CHAPTER I

CORROSION CHARACTERISTICS OF BRASS
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Copper-zinc alloys i.e., brasses are amongst the oldest known to man. The Romans were the first people to make brass. Although unacquainted with zinc, Romans prepared brass by melting copper with calamine - an ore of zinc. This method was followed upto the middle of nineteenth century and the product was known as calamine brass.

The copper-zinc alloys are prepared by melting together various elements and casting the metallic melt as bars and billets. These are, then, processed in requisite physical form by rolling, extruding or piercing. The coarse dendritic structure of cast alloys is refined during the working process leading to improvement in physical properties.

The properties responsible for the importance of copper alloys are -
- generally good corrosion resistance.
- good electrical and thermal conductivities.
- good workability at hot and cold temperature.
- ease of welding, brazing or soldering.
- high malleability and ductility.
Copper and zinc melted together in various proportions produce brasses. Six different phases are formed which are named as alpha, beta, gamma, delta, epsilon and eta. As the copper content decreases the alloys become increasingly difficult to cold work and hence alloys having more than 42% zinc have limited commercial applications. Alloys containing less than 58% copper have all the desirable properties listed above. Typical uses of copper zinc alloys in conditions where corrosion resistance is important are given in Table 1.1, page 9.

Aside from gold, copper alloys are the only alloys which have natural red to yellow colour. As the copper content decreases from 100%, the brasses vary in colour.

- 90% Cu - 10% Zn : rich bronze hue
- 85% Cu - 15% Zn : golden hue
- 70% Cu - 30% Zn : yellow hue
- 60% Cu - 40% Zn : reddish-yellow hue

Copper and its alloys are very resistant to corrosion. The corrosion resistance of copper is due to its relative chemical inertness and due to the formation of a protective film. Copper lies towards the bottom of electrochemical series of metals, well below hydrogen. When an electrolytic couple is formed between copper and another metal, copper is, in most cases, the cathode so that it is electro-chemically protected.
Types of Corrosion

Copper-zinc alloys are subject to two special types of corrosion processes:

(1) Season cracking
(2) Dezincification.

Season cracking is a form of stress corrosion cracking. It is mostly intergranular, occurring even in mildly corrosive conditions, when external stress exists in brass after cold work. Season cracking can be effectively controlled by relief annealing (at temperatures high enough to permit crystalline readjustment but not high enough to permit softening) or by the employment of balancing conditions in the last cold working operations. Presence of elements or compounds at grain boundaries decreases resistance to this type of failure by causing intergranular weakness.

In dezincification, zinc atoms are removed from the solid solution more readily than copper atoms. Dezincification of brass occurs in acids, acidic and salt water and some impure and hard waters. It may also occur in heating thin sections of brass through vapourization of zinc from the surface.

Alloys containing 80% copper or less may dezincify severely under corrosive conditions. Muntz metal has the least resistance in this respect. Corrosion
resistance as indicated by the loss of strength and penetration by pitting at the water line or by dezincification changes only slightly until the copper content drops below 85%.

The occurrence of stress corrosion follows the same pattern i.e., alloys of higher zinc content are most susceptible. A marked increase in resistance is shown by alloys containing more than 85% copper.

However, in the case of sulfur corrosion, the behaviour is reversed. Low copper alloys are most resistant to sulfur corrosion and high copper alloys are the least resistant. There is no abrupt change in the resistance to sulfur corrosion in the 80-85% copper range.

Copper base alloys in galvanic coupling with a less noble metal like aluminium, steel or zinc, increase the corrosion of latter metals. However, copper and iron are coupled with each other in handling fresh water and slightly corrosive liquids.

Influence of Medium

The corrosion of copper-zinc alloys in aqueous solution is considerably influenced by concentration of dissolved gases. Sulphur dioxide dissolved in water is more active than dissolved oxygen due to its action as a mild oxidising acid. Dissolved carbon dioxide appreciably
Increases corrosion rate. Hydrogen sulphide accelerates the corrosion of copper-zinc alloys.

Copper-zinc alloys show a very good resistance to unpolluted fresh water. Non-scale forming fresh waters containing aggressive carbon dioxide show a high corrosion rate for high zinc brasses. Dissolved salts vary considerably in their influence on the corrosion of copper-zinc alloys.

Huntz metal suffers from rapid dezincification in sea water. When dezincification is not an influencing factor, the corrosion rates of alloys containing more than 65% copper are quite low. In warm and hot waters, the susceptibility towards pitting is increased considerably.

Copper-zinc alloys show very high corrosion rates in nitric acid, sulfurous acid, hydrochloric acid; sulfuric acid is less corrosive than hydrochloric acid. In absence of oxygen, the corrosion rate of copper-zinc alloys in dilute sulphuric acid is practically negligible. Acetic acid, and other fatty acids attack brasses.

Alkalies attack the copper-zinc alloys, this attack is enhanced by increased aeration and elevated temperatures. Ammonium hydroxide is much more corrosive than alkalies.

Acidic non-oxidising salts which hydrolyse to give acidic solutions behave in a manner analogous to that of
dilute solutions of corresponding acids. In neutral salts, the order of corrosivity is NaI > NaBr > NaCl > NaF. Alkaline salts attack the copper-zinc alloys at the rate of 0.002 to 0.005 ipy. Oxidising salts corrode copper-zinc alloys at high rates. Salts of metals more noble than copper, corrode copper-zinc alloys.

Presence of mercury induces intercrystalline cracking on brasses stressed internally.

Dry halogens, anhydrous hydrofluoric acid, ammonia are non-corrosive to brasses but in the presence of moisture, they are very corrosive. Sulfur dioxide shows corrosive effect when its concentration is more than 0.9% and when humidity rises above 70%. Hydrogen sulphide corrodes brasses even at low humidity. Alloys containing more than 30% zinc resist the action of hydrogen sulfide better. Dry carbon dioxide is not corrosive to brasses but in the presence of moisture and oxygen, it is mildly corrosive. Carbon monoxide and nitrogen are non-corrosive to brass.

Methanol, formaldehyde, butyraldehyde, benzaldehyde and antifreeze solutions containing alcohols or glycols corrode copper-zinc alloys. Organic chlorides, bromides and fluorides have a very little effect.
Effect of Alloying Constituents

Iron and manganese accelerate dezincification but tin retards it, especially in cast alloys. An addition of tin to brasses improves corrosion resistance, increases strength and hardness and tends to lighten colour. Of the naval brasses, manganese bronze (68.0% Cu, 39.9% Zn, 0.1% Mn, 1.0% Sn, 1.0% Fe) has the best mechanical properties and corrosion resistance. Arsenic, antimony and phosphorous in the amounts of 0.3-0.05% are added to admirality brass but arsenic is most widely used.

An addition of aluminium upto 2.0% increases strength and corrosion resistance of various brasses. Aluminium brass (76% Cu, 2% Al, 22% Zn) is very useful for condensers, its advantage being the high resistance to impingement attack which is destructive to admirality and common brasses. High resistance is due to the presence of aluminium which promotes the development of a strong tenacious surface in which aluminium oxide is an important constituent. This film resists attack by high velocity cooling water and it is self-healing when damaged by erosion. An addition of 0.02-0.05% arsenic to aluminium brass increases its resistance to dezincification. The effect of alloying constituent on dezincification of brass is discussed in Chapter VII.

Nickel-copper-zinc alloys known as nickel silvers have high resistance to corrosion, pleasing white colour and excellent properties.
TABLE I-1

Typical Uses of Copper-Zinc Alloys Where Corrosion Resistance is Important

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muntz metal</td>
<td>Architectural trimming; nuts and bolts; condenser, evaporation, and heat-exchanger tubes; condenser plates; valve stems.</td>
</tr>
<tr>
<td>Yellow brass</td>
<td>Grillwork; radiator cores; tanks; fasteners; pins, rivets, and screws; springs; sink strainers.</td>
</tr>
<tr>
<td>Cartridge brass</td>
<td>Radiator cores; tanks; fasteners; pins and rivets; springs; ammunition components.</td>
</tr>
<tr>
<td>Low brass</td>
<td>Architectural trimming; battery caps; bellows; musical instruments; flexible hose; pump liners.</td>
</tr>
<tr>
<td>Red brass</td>
<td>Architectural trimming; weather strip; fasteners; fire extinguishers; plumbing pipe; name plates and tags.</td>
</tr>
<tr>
<td>Commercial bronze</td>
<td>Screening; weather strip; line clamps, rivets, and screws; marine hardware.</td>
</tr>
<tr>
<td>Leaded brasses</td>
<td>Architectural trimming; hinges; rivets, nuts and screws; watch and clock parts; instrument plates.</td>
</tr>
<tr>
<td>Manganese bronze</td>
<td>Balls; shafting; valve stems and bodies.</td>
</tr>
<tr>
<td>Naval brass</td>
<td>Balls; propeller shafts; valve stems; rivets, nuts, and bolts; condenser plates.</td>
</tr>
<tr>
<td>Admiralty brass</td>
<td>Condenser, evaporator, heat exchanger and distiller tubes; forrules.</td>
</tr>
<tr>
<td>Aluminium brass</td>
<td>Condenser and heat-exchanger tubes.</td>
</tr>
</tbody>
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REFERENCES


