Chapter 23

Dealloying

Locations

Dealloying, other than in cast irons (see Chap. 22, "Graphitic Corrosion"), usually occurs in copper-containing alloys. Corrosion is confined primarily to feedwater systems and afterboiler regions. Areas that can suffer attack include high-pressure feedwater heaters, bronze pump impellers, Monel steam strainers, and boiler peripherals such as brass pressure-gauge fittings. Condensers and heat exchangers are also frequently affected.

General Description

Dealloying is a corrosion process in which one or more alloy components are removed preferentially. The corroded region usually has a markedly different structure than the original alloy. However, macroscopic dimensions of the corroded part often remain unchanged. The process is also referred to as *selective leaching,* or *parting.* Obviously, dealloying can occur only in alloys containing two or more elements. Particularly susceptible alloys are cupronickels (in which nickel is removed) and brasses (in which zinc and aluminum are leached). The name given to a particular dealloying process derives from the leached element. For example, in common brasses where zinc is removed, dealloying is referred to as *dezincification.* In situations where nickel is removed from cupronickels, dealloying is referred to as *denickelification.*

Figure 23.1 Plug-type dezincification beneath a deposit in admiralty brass tube.

There are two commonly recognized forms of dezincification. Attack is either of a *plug* or *layer* type. Small localized areas of metal loss occur in the tube wall, producing plugs that can be blown out of pressurized tubes (Fig. 23.1). More general attack is called *layer-type dezincification* (Fig. 23.2). Cupronickels are more prone to layer-type attack than to plug-type deterioration. However, cupronickel wastage is usually slight compared to attack in brasses. It is likely that fundamental mechanisms of plug-type and layer-type attack are similar. However, plug-type attack can produce localized wastage rates of up to several hundred milliinches per year, while much milder attack is common with layer-type dealloying.

Destannification (loss of tin) can occur in gunmetal and some phosphor bronzes. This is especially the case in steam environments and in hot feedwaters. Monel steam strainers have been attacked when exposed to steam containing sulfur compounds at elevated temperatures (Fig. 23.3).

Figure 23.2 Layer-type dezincification of a brass pump component.

Dealuminification of duplex aluminum bronzes has been reported in waters having both high and low pH.

Critical Factors

Deposits, soft waters (especially those containing carbon dioxide), heat transfer, stagnant conditions, either high- or low-pH waters, and high-chloride waters accelerate most forms of dealloying in copper-containing alloys. Addition of small amounts of arsenic, antimony, or phosphorus to admiralty brasses has materially reduced the tendency to dezincify. However, attack may still occur under extreme conditions.

Identification

In cupriferous alloys, copper is almost never selectively removed. Rather, other elements are dissolved, leaving behind a comparatively soft, porous mass of copper. Attacked metal is relatively brittle and can be broken easily by impact or bending. Frequently, surfaces will be riddled with cracks, but will retain original dimensions. Attacked areas will usually

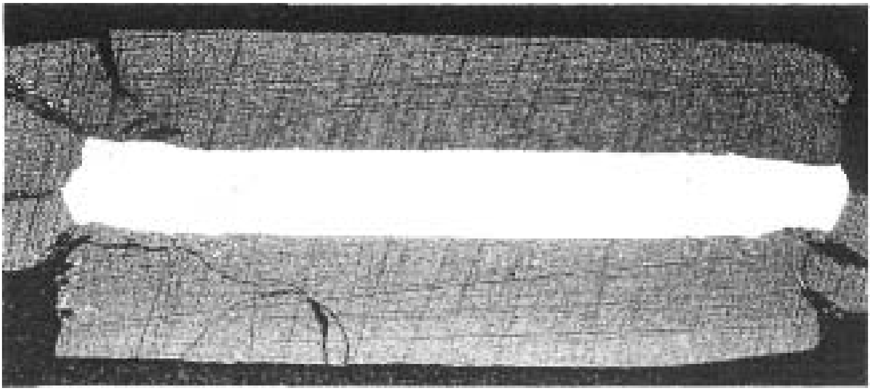

Figure 23.3 Cross section through a corroded Monel metal steam strainer. The dark area consists of oxides, sulfides, and elemental copper (Magnification: 15X.)

Figure 23.4 Peeling surfaces on a cupronickel high-pressure feedwater heater tube.

change to a deep red or salmon color of elemental copper (Figs. 23.1 and 23.2).

High-pressure feedwater tubes made of cupronickel may experience a unique form of dealloying. Air may gain access to shell-side surfaces during outages, causing considerable oxidation. Subsequent normal operation causes the surface oxides to be reduced to elemental copper. Eventually, sheets of oxide and/or reduced metal may peel off surfaces, giving the tubes an odd, sunburned appearance (Fig. 23.4). Alloys such as 70:30 cupronickels are particularly susceptible to this form of exfoliation. Alloys such as 80:20 are susceptible to a lesser extent. Such wastage is rare in 90:10 cupronickels.

Elimination

Surfaces should be kept free of deposits. In general, outages should be as short as is practical. Air contact should be prevented by steam or nitrogen blanketing. Water and steam quality must be controlled so that chloride- and sulfur-compound concentrations are minimized. Substitution of alternative alloys may be necessary. Use of inhibited grades of admiralty brass should be insisted upon when conditions dictate.

Related Problems

See Chap. 22, "Graphitic Corrosion."

CASE HISTORY 23.1

Industry:	Utility
Specimen Location:	Turbine steam strainer
Specimen Orientation:	Vertical
Years in Service:	16
Water-Treatment Program:	Phosphate
Drum Pressure:	1500 psi (10.3 MPa)
Specifications:	Monel wire, 0.15 in. (0.4 cm) diameter
Fuel:	Coal

A Monel turbine steam strainer was discovered to contain many broken elements. The metal was converted to oxide, sulfide, and elemental copper (Fig. 23.3). The deteriorated metal consisted of numerous elemental copper particles embedded in an oxide–sulfide matrix. Cracks in the wasted metal were lined with elemental copper.

Failure was attributed to carryover of sulfur-containing compounds in the steam. The system had a history of poor steam purity and carryover of boiler water into the superheater.

CASE HISTORY 23.2

Industry:	Utility
Specimen Location:	Inlet first pass of high-pressure feedwater heater
Specimen Orientation:	Horizontal
Years in Service:	7
Water-Treatment Program:	All volatile
Pressure:	400 psi (2.6 MPa)
Tube Specifications:	⅝ in. (1.6 cm) outer diameter, 70:30 cupronickel

Feedwater heater tubes were thinned by cyclic oxidation followed by reduction of oxides in service (Fig. 23.4). Wall thickness was reduced by as much as 15%.

During the previous 2 years, the boiler had experienced frequent outages in which air leaked into the heater shell and caused surface oxidation. Conversion of oxide to elemental copper occurred during normal operation.