weldment made by joining two dissimilar metals results in a joint that will exhibit poor mechanical and corrosion performance. To avoid a dissimilar metal weldment, the interior surfaces of the stripper’s upper and lower chambers and tubesheets are explosively clad with titanium. Cladding provides a titanium surface onto which the titanium tubes can be welded. A limitation in this configuration is that stainless steel cannot be used as the tubing material due to the incompatibility of the two metals during fusion welding. Previously, when re-tubing a titanium stripper, the choice of material has been limited to titanium, which historically has been subject to large swings in price and availability.

Zirconium

It is generally recognized that zirconium is an ideal candidate for urea service. It had been successfully implemented in acetic acid production and other extreme corrosive organic processes, showing virtually no corrosion. In urea service, zirconium’s limited initial application was largely due to the perceived exotic nature of the metal by plant designers, end users, and fabricators. However, the limited number of process units that were installed have proven the concept of zirconium in urea service. In non-urea applications, heat exchangers constructed of solid zirconium have exhibited virtually no corrosion, even after 25 years of chemical processing service (Ref. 9).

Zirconium has an added advantage in that its thermal conductivity is approximately twice that of titanium. This attribute allows equipment designed to the same specifications as titanium to operate at a higher efficiency.

One of the primary factors limiting the use of zirconium is the fact that it cannot be welded to other metals using standard techniques. The similarities in physical properties between zirconium and titanium might lead one to believe that they could be successfully fusion welded since the metals are completely miscible in each other, forming a complete solid solution alloy series with no intermetallic compounds or discrete phases. Indeed, a weld (although hard and brittle) can be made between zirconium and titanium.

Due primarily to the difference in lattice size of the respective oxides, the resultant alloys in the welded section suffer the consequence of being less corrosion resistant than either of the parent metals. This fact, coupled with the lower-ductility weld zone, prevents fusion welding from being a commonly used method of joining the two reactive metals, especially in a highly corrosive environment.

Zirconium and ferrous alloys cannot be welded successfully by standard techniques because the physical and chemical properties are too different.

As with titanium-to-titanium fusion welds, fusion welds of zirconium-to-zirconium make high quality joints when proper welding techniques are used.

Stainless Steel: The original workhorse of the industry

Stainless steels have a long history in urea service. Due to their relative affordability and widespread use throughout multiple industries, there are a
large number of specialized alloys for specific applications and much work has been done on improving the performance of stainless steel for use in urea strippers. Most of this work focuses on two strategies: tightening the compositional limits on the stainless alloys used in the most aggressive parts of the plant and the introduction of passivation air into the process stream.

The performance of stainless steels in urea service has been found to be very sensitive to the chemical composition of the stainless steel being used. For this reason, Type 316L Urea Grade stainless steel was developed with extra-low carbon content and the other elements very tightly controlled. Other alloys have also been developed with some success, including 25Cr-22Ni-2Mo and other proprietary alloys. The tight chemical specifications in these steels reduce much of the performance variability by altering the concentration of elements that do not perform well in urea service.

The addition of passivation air to the process stream is necessary to protect stainless steel from rapid failure. For stainless steel in urea service, the chromium component forms an adherent oxide layer that protects the base metal from excessive corrosion. For this reason, it is necessary to ensure that the surface of the steel is continuously wetted by oxygenated process solution. If the conditions become reducing, the chromium oxide layer loses its effectiveness and corrosion may occur at a more accelerated rate.

Another related problem occurs when the oxygenated process solution leaks into a crevice. In this situation, the crevice sets up an environment that is no longer oxidizing enough to maintain the protective layer thus making the use and application of passivation air problematic. Compressors, pumps, and distribution systems must be installed to supply a steady stream of air at the correct rate. If any component should fail and interrupt the air supply, the plant equipment can experience severe and rapid corrosion.

Adding air to the process stream may also reduce the efficiency of the overall process by introducing an inert substance that must then be removed downstream. Any passivation air added to the urea process must be removed after stripping; this removal adds both process costs and hazards.

Even with these control measures in place, stainless steel still exhibits corrosion. Furthermore, using stainless steel puts an upper temperature constraint on plant operators of about 205°C, reducing reaction rates, yields, and capacity.

Steel and Zirconium Bi-metallic Tubes

Bi-metallic tubing is a large-scale adoption of zirconium that uses stainless steel as the material of construction for the structural component of the tubes with a mechanically fitted interior liner of zirconium. This design is intended to put the most corrosion-resistant material on the inside of the tubes where the greatest potential for corrosion exists. It allows the stainless steel jacket to bear the structural load and gives fabricators a stainless steel outer layer of tube to weld into a stainless steel tubesheet. Bi-metallic strippers have been successfully employed at many urea plants and can be successfully utilized, given careful adherence to known operating conditions and limitations. However, even with close adherence to proper operating conditions, the tubes at the bottom of the stripper will continue to suffer corrosion related issues due to the high temperature associated with the process.

A more robust solution over the current bi-metallic design is desired to ensure a higher factor of safety with respect to materials design and performance. For example, because the upper and lower stripper chambers and the tubesheets in a typical bi-metallic unit are manufactured from solid un-clad stainless steel, passivation air is still needed to prevent rapid corrosion. Furthermore, the lack of a true bond between the zirconium and stainless steel may allow carbamate solution to penetrate between the zirconium liner and the stainless steel outer
tube. As this penetration is localized and occurs outside the bulk fluid flow, a crevice environment is created in which the media is not thoroughly oxygenated. In such cases, the isolated fluid becomes very corrosive to the stainless steel and is often times in a location where detection is difficult.

The Current Situation

Currently, two of the dominant materials of construction in service in urea strippers are bi-metallic and titanium. As we’ve discovered, both configurations have their respective advantages and disadvantages.

Titanium has a generally predictable life expectancy in urea service. Unit life is dictated by erosion generally observed inside the top part of the stripper tubes. To extend the life of titanium strippers, operators have rebuilt the unit half way through the unit’s service life or physically turned the unit 180 degrees. Some operators have experienced operational issues with corrosion products, principally titanium oxide, being released into the urea plant downstream of the stripping process. Due to the current cost and availability of titanium, costs of major maintenance associated with rebuilding a stripper at mid-life and other operational issues, other materials options are being evaluated.

Due to the limitations with bi-metallic and/or titanium, new tubing solutions are being evaluated to service numerous existing and planned urea plants.

OmegaBond™ Tubing Solutions

ATI Wah Chang developed a new set of material solutions to address the problems previously discussed. The result is a robust, novel approach that serves as a platform to put the optimal corrosion resistant material in the process where it is needed. At their core, these solutions provide high-integrity, repeatable metallurgical bonds between two different materials while avoiding the limitations of fusion welding. The metallurgical bond provides the necessary integrity and prevents the corrosive process solution from attacking vulnerable material. This enables, for example, zirconium to be used as the tubing material in a titanium stripper without using problematic dissimilar-metal fusion welds. This new technology has the capability to greatly simplify stripper tubing retrofits while upgrading the metallurgy used in the stripper.

These new tubing solutions utilize solid-state joining technology where the interface between the two metals never reaches a molten state. By not allowing them to melt together, an alloy of the two metals does not form. Instead, they are plastically “forged” together at a temperature well below the melting point. The resultant joint has virtually no diffusion zone, no inter-metallic compounds, and no alloying. Likewise, the heat-affected zone is negligible.

The two primary solid-state joining technologies in use in this development are extrusion bonding and inertia welding. Due to the lack of a significant transition zone, both create high integrity, repeatable bonds that are strong and ductile. Likewise, the corrosion resistance should be the same as the parent metal.

Extrusion Bonded Tube

The process of extrusion bonding entails several metallurgical process steps. The outer titanium billet is prepared with a large axial hole. The inner zirconium liner is prepared and fitted inside the titanium billet. The two are then assembled in a proprietary process that includes machining, cleaning, and assembly.

Extrusion-bonded tube sample after flattening indicates the strength of the extrusion bond between zirconium and titanium. No dis-bonding was observed, even after severe bending.
Extrusion bond samples in various stages of size reduction

The billet is then extruded and a metallurgical bond is formed between the inner zirconium and the outer titanium. The extruded tube is then cold reduced in multiple steps and finished to the appropriate final size. The resultant extrusion-bonded tubing exhibits a seamless protective barrier on the titanium, and with a metallurgical bond, there is no opportunity for corrosive solution to leak between them.

Metallurgical bond in extrusion-bonded tube, 200X, anodized

Inertia Welded Tube

Inertia welding is a process also commonly known as friction welding. It consists of spinning one of the two pieces to be joined at a pre-determined speed. The other piece is held in a fixed mandrel. Just prior to pressing the parts together, the drive is disconnected from the flywheel of the rotating part. As the parts are pressed together, the rotational inertia is converted to heat. The interface of the two parts is locally heated to about 80 percent of the melting point and the axial force applied forges the parts together. In the immediate joint, the two metals plastically deform, swirling and mixing. As this happens, the soft metal at the interface is forged out of the joint, forming a flash of material that must be removed. Since this joining occurs below the melting point and for a very short period of time, there is no alloying of the metals.

The frictional heating that occurs is highly localized and dissipates quickly. The corrosion properties of the metal adjacent to the joint are virtually the same as the parent metal. One notable characteristic of this type of weld is that it is highly repeatable. Once the parameters of surface condition, rotational speed, and axial force are determined, there is very little variability in the quality of weld between individual specimens.

30X Magnification: The darker layers at the interface in the photo show the very fine grained metal “flash” that was in the process of being ejected from the joint when it cooled.

500X Magnification: Inertia welds showing metallurgical bond with no diffusion layer. The photograph shows the swirling patterns formed while joining.
Using these two primary enabling technologies, ATI Wah Chang and Snamprogetti envision a few potential configurations for retrofitting existing titanium strippers or constructing new titanium units.

The first configuration of the new tubing solutions consists of lining a titanium tube with a thin liner of zirconium using the extrusion bonding technology. This extrusion bonded tube can then be welded directly into a titanium clad tubesheet.

The second configuration of the new solutions consists of a solid zirconium tube with solid titanium tube inertia welded onto the ends. This also gives a solid titanium substrate that can be welded directly into the titanium clad tubesheet. In practice, the inertia weld could be located inside the tubesheet, outside of the hottest part of the stripper. The ferrule that fits into the top of tube could be modified to protect the titanium end and the inertia weld from erosion from the high velocity fluid in that region of the tube.

The third configuration consists of a solid zirconium tube inner liner with extrusion bonded tubes that are inertia welded onto either end. This configuration provides a sound titanium outer surface for direct fusion welding onto the titanium clad tubesheet, together with the protection of solid zirconium for the length of the tube.
Mechanical and Corrosion properties of New Tube Solutions

Testing and evaluation of the mechanical and corrosion properties of these new tubes is ongoing. There are currently samples being evaluated through field trials in operating strippers. Presently, all materials in urea service appear to perform as expected.

Extensive testing and prototype manufacturing is underway and preliminary test results in the following paragraphs:

Bend test results of inertia-welded joints. Note that specifications for parent metal requires a bend radius of 5T or smaller.

Bend tests of longitudinal sections of tube (similar to the type shown above) indicate that Omegabond tubes are highly ductile. In 36 samples bent to 2.5T radius, there were no breakages. In 12 samples bent to 1.8T radius, there were no breakages.

Crushed final-size extrusion bonded tube, 12X magnification

Tube-crush tests have been conducted on final-size extrusion bonded tubes. Samples were then mounted and anodized for metallographic examination. At the apex of the tube bend where the deformation is the greatest there was no delamination.

Solid Zr702 and TiGr2, with inertia weld, bent in a standard tube bender.
Two different weld tests have been conducted on extrusion bonded tube that examined how the extrusion bond was affected by heat input from fusion welding. Both tests were intended to simulate the tube-to-tubesheet joint.

In the first test, an extrusion bonded tube was welded into a 1-inch-thick plate of titanium. The welding parameter called for maximum heat input to simulate a worst-case situation. The second test was conducted using an approved weld procedure from the titanium tube-to-titanium tubesheet strip-per design. Metallographic examination was performed on both samples, and in both cases, there is no evidence of disbonding between the Zr and Ti extrusion bond.

The tensile strength of Omegabond tubes is comparable to that of the parent metals at both room temperature and elevated temperature tests (250°C). Results are summarized below for 0.2% offset yield strength.
Testing of the ultimate tensile strength produced similar results. In mechanical testing of the inertia welded samples, the yield and failure occurred in the Zr, away from the joint.
Laboratory corrosion testing is currently underway on all configurations of Omegabond tubing. A preliminary campaign utilized the Huey test procedure in 65% boiling nitric acid and compared the corrosion rates of inertia welded samples to fusion welded samples. Results of that testing regimen are shown below.

**Advantages and Applications of Omega-Bond™**

As detailed above, OmegaBond tubing offers direct and indirect benefits to urea producers. The direct benefits include the enhanced performance of the urea stripper due to improvements in materials technology and unit design. The indirect benefits include expected improvement in urea plant operating maintenance, operating cost reduction, and improved return on capital investment.

The new products will effectively facilitate the use of corrosion- and erosion-resistant reactive metals in the most severe urea service by incorporating bonding technologies that eliminate the potential of process fluid penetrating and damaging process tubing. OmegaBond products can be retrofitted or fabricated by conventional methods into existing titanium-clad or newly-constructed urea strippers.

These new products will also enable urea plants to run at higher efficiency with less downtime. Due to the design of these advanced solutions and the elimination of stainless steel, the use of additional passivation air in the stripper can also be eliminated. Eliminating the cost of maintaining associated compressor systems and air removal after stripping will result in energy, labor, and other unit cost savings. The improvements in stripper technology will likely allow units to be operated at a higher temperature which may enhance the stripping reaction. Most importantly, this new materials technology will address many of the maintenance concerns that some urea producers face. The cost of unit downtime can be significant; for example a 2,000 ton per day plant supplying urea at $250 USD per ton incurs an opportunity cost in excess of $500,000 USD for each day of unscheduled downtime.
Bibliography / References:


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