Choosing Specialty Metals for Corrosion-Sensitive Equipment

Dean Gambale
Tantaline

Specialty metals should be considered for processes that push beyond the corrosion limits of steel. New composites and surface alloy technologies expand the options for defending against corrosion.

Chemical processing facilities are engaged in a never-ending battle against corrosion to ensure that processes operate safely and reliably. Corrosion can affect many types of materials, from metals to ceramics, and even polymers and plastics. Many processes employ a variety of materials to protect against corrosion and its ensuing problems.

Some types of corrosion-sensitive equipment, such as valves, fittings, and instrumentation, require special attention. This is because they corrode more quickly than other components in a typical process stream, and even small amounts of corrosion (about 0.002 in.) can have a large impact on performance.

This article focuses on corrosion-sensitive equipment typically found in processing plants and the specialty-metal material options and techniques that should be considered when stainless steel and fluorinated polymers are insufficient.

Specialty metals

For corrosion-related applications, the term specialty metal generally refers to titanium, nickel alloys, zirconium, and tantalum. Specialty metals provide corrosion resistance and mechanical stability where other materials, such as standard steels, are inadequate. Stainless steels are mechanically excellent, but their corrosion resistance is limited, especially in concentrated acids at elevated temperatures. Although they are usually found in the most severe applications, specialty metals are attractive for use in corrosion-sensitive equipment in several industries, including chemical processing, next-generation energy production, oil and gas (onshore and offshore), pharmaceuticals, and foods and beverages.

Fluoropolymer-coated steel offers both the excellent corrosion resistance of the polymer (*e.g.*, polytetrafluoroethylene, PTFE) and the mechanical strength of the steel. These coatings are suitable for many corrosive applications, but as with any material, they are not universal solutions. For example, polymer coatings may not be ideal, or even feasible, for instrumentation, because polymers are electrically nonconductive and thermally insulating.

Many polymers are not able to withstand temperatures above 300°F. As the temperature increases, the polymer softens, compromising the mechanical integrity of the coating and thus equipment performance. This problem is especially relevant under certain conditions, such as a combination of high temperature and pressure, a high flowrate, and/or the presence of mildly abrasive particles. In some applications, the porosity of the polymer can allow corrosive gases to diffuse through the coating and corrode the base steel. In other cases, a polymer lining's pores could become contaminated, which can be especially hazardous for pharmaceutical batch processing.

In general, process equipment made from specialty metals is mechanically rugged and provides excellent corrosion resistance for many processing applications. Each specialty metal has its own niche — a specific metal's strengths and weaknesses may make that material suitable or unsuitable for a particular processing environment or application.

When selecting materials, consider:

- estimated service life
- reliability with respect to safety and economic consequences of failure
- overall availability and delivery time
- associated material costs.

Corrosion resistance

Corrosion resistance, which is expressed as the rate of corrosion of the metal in the target media, is the most important criterion for evaluating a specialty metal, since this characteristic directly impacts the estimated service life of the equipment. Corrosion resistance data from laboratory tests are often summarized in an iso-corrosion chart, which plots the material's corrosion rate for a range of temperatures and concentrations. Each curve represents a corrosion rate of 5 mil/yr, with points below representing a lower corrosion rate and points above representing a higher one. Comparing iso-corrosion curves indicates the relative performance of materials in a particular medium.

Although iso-corrosion curves typically depict a corrosion rate of 5 mil/yr, it is important to note that a valve corroded at this rate would quickly experience problems, such as leaks and the inability to create tight seals.

Figure 1 presents the iso-corrosion curves and relative corrosion resistances of various specialty metals in sulfuric acid (H_2SO_4) and in hydrochloric acid (HCl). In both acids, tantalum's corrosion resistance is best, followed by zirconium, nickel alloys (Hastelloy), and titanium.

Tantalum

Tantalum is a reactive metal — *i.e.*, it reacts with oxygen to form a protective oxide layer. What distinguishes tantalum from other reactive metals is the tenacity of its oxide layer and the ease with which it forms. It provides superb corrosion resistance comparable to that of glass. This makes it practically inert to most oxidizing and reducing agents, except fuming sulfuric acid, concentrated hydrofluoric acid, and hot strong alkalis. Taking no other factors into consideration, tantalum metal is an ideal choice for superb corrosion resistance.

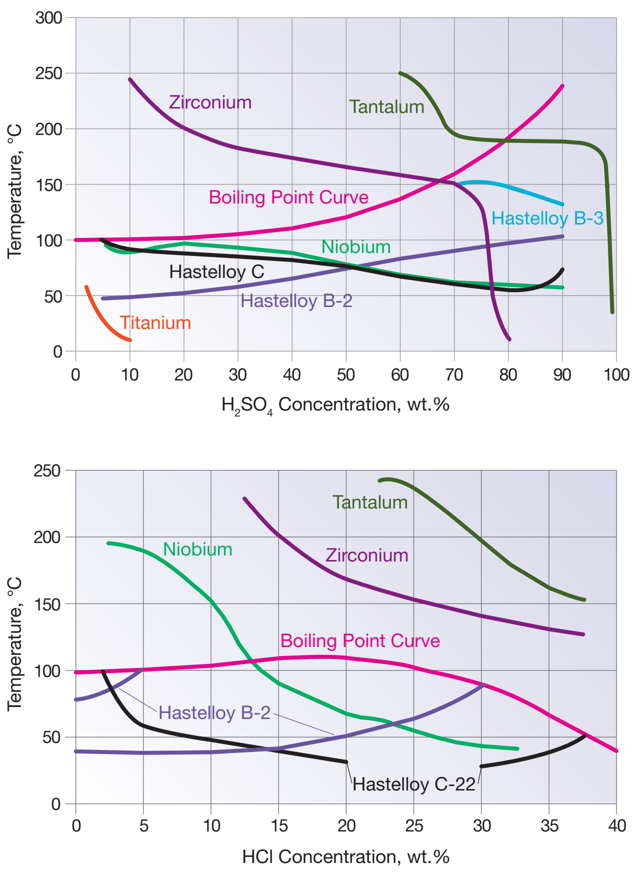
However, tantalum metal has some practical limitations. First, it is very expensive and typically cost-prohibitive, even when formed around and cladded on top of other materials (*e.g.*, steel). Second, the availability of valves, fittings, instrumentation, and other process equipment made of tantalum is very limited. Therefore, tantalum (at least in its traditional forms) is only considered for valves, fittings and instrumentation in process conditions where no other material could adequately protect against the corrosive environment.

Tantalum is commonly used in applications that involve handling hot concentrated acids (*e.g.*, sulfuric, hydrochloric, and nitric) in polymer production, metal pickling, acid production, and specialty chemical manufacturing. Due to its negligible corrosion rate, tantalum is also used in the pharmaceutical and food manufacturing industries, where even the smallest amount of metallic impurity cannot be tolerated *(1)*.

Surface alloys, linings, and coatings

Surface alloys, linings, and coatings were developed to combine the best properties of multiple materials. In the case of corrosion protection, the goal is to protect inexpensive standard steel components with corrosion-resistant materials, which are typically more costly.

Coatings are typically applied by dipping, plating or spraying metals onto a substrate surface (*e.g.*, carbon steel). Various levels of corrosion protection can be achieved depending on the materials used. The common feature of coatings is that their bonding mechanisms are predominately mechanical in nature. As a result, coatings



▲ **Figure 1.** Tantalum's corrosion resistance is best for both sulfuric acid (top) and hydrochloric acid (bottom), whereas Hastelloy B-2 performs poorly according to both iso-corrosion curves.

Surface alloys are an excellent option for applications that require extreme corrosion resistance on complex process equipment.

can be susceptible to chipping, spalling, or delamination with mechanical deformation.

Linings such as fluoropolymers (*e.g.*, perfluoroalkoxy, PFA) and metal claddings can also provide corrosion resistance. Like coatings, linings are held in place mechanically. Although linings are versatile enough to be applied to both large and small equipment, they are relatively thick, usually several millimeters, and held in place mechanically. Claddings are formed over a substrate, and in many cases are considered loose linings because there is little to no physical attachment to the substrate.

Surface alloys are very different from coatings and linings in their final form and effectiveness. Recent developments in processing tantalum metal have made it possible to create tantalum surface-alloy materials that are suitably rugged and durable for use in the manufacturing of process equipment and that are priced 20–30% lower than specialty alloys like nickel, titanium and zirconium metal alloys.

This surface treatment employs a process that grows tantalum metal into a base substrate, such as stainless steel, until a thin, uniform, rugged surface of pure tantalum metal is created. This surface exhibits all the chemical properties of pure tantalum, but without the higher cost. Since it is a surface alloy that is metallurgically alloyed to the substrate, the resulting material is extremely rugged and durable and can withstand severe deformation, such as 180-deg. bends, indentations, and scratches.

With the corrosion resistance of tantalum and the ruggedness of standard materials, surface alloys are an excellent option for applications that require extreme corrosion resistance on complex process equipment. Surface alloy products are limited in size by the reactors in which they are created, but they have the advantage of being used on standard and readily available steel substrates.

Zirconium

Zirconium alloys exhibit excellent resistance to corrosive attack and are suitable for 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 relatively pure zirconium, and Grade 705 is alloyed with 2.0–3.0% niobium. Of the alloys, Zr 702 has slightly better corrosion resistance in sulfuric acid than does Zr 705; however, Zr 705 has better strength properties, due to the addition of niobium, and it is easier to form *(2)*.

Zirconium's corrosion resistance comes from the natural formation of a dense, stable, self-healing oxide film on its surface. Unalloyed zirconium has excellent resistance to sulfuric acid at concentrations up to 60% at the boiling point (135°C), as well as resistance to hydrochloric acid at various concentrations below the boiling point. Zirconium is also highly resistant to most alkali solutions, up to their boiling point. Zirconium's corrosion resistance is comparable to that of titanium in many ways, although it is much more robust than titanium in organic acids, such as acetic, citric, and formic acids at various concentrations and elevated temperatures. Despite these attributes, zirconium is vulnerable to corrosive attack by fluoride ions, wet chlorine, aqua regia (nitro-hydrochloric acid), concentrated sulfuric acid (up to 80% concentration), and ferric and cupric chlorides *(3)*.

Zirconium is most commonly found in industrial applications that produce hydrogen peroxide, manufacture rayon, and handle phosphoric acid, sulfuric acid, and ethylbenzene.

Titanium

Titanium is available in a range of different alloys. The most corrosion-resistant grades are Titanium 7, 11 (containing 0.15% palladium), and 12 (containing 0.3% Mo and 0.8% Ni).

In the chemical process industries, titanium and its alloys offer good corrosion resistance in many process environments. Titanium provides more protection than stainless steel because it has a greater affinity for oxygen and more readily forms a protective oxide layer. As a result, titanium performs well in media such as seawater, wet chlorine, and organic chlorides. Although titanium offers good corrosion resistance to these solutions, it is not immune to them, especially at elevated temperatures, such as seawater heated to above 110°C *(1)*.

Titanium is commonly used in pulp and paper production, chemical processing applications (*e.g.*, chlorine production), and marine applications, such as those involving seawater or brackish water.

Nickel alloys

Nickel alloys are often selected when steels do not offer adequate corrosion resistance. The most important alloying elements are chromium and molybdenum, as well as iron, copper, and silicon. Varying the concentrations of Cr and Mo in the alloy allows nickel alloys to be used successfully in a wide range of corrosive environments, including acid, salt and alkali applications. The addition of chromium (15–30%) improves the corrosion resistance to oxidizing solutions, while the addition of molybdenum (up to 28%) significantly improves the resistance to nonoxidizing acids.

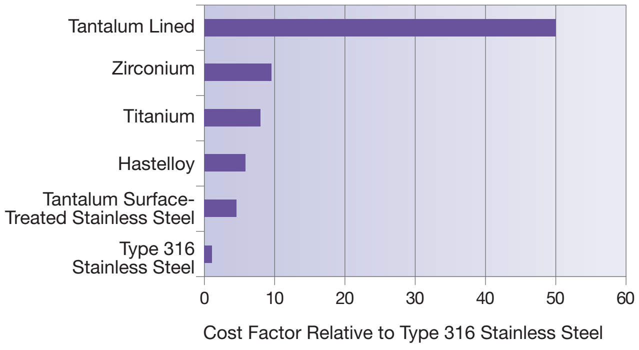
Of the more corrosion-resistant and common nickel alloys, C-22, C-276, and B-2 (Table 1) all have good corrosion resistance in a variety of media. The corrosion resistance of these alloys in HCl depends heavily on the molybdenum content — the alloy with the highest concentration of molybdenum, B-2, exhibits the best corrosion resistance. In other acids, such as HNO_3, chromium is the most important alloying element. Under ideal conditions, these alloys perform well in pure deaerated H_2SO_4 and HCl but deteriorate rapidly in the presence of oxidizing impurities, such as oxygen and ferric ions. Another important factor when considering these alloys is the presence of chlorides, which generally accelerate corrosion, although the degree of acceleration differs for various alloys *(3)*.

Nickel alloys are applicable in a wide range of acids, salt solutions, and caustic environments, and are suitable in the chemical, petrochemical, oil and gas, nuclear, power, and paper industries. Nickel alloys are discussed in detail in Ref. 4.

Table 1. Nominal compositions (wt.%) of common nickel alloys.

Alloy	Ni	Cr	Mo	Fe	Cu	Si	Other
C-22	56	22	13	3	0.5*	0.08*	W 3; Mn 0.5*; C 0.01*; V 0.35*
C-276	57	16	16	5	0.5*	0.08*	W 4; Mn 1*; C 0.01*; V 0.35*
B-2	69	1*	28	2*	0.5*	0.1*	W 0.5*; Mn 1*; C 0.01*

* Maximum ** Minimum



▲ **Figure 2.** With the exception of tantalum surface alloys, the effectiveness of a specialty metal is roughly in line with its cost.

Supply chain considerations

The availability of and delivery time for many specialty metal valves is usually not optimal. Several conditions in today's market have contributed to this problem. Specialty metal prices are relatively high, and because valves, fittings, and instrumentation come in such a wide range of sizes, types, and styles, stocking all of these combinations in the various specialty metals is cost-prohibitive. Furthermore, because prices fluctuate, most manufacturers and distributors are unwilling to stock significant quantities for fear of their inventories losing value. Hence, these materials are typically purchased and equipment manufactured on an as-ordered basis. As a result, delivery estimates of 12–18 weeks are not uncommon.

If lead times are a concern for a project that requires specialty metals, an alternative is to consider specialty metal surface treatments. Treating standard stainless steel valves, fittings, and instrumentation with a tantalum surface alloy creates products that have the corrosion resistance of tantalum and the availability of standard stainless steel materials. Typical lead times for such products are 3–6 weeks.

Comprehensive replacement cost

It is important to remember that the true cost of replacing equipment is not simply the cost of the part itself. Product contamination, loss of production, safety, and the high maintenance costs associated with premature failures must also be considered.

In many processing environments, the additional costs that are usually associated with more-corrosion-resistant materials are invariably less than the disruptions and distractions caused by failed equipment. This is especially true for large facilities with integrated processes.

However, this may not be true for pilot plants and laboratories. There, it may be more cost-efficient to replace cheaper valves more often, as access to the equipment is relatively easy and the cost of downtime is small.

When evaluating material costs, consider the total cost of ownership, rather than the initial out-of-pocket costs only. In most cases, it is more cost-effective to specify materials that will provide an extended service life. This is especially true for equipment installed in locations where replacement is difficult or that is critical to the safety and performance of the entire operation.

Compared to Type 316 stainless steel or polymers, specialty metals are relatively expensive (Figure 2) and, therefore, are reserved for applications that require the properties and characteristics of specialty metals. Although metal prices continuously fluctuate, most solid specialty metals cost 4.5 to 10 times as much as Type 316 stainless steel. The cost of a solid-tantalum-lined valve could be 50 or more times that of a stainless steel valve. As a cladding, tantalum is still significantly more expensive than any of the specialty alloys. However, the price of tantalum surface alloy is typically lower than the cost of other specialty metals because the tantalum metal is used very efficiently.

Valves

Valves are essential for controlling flowrate, temperature, concentration, and pressure. Because valves control these vital process parameters, their operation and perfor-

▲ **Figure 3.** The corrosion resistance of process equipment, such as tube fittings (left), cam and groove couplings (center), and heat exchanger plates (right), can be enhanced with a surface alloy that can withstand acidic environments.

mance are critical. A small amount of corrosion may have a large impact on the performance of a valve.

For example, standard 2-in. piping can typically withstand several thousandths of an inch of corrosion with little or no impact on the process (it might not even be noticed). However, if a ball valve were to corrode by a few thousandths of an inch, it could lose its ability to completely shut off or accurately control flowrate.

Furthermore, a valve's geometry can disturb the flow pattern and introduces turbulence, which increases the corrosion rate. This creates turbulence and increases erosion. As a result, erosion and corrosion are both accelerated.

Fittings

Fittings (Figure 3) are also typically sensitive to the effects of corrosion. Because fittings are often used as piping transitions, laminar flows are disturbed when streams combine, flow is reduced, or reagents are injected. These conditions create turbulence, higher erosive forces, and spikes in the concentration and temperature of processing streams.

Because of these localized effects, it is not uncommon for fittings to fail before other process equipment.

Instrumentation

For many types of instrumentation to be effective, corrosion products must be minimized in order to maintain the original equipment's performance. Failure to keep instrumentation free of corrosion products could jeopardize the instrument's electrical conductivity, thermal conductivity, and flow characteristics, all of which are critical for accurate measurement.

As a result, small amounts of corrosion could have a large effect on an instrument's ability to quickly and accurately indicate process conditions. This will ultimately lead to process instability and drift.

Closing thoughts

Deciding whether to use specialty metals for corrosion-sensitive equipment involves tradeoffs. Rarely does a single material combine the optimum service life, reliability, availability, and material cost. However, advances in materials science are opening up new possibilities for corrosion resistance. Materials with superb corrosion resistance but extremely high costs (such as tantalum) can be combined with standard inexpensive materials (usually stainless steel) to create a readily available surface alloy with superb corrosion resistance that costs 20–30% less than specialty alloys.

The battle against corrosion never ends, but engineers armed with knowledge and the best-performing, most-economical materials are sure to put up a good fight. CEP

DEAN GAMBALE is president of Tantaline (E-mail: dgambale@tantaline.com; Phone: (888) TANTALUM), where he oversees company operations in the U.S., including sales, marketing, and business development. In his more than 14 years of engineering experience, Gambale worked at E Ink Corp., H. C. Starck, and WL Gore & Associates. He holds a BS in chemical engineering from Penn State Univ. and an MBA from the Univ. of Delaware.

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Further Reading

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