High Strength Corrosion Resistant Metals

Abstract
There are a number of ways to improve the corrosion and abrasion resistance of metals, including alloying, anodizing, nitriding and application of protective thin films. Alloying involves generating a binary phase diagram to determine the optimum composition and temperature dependence. For example, copper alloys known as “bronzes” offer high strength, abrasion resistance and high temperature corrosion resistance for certain compositions. These alloys include aluminum bronze (Cu$_x$Al$_y$: y ~ 5%), aluminum nickel bronze (AlNiCu: ~ 4% Ni), aluminum niobium bronze (AlNbCu) and aluminum manganese bronze (AlMnCu: 2 – 5%Mn). Because oxides are generally more chemically and thermally stable than metals, anodizing is essentially oxidizing the surface of the metal to form a protective and abrasion resistant oxide. Nitriding accomplishes much the same as anodizing except the metal surface is exposed to a nitrogen plasma and the surface layer is a hard metal nitride. Thin oxide, nitride, and carbide films applied to a surface can significantly improve corrosion resistance and abrasion resistance, particularly for reactive metals such as aluminum, silver, titanium, nickel, iron, zirconium and copper. All these treatments can significantly extend the lifetime of the metal surface and components and lower implementation and usage costs.

Introduction
Corrosion and corrosive wear of metal components are ubiquitous problems affecting virtually all metallic surfaces. Wear and corrosion of materials are the most important failure mechanisms in industry [1]. They cost industrial economies hundreds of billions of dollars each year. According to the National Association of Corrosion Engineers (NACE), the cost of corrosion in the USA in 2006 was 430 billion dollars, which amounts to about 3.5 % of the Gross Domestic Product (GDP). Similar studies show that wear imposes similar level of costs with one estimate being 0.75% of the GDP [2]. Corrosion can also degrade integrated circuit interconnects. Corrosion and wear can also behave synergistically to further degrade performance and reduce the lifetime of the metal surface, component or part [3]. Corrosion is the degradation and removal of a material’s surface into its constituent atoms due to chemical reactions (e.g., oxidation, sulfidation, chlorides/salts), and is essentially an electrochemical process in reaction with an oxidant such as oxygen or sulfur. However, due to synergistic effects, material loss can be larger than the sum of the losses due to wear and corrosion acting separately.

The severity of corrosion is determined by chemical kinetics, which can have a strong dependence on temperature. Formation of Fe$_2$O$_3$, or rust, on an iron surface is due to oxidation of the iron atoms in solid solution and is a common example of electrochemical corrosion. Corrosion can also occur in materials other than metals, such as ceramics and polymers.
Corrosion can also be self-limiting when a protective scale forms on the surface of the metal. Corrosion can be classified as dry, wet, or stress-enhanced corrosion [4]. Dry corrosion is a chemical process that involves interaction of a gaseous environment with a solid surface, for example, oxidation in air. Gaseous sulfides and halides can also be strongly corrosive to metal surfaces. Wet corrosion involves exposing the surface to liquids, which may or may not function as electrolytes (wet galvanic or nongalvanic). Ionic charge transport in an electrochemical redox process occurs in galvanic corrosion, which involves an aqueous medium with dissolved salts. If a deposit does not form, corrosion can proceed until the entire object or component is consumed. In wet nongalvanic corrosion, the surface is dissolved by the aqueous medium in a non-redox reaction. Again, it is possible for the entire solid structure to be dissolved.

Stress enhanced corrosion is characterized by corrosion concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion controlled process, it occurs on exposed surfaces. Passivation and chromate conversion can increase the corrosion resistance of a surface. Applied stress or fatigue can enhance localized corrosion, even in otherwise benign conditions. Stress-corrosion cracking occurs when a surface is simultaneously exposed to a corrosive environment and applied stress. Intergranular regions and intragranular regions are extremely susceptible to this type of corrosion. Corrosion fatigue occurs when loads and stresses are variable.

A number of surface treatments are possible to mitigate the above types of corrosion, including:

- Corrosion resistant alloys
- Anodizing
- Nitriding
- Galvanization
- Corrosion resistant thin film coatings
- Reactive coatings
- Cathodic protection

**Corrosion Resistant Alloys**

Some metals are more intrinsically resistant to corrosion than others, either due to the fundamental nature of the electrochemical processes involved or due to the details of how reaction products form. Corrosion resistance can also be increased by alloying the metal with another metal that forms a passivation layer. Examples of corrosion resistant metal alloys are:

- **Aluminum bronzes** (Cu,Al; γ ~ 5%), **aluminum nickel bronze** (AlNiCu: ~ 4% Ni), aluminum niobium bronze (AlNbCu) and aluminum manganese bronze (AlMnCu: 2 – 5%Mn)
- Stainless steel (Fe-Ni-Cr alloys)
- Superalloy: Inconel (Ni-Cr-Fe alloy)
- Superalloy: Incoloy (Ni-Cr-Mo alloy)
- Superalloy: Hastelloy (Ni-Cr-Mo-Fe-W-Co)
- Ti-Al-Nb
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Take aluminum bronzes as an example. Aluminium bronzes have higher strength and corrosion resistance compared to other bronze alloys [5]. These alloys are most commonly used in applications where their resistance to corrosion makes them preferable to other engineering materials (stainless steel, for example). Applications include bushings (see Figure 2), plain bearings, aircraft landing gear components, engine components (especially for naval and sea going vessels), underwater fastenings, dies, molds, valve seats and ship propellers.

Aluminium bronzes tend to have a golden color. Figure 1 compares aluminum, aluminum bronze and brass surfaces and Figure 2 shows various aluminum bronze bushings. These alloys are highly corrosion and oxidation resistant, even at temperatures near 1000 °C, and have low reactivity with sulfurous compounds and other exhaust products of combustion and chemical reformers. They are also resistant to corrosion in salt water. Corrosion resistance is due to the aluminium component of the alloys, which reacts with atmospheric or system oxygen to form a thin, wear resistant aluminum oxide (Al₂O₃) surface layer and acts as a barrier to corrosion of the copper-rich alloy. As shown above, the addition of various metals can enhance corrosion resistance. Table 1 lists the various types of aluminum bronze alloys. Figure 3 shows the binary phase diagram for Cu-Al.

Note that high temperature performance is achieved by the δ-phase.

Figure 1. Comparison of aluminum, aluminum bronze and brass surfaces.  

Figure 2. Picture of aluminum bronze bushings.

Figure 4 shows a picture of the alumina scale on an aluminum bronze surface subjected to high temperatures in an oxygen atmosphere [6].

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In addition to high wear and corrosion resistance, aluminium bronzes display biostatic properties, i.e., the copper component of the alloy prevents colonization by marine organisms including algae, lichen, barnacles and mussels, and therefore can be preferable to stainless steel or other non-cupric alloys in
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applications where such colonization is undesirable. Because of their gold color and chemical inertness, aluminium bronze alloys are now being used to replace gold for the casting of dental crowns.

![SEM image of oxide scale formed on an aluminum bronze film](image)

Figure 4.  SEM image of oxide scale formed on an aluminum bronze film [6].

Aluminium bronzes are in the highest demand from the following industries and areas:
- General sea water-related service
- Water supply
- Oil and petrochemical industries
- Specialized anti-corrosive applications such as chemical reactors
- Certain structural retrofit building applications
- Engine parts

The other materials listed above function in much the same way as aluminum bronze. Because of their high temperature corrosion resistance, superalloys are used extensively in gas and jet engine turbine blades. The family of corrosion resistant nickel (Ni) alloys (e.g., Inconel) is shown in Figure 5, and includes those listed above.
Metal dusting is a catastrophic corrosion process which occurs at high temperatures (400-900°C) under strongly carburizing and reducing atmospheres such as those from coal gasification, coal liquefaction, petrochemical processes, in synthesis gas reactors and in ammonia (NH\textsubscript{3}) and methanol (CH\textsubscript{3}OH) production. Fe, Ni and Co, as well as alloys based on these metals, are all susceptible. The corrosion manifests itself as a break-up of bulk metal to metal powder, hence the term, metal dusting. Inconel 617 has excellent corrosion protection properties and is used in high temperature microchannel chemical reactors to mitigate metal dusting. One method of assessing corrosion is measurement of mass loss due to electrochemical reactions. Figure 6 compares the mass loss rate of various Inconel alloys exposed to CO-20%H\textsubscript{2} at 621°C. Aluminum bronze alloys are extremely effective at preventing metal dusting. Al\textsubscript{0.05}Cu\textsubscript{0.95} and Al-Ni-Cu are particularly effective at high temperatures.
Anodization

Anodizing is an extremely effective, and simple, process used to increase the corrosion resistance and abrasion resistance of metal surfaces. Metal alloys, such as aluminum, are anodized to increase corrosion resistance, increase surface hardness, allow dyeing (coloring), and improve lubricity and adhesion. The anodic layer is nonconductive and surface morphology is generally quite rough. The surface of a conducting solid is modified by means of an electrolytic reaction [7]. For example, an anodized aluminum layer is grown by passing a direct current through an electrolytic solution, with the aluminum component serving as the anode (the positive electrode). The electrochemical reaction releases H₂ at the cathode (the negative electrode) and O₂ at the surface of the aluminum anode, creating a build-up of aluminum oxide (alumina: Al₂O₃). The reaction process on a metal surface (S) can be expressed as:

1) Anode reaction: S + A⁻ → SA + ne⁻ (where A⁻ = ions in solution with charge = ne⁻)
2) Cathode reaction: S' + B⁺ + ne⁻ → S'B (B⁺ = positive ions)
3) Anode/water reaction: S_n + mH₂O → S_nO_m + 2mH⁺ +2me⁻
4) Cathode/water reaction: S' + 2me⁻ + 2mH₂O → S' + 2mH₂O⁻ + mH₂
5) Net oxidation reaction: S_n + mH₂O → S_nO_m + mH₂

Thus, hydrogen is released in the anodization process.

While a number of reactive metals are anodized (Al, Ti, Mg, Zn, Ta, Nb), aluminum (Al) is the most well known. The reaction for anodization of Al is: 2Al + 3H₂O → Al₂O₃ + 3H₂.

In addition to corrosion protection, anodizing can change the color of the surface. An array of colors possible with anodized titanium (TiO₂) is shown in Figure 7. Colors are achieved by varying the thickness of the TiO₂ by means of interference effects. Note that a titanium nitride has a gold color, as discussed in a recent article. Similar colors can be achieved with niobium and tantalum [8,9].

Figure 7. Colors of anodized titanium.

Because the thermal conductivity and thermal expansion coefficient of the surface oxide is orders of magnitude lower than that of the metal surface, anodized surfaces can experience several problems. Most significant of these is thermal stress, in which the anodized surface expands orders of magnitude less than the metal surface [10]. Since the oxide layer is constrained by the metal surface, the oxide layer cannot deform and, as a result, significant stresses and strains can develop. In the case of Al, the coating will crack from this thermal stress if exposed to temperatures above 80 °C. Because the coating is highly adherent to the metal surface, the coating can crack, but it will not peel [10]. The melting point of alumina is 2050 °C, much higher than that of pure Al (658 °C). In typical commercial Al anodization
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processes, aluminium oxide is grown down into the surface and out from the surface by equal amounts. So anodizing will increase the part dimensions on each surface by twice the oxide thickness. For example, a coating that is 2 μm thick will increase the part dimensions by 1 μm per surface. Anodized Al surfaces are harder than untreated Al, but have low to moderate wear resistance, which can be improved with increased oxide thickness and sealing.

Nitriding

Nitriding and nitrocarburizing serve much the same purpose as anodizing, increasing the corrosion and wear resistance of a metal surface [11,12,13]. Nitriding is a basically a heat treating process that diffuses nitrogen (N₂) into the metal surface to create a case-hardened and corrosion resistant surface. Plasma nitriding is used most generally for converting the metal surface to a nitride, but it is also accomplished using gas and chemical treatments. It is a commonly used to harden and increase the corrosion resistance not only of steels but also for Ti, Al and Mo. The plasma nitriding process consists of ion bombardment by nitrogen ions from a plasma onto a metal surface, which incorporates high concentrations of gas into the surface and forms a metal nitride with atoms on the surface [14,15,16].

An additional advantage of this process is that it also allows in-situ surface cleaning by sputtering and hydrogen reduction. Typically a plasma containing NH₃, N₂ or N₂-H₂ is used along with substrate heating to 500-600°C to nitride steel. The term “ionitriding” refers to the plasma nitriding process [17]. Bombardment from a nitrogen plasma can be used to plasma nitride a steel surface prior to the deposition of a TiN film [18]. Plasma carburizing [19] is done in a carbon containing environment and low temperature plasma boronizing can also be performed [20].

Plasma nitriding enhances the corrosion and wear resistance of austenitic steels, electroplated hard chrome, titanium medical implants, injection nozzles and gears and cast automotive parts [21]. As with all ion implantation processes, the thickness of the nitride layer depends on several factors: temperature, time, dose, crystal structure and ion energy [13, 21]. Figure 8 shows SEM images of a nitride layer in X5CrNi18 and X6Cr17 steels and Figure 9 shows the dependence of diffusion depth of Fe₄N in EN 19 steel on time and temperatures of 450°C and 530°C [21]. The lattices of X5CrNi18 and X6Cr17 steels are different with diffusion being faster in the lattice with a body centered cubit (b.c.c) crystal structure of X6Cr17 steel. Note that Fe₄N thickness increases significantly faster at the higher nitriding temperature.
Figure 8. SEM image of nitride layer in X5CrNi18 and X6Cr17 steels [13].

Figure 9. Dependence of $\text{Fe}_6\text{N}$ diffusion depth in EN 19 steel with time temperatures of 450°C and 530°C [21].
The effectiveness of a corrosion resistant treatment is assessed by how much weight is lost during exposure to the corrosive environment [3,5]. Total mass loss due to corrosive wear [3] can be expressed as:

\[ M_{\text{tot}} = M_{\text{mech}} + M_{\text{C}} + M_{\text{syn}} \]

Where \( M_{\text{mech}} \) is mass loss due to purely mechanical wear (no corrosion), \( M_{\text{C}} \) is mass loss due to static corrosion (no mechanical wear) and \( M_{\text{syn}} \) is mass loss due to synergistic effects. Friction and wear enhance the sensitivity of the surface to corrosion and conversely, corrosion may modify the effects of friction [22]. As a result, \( M_{\text{syn}} \) can be expressed as the sum of two components: \( M_{\text{C-W}} \) and \( M_{\text{W-C}} \) (wear enhanced corrosion and corrosion enhanced wear). Thus:

\[ M_{\text{tot}} = M_{\text{mech}} + M_{\text{C}} + M_{\text{C-W}} + M_{\text{W-C}} \]

Table 2 shows mass loss of Ti-6Al-4V alloy with tribo-corrosion testing. For Ti-6Al-4V, wear was found to significantly increase electrochemical reaction rate; \( M_{\text{C-W}} \) is three orders of magnitude higher than \( M_{\text{C}} \). However, corrosion has negligible effect on wear rate (\( M_{\text{C-W}} \ll M_{\text{mech}} \)).

Possible mechanism of tribo-corrosion involves effects such as infiltration of liquid through nano-scale porosities or pathways in the film, followed by electrochemical reaction with the substrate leading to the reduction of adhesion strength.

Table 2. Total mass loss and its components after tribo-corrosion tests [4].

<table>
<thead>
<tr>
<th>Component</th>
<th>Material loss (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_{\text{tot}} )</td>
<td>2.7x10^{-2}</td>
</tr>
<tr>
<td>( M_{\text{mech}} )</td>
<td>2.3x10^{-2}</td>
</tr>
<tr>
<td>( M_{\text{C}} )</td>
<td>1.1x10^{-6}</td>
</tr>
<tr>
<td>( M_{\text{C-W}} )</td>
<td>3.4x10^{-3}</td>
</tr>
<tr>
<td>( M_{\text{W-C}} )</td>
<td>2.0x10^{-4}</td>
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</tbody>
</table>

One important application for nitriding is the protection of hot forged cast steel parts, and parts for diesel automotive engines in particular [21, 23].

**Thin Films**

Corrosion and wear resistant thin film materials are now used in many applications instead of anodizing, nitriding and nitrocarburizing metal surfaces, and are often used to increase corrosion resistance of already-treated surfaces [17]. Because thin film materials are not constrained by bulk thermodynamics, virtually any composition can be synthesized. To this end, a wide range of thin film materials, much more expansive than the above treatments can address, is used to increase corrosion resistance and decrease corrosive wear of metal and other types of surfaces. Many of the corrosion resistant thin film
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materials, however, also have their counterparts as bulk materials (see above). Additionally, we now have a full range of oxides, nitrides, oxynitrides, carbides and nanocomposites at our disposal [16].

Corrosion resistant thin films have the following general characteristics:

- Inert to the environment
- Wide range of thicknesses
- High density
- Multilayers possible
- Nanocomposites possible
- Continuous over the entire area (prevent permeation)
- Low permeability
- Very low porosity
- Low stress
- Large area coverage

Examples of corrosion and wear resistant thin film materials are TiN, TiAlN, diamond like carbon (DLC), CrN, TiAINb, TiC, aluminum bronzes \((Cu_xAl_y: y \approx 5\%\)\), aluminum nickel bronze \((AlNiCu: \approx 4\% Ni)\), aluminum niobium bronze \((AlNbCu)\) and aluminum manganese bronze \((AlMnCu: 2–5\%Mn)\).

Aluminum bronze films have demonstrated superior high temperature corrosion resistance in reducing oxidation in hydrogen atmospheres. There are literally dozens of corrosion and wear resistant composites; examples include TiN/Si3N4, TiC,Ny/SiCN, TiAIN/CrN, DLC/TiC/TiN/Ti, TiBN, CrN/NbN and TiN/CrN [24]. All these nanocomposites have hardness in the “superhard” range.

Corrosion and wear resistance of a nitride or carbonitrided surface can be further enhanced by application of a “duplex” protective thin film [3, 21]. Figure 10 shows a SEM image of a TiN thin film deposited over plasma nitrided high speed steel [21] and Figure 11 shows a DLC film deposited on a nitried 316L stainless steel surface [3]. Both these materials are being developed for biomedical applications such as corrosion protection of hip and knee prostheses. Figure 12 compares the hardness of untreated TiAl5Fe2.5, nitried TiAl5Fe2.5 and nitried TiAl5Fe2.5 with a TiN overcoat [21]. Note that hardness increases significantly with plasma nitriding and further increases with the TiN coating.
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Figure 10. TiN film deposited over plasma nitrided high speed steel [21].

Figure 11. DLC coating deposited over plasma nitrided 316L stainless steel [3].
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Figure 12. Comparison of the hardness of untreated TiAl5Fe2.5, nitrided TiAl5Fe2.5 and nitrided TiAl5Fe2.5 with a TiN overcoat [21].

Tribo-corrosion properties of CrN coatings show promise. When applied to 301 stainless steel, CrN coatings reduced corrosive wear resistance by a factor of 200 compared to mechanical wear [3]. Corrosion protection is critical for reflective surfaces exposed to atmospheric conditions [25, 26]. Thin film materials such as TiN, ZrN, TiAlN, TaN and related alloys are also used as corrosion resistant and wear resistant decorative coatings [27, 28]. Highly reflective thin film materials such as Al and Ag are susceptible to chemical attack by oxygen and sulfur in the air. Additionally, these metals must be protected by transparent thin film coatings. Materials such as AlN, Al2O3, Si3N4, TiO2 and SiO2 are most often used for these applications. However, Ta2O5, Nb2O5 and ZrO2 as well as multilayer coatings are also used [25, 25, 26, 27].

Note that in most cases (except DLC) the highest quality thin films are deposited by magnetron sputtering. Sputtering targets for these thin film materials are available at Materion. Evaporation and thin film materials are also available.

We have presented treatments that are used to mitigate corrosion and tribo-corrosion of metal surfaces. Metal alloying, anodizing, plasma nitriding and carbonitriding and thin film deposition are all effective at reducing corrosion and corrosive wear. The most versatile and cost effective treatment is protective thin film materials. Additionally, thin films can be deposited over large areas.

Recommended reading:


Reference:

5.  See (http://properties.copper.org)