Metal Valves for Highly Corrosive Application

This article highlights important issues to consider when selecting corrosion resistant metal valves for difficult corrosion applications, i.e. applications where standard valves (in steel, in stainless steel or polymer lined) do not offer an acceptable performance.

By Dean Gambale, CEO Americas of Tantaline Inc.

Unless materials are either grown on trees or come directly from livestock, nearly every material that we are familiar with today has either been directly or indirectly processed by valves. Valves are critical to the control, safety, and reliability of processes in order to create the products that we use every day.

When considering valves and highly corrosion resistant materials for your operation, there are always tradeoffs. The ideal properties of life, reliability, availability, and material costs are rarely realized in one single material set and usually a compromise must be made that boils down to corrosion performance versus costs.

When to consider specialty metal valves

Stainless steels and polymer lined valves provide corrosion protection for a great number of applications. However there are applications where stainless steels are not capable of providing the desired corrosion protection and polymer solutions are less than ideal due to various process conditions that may exist. In these cases, corrosion resistant metals and alloys such as titanium, nickel alloys, zirconium and tantalum must be considered.

These corrosion resistant metals and alloys deliver corrosion resistance and mechanical stability where no other materials are suitable. Whilst the use of corrosion resistant metals are nowhere near as widespread as stainless steel and polymer liners, these materials have found a home in some of the most severe applications, spanning many industries such as: chemical processing, oil and gas, specialty chemical, pharmaceutical, food, off-shore, and marine industries.

There are a variety of corrosion resistant alloys and metals that are commercially available for valves and this article will take a close look at and compare the different material options that are available to engineers both new and traditional. This article will also explain the differences in the corrosion resistance, reliability, availability and material cost perspectives as well as explain the advantages, possibilities and potential pitfalls of each material option.

In highly corrosive applications, the fine balance between a valve's performance, safety, and costs while also taking into account numerous process related variables becomes difficult.

The initial choice for at least moderate corrosion protection is to evaluate stainless steel solutions. These materials are mechanically excellent, but their corrosion resistance is limited especially in concentrated acids at elevated temperatures. When additional protection is needed engineers also turn to polymer coatings. For example, flouropolymer coatings have been able to combine the great corrosion resistance of PTFE and the mechanical strength of steel in one product. These polymeric coatings have been able to satisfy a large need in the corrosion industry, however as with any material, they are not the solution for every application. Polymeric solutions struggle at elevated temperatures (greater than 200°C or 390°F) which can cause the mechanical integrity of the coating to compromise the performance of the valve. This is especially true if the combination of high temperature and pressures, high flow rate, or mildly abrasive particles exist. In some applications, the porous nature of the polymers can lead to corrosive gases diffusing through the coatings or contamination of the valves which can be especially important in pharmaceutical batch processing. In valve applications where typical stainless steel or polymeric solutions do not offer a level of performance that is acceptable corrosion resistant metals must be considered.

In general, valves utilizing corrosion resistant metals and alloys are mechanically rugged, offer good to superb corrosion resistance, and are robust in a large range of processing conditions. Depending on the conditions and severity of the application, there most likely exists a metal alloy solution. Some things for the engineer to consider when selecting materials include:

- Estimated service life
- Reliability (Economic consequences of failure)
- Availability and delivery time
- Material costs

Estimated service life

The corrosion rate is the single most important variable when trying to estimate service life of a valve and the suitability of each metal, titanium, nickel alloys, zirconium and tantalum. To compare the corrosion resistance of each of these materials, Figure 1 represents the relative corrosion resistances of the various corrosion resistant metals in sulfuric acid (H_2SO_4) and Figure 2 is the metals comparison in hydrochloric acid (HCl). Typically corrosion rates are shown in 5 mills (0.005'') per year however, keep in mind for valves this would be a large corrosion rate and would lead to significant leaks rather quickly.

As can be seen in these charts, tantalum is the most corrosion resistant material, followed by zirconium, nickel alloys ('Hastelloy®' is the common trade name

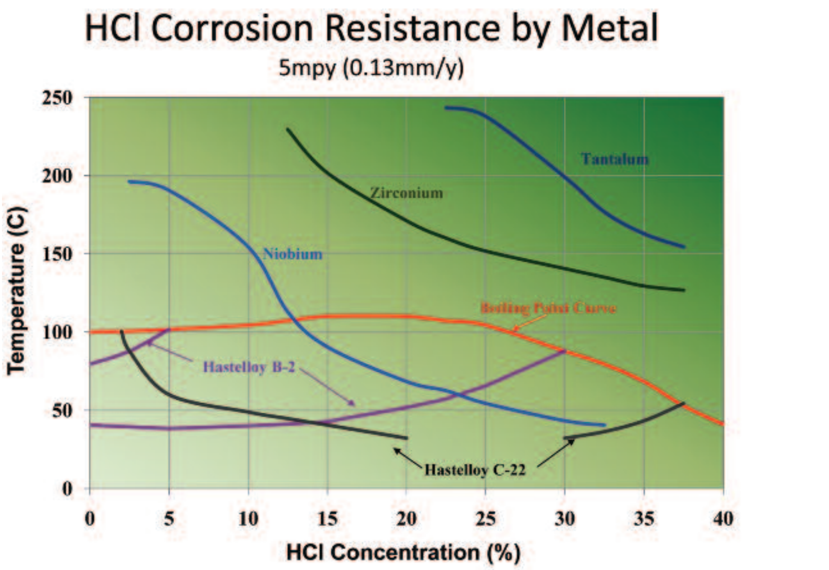

Figure 1

produced by Haynes International) and titanium in both solutions.

Tantalum gets its extreme corrosion resistance from a tenacious oxide layer which makes it the most corrosion resistant metal that is in common use today. Tantalum's superb corrosion resistance is practically inert to most oxidizing and reducing acids, except fuming sulfuric, hot alkalis, and hydrofluoric acid and is most comparable to glass. From a purely corrosion resistant point of view, tantalum metal is an ideal choice, however the problem with tantalum metal is it is typically cost prohibitive even when cladded on valves. Therefore tantalum, at least in its traditional forms, is reserved for process conditions where no other material will perform adequately.

Recent developments in tantalum processing has enabled valves as well as fittings, instrumentation and other processing equipment to be treated with a surface alloy of tantalum metal. This surface treatment, marketed under the name 'Tantaline', is based on a chemical vapor deposition process that grows tantalum metal into a base substrate and creates a thin, uniform, rugged surface of pure tantalum metal. The result is a valve with the superb corrosion resistant properties tantalum metal without being cost prohibitive. However, this option should be avoided with slurries or solutions that contain abrasive particles that could lead to mechanical erosion and abrasion of the surface.

The corrosion resistance of zirconium alloys is excellent and works well in many organic and inorganic acids, salt solutions, strong alkalis, and some molten salts.

Zirconium is produced as two major alloys for chemical processing applications; grade 702 is "pure " zirconium, while grade 705 is zirconium alloyed with 2.0 – 3.0% niobium. Of the alloys, Zr 702 has better corrosion resistance than Zr 705, however Zr 705 has better strength properties due to the addition of niobium.[5]

Zirconium's natural formation of a dense, stable, self-healing oxide film on its surface gives unalloyed zirconium excellent resistance to organic acids and most alkali solutions up to their boiling point. For all of zirconium's attributes it still can be corrosively attacked by fluoride ions, wet chlorine, aqua regia, concentrated sulfuric acid above 80% concentration, and ferric or cupric chlorides.[1]

Titanium is available in a range of different alloys with the most corrosion resistant grades being titanium 7, 11 (containing 0.15% palladium), and 12 (containing 0.3% Mo and 0.8% Ni). Titanium and its alloys offer good corrosion resistance and perform well in media such as seawater, wet chlorine and organic chlorides.

Titanium's corrosion resistance begins to break down especially at elevated temperatures and struggles with seawater at temperatures greater than 110°C.[1]

Nickel alloys are commonly used in valves for corrosive applications and are typically found in a range of acid, salt and alkali applications with some of the most corrosion resistant nickel alloys being C-22, C-276, and B-2.

The weakness of nickel alloys stems from contamination and impurities in the process stream. Under ideal conditions, B-2 alloy works well in pure de-aerated H_2SO_4 and HCl, but deteriorate rapidly when oxidizing impurities, such as oxygen and ferric ions are present. Another important consideration is the presence of chlorides (Cl-) as they generally accelerate the corrosion attack.[4]

Reliability (economic consequences of failure)

So what is the cost of a failed valve? It is typically much more than the valve itself,

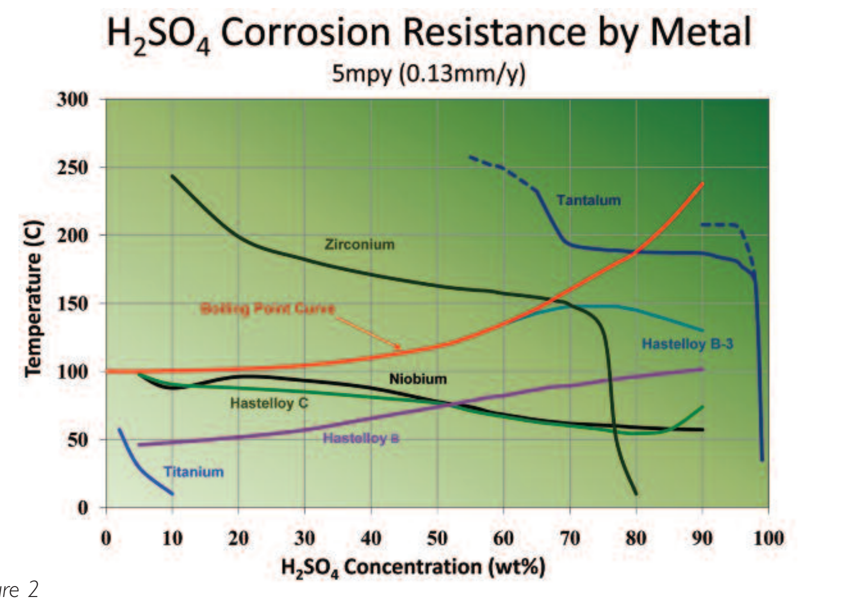

Figure 2

and engineers must carefully consider the costs of product contamination, production down time, safety and maintenance costs associated with premature valve failures. Typically in large processing environments the additional costs to obtain the next level of corrosion resistance is easily offset by the disruptions caused by failed and leaky valves. In lab and pilot scale size operations when production is not a key concern and access to equipment is easily scheduled frequent valve replacement may be a more economical approach.

Availability and delivery time

For highly corrosion resistant metals, Ti, Ni Alloy, Zr and Ta, it is not uncommon to see lead times ranging from 12 -24 weeks. One of the reasons for these long lead-times is that nearly all valves produced from these highly corrosion resistant metals are made to order and because of their relatively high costs, the supply chain is not willing to hold any inventories. In many production environments this is sub-optimal as the burden of inventory is placed on the end user.

In the current market, to obtain the performance of highly corrosion resistant metals with significantly less lead times one might considerer metal surface treatments. There exist commercial processes that could take standard stainless steel valves and upgrade their performance to that equal of tantalum creating a tantalum surface alloy. Because standard stainless steel valves are used, lead times for these valves ranges from 3 – 6 weeks.

Material costs

Highly corrosion resistant metal valves are typically reserved for applications that truly need their properties since their costs are significantly higher than 316 stainless steel or even polymer lined valves. Although metals prices are continuously fluctuating the latest estimates for a solid corrosion resistant metal solution is anywhere from 4.5 – 10 times the cost of 316 stainless steel solution. The exception is tantalum metal. Tantalum metal is typical on the extremely high-end of the cost curve at 50+ times that of 316 stainless, however due to advances in tantalum processing, tantalum treated valves are also available at the low-end of the cost curve typically costing less than nickel alloys.

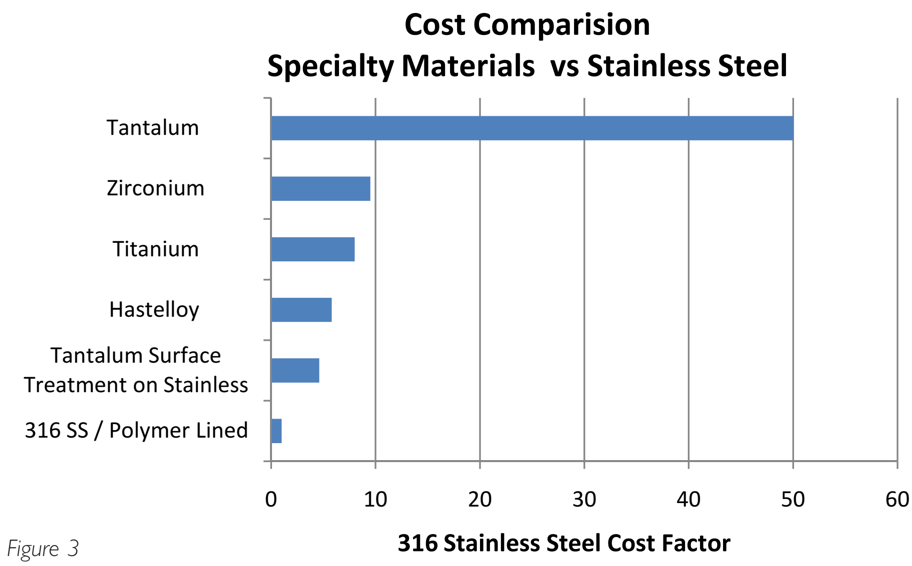

Figure 3

Conclusion

Advances in materials technology are helping to limit the compromises and tradeoffs engineers have been forced to make. Through composites, engineers are always trying to take the best properties of various materials and combine them into a single product. One referenced to in this article takes the superb corrosion resistance of tantalum, and combines it with the strength and availability of stainless steel by growing a tantalum metal surface on the substrate with the goal of creating a highly corrosion resistant valve, that is readily available at competitive prices. Whilst no material or composite is the solution for every application it's only through advances in materials will the battle against corrosion be won…Or at least under control.

Footnotes:
1. Handbook of Corrosion Engineering, Pierre R Roberge, McGraw Hill, 2000
2. CORROSION Volume 1 & 2, L. L. Sheir, R. A. Jarman, G. T. Burstein, Butterworth Heinemann 1994
3. Metals Handbook: Corrosion , Corrosion of Nickel-Base Alloys, in. Metals Park, Ohio, ASM International, 1987, pp. 641–657.
4. andbook of Corrosion Engineering, Pierre R Roberge, McGraw Hill, 2000, pp. 676-678
5. ATI Wah Chang Allegheny Technologies, Zirconium in Sulfuric Acid Applications Technical Datasheet, 2003 pp. 3.

About Dean Gambale

Mr Gambale has spent thirteen years of his professional career focusing on cutting edge materials and how to create useful products that solve real problems and bring value to the customers. He graduated from Penn State University with a BSc in Chemical Engineering and after that he gained an MBA at the University of Delaware. After his studies, he worked at W.L. Gore & Associates for ten years doing product development and product management. Focused on materials utilizing PTFE composites and surfaces and spent three years at H.C. Starck as business development manager focusing on tantalum metal products and technologies and he is an officer of the local Boston AICHE. Currently, Mr Gambale is the CEO Americas of Tantaline Inc. Tantaline's technology focusing on the creation of rugged, durable and extremely corrosion resistant tantalum metal surface alloys for use in the chemical processing, oil & gas and pharmaceutical industries.

Tantaline will be at the Valve World Exhibition, stand number N767.