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Copper Alloys for Marine Environments

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CDA Publication No 206
May 2011
Revised December 2012

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Cover page picture acknowledgement:
Copper-nickel splash zone sheathing on a platform in the Morecambe Field
(Courtesy Centrica Energy Upstream, East Irish Sea)

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1.0 Introduction

The aim of this publication is to provide engineers with an appreciation of copper alloys commonly used in marine applications. It will provide an overview of the range of alloys and their properties, and give references and sources for further information.

Copper is a metal that is extracted from the earth, is essential to the development of all forms of life and has been vital in the progress of civilisation. Alongside gold, it is the oldest metal used by man and its history of use dates back more than 10,000 years.

Since antiquity, both wrought and cast forms of copper alloys have shown high resistance to the ravages of the marine environment, like the bronze cannon in Figure 1. Seawater is corrosive to most construction materials and, with properties which have been developed and modified to meet today's exacting engineering challenges, copper alloys continue to offer solutions to a range of industries requiring reliability in seawater.

The metal copper is very versatile, having good resistance to corrosion in marine atmospheres and in seawater with moderate flow velocities. Its properties, both in terms of corrosion resistance and mechanical strength, can be further improved by alloying. There are many copper alloys suitable for marine service and the main groups are:

Coppers
Copper-nickels
Bronzes
Brasses
Copper-beryllium

All copper alloys can be machined accurately and cost-effectively and to a good standard of tolerance and surface finish. Some copper alloys have excellent machinability as a primary attribute - specifically leaded brasses, which set the standard by which all other metals are judged. Other copper alloys are made with a variety of combinations of properties such as strength, wear resistance, anti-galling and cold formability. These may be less easily machined, but are still easier to machine than many other types of material.

For seawater systems, copper-nickel and aluminium bronze are often preferred, although other copper alloys are used in marine service and have their specific advantages. Copper alloys differ from other metals in that they have an inherent high resistance to biofouling, particularly macrofouling, which can eliminate the need for antifouling coatings or water treatment.

Figure 1 - Underwater photo of royal crest still plainly visible on a bronze cannon on a warship wrecked in 1744
(Courtesy Odyssey Marine Exploration)

2.0 Copper Alloy Groups: Properties and Applications

There are many copper alloys which fall within each group and a selection are examined here. Copper Development Association publication 120 *Copper and Copper Alloys*(1) gives a more comprehensive breakdown of standards, compositions and properties. Typical applications for marine environments include heat exchangers and condensers, seawater piping, hydraulic tubing, pump and valve components, bearings, fasteners, marine fittings, propellers, shafts, offshore sheathing and aquaculture cages.

The alloy groups, and alloys within each group, are described in Table 1.

Table 1 – Alloy Groups

Alloy Group	Alloy Types
Coppers	Cu
Copper-nickels	90-10 Cu-Ni 70-30 Cu-Ni Cu-Ni-Cr Cu-Ni-Sn Cu-Ni-Al
Bronzes	Cu-Sn-P (phosphor bronze) Cu-Sn-Zn (gunmetal) Cu-Al (aluminium bronze/nickel aluminium bronze) Cu-Si (silicon bronze)
Brasses	Cu-Zn
Copper-beryllium	Cu-Be

Copper and copper alloys are produced to conform with a wide variety of national and international specifications prepared to suit different conditions and requirements. They are ductile and may be manufactured by extrusion, forging, rolling, drawing, hot stamping and cold forming. They can also be cast by all of the traditional casting methods such as sand and die, and by continuous and centrifugal methods.

Table 2 gives a selection of EN standards for copper and copper alloy product forms. It is clear that, by selection of the appropriate wrought or cast route, almost any shape can be obtained. For example, by the use of centrifugal casting, tubes in bronzes may be made which would either not be covered in the wrought specifications or be of non-standard sizes.

Minimum mechanical properties will depend on the product form, specification used, dimensions and material condition. Mechanical properties of copper alloys can range from 'moderate' in the case of the coppers to 'extremely high' for the Cu-Ni-Sn, Cu-Ni-Al and Cu-Be alloys. Annealed values can be increased by cold work for copper and alloys such as brasses, phosphor bronzes and copper-nickels, but the highest values are achieved from age hardened alloys which are heat treated to strengthen the metal matrix by forming precipitates in the structure. Copper alloys do not undergo a ductile-brittle transition, as mild steel does, and are ductile down to cryogenic temperatures. The highest strength of any copper alloy is given by the copper-beryllium alloys, which may be hardened by a combination of cold working and age hardening to values comparable to that of high strength steel.

Table 3 shows the range of conditions available for copper alloys in the USA. The terms used in the table will be recognised

Table 2 – Selection of European Standards for Product Forms in Copper and Copper Alloys

Product Form	EN No	Full Standard Title
Plate, sheet, strip and circles	1652	Copper and copper alloys. Plate, sheet, strip and circles for general purposes
Strip (springs and connectors)	1654	Copper and copper alloys. Strip for springs and connectors
Seamless tubes	12449	Copper and copper alloys. Seamless, round tubes for general purposes
Seamless heat exchanger tube	12451 12452	Copper and copper alloys. Seamless, round tubes for heat exchangers Rolled, finned seamless tubes for heat exchangers
Rod	12163	Copper and copper alloys. Rod for general purposes
Wire	12166	Copper and copper alloys. Wire for general purposes
Profiles and rectangular bar	12167	Copper and copper alloys. Profiles and rectangular bar for general purposes
Forgings	12420	Copper and copper alloys. Forgings
Ingots and castings	1982	Copper and copper alloys. Ingots and castings

Table 3 – Examples of Temper Designation for Copper Alloys (ASTM B601 – Standard Classification for Temper Designations for Copper and Copper Alloys – Wrought and Cast)

Temper Designation	Temper Name or Condition
Annealed Conditions	
O10	Cast & Annealed
O20	Hot Forged & Annealed
O60	Soft Annealed
O61	Annealed
O81	Annealed to Temper: ¼ Hard
OS015	Average Grain Size: 0.015mm
Cold Worked Tempers	
H01	¼ Hard
H02	½ Hard
H04	Hard
H08	Spring
Cold Worked & Stress Relieved Tempers	
HR01	H01 & Stress Relieved
HR04	H04 & Stress Relieved
Precipitation Hardened Tempers	
TB00	Solution Heat Treated
TF00	TB00 & Age Hardened
TH02	TB00 & Cold Worked & Aged
TM00 / TM02 / TM08	Mill Hardened Tempers
Manufactured Tempers	
M01	As Sand Cast
M04	As Pressure Die Cast
M04	As Investment Cast

Table 4 – Letter Symbols for Property Designations (EN 1173)

A	Elongation
B	Spring bending limit
G	Grain size
H	Hardness (Brinell for castings, Vickers for wrought products)
M	(as) Manufactured, i.e. without specified mechanical properties
R	Tensile strength
Y	0.2% proof strength

in the UK and Europe but European specifications, which were introduced to give one harmonised series of standards for all European countries, use different terminology to describe the same range of conditions.

European copper and copper alloy material condition (temper) designations are defined in EN 1173. The principal mandatory properties for material condition are defined by a letter as in Table 4. For example, tensile strength R250 indicates the minimum of 250 N/mm^2, while a hardness of H090 indicates a minimum value of 90 (Vickers for wrought materials and Brinell for cast). Copper and copper alloys may be selected to an R or H value but not both.

For further details of material designations see Copper Development Association Publication 120(1) and standards such as BS EN 1652:1998 'Copper and copper alloys - plate, sheet, strip and circles for general purposes' and others referred to in Table 2.

Copper alloys are also used for their physical properties, having very high levels of thermal and electrical conductivity. The high thermal conductivity associated with copper and many of its alloys means that heat is quickly dissipated from components and this is used to good effect in heat exchangers. Coppers, copper-nickels and aluminium brass make use of their thermal conductivity in exchangers such as oil coolers and steam condensers. High melting points are a safety feature in the case of fire; they will not creep (flow) like some materials such as aluminium and plastics. Table 5 compares the physical and mechanical properties of copper, aluminium brass, an aluminium bronze and a copper-nickel alloy.

The following sections examine alloys from each group and define typical applications, compositions and mechanical properties. Corrosion behaviour and other properties are highlighted where important for these alloys.

It is important to note that, throughout this publication, tables refer to both EN and UNS nomenclatures. The comparison is based on similarity of composition only and it may not be exact. Also, related specifications may call up differences in properties and testing. The information here is given for general guidance only and full standards should be referred to for specific information.

2.1 Coppers

There are two main grades of copper:

- Electrical (99.99% Cu) e.g. CW004A
- Engineering (99.90% Cu) e.g. CW024A

Coppers have a high purity and a single phase metallurgical structure which makes them formable and ductile. The engineering grade, Copper DHP (Deoxidised High Phosphorus - CW024A) is commonly used for tubing in marine environments and is deoxidised with phosphorus to facilitate brazing.

The thermal conductivity of copper, 394 W/mK, is about twice that of aluminium and thirty times that of stainless steel. This means that copper is used for components where rapid heat transfer is essential such as heat exchangers.

Mechanical properties are given in Table 6. The tensile strength can be increased from the annealed condition by cold work. Mechanical properties of electrical and engineering coppers are identical. Applications are given in Table 7.

In addition to high thermal and electrical conductivity, coppers have good corrosion resistance in the marine atmosphere and seawater, showing very little pitting or crevice corrosion, together with high resistance to biofouling. However, when seawater conditions are polluted with ammonia and sulphides, higher corrosion rates or pitting can be experienced.

There are also limitations on the flow velocity in copper pipework to avoid erosion corrosion (see page 18 regarding Erosion Corrosion and Figure 11). Other alloys such as aluminium brass or copper-nickels are preferred if the flow velocities are too high for copper.

Table 5 – Typical Physical and Mechanical Properties

Alloy	EN No (UNS No)	Melting Point °C	Density (g/cm^3)	Coeff of Expansion x 10^{-6}/°C	Electrical Conductivity % IACS	Thermal Conductivity (W/mK)	Tensile Strength (N/mm^2)	Elongation (%)	Hardness HV
Copper	CW024A (C12200)	1083	8.94	18	97*	394	200-400	5-50	40-120
Aluminium brass	CW702R (C68700)	971	8.3	20	23	101	340-540	20-60	80-160
Nickel aluminium bronze	CW307G (C63000)	1075	7.95	18	15	38	430-770	5-15	170-220
90-10 copper-nickel	CW352H (C70600)	1150	8.91	16	10	40	290-520	8-35	80-160

* If high electrical conductivity is essential (up to 103% IACS), then the electrical grade of copper CW004A should be used.

Table 6 – Typical Mechanical Properties of Engineering Copper

Alloy	EN No	UNS No	0.2% Proof Strength N/mm^2	Tensile Strength N/mm^2	Elongation %	Hardness HV
Engineering Copper	CW024A	C12200	50-340	200-400	5-50	40-120

Table 7 – Typical Applications for Engineering Copper

Alloy	Applications
Engineering Copper	Seawater piping, heat exchangers, fuel lines, nails

Summary

- Coppers have very high purity
- 0.2% proof strength 50-340 N/mm^2; tensile strength 200-400 N/mm^2
- High thermal and electrical conductivity
- Good corrosion resistance in the marine atmosphere and seawater
- High resistance to biofouling
- Avoid exposure to polluted seawater and high flow velocities
- Seawater piping, heat exchangers, fuel lines and nails.

2.2 Copper-nickel Alloys

The copper-nickel alloying system is relatively simple, enhancing the overall properties of copper in terms of strength and corrosion resistance while maintaining a high inherent resistance to biofouling. The 90-10 copper-nickel alloy (CW352H, C70600) is the most commonly used wrought copper alloy for marine engineering and can be found in seawater systems for naval and commercial shipping and offshore oil and gas production, as well as in desalination and aquaculture. Alloys with higher nickel content, and those which are more highly alloyed with chromium, aluminium and tin, are used where greater resistance to flow conditions, sand abrasion, wear and galling are required, as well as higher mechanical properties or castability.

Table 8 shows typical applications for the copper-nickel alloys and Tables 9 and 10 show compositions and mechanical properties respectively. In overviewing these alloys, they are separated into two groups: the general engineering 90-10 and 70-30 copper-nickel alloy grades and the high strength grades.

2.2.1 90-10 and 70-30 Copper-nickel Alloys

While the more economical 90-10 copper-nickel alloy (CW352H, C70600) is the most widely used, the 70-30 copper-nickel alloy (CW354H, C71500) is stronger and can withstand higher flow velocities, making it favoured in the UK for submarine systems. Iron and manganese levels are important in optimising the corrosion resistance of both alloys and it is important these are within the limits given in international standards.

There is also a modified 70-30 alloy containing 2% Mn and 2% Fe (CW353H, C71640), which is only commercially available as condenser tubing. It was developed for higher resistance to erosion corrosion in the presence of suspended solids. It has been extremely successful in

Figure 2 - Copper-nickel pipework aboard ship
(Courtesy Eucaro Buntmetall GmbH)

Table 8 – Typical Applications for Copper-nickel Alloys

Alloy	Applications
General Engineering	
90-10 Cu-Ni and 70-30 Cu-Ni	Seawater cooling and firewater systems, heat exchangers, condensers and piping, offshore platform leg and riser sheathing, MSF desalination units, aquaculture cages and boat hulls
Cu-Ni-Cr	Wrought condenser tubing Cast seawater pump and valve components
High Strength Copper-nickels	
Cu-Ni-Al	Shafts and bearing bushes, bolting, pump and valve trim, gears, fasteners
Cu-Ni-Sn	Bearings, drill components, subsea connectors, valve actuator stems and lifting nuts, subsea manifold and ROV lock-on devices, seawater pump components

Table 9 - Nominal Compositions of Copper-nickel Alloys (weight %)

Alloy	EN No or Other Identification	UNS No	Cu	Ni	Fe	Mn	Al	Sn	Other
Cu-Ni	CW352H	C70600	Rem	10	1.5	1			
	CW353H	C71640	Rem	30	2	2			
	CW354H	C71500	Rem	30	0.7	0.7			
Cu-Ni-Cr	Def Stan 02-824 Part 1	-	Rem	30	0.8	0.8			1.8Cr
	-	C 72200	Rem	16	0.7	0.7			0.5Cr
Cu-Ni-Al	Nibron Special™	-	Rem	14.5	1.5	0.3	3		
	Def Stan 02-835	C72420	Rem	15	1.0	5	1.5		0.4Cr
Cu-Ni-Sn	-	C72900	Rem	15				8	

Table 10 - Typical Mechanical Properties of Copper-nickel Alloys

Alloy	EN No or Other Identification	UNS No	0.2% Proof Strength N/mm²	Tensile Strength N/mm²	Elongation %	Hardness HV
Cu-Ni	CW352H	C70600	100-350	290-420	12-40	80-160
	CW353H (tube only)	C71640	150 min	420 min	30 min	110
	CW354H	C71500	130-450	350-520	12-35	90-190
Cu-Ni-Cr	Def Stan 02-824 Part 1	-	300 min	480 min	18 min	
	-	C72200	110 min	310 min		
Cu-Ni-Al	Nibron Special™	-	555-630	770-850	12 min	229-240
	Def Stan 02-835	C72420	400 min	710 min	18 min	170
Cu-Ni-Sn	-	C72900	620-1030	825-1100	2-15	272-354

Table 11 - Typical Guidelines for Flow Velocities for 90-10 and 70-30 Copper-nickel Alloys in Seawater Systems, m/s(5)

	Maximum Velocities	
	C70600 (90Cu10Ni)	C71500 (70Cu30Ni)
Condensers and Heat Exchangers		
Once through	2.4	3.0
Two-pass	2.0	2.6
Piping		
$\leq$ 76 mm I.D with long radius bends	2.5	2.8
77-99 mm I.D with long radius bends	3.2	3.5
$\geq$100 mm I.D with long radius bends	3.5	4.0
Short radius bends	2.0	2.3

For long radius bend, r $\geq$ 1.5 O.D. NB: The minimum velocity for any tube/alloy is 0.9m/s

multi-stage flash desalination plants, particularly in the heat rejection and brine heater sections.

A fourth alloy has 16% Ni and 0.5% Cr (C72200) and was developed to allow higher flow velocities in condenser tubing.

General corrosion rates in seawater are normally between 0.02-0.002 mm/year, decreasing to the lower end of the range with time. Data for the increasingly low corrosion rates of 90-10 and 70-30 copper-nickel alloys are shown in Figure 3.

Copper-nickels have high resistance to chloride pitting, crevice corrosion and stress corrosion cracking and do not have localised corrosion limitations caused by temperature, as do stainless steels(3). Piping is typically used up to 100°C. However, it is important to keep flow velocities below certain limits to avoid erosion corrosion. For tube and pipe these limits depend on alloy, diameter, sand loadings and system design; more explanation is given in Section 3.3. Table 11 gives an example of guidelines as given in Defence Standard 02-781(5). The CW353H (C71640) and C72200 alloys can be used at relatively higher flow velocities.

Ammonia stress corrosion cracking in seawater or sulphide stress cracking/hydrogen embrittlement are not problem areas with these copper-nickels. However, ammonia can cause increased corrosion rates and can also cause low temperature hot spot corrosion in heat exchanger tubes where there is little or low flow(6,12). Sulphides can cause pitting and increased corrosion rates, usually in situations when aerated water mixes with sulphide containing waters. An established oxide film offers a good degree of resistance to such corrosion, as does ferrous sulphate dosing(3).

The 90-10 and 70-30 copper-nickel alloys are essentially ductile and available in all product forms. Their strength is increased by cold work but not age hardening. They can be joined by brazing and welding(7).

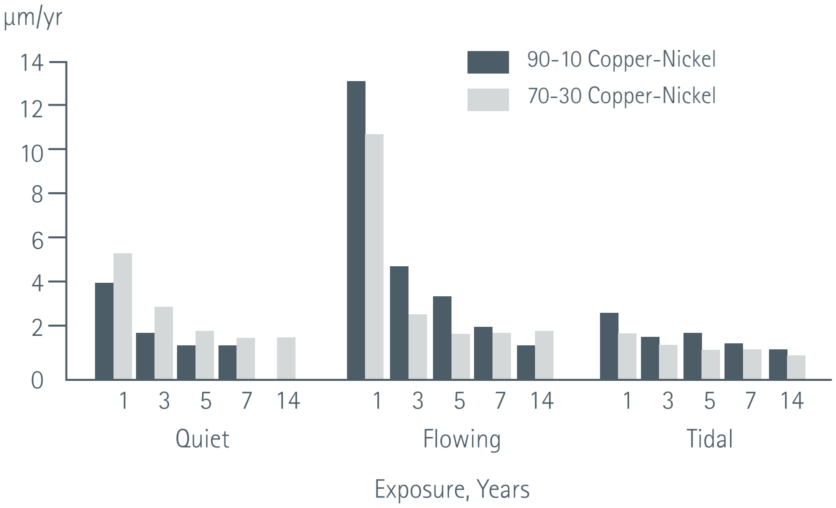

Figure 3 - Fourteen year corrosion rate data (2) at LaQue Center for Corrosion Technology, North Carolina, for 90-10 and 70-30 copper-nickels

Table 12 - Standards and Typical All-Weld-Metal Compositions of Filler Metals

Alloy	AWS*	International Standard**	Composition - Weight %				
			Cu	Ni	Mn	Ti	Fe
Covered electrodes							
70Cu-30Ni	A5.6 ECuNi	-	67	30	1.8	0.15	0.6
65Ni-30Cu	A5.11 ECuNi-7	EN ISO 14172 E-Ni 4060 (ENiCu30Mn3Ti)	30	63	3.5	0.2	2
Filler wires							
70Cu-30Ni	A5.7 ERCuNi	EN ISO 24373 S Cu 7158 (CuNi30Mn1FeTi)	67	31	0.8	0.3	0.5
65Ni-30Cu	A5.14 ERNiCu-7	EN ISO 18274 S Ni 4060 (NiCu30MnTi)	29	64	3.2	2.2	<1

* AWS - American Welding Society
** Preceded by national standard designation e.g. 'DIN EN ISO 18274'

Table 12 gives appropriate standards and typical weld metal compositions for weld consumables used. Note, the 70-30 Cu-Ni electrodes and filler metals are normally preferred for both 90-10 and 70-30 alloys. No post weld heat treatment is required to maintain corrosion resistance. Copper-nickel can also be welded to steel using the appropriate 65Ni-30Cu consumables.

A copper-nickel alloy with 30% Ni and 2% Cr was developed as a casting and is used by the UK Royal Navy (Def–Stan 02-824) as an alternative to nickel aluminium bronze for pumps and valves(8).

Further detailed information on these alloys and downloadable published papers about the corrosion performance, mechanical properties, fabrication and biofouling properties of copper-nickels can be found at www.coppernickel.org(4).

Summary

- 90-10 and 70-30 copper-nickels are the main grades and developed by the Royal Navy
- 0.2% proof strength 100-420 N/mm^2; tensile strength 290-520 N/mm^2
- High corrosion resistance. Piping typically used up to 100°C
- Good thermal conductivity
- Ductile and weldable
- Avoid polluted seawater and flow velocities higher than standard guidelines
- Biofouling resistance similar to copper
- Seawater systems, piping, condensers and heat exchangers, sheathing on offshore structures and boat hulls.

2.2.2 High Strength Copper-nickel Alloys

Two principal alloying routes have been used to enhance the mechanical strength of copper-nickel alloys: the Cu-Ni-Sn which relies on spinodal decomposition of the structure and Cu-Ni-Al system where precipitation hardening is used - see Tables 8, 9 and 10. Both types of alloy are able to achieve high strengths matching that of carbon steel. They are used subsea and applications include actuator stems, bushes, bearings and connectors.

2.2.2.1 Cu-Ni-Sn

Cu-Ni-Sn alloys are used subsea where bearing performance, non-magnetic, low-fouling, anti-galling or high strength properties are required such as for stems, bushes and bearings.

They have high strength, with proof strengths typically 690 to more than 1000 N/mm^2(9), and this is due to a process called spinodal strengthening which develops sub-microscopic chemical composition fluctuations in the alloy matrix by a controlled thermal treatment. They are weldable with a post-weld heat treatment being required for weldments if strength is a critical requirement. In marine applications, they are often selected where sliding movement and good resistance to corrosion and biofouling are required. The alloys retain 90% of room temperature strength at elevated temperatures as high as 300°C.

C72900 is one of the highest strength, low friction, non-magnetic, non-galling copper-based materials available that will work in most sour service conditions. Its seawater corrosion rate is very low, with high resistance to erosion corrosion even in sand-laden seawater. For practical purposes, it is not subject to hydrogen embrittlement in seawater and generally has acceptable resistance to embrittlement in dilute amine solutions.

2.2.2.2 Cu-Ni-Al

In Cu-Ni-Al alloys, the aluminium increases the strength by a conventional precipitation hardening mechanism, principally consisting of Ni_3Al (known as gamma prime). Additional elements are introduced to the basic Cu-Ni-Al ternary alloy to increase the effectiveness of this phase such as Fe, Nb and Mn. 0.2% proof strength levels of around 600 N/mm^2 are achievable, together with good anti-galling properties, whilst retaining low corrosion rates and resistance to hydrogen embrittlement. The alloys have been refined over the years to improve resistance to ammonia stress corrosion cracking(10).

Summary

- Copper-nickels can be strengthened by adding Al or Sn
- Cu-Ni-Sn is strengthened by sub-microscopical chemical fluctuations called spinodal strengthening to proof strengths of 690-1000 N/mm^2
- Cu-Ni-Al can be precipitation hardened
- Good corrosion and biofouling resistance, high strength, bearing and anti-galling properties
- Shafts, bearings, bolting, valve components, subsea clamps and connectors.

2.3 Bronzes

Traditionally, copper-tin alloys are associated with the word 'bronze'. However, today, the term refers to Cu-Sn alloys with further alloy additions to give improved strength such as Cu-Sn-Zn alloys (gunmetals) and Cu-Sn-P (phosphor bronzes). Importantly, it also now covers copper alloys which do not have a tin addition but are considered to provide the high qualities associated with the word bronze including Cu-Si (silicon bronzes) and Cu-Al (aluminium bronzes). Bronzes have superior resistance to ammonia stress corrosion cracking compared with brasses(3). Table 13 shows bronze alloys and typical applications. Compositions and mechanical properties are shown in Tables 14 and 15.

2.3.1 Phosphor Bronze

In binary Cu-Sn alloys, up to about 8% tin allows the alloy to be readily cold formed and significant increases in hardness and strength can be achieved. The mechanical properties are further improved by small alloying additions of phosphorus of up to 0.4%, leading to the name phosphor bronze. Castings can contain more than 8% Sn and, if so, may require soaking at temperatures of about 700°C until a second tin-rich phase disappears returning to a more corrosion resistant single phase alloy.

On the whole, the higher the tin content, the higher the seawater corrosion resistance. When properly manufactured, these alloys tend to corrode evenly and have little tendency to pit. The higher tin bronzes have good resistance to polluted seawater when compared to other copper alloys(6).

Summary

- Phosphor bronze alloys are tin bronze with ~0.4% P
- Good corrosion resistance with little tendency to pit
- 0.2% proof strength 170-1000 N/mm^2; tensile strength 390-1100 N/mm^2
- Springs, bearings, gears, fasteners.

2.3.2 Gunmetals

Gunmetals have been widely used in shipbuilding and marine engineering and are tin bronze castings which commonly have a small zinc addition which improves castability. As an alloy family, they can contain between 2-11% tin and 1-10% zinc. Modified forms may contain lead (up to 7%) giving leaded gunmetal or nickel (up to 6%) giving a nickel gunmetal. The term 'gunmetal' is used because, at one time, they were used for gun barrels. Gunmetals have good corrosion resistance and are not prone to dezincification, stress corrosion, crevice corrosion or pitting. For use in seawater, sound casting practices(11) and low levels of porosity are necessary. It is also preferable to choose a gunmetal with a tin content above 5% and with a low percentage of lead; the more common grades have 5, 7 or 10% tin.

Lead contents of up to 6% have little effect upon the corrosion resistance of gunmetal under atmospheric conditions and in normal seawater at moderate flow velocities. When the flow velocity is high, less than 3% lead in such components as centrifugal pump impellers may be advantageous(11). The addition of lead to gunmetal ensures pressure tightness so that they can be used for valve bodies and pump casings.

Summary

- Gunmetals are tin bronze castings; commonly with a small addition of zinc. Lead can ensure pressure tightness in valves and pumps
- Not prone to dezincification, ammonia stress corrosion or pitting
- Valves bodies and pump casings, gears and bearings.

2.3.3 Aluminium Bronzes

Aluminium bronze refers to a range of copper-aluminium alloys which combine high strength and corrosion resistance and are widely used in both cast and wrought forms. These alloys are basically copper with 4-12% Al. They have a thin, adherent surface film of copper oxides and aluminium oxides, which will heal very rapidly if damaged. Furthermore, they have good resistance to erosion and wear, as well as good corrosion fatigue properties.

For up to about 8% Al, the alloys are alpha phase and can be readily rolled and drawn. At 8-12% Al, a second phase, beta, is formed and the alloys can be wrought or cast. Additions of iron, manganese, nickel

Table 13 – Typical Applications for Bronzes

Alloy	Applications
Phosphor bronze (cast and wrought)	Springs, bearings, gears, fasteners, rods, slides
Silicon bronze	Fasteners: screws, nuts, bolts, washers, pins, lag bolts and staples
Aluminium bronze Nickel aluminium bronze (cast and wrought)	Sea cocks, pumps, valves, bushes Propellers and shafts, pumps, valves. Bushing and bearings, fasteners, tube plate for titanium tubing in condensers
Gunmetal (castings)	Pumps and valves, stern tubes, deck fittings, gears and bearings, bollards, fairleads

Table 14 – Nominal Compositions of Typical Bronzes (weight %)

Alloy	EN No or Def Stan	UNS No	Cu	Ni	Fe	Mn	Zn	Al	Sn	Other
Phosphor bronze	CW453K CW451K	C52100 C51000	Rem Rem						8 5	0.3P 0.2P
Silicon bronze	CW116C	C65500	Rem			1				3Si
Aluminium silicon bronze	CW302G	C64200	Rem					7.5		2Si
Nickel alumunium bronze	CC333G Def Stan 02-833	C95800 -	Rem Rem	4 5	4.5 5			9 10		 Ni>Fe
Gunmetal	CC491K	C83600	Rem				5		5	5Pb

Table 15 – Typical Mechanical Properties of Bronzes

Alloy	EN No or Def Stan	UNS No	0.2% Proof Strength N/mm²	Tensile Strength N/mm²	Elongation %	Hardness
Phosphor bronze	CW453K	C52100	170-1000	390-1100	1-60	85-270HV
Silicon bronze	CW116C	C65500	200-890	380-900	3-50	90-220HV
Aluminium silicon bronze	CW302G	C64200	250-350	500-650	10-25	125-160HV
Nickel aluminium bronze	CC333G Def Stan 02-833	C95800 -	280 min 245 min	650 min 620 min	12 min 15 min	150HB
Gunmetal	CC491K	C83600	110 min	230 min	10 min	65HB min

or silicon can also be present. Generally, the corrosion resistance of the aluminium bronzes increases as the aluminium, and other alloying additions, increase. At 9-10% Al, additions of 4-5% iron and nickel produce alloys with both high strength and corrosion resistance in non-polluted waters. A derivation, aluminium silicon bronze CW302G, finds application notably where low magnetic permeability is required. It is also covered by Def Stan 02-834 which gives a maximum magnetic permeability value of 1.05. This aluminium bronze is typically used for chains and deck fittings on minesweepers.

The metallurgical structure of aluminium bronze alloys is very complex and described together with corrosion properties and applications in detail by Meigh(13) and Campbell(14) and the implications are nicely summarised by Francis(6). Careful control of chemistry and processing is required to ensure the structure is maintained in an optimum condition and does not form less corrosion resistant phases which can promote selective phase attack. Nickel and iron provide increased ductility and improved castability and are also the two alloying additions which retard decomposition of beta phase in the structure or alter the decomposition to provide higher corrosion resistance. These alloys are known as the nickel aluminium bronzes or NABs. Those with 5% each of nickel and iron are widely used and exhibit useful precipitation hardening characteristics. The corrosion resistance can be improved by a heat treatment of 675±25°C for 4 to 6 hours followed by air cooling for castings and 725±25°C for wrought material and is particularly advantageous after welding(6,13).

Aluminium bronze alloys have a high order of resistance to ammonia stress corrosion cracking and, although there have been some instances of failure in high pressure steam, extremely high resistance is found in marine environments. Selective phase attack has occasionally been observed at crevices and other shielded areas on NAB. This is due to a drop of pH within the crevice resulting in a normally cathodic phase in the structure called kappa III becoming galvanically less noble to the surrounding alpha phase. It is more pronounced when the NAB is coupled to more noble alloys in non-chlorinated systems. It can be avoided by ensuring exposure to aerated flowing seawater when going into service so the protective surface films in exposed surrounding areas become established, or by galvanic coupling to less noble alloys in the system or cathodic protection(6).

Of the copper alloys, NAB has a very high resistance to cavitation and has become an established alloy for ship propellers; an example is shown in Figure 4.

Summary

- Aluminium bronzes are Cu-Al alloys used in wrought or cast forms as pumps, valves, propellers, bushes, bearings, shafts and fasteners
- Complex metallurgical structure requiring careful processing

Figure 4 - Nickel aluminium bronze ship propeller
(Courtesy Stone Marine Propulsion)

- Nickel aluminium bronze (NAB) is widely used for marine applications
- 0.2% proof strength 280-680 N/mm^2; tensile strength 600-850 N/mm^2
- Excellent resistance to cavitation and used for ships' propellers.

2.3.4 Silicon Bronzes

The most common silicon bronze contains about 3% silicon and 1% manganese(6). It has very good seawater corrosion resistance and resistance to stress corrosion by ammonia. It has been widely used for screws, nuts, bolts, washers, pins, lag bolts and staples in marine environments, as well as screws used in wooden sailing vessels.

Silicon bronzes have an alpha phase metallurgical structure and the silicon provides solid solution strengthening. Strength and hardness can be increased by cold work. They generally have the same corrosion resistance as copper, but with higher mechanical properties and superior weldability. They are tough with good shock resistance and galling resistance.

Summary

- Silicon bronze commonly contains 3% Si
- Very good resistance to corrosion and stress corrosion
- 0.2% proof strength 200-890 N/mm^2; tensile strength 380-900 N/mm^2
- Used as fasteners, screws, nuts, bolts, washers, pins, staples.

Figure 5 - Silicon bronze rigging toggle for mast support
(Courtesy Marine Store)

2.4 Brasses

Copper-zinc alloys are commonly known as brasses and often have small additions of other elements to enhance their properties, such as tin or arsenic for inhibition of dezincification or lead to aid pressure tightness or machining. Their strength increases with zinc content and also with additional alloying elements. Detailed information about them can be found in Copper Development Association Publication 117 *The Brasses - Properties and Applications*(15) and Tables 16 to 18 provide information about typical alloys used in the marine environment.

There are two distinct groups of brasses used for marine service, which can be distinguished by their metallurgical structure:

- Alpha brasses have a single phase structure and contain up to about 37% zinc
- Alpha-beta (duplex) brasses have two phases - the second phase, beta, starts to form above about 37.5% zinc.

Alloying additions such as aluminium and silicon have a 'zinc equivalence', which means that the beta phase can form at lower zinc contents than if they were absent. Alpha brasses are used for wrought products but tend to crack when hot worked. The most popular alloys for hot working processes such as stamping or forging are alpha-beta brasses based on a composition of 60% copper, 40% zinc. At the hot working temperature (650-750°C), these brasses are in the predominantly plastic beta phase and have a mixture of alpha and beta phases at room temperature. Components such as tubesheet and valve bodies are made by hot working.

CW700R is an alpha brass with around 1% each of aluminium, nickel and silicon; Tungum® is a well-known tube product (Figure 7)(16) and has been successfully used in marine environments, particularly for hydraulic control and instrumentation lines. It can be precipitation hardened and has performed extremely well in seawater and marine atmospheres. The alloy is defined under BP Specification GP 36-15-1 for mitigating/preventing external corrosion in topside small bore tubing for operating pressures up to 5000psi.

Al, Sn, Mn additions also give a range of 'high tensile strength' alpha-beta brasses which can be cast, hot-rolled, forged or extruded; applications include propellers and marine hardware including shackles (Figure 6). Cast and wrought manganese bronze alloys are in this category – the term 'bronze' here is a misnomer. Alloys with about 3% Mn and similar amounts of aluminium and nickel have given good service as medium duty propellers.

Brasses can give good service in seawater but require consideration of two types of corrosion processes in their selection and system design - dezincification and ammonia stress corrosion cracking.

Figure 6 - Manganese bronze dee shackle. The term bronze is a misnomer. The alloy is really a brass.
(Courtesy Marine Store)

Dezincification is a form of selective phase corrosion and can occur in seawater. This is a form of corrosion in which the alloy is corroded and a porous matrix of copper is left behind. The rate of attack can be severe, for example 20 mm/year in 60-40 brass and, as the copper deposit is porous and brittle, leakage may occur, for example in condenser tubing and tube plates.

Brasses with up to about 15% zinc are immune to dezincification. Above about 15% zinc, additions of arsenic (0.02-0.06%) can successfully inhibit dezincification in alpha brasses such as aluminium brass used for condenser and heat exchanger tubing, whereas about 1% tin can slow down the process in both alpha and alpha-beta alloys. An example is naval brass, a duplex alloy used for tubesheets in heat exchangers, where the rate of corrosion can be slow enough in thick sections to allow acceptable practical service lives.

DZR (dezincification-resistant CW602N) brass is really a type of hybrid as it has a two-phase structure at high temperatures required for hot forming, but can then be given a heat treatment (500-525°C for 2 hours followed by an air cool) to convert it to an all alpha structure. Arsenic as an alloying addition stabilises the alpha phase and ensures that the brass has resistance to dezincification in service.

All brasses are susceptible to ammonia stress corrosion cracking, which requires a combination of the presence of ammonia, or one of its compounds, and an applied tensile stress. It is more likely to occur in marine atmospheres as, under submerged conditions, very high stress levels are needed. A stress relief anneal at 280-300°C can avoid stress corrosion and both dezincification and stress corrosion can be prevented under submerged conditions by cathodic protection with zinc or iron anodes or impressed current. As an example, cathodic protection is required to avoid dezincification on manganese bronze propellers.

Summary

- Tough, more ductile than copper
- 0.2% proof strength 120-380 N/mm^2; tensile strength 280-580 N/mm^2
- Can be subject to dezincification. This can be controlled by alloying or cathodic protection (CP).
- Susceptible to ammonia stress corrosion cracking, particularly in marine atmospheres. Can be prevented by stress relieving and, when submerged, by use of cathodic protection
- Aluminium brass (an alpha brass used for tube and pipe) contains As to prevent dezincification. Tin is used in naval brass (alpha beta brass) and will slow down dezincification e.g in heat exchanger tube plates
- Tungum® (commonly used for marine hydraulic control and instrument lines) contains Al, Ni and Si. High resistance to dezincification
- High tensile brass (can be called manganese bronze) needs cathodic protection to avoid dezincification. Uses include medium duty propellers, shafts, deck fittings.

Figure 7 - Tungum® brass tubing on decompression chamber housing living and sleeping sections for divers (Courtesy Drass Galleazzi Underwater Technology)

Table 16 – Typical Applications for Brasses

Type of Brass	Applications
Aluminium brass	Seawater tube and pipe
Naval brass	Tubesheet
Aluminium-nickel-silicon brass	Hydraulic, pneumatic and instrument lines
Dezincification-resistant brass (DZR)	Through hull fittings
Manganese bronze (cast and wrought)	Propellers, shafts, deck fittings, yacht winches
UR 30™ (proprietary alloy)	Aquaculture

Table 17 – Nominal Compositions of Typical Brasses (weight %)

Alloy	EN No or Other Identification	UNS No	Cu	Ni	Fe	Mn	Zn	Al	Sn	Other
Aluminium brass	CW702R	C68700	78				Rem	2		0.04As
Naval brass	CW712R	C46400	61				Rem		1	Pb
Aluminium-nickel-silicon brass	CW700R *Tungum®	C69100	83	1.2			Rem	1		1Si
Dezincification-resistant brass	CW602N	C35330	62				Rem			2.0Pb 0.06As
Manganese bronze (high tensile brass)	CW721R	C67500	58		0.8	1.5	Rem	1	0.7	1Pb
Proprietary alloy	UR 30™	-	64				Rem	0.6	0.6	Various

*Tube only

Table 18 – Typical Mechanical Properties of Brasses

Alloy	EN No or Other Identification	UNS No	0.2% Proof Strength N/mm²	Tensile Strength N/mm²	Elongation %	Hardness HV
Aluminium brass	CW702R	C68700	140-380	340-540	20-60	80-160
Naval brass	CW712R	C46400	160-360	340-540	10-30	80-160
Aluminium-nickel-silicon brass	CW700R *Tungum®	C69100	230-350	430-500	40 min	120-140
Dezincification-resistant brass	CW602N	C35330	120-200	280-450	20-40	80-140
Manganese bronze	CW721R	C67500	200-380	450-580	15-30	130-170

2.5 Copper-beryllium

Copper-beryllium has high corrosion resistance and exceedingly good biofouling resistance. Tables 19, 20 and 21 give typical applications, composition and mechanical properties respectively.

In its age hardened condition, copper-beryllium attains the highest strength and hardness of any commercial copper-based alloy(17). The tensile strength can exceed 1300 N/mm^2 depending on temper, while the hardness approaches 400HV.

It has high galling resistance, is immune to hydrogen embrittlement and chloride-induced stress corrosion cracking. It has a range of marine applications including corrosion resistant, anti-galling cylinders for undersea cable communication system repeater housings, as well as connectors and drill components.

Summary

- In age hardened condition can achieve highest strength of any copper alloy
- 0.2% proof strength 200-1300 N/mm^2; tensile strength 410-1400 N/mm^2
- Low corrosion rates
- High biofouling resistance
- High galling resistance.

Table 19 - Typical Applications for Copper-beryllium

Alloy	Applications
Copper-beryllium	Springs, drill components, subsea connectors, actuators, locking rings, lifting nuts, valve gates

Table 20 – Nominal Composition of Copper-beryllium (weight %)

Alloy	EN No	UNS No	Cu	Be	Others
Copper-beryllium	CW 101C	C17200	Rem	1.9	0.5

Figure 8 - Copper-beryllium repeater housing assembly
(Courtesy Materion Brush Perfomance Alloys Ltd)

Table 21 - Typical Mechanical Properties of Copper-beryllium

Alloy	EN No or Other Identification	UNS No	0.2% Proof Strength N/mm^2	Tensile Strength N/mm^2	Elongation %	Hardness HV
Copper-beryllium	CW101C	C17200	200-1300	410-1400	2-20	100-420

3.0 Corrosion Behaviour of Copper Alloys in Seawater

Although copper alloys have a long service history in marine environments, their corrosion behaviour can be poorly understood and confused with other alloy systems. This section is intended to provide an overview of the pertinent issues related to copper alloys. For a more detailed account, the reader is referred to *The Corrosion of Copper and its Alloys: A Practical Guide for Engineers* by Roger Francis(6).

Copper alloys attain their corrosion resistance by the formation of protective surface films. These are visible to the naked eye, form gradually over a period of time - both in the atmosphere and in seawater - and are due to a reaction between the air or seawater and the surface of the alloy.

In the atmosphere, copper develops a brown patina in a few days, which gradually weathers into a green patina. Continued weathering results in conversion of sulphide films to the basic copper sulphate patina which, when complete, gives the distinctive light green colour of older copper roofs. In marine climates, the surface patina will also contain some copper chloride. The eventual development of the light green patina can take 7 to 9 years in marine environments.

Data(18) from exposure tests of up to 20 years duration in various marine sites show a high corrosion resistance to the marine atmosphere for a variety of copper alloys and has found corrosion rates in the range $1.3\text{-}26\times10^{-4}$ mm/year, apart from alloys susceptible to dezincification where the corrosion rate was much higher(6,18).

Under immersed conditions, the surface films are formed by interaction with the seawater itself. These films can be multi-layered and complex, involving forms of oxides and chlorides with the composition depending on the alloy group. They do, however, take several weeks to mature and it is important that, during this initial exposure, and particularly during commissioning, the alloys are exposed to clean aerated conditions to obtain the best protection. In general, the long term, steady-state corrosion rate for copper and its alloys is in the order of 0.025mm/year or less, and that for copper-nickel alloys can be as low as 0.002mm/year.

It is important to realise that, unlike stainless steels, copper alloys are not sensitive to chloride stress corrosion cracking or chloride induced pitting and crevice corrosion, nor do they have the temperature dependence associated with these types of corrosion.

However, under certain conditions, copper alloys do show susceptibility to some types of corrosion and it is by understanding these in more detail that they can be avoided.

3.1 Selective Phase Corrosion

One form of selective phase corrosion has already been mentioned, namely dezincification of brasses. The alloy tends to corrode leaving a brittle porous coppery matrix, see Figure 9.

Figure 9 - Dezincification of a 60-40 brass valve stem

It is avoided, or significantly reduced, by using particular brass alloys which have additions specifically to avoid or reduce it (see Section 2.4) or by applying cathodic protection. In aluminium bronze alloys, there is a similar type of corrosion - often with a coppery appearance and sometimes called de-aluminification(13). However, selective phase corrosion is a more accurate description as it is caused by the relative difference in electrochemical potential of the structural phases. The situation is greatly improved by measures already discussed in Section 2.3.3 on page 13.

3.2 Stress Corrosion Cracking

Stress corrosion cracking in copper alloys in marine environments is normally due to ammonia or associated compounds. In marine environments, this is more likely to affect brasses than the other groups, as already mentioned in Section 2.4, where guidance has already been given on how to avoid it. Bronzes and copper-nickels are generally considered resistant to stress corrosion in seawater and marine atmospheres for most practical applications. Mercury and its compounds can also cause stress corrosion cracking in copper alloys; the attack is liquid metal embrittlement requiring a threshold stress which varies from alloy to alloy(6). Offshore, mercury is present as a contaminant in many oil and natural gas wells and can be problematical for metals in general, thus frequently requiring its removal at an early stage.

3.3 Erosion Corrosion

Erosion corrosion is also known as impingement attack and can occur in copper alloys when the flow velocity exceeds a critical flow called the 'breakaway velocity'. This occurs when the relative shear stress caused by the flowing seawater on the protective surface films is sufficient to damage them. The attack often takes the form of pits and, when severe, is said to appear like horseshoe imprints with the horse walking upstream.

The critical flow velocity and shear stress depend on the alloy and the geometry of

Figure 10 - Erosion corrosion in a 90-10 copper-nickel tube due to excessively high flow velocities

the component. This is well understood for condenser and heat exchanger tube, and piping, in seawater systems. British Standard BS MA 18(19) provides maximum flow velocities for various alloys and diameters for piping. Reference 20 provides data for 90-10 copper-nickel, and a guide for condensers and piping is given in Def Stan 02-781(5) and reproduced in this publication as Table 11. Reference 21 offers its own flow rate guidelines for condenser tubes and includes reductions for waters containing entrained solid matter, Table 22. Many suppliers will also offer guidelines.

Such guidelines have worked well and, although conservative, have taken into account normal velocity raisers within piping systems such as bends, which can cause areas of high local flow velocities. Nevertheless, extreme turbulence should be avoided. Instances where this may occur include tight radius bends, partial blockages and areas downstream of partially throttled valves.

In relative terms, coppers, silicon bronze and low zinc brass alloys have the lowest resistance to erosion corrosion; higher zinc brasses are better, with copper-nickels and nickel aluminium bronzes having the greatest tolerance to higher velocity seawater.

Castings such as gunmetals (copper-tin-zinc) and aluminium bronzes have good resistance to erosion corrosion. Both groups are used for components such as pumps and valve bodies. The nickel aluminium bronze alloy is also used for propellers as it has excellent resistance to cavitation compared to many other copper and non-copper-based alloys.

Figure 11 shows the relative level of flow velocities for four alloys. 70-30 copper-nickel can be used at higher velocities than 90-10 and aluminium brass. 30Ni-2Mn-2Fe copper-nickel would be expected to resist higher flow velocities than 70-30 Cu-Ni and the 16Ni-0.5Cr copper-nickel alloy would be higher again(23).

For other geometries, hydrodynamics and exposure regimes, higher flow velocities can be allowable. For example, the maximum flow velocity within a 90-10 copper-nickel pipe at 100mm diameter or greater is typically 3.5 m/s, whereas the hydrodynamics of ship hulls are somewhat different to piping systems and allow higher velocities. Hull experience to date has shown minimal corrosion after 14 months at 24 knots (12 m/s) for the 90-10 alloy(3), whereas the highest recorded velocity is 38 knots (19 m/s) for a patrol boat which showed no measurable thickness loss after 200 hours at maximum operating speed. The upper service velocity for hulls is still to be established. Higher flow rates are also tolerable for intermittent flow in pipes; copper alloys have been used very successfully in firewater systems, where water velocities are typically 10 m/s (Figure 12).

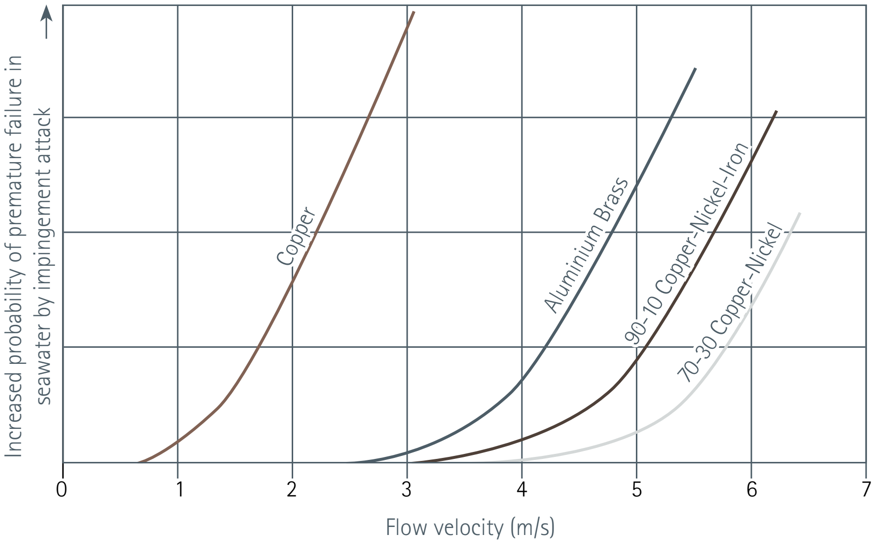

Figure 11 - Relative breakdown velocities for copper alloys in seawater ex Gilbert(22)

Table 22 – Flow Rate Guidelines ex Reference 20 and the Influence of Solid Matter

Condition	C 70600	C 71500
Cooling water with low solid* content	2.4 m/sec	2.7 m/sec
Cooling water with high solid* content	2.0 m/sec	2.2 m/sec

*sand and biological matter

3.4 Crevice Corrosion

Crevice corrosion can occur in copper alloys but is vastly different from the mechanism which occurs in stainless steels. It is a metal concentration cell effect, where copper ions build up in the crevice and are not washed away, such that the crevice becomes more noble than the surrounding exposed area and the surrounding area becomes the anode. The corrosion is therefore outside and not inside the crevice and is shallow in nature and not a threat to the life of the system or component. One exception is for NAB, which takes the form of a selective phase corrosion attack under the crevice, and this has been addressed earlier on page 13.

3.5 Polluted Conditions

All copper alloys are sensitive to polluted conditions(24). This is because the surface films formed become predominantly sulphide, which are less protective and lead to pitting and higher corrosion rates when re-exposed to oxygenated water. Minimum flow velocities of around 1 m/s are often included in tube and piping design to avoid sediment deposition which can interfere with heat transfer and lead to sulphide corrosion if sulphate reducing bacteria are present.

Table 23 gives a scenario for copper-nickel designed to avoid sulphide corrosion during commissioning and refit for pipes and tubes in seawater systems. Def Stan 02-781(5) also covers the effects of pre-treatment; although this reference is a naval standard, it gives information which is also relevant to non-naval service. Ferrous sulphate dosing is the traditional method of improving the resistance for aluminium brass and copper-nickels against sulphides in polluted sea water systems. Chlorination at low levels can also improve the corrosion resistance of copper-nickels(6). However, dosing both ferrous sulphate and chlorine at the same time can lead to a floc being formed and requires staggered dosing regimes.

Figure 12 - Between 150-200 tons of 90-10 copper-nickel have been installed on individual drill ships for the fire fighting system
(Courtesy KME Germany AG & Co KG)

Table 23 – Typical Guidelines to Avoid Sulphide Corrosion during Commissioning, Shutdown and Standby Conditions(4)

Duration	Conditions in the system	
	Clean seawater or fresh water without deposits	**Polluted seawater or fresh water where deposits are present**
4 days	• Keep the system filled	**Commissioned System:** • Avoid very high flow rates • If possible, clean the system and fill with clean seawater or fresh water **New System:** • Clean the system and fill with clean seawater or freshwater
> 4 days	**Possibility I:** • Keep the system filled • The system has to be replaced by oxygenated seawater within 2-3 days to avoid decomposition	**Possibility I:** • Dispose of the polluted water and refill with clean seawater or fresh water • The system has to be replaced by oxygenated seawater within 2-3 days to avoid decomposition
	Possibility II: • Drain down the system, clean and keep it dry.	**Possibility II:** • Drain down the system, clean and keep it dry.

3.6 Splash Zone Protection

In addition to atmospheric and fully submersed conditions, on offshore structures there is a position on platform legs and pilings, which is not fully immersed and not fully in the atmosphere, called the splash zone. Steel cannot be sufficiently protected by cathodic protection and coatings can be damaged by the erosive nature of aerated splashing seawater. Copper-nickel sheathing welded onto the steel structure has been found to provide effective protection in this area with over 25 years experience, see Figure 13 (25,26).

Figure 13 - 90-10 copper-nickel splash zone protection on a platform in the Morecambe Field, UK
(Courtesy Centrica Energy Upstream, East Irish Sea)

4.0 Galvanic Behaviour

Galvanic corrosion is the enhanced corrosion which occurs to the least noble metal within a mixed metal system, in electrical contact with the other metals and exposed to an electrolyte. The least noble alloy is called the anode and the more noble alloy the cathode. If the galvanic current is significant, the anode will corrode more than it normally would in an uncoupled situation and the cathode will corrode less. This forms the basis for cathodic protection, where less noble materials (e.g. zinc, aluminium or iron alloys) are connected intentionally as sacrificial anodes in order to protect other alloys in the system.

Where seawater is the electrolyte, a Galvanic Series can be used, such as that shown in Figure 14, in order to predict which of the metals in contact is the least noble and whether higher corrosion rates may occur than might otherwise be expected. The alloys nearer the top of the chart are less noble (more anodic) in seawater than those towards the bottom and would be expected to corrode preferentially. The further apart in the series the coupled alloys are, the greater the potential difference between them and the more likely it is for corrosion to occur. It is seen that copper alloys are in the middle of the Series whereas steel, zinc and aluminium are appreciably less noble and would be expected to corrode preferentially when coupled to them in a system. Passive stainless steels, nickel alloys, titanium and graphite are all more noble than copper alloys, and the copper alloys would therefore risk galvanic corrosion.

However, other factors can play a part. The relative surface areas of the galvanically coupled metals, exposed to the seawater, have an important influence on the extent of corrosion. The surface area of the cathodic alloys exposed to seawater normally limits the galvanic current. Therefore, a small cathodic area in contact with a large anodic area can have little effect on the overall corrosion rate of the less noble, anodic material. Alternatively, if the relative area of the more noble, cathodic area is high, then excessively high corrosion rates of the anode might be experienced.

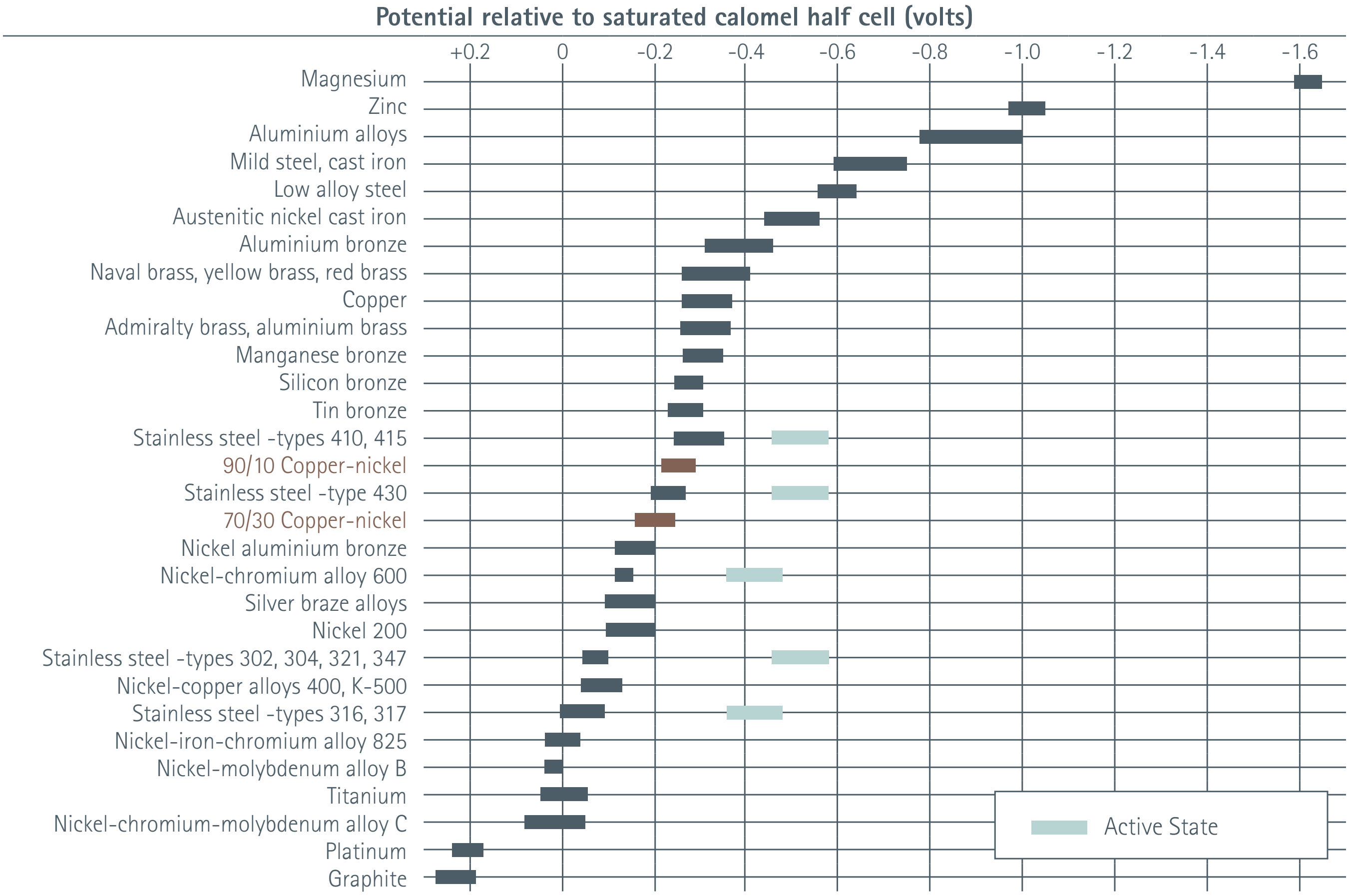

Figure 14 - Galvanic Series in seawater

In general, the copper-based alloys have similar nobility and are all galvanically compatible with each other in seawater unless the surface area of the more noble copper alloy is significantly greater than the less noble alloy. The copper-nickel alloys are slightly more noble than the nickel-free copper base alloys, but the differences in corrosion potential rarely lead to serious galvanic effects. 90-10 copper-nickel is slightly less noble than 70-30 copper-nickel and both are less noble than nickel aluminium bronze but more noble than manganese bronze. Nickel aluminium bronze is therefore preferred as a propeller material for a copper-nickel hulled boat as the unfavourable area ratio would lead to accelerated corrosion of manganese bronze.

In more recent times, it has become appreciated that galvanic corrosion can be less pronounced for some metal combinations in chlorinated rather than in non-chlorinated seawater systems. Copper-nickel is significantly more galvanically compatible with stainless steels when the system is chlorinated.

Problems with galvanic corrosion can usually be avoided by following the rules below:

- Use alloys situated close together in the Galvanic Series
- Where this is not possible, make the key component of a more noble material
- Ensure that the less noble material is present in a much larger area than the more noble material
- Paint the more noble material. This can be beneficial as it reduces the exposed area of the more noble material, even when the paint film is incomplete. An imperfect coating, if the less noble alloy alone was painted, would lead to intensified attack at breaks in the paint film.
- Insulate to prevent metal-to-metal contact and break the galvanic current e.g. using non-conducting sleeves and gaskets, distance pieces. For a more detailed analysis of galvanic corrosion, and how to avoid it, the reader is referred to *Galvanic Corrosion: A Practical Guide for Engineers* by R Francis(27).

Of additional importance to the behaviour of copper alloys is that galvanic coupling to less noble alloys, or the use of cathodic protection, as in Figure 15, can inhibit their biofouling resistance. See Section 5.0 on page 24.

Figure 15 - Comparison of a cathodically protected (left) and freely exposed 90-10 copper-nickel panel (right) after 12 month exposure at Langstone Harbour, UK. The panel free of cathodic protection shows no macrofouling (29)

5.0 Marine Biofouling

Marine biofouling is found on structures such as pilings, offshore platforms, boat hulls, and even within piping and condensers. The fouling is usually most widespread in warm conditions and in low velocity (<1 m/s) seawater. Above l m/s, most fouling organisms have difficulty attaching themselves to surfaces unless already secured. There are various types of fouling organisms, particularly plants (slime algae), sea mosses, sea anemones, barnacles and molluscs (oysters and mussels). In steel, polymers and concrete marine construction, biofouling can be detrimental, resulting in unwanted excess drag on structures and marine craft in seawater or causing blockages in pipe systems. Removal by mechanical means is often required, or prevention methods such as antifouling coatings on structures or chlorination of pipework systems can be used.

Marine organisms attach themselves to some metals and alloys more readily than they do to others. Steels, titanium and aluminium will foul readily. Biofouling has been found to have low adherence to many higher copper-based alloys. This is particularly so for macrofouling (grasses and shell fish), although microfouling (slimes) will still occur but to a reduced extent. When exposed for long periods under quiet conditions, some macrofouling can eventually occur but this has been observed to slough away at intervals and can readily be removed by a light wiping action. Copper-nickels have very good resistance in this respect showing a similar behaviour to copper itself(28). The 90-10 copper-nickel alloy has found several applications that take advantage of its combined good corrosion and biofouling resistance, including water intakes, boat hulls and insulated markers and sheathing on legs of offshore structures. Copper alloys, such as UR 30™ brass alloy in Figure 16, are being used for aquaculture cages.

The most important requirement for optimum biofouling resistance is that the copper alloy should be freely exposed or electrically insulated from less noble alloys and cathodic protection. Galvanic coupling to less noble alloys and cathodic protection can prevent free copper ion release from the surface film and reduce the biofouling resistance(29). However, there are some indications that the resistance is in part associated with the nature of the surface films as well(3).

Figure 16 - Since 2005, Van Diemen Aquaculture in Tasmania has successfully used Mitsubishi-Shindoh's UR 30™ brass alloy in salmon cages supplied by Ashimori Industry Company. There are 28 salmon cages in the estuary with extreme conditions of reversing high velocity currents, salinity gradients and high summer water temperatures. (Courtesy of Van Diemen Aquaculture)

6.0 Summary of Good Practices

Corrosion is a complex topic for any type of metal. Table 24 gives a simple description of the main initial considerations to control unnecessary corrosion of copper alloys and the pages in this publication where items are discussed. For a more in-depth understanding of these and other issues the reader is referred to *Corrosion of Copper and its Alloys – A Practical Guide for Engineers*(6) and *Galvanic Corrosion: A Practical Guide for Engineers*(27).

Table 24 – Typical Considerations for Good Practices

Issue	Typical options	Page No
Maintain low corrosion rates	**Galvanic** 1. Avoid mixed metal connections where the copper alloy chosen is the anode, particularly where it has a relatively small surface area 2. Insulate the connection or apply distance piece to stop galvanic connection 3. Coat cathode	22,23
	Flow 1. Stay within flow velocity guidelines 2. Avoid tight angle bends, misalignments and other obstructions which can cause areas of local turbulence	9,18,19
Pitting (in copper alloys, this is largely due to polluted seawater)	1. Avoid extended exposure to quiet and stagnant conditions or polluted waters which can encourage sulphides and sulphate reducing bacteria 2. Periodically clean systems to remove deposits 3. Plan and implement good commissioning and start-up procedures aimed at achieving good surface film formation 4. Ferrous sulphate dosing	20,21
Stress corrosion cracking (normally due to ammonia or its compounds)	1. Stress relief heat treatment 2. Cathodic protection if immersed 3. Select copper alloy which has a high resistance	14,15,18
Selective phase corrosion	**Brasses** 1. Select alloy composition which is immune to dezincification or is inhibited against it 2. Cathodic protection	14,15,18
	Aluminium Bronzes 1. Process to avoid unwanted structural phases 2. Heat treatment 3. Build up sound surface films at outset 4. Galvanic or cathodic protection	13
Unexpected levels of fouling	1. Avoid surface contamination 2. Insulate from galvanic or cathodic protection 3. Avoid extended exposure in quiet waters (Fouling will normally only be loosely attached and readily removed by a light scraping or pressurised water clean applied before it dries out.)	23,24

7.0 Recyclability

Figure 17 - Dismantling Oscar 1 Class Submarine
(Courtesy Keel Marine Ltd)

Copper and its alloys are fully recyclable without loss of properties. Globally, 34% of the copper used in new alloys comes from recycled scrap; it is currently 45% in Europe(30). This provides benefits in energy saving and preservation of resources which contribute to the sustainable credentials of copper and copper alloys.

One example is a 95 tonne nickel aluminium bronze propeller for a container ship produced by Stone Manganese, which used almost 100% scrap processed from in-house process scrap and carefully selected bought-in scrap. It was produced in one continuous pour and was fed with liquid bronze for 24 hours.

Another example is that 180 tonnes of tin/aluminium bronze alloys and 72 tonnes of high purity copper wire were recovered for recycling from the Russian Oscar 1 class submarine, as shown in Figure 17.

8.0 References and Further Information

8.1 References

1 Copper and Copper Alloys: Compositions, Applications and Properties. Copper Development Association Publication 120. December 2004

2 Seawater Corrosion of 90-10 and 70-30 Cu-Ni 14 Year Exposures. Materials Performance. K Efird and D Anderson. November 1975

3 Copper-Nickel Alloys for Seawater Corrosion Resistance and Antifouling – A State of the Art Review. C A Powell and H T Michels. Corrosion 2000. NACE. March 2000

4 www.coppernickel.org

5 Protection of Seawater System Pipework and Heat Exchanger Tubes in HM Surface Ships and Submarines. DEF Stan 02-781. UK MoD.

6 Corrosion of Copper and its Alloys - A Practical Guide for Engineers. R Francis. NACE International. 2009

7 Copper-nickel Fabrication: Handling Welding, Properties, Resistance to Corrosion and Biofouling, Important Applications. Copper Development Association Publication 139. 2013

8 Development of Cast Copper-nickel Chromium Alloy for Naval Service. Metals and Materials. Vol. 6. No 12. C A Powell. December 1990

9 Engineering Guide, Toughmet 3AT and 3CX. Kushna et al, Brush Wellman. 2002

10 High Strength Copper-nickels. C Tuck, Langley Alloys. 2008. www.coppernickel.org

11 Gunmetal Castings. F Hudson, Macdonald and Co. London. 1967

12 The Selection of Materials for Seawater Cooling Systems - A Practical Guide for Engineers. R Francis. Published by NACE International. 2006

13 Cast and Wrought Aluminium Bronzes - Properties, Processes and Structure. H Meigh, Maney Publishing. 2000

14 Aluminium Bronze Corrosion Resistance Guide. H Campbell. Copper Development Association Publication 80. 1981

15 The Brasses: Properties and Applications. Copper Development Association Publication 117. 2005

16 Tungum - Specification and Application Guide. Tungum Ltd. 2009. www.tungum.com

17 Guide to Beryllium Copper. Materion Brush Performance Alloys

18 Shreir's Corrosion Vol 3. Corrosion of Copper and its Alloys. pp1937-1973. C D S Tuck, C A Powell, J Nuttall, In: J A Richardson et al. (eds.). Amsterdam: Elsevier. 2010

19 Salt Water Piping Systems in Ships. British Standard MA 18

20 Pipelines of Copper-nickel Alloys - Part 2 - Basic Principles for Design, Fabrication and Testing. DIN 85004

21 Kühlwasserrichtlinie: Wasserbehandlung und Werkstoffeinsatz in Kühlsystemen (Translation: Guideline for Cooling Water: Water Conditioning and Material Selection in Cooling Systems) VGB-R 455P,2. Auflage 2000, page 33

22 Corrosion Resisting Properties of 90-10 Copper-Nickel Iron Alloys with Particular Reference to Offshore Oil and Gas Applications. P T Gilbert. British Corrosion Journal. Spring 1979

23 Alloy C72200 – A Cost-Effective Alternative to C71640 and Titanium. Olin Fineweld Tube - Technical Letter

24 Guidelines for the Use of Copper Alloys in Seawater. A H Tuthill. Combined Nickel Institute and Copper Development Association Publication. 1987

25 Long Term Exposure Trials Evaluating the Biofouling and Corrosion Resistance of Copper-nickel Alloy Sheathing Materials. S Campbell and C A Powell. 12th International Congress on Marine Corrosion and Fouling. Southampton, 2004

26 Review of Splash Zone Corrosion and Biofouling of C70600 Sheathed Steel During 20 Years Exposure. C A Powell and H Michels. Eurocorr 2006. Maastricht

27 Galvanic Corrosion: A Practical Guide for Engineers. R Francis. NACE International Press. 2001

28 The Interrelation of Corrosion and Fouling of Metals in Seawater. Materials Performance, Vol 15, No 4, pp16-25. K D Efird. April 1976

29 Preventing Biofouling with Copper-nickel. Copper Development Association Publication 157. 2002

30 World Copper Factbook. International Copper Study Group Publication. 2012

8.2 Other Useful Documents

- Marine Corrosion. T Howard Rogers. George Newnes Ltd. London. 1968
- The Selection of Materials for Seawater Cooling Systems - A Practical Guide for Engineers. R Francis. Published by NACE International. 2006
- Metal Corrosion in Boats. N Warren. Adlard Coles Nautical. 1998
- Marine Corrosion. Causes and Prevention. F LaQue. John Wiley and Sons. 1975
- Copper and Copper Alloy Castings. Properties and Applications. Copper Development Association Publication TN 42. 1991
- Copper Alloy Bearings. Copper Development Association Publication TN45. 1992
- The Copper Advantage: Guide to Working with Copper and Copper Alloys. Copper Development Association Inc Publication. 2010
- Cost-Effective Manufacturing. Machining Brass, Copper and its Alloys. Copper Development Association Publication TN 44. 1992
- Recommended Machining Parameters for Copper and Copper Alloys. DKI Monograph i.18. 2010
- Biofouling Resistance of Cupronickel - Basics and Experience. W Schleich and K Steinkamp. Stainless Steel World 2003 Conference. Maastricht. November 2003.

8.3 Information Sources

For detailed information on copper-nickels see downloadable papers on www.coppernickel.org. The web pages are organised by an International Copper Association international committee of copper-nickel product manufacturers and Copper Centres.

Technical publications on corrosion, fabrication and properties of copper alloys are available from:

Copper Development Association websites:
www.copperalliance.org.uk (UK)
www.copper.org (USA)
www.coppernickel.org

Aquaculture: Copper Alloys In Aquaculture
http://en.wikipedia.org/wiki/Copper_alloys_in_aquaculture

Notes

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