Copper Alloys in Heat Exchangers Copper in Industry

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December 1998

Foreword

Although, several decades ago, shipbuilding used to tea major of copper alloys, its percentage importance in the field of heat exchange applications has decline ever since. In view of the growth experienced by other uses, such as desalination, thermal power generation (both nuclear and furl-based) and petrochemical plants.

The Author is unaware of any recent world wide survey of copper alloy tube usage in heat exchange application, but a likely subdivision of present-days production of some 40.000 MT of these materials by end use (excluding copper tube for air conditioning and refrigeration, which may account for an additional 150.000 to 170.000 MT per year) could be as follows:

- Desalination	15.000 MT
- Power generation	12.000 MT
- Petrochemical and oil industry	7.000 MT
- Ship building	3.000 MT
- Other miscellaneous	3.000 MT
Total	40.000 MT

This figure is inclusive of replacement spares (especially for power and petrochemical plants) and show a share decline over that prevailing around 1970-80, when it stood at 80.000 MT.

But the decline is attributable mainly to the consequences of world business stagnation, as reflected in a virtual standstill of new plant construction for the first three end-uses.

The experience gained over the years in large desalination and power plants, however, has significantly contribute to increase operation know-how and tube life for the copper metals, and these benefits. Also accrued to the shipbuilding industry, which was the first to foster the development of such crucial alloys as admiralty and aluminum brass, as well as of iron-bearing cupronickels.

Copper alloys for Ship Heat Exchangers
TABLE 1-Main copper alloys for marine heat exchangers

Alloys (ISO Designation)		**Heat Exchanger Component**		
		Tube	**Tube-plate**	**Shell**
Brasses	Admiralty brass Cu Zn 29 Sn1	×		
	Aluminum brass Cu Zn 21 Al 2	×		
	Muntz metal Cu Zn 40		×	
	Naval brass Cu Zn 39 Sn 1		×	
Cupro-nickel	90/10 Cupro-nickels Cu Ni 10 Fe 1 Mn	×	×	×
	70/30 Cupro-nickel Cu Ni 30 Ma 1 Fe	×	×	
	66/30/2/2 Cupro-nickel Cu Ni 30 Mn 2 Fe 2	×		
Aluminum	95/5 aluminum bronze Cu Al 5 As	×		
	Iron-aluminum bronze Cu Al 8 Fe 3		×	×
	Nickel-aluminum bronze Cu Al 9 Ni 6 Fe 5		×	

Tonnagewise, it should to remembered that tubes are the most important semis, representing well over two-thirds of the heat exchangers weight; another 6 to 7% is represented by the tube plates, and the rest is made of shell and diaphragms, which however are often made of cheaper materials, like steel.

The brasses whether in tube or plate form account for about 70% of total production, mainly owing to their low price and satisfactory performance in most service environments.

The Brass

Brass is basically a copper-zinc alloy, to which, in heat exchanger application one or more specific additions are made for particular purposes.

So, for example, admiralty brass also contain tin against erosion-corrosion, and arsenic to combat dezincification; in aluminum brass, aluminum is used instead of tin, but arsenic is retained for the same reason, Similarly,muntz metal is usually inhibited against dezincification by arsenic addition and, when tin is added purposely, muntz metal becomes naval brass.

From the structure/end use combination, we can subdivide these alloys into two families:

a) Alpha phase alloys, suitable for cold working into thin wall seamless tubes, and

b) Alpha plus beta phase alloys, suitable for hot rolling into heavy wall tube plates.

Of the two families, the first one is the most sensitive to impurity levels, due to more severe operating conditions and longer fabrication route. For them, the following limitations have been proposed as far as impurities are concerned:

- Lead: 0.01% max., to avoid microcracking during drawing.

- Iron: 0.03% max., to facilitate uniformity of annealing.

- Manganese: 0.02% max., to avoid manganese sulphide inclusions.

- Silicon: 0.02% max., to control inclusion content.

- Phosphorus: 0.10% max., to avoid detrimental synergism with arsenic (Limited to 0.020-0.035%) in fostering integranular corrosion attack.

- Magnesium: 0.005% max., to avoid dezincification when combined to arsenic.

- Sulphur: 0.005% max., to limit sulphide inclusions.

- Tin:0.03% max., (in aluminum brass) to improve annealability

- Aluminum: (in admiralty brass) to limit inclusions.

- Antimony, Tellurium, Selenium $\}$: 0.01% Max., each, to improve annealability

- Bismuth: 0.005 max., to avoid microcracking during drawing.

Such a careful control of composition can obviously be achieved only by using high quality raw materials and closely monitoring all the melting and casting processes, but the critical nature of the heat exchangers, function in a ship more than justifies such preventive measures to limit outages to a minimum.

The Cupro-Nickels

These alloys were developed in their present-day composition around World War Two over come erosion-corrosion (impingement) problems encountered with brass tubes under continued peck load operating conditions. They key to their wide-spread use lies in a balanced addition of iron and manganese, which strengthens the metal matrix and the surface protective film, while increasing its self healing propensity. While copper and nickel are entirely miscible over the full range of compositions two basic alloys have been selected, namely the 90/10 and 70/30 copper-nickel combinations, the latter being generally reserved for the most service (temperature, water velocity, ammonia pollution) conditions.

As they contain 10to 30% nickel, both are more expensive than brasses and should therefor be selected when actual operating conditions dictate their choice: higher water speed, ammonia contamination, presence of suspended solids, higher temperatures, ect. It may be said that copper-nickels are immune from stress corrosion cracking but more and susceptible to deposit attack as their nickel content increases, which means that their surface should be kept as clean as possible from any from of screening, such as stones, silt, shells, scales, etc., also, some minimum water flow velocity should be maintained to avoid stagnation.

For cupro-nickels, too, impurity limitations have been proposed and adopted by the more sophisticated users and manufacturers, as follows.

- Lead: 0.01% max., to avoid microcracking during drawing.

- Bismuth: 0.005% max., for the same reasons as lead.

- Zinc: 0.2% max., to avoid zinc sulphide inclusions.

- Tin: 0.02% max., to maintain annealability

- Aluminum: 0.02% max., to avoid alumina

- Phosphorus: 0.010% max., to maintain annealability

- Carbon: 0.05% max., to improve ductility during hot working

- Sulphur: 0.01% max., to avoid sulphide inclusions

  Sntimony
- Tellurium :0.01% max., each, to maintain annealability.
  Selenium

When used in the hot-worked condition, i.e. for tube plates. The chemical composition of cupro-nickel would in theory require less care than in the case of tube, but owing to the high cost of the material and the grater difficulty of manufacture when compared to duplex brasses, any lowering of inspection standards would be unwarranted.

Furthermore, it appears that cupro-nickels, and aluminum bronzes as well, are more easily inspected by ultrasonic techniques than the brasses, the latter giving rise to severe sound wave scatter at grain boundaries; flaws in heavy wall components made of the more expensive and less workable cupro-nickels or aluminum bronze alloys can thus be subjected to more stringent and more efficient inspection procedures.

The Aluminum Bronzes

Developed at the turn of this century more like an academical curiosity than for particle proposes, the copper-aluminum alloys, or aluminum bronzes, started their progress into industrial usage as casting materials for sea-water components like ship propellers, value bodies, pump impellers and the like. Their excellent hardness, toughness and wear resistance led to investigation into the possibility of developing easily cold workable alloys while retaining the useful properties of castings. Raw material purity and very close chemical composition limits for the main alloying elements like copper, aluminum and iron were soon recognized as a per-requisite, and a few specialized companies in Erope and the U.S.A. soon emerged as worldwide suppliers.

In the heat exchanger industry, we have to deal with three main alloys.

The single-phase (alpha) 5% aluminum bronze usually inhibited against dealuminification by the addition of about 0.3% arsenic.

The single phase 8% aluminum bronze, also containing some 3% iron as a strengthener (a small amount of iron-rich phase would some time be found as rosette like precipitate within the alpha matrix).

The multiphase 9% aluminum bronze with 4-5% iron and 5-6% nickel additions; here, the alpha phase grains are partially surrounded by various types of a high temperature “beta” phase during cooling through an eutectoid boundary, while a number of intermetallic Cu-Al-Fe-Ni compounds (Kappa phase) are dispersed throughout.

The first two alloys are easily cold workable, and 5% aluminum bronze is a typical tube material whose performance is intermediate between those of aluminum brass and 90/10 cupro-nickels. As is its cost; for instance, it has improved resistance to impingement attack, and erosion over brasses, and a lesser sulphide susceptibility than the cupro-nickels. Being rather limited in usage, it is less readily available off-the shelf than other materials, but has been used very satisfactory in sea-side petroleum refineries and steel mills in Saudi Arabia, Italy and the U.S.A.

The 8% aluminum-3% iron aluminum bronze is also cold workable, but most of its uses are in the "as hot rolled" condition for tub plates, baffles, supports and heat exchanger shells; in welded fabrications, it is also a very good material for water boxes. Tow main factors have to be monitored in its practical use:

- Being near to the + β boundary in the equilibrium diagram care should be taken to avoid retention of residual "beta" phase by excessively of this less noble part of the alloys is to be expected.

- In welded application, part from avoiding the effects of fast cooling in the HAZ (heat affected zone), impurities such as tin, lead, bismuth should be limited to well under 0.01% otherwise HAZ hot shortness cracking would ensue.

Finally, in the case of the nickel aluminum bronze, much care is needed to adjusted the chemical composition in order to ensure freedom from interconnected "beta" phase which would lead to extensive and destructive dealumiuification; the simplest and most effective way being to add nickel at a 6:9 ratio to the aluminum content, whereby the former will combine with the latter by forming the hard, relatively noble kappa phase, and effectively reducing the aluminum content in the matrix to the alpha phase domain.

Heat Exchanger Services Conditions

The service condition of a copper based heat exchanger, when used on bard ship, are very different from those of land equipment, and these differences in turn will be reflected in the heat exchanger design and operation practice, as detailed here below.

Types of Cooling Waters

As the ship, or boat, travels along its journey, it may encounter a wide rang of seawaters, from very warm to very cold, from polluted harbor to clean high sea, from extremely turbid to crystal clean; but its heat exchangers tube remain the same all throughout and must ensure safe and reliable service.

This means that some reasonable sort of compromise should be found between conflicting requirement; for instance. Water flow velocities should be specified not only at the upper, but also at the minimum level (I.e. the heat exchanger water inside) as a function of tube material (see Table II); the maximum velocity values may increase significantly for the brasses in river or lake water (safe waters), where the other alloys are seldom used. In estuary or brackish water, however, whose composition and aggressively may change very quickly, conservation values are recommended.

In addition, and especially for ships which have dwelt for a long time in warm waters, an increased frequency of inspection is recommended, coupled with periodic oration at high water velocity to assist the removal of silt, etc. it is unfortunate that, on most ships, cooling water pretreatment (such as efficient filtering, chlorinating against biofouling, ferrous sulphate dosing on brass surfaces to improve their resistance to impingement) is generally impractical, contrary to large, land based plants.

Table II-Minimum and maximum water flow velocities in copper based tubes operated in clean sea water (moderately polluted sea water value are shown in brackets).

Material	Velocity (m/s)	
	Min	Max
Admiralty	0.3(0.3)	1.5 (1.0)
Aluminum	0.5(0.5)	2.5 (1.8)
5% Aluminum bronze	i.5(1.8)	3.0 (3.0)
90/10 Cupro-nickels	0.8 (1.2)	3.2 (3.0)
70/30 cupro-nickels	1.0 (1.5)	4.5 (4.0)
1.0 (1.5)	1.0 (1.5)	5.5 (4.5)

Space limitations

On many ships, especially on warship,. Space is limited and the heat exchangers must be small, light weight and easy to accommodate into unusual locations. This, in general, means that they should be operated at comparatively high cooling water velocities, i.e. they are tubed in the high nickel alloys.

It is then useful to remind sea captains of the need to retain some minimum level of water flow within the bundle, and the heat exchangers designers that they should not adopt thinner wall tubes (for improved heat transfer and reduced risk of hot-spot attack), but also well- baffled steam intake ports and somewhat closer support spacing, to minimize vibration and local over heating of tube walls.

In particular, both users and designers should remember that “corrosion allowance” on a copper-base tube really makes little sense, as the danger lies mainly with localized attack (impingement on tube ends, pitting, deposit attack, occasional stress-corrosion of brasses, fatigue and corrosion-fatigue, “channel” attack due to ammonia-rich condensate percolation, and so on) rather than with generalized corrosion, whose ready-state progress is very small indeed (from 2 to 5 microns per year): they could , therefore , improve the efficiency and the economics of heat exchangers by sing I mm wall thichnesses , file taking concurrent account of the appropriate reminds for each operation malpractice , as described in the technical literature over he last 40 years .

Start-up and Maintenance

We will never over-emphasize the importance of start-up conditions of copper-based heat exchangers for heir tubes’ life: only when appropriate measures are taken to ensure the formation of a uniform, well adherent film of the appropriate composition is the underlying metal wall really guaranteed against most forms of general, and especially localized, corrosion.

There are a few steps in start-up (and in maintenance as well) worth mentioning in this connection.

a) Good tube quality*:* it is essential, for long tube life, that only tubes coming from well-qualified (i. e. having a Quality Assurance System in operation and a significant record of satisfactory supplies) manu-facturers be used; parameters to be controlled on the tube lots include: chemical composition, tensile and hardness properties, grain size, dimensional accuracy and consistency (OD and wall thickness tolerances, eccentricity, ovality), freedom from hidden defects (100% eddy-current testing must be requested on the entire tube length , rather than obsolete , inaccurate and corrosion-wise dangerous pressure tests) especially for the tube inner wall surface , freedom from residual stresses and residual lubricants and\or cracked carbon films , adequate packing in moisture-free conditions (e. g. by using silica gel as a desiccant) and well constructed boxes (an outline of these requirements for the main copper alloys is given in a new standard specification , quoted under Ref. l.)

b) Appropriate Storage of New Tubes (including spares): the external atmosphere can adversely affect the protective film formation, by causing local attack due to aggressive components (SO_2, CO_2 NH_2, etc) or condensation/evaporation of water vapor droplets (differential aeration); tubes shall therefore be stored in closed sheds, sheltered from atmospheric agents and within well preserved boxes.

c) Careful Assembly of tubes into the heat exchanger : this involves defining appropriate means to facilitate parallel insertion into the shell (plastic pointers are recommended), adequate hole clearances into supports (about 0.10 mm on OD) and tube plates (these are so chosen as to ensure about 6.8% permanent expansion of tubes into pre-rolled holes), appropriate rolling-in sequences (a cross-wise system is generally desirable) and preservation from the effects of atmospheric pollution and of the presence of foreign materials in the tube bores (such as chips, swarf, loose, loose objects, rolling-in lubricants, etc.)

d) Heat Exchanger Pressure Testing with clean soft water, possibly containing some corrosion inhibitor by thorough drying with warm compressed air and tight sealing under nitrogen or at least in the presence of adequate amounts of a desiccant.

e) Pre-Treatment of Bundle Inned Surfaces in case of long-time storage, again by means of proprietary combinations of BTA and MBTA saline solutions circulated for acouple of days; also, some satisfactory hot steam for some days, owing to the formation on tube inner surfaces of a sufficiently uniform layer of protective corrosion products.

f) Start-Up with clean water in the absence of applied load for a couple of weeks ; the water flow velocity should be reduced to between one third and one half its design value, and the water should be kept free from such pollutants as ammonia and suphides, while still retaining sufficient oxygen to assis in the formation of the initil protective film. Obviously, prior to start-up, the heat exchanger should be thoroughly inspected and cleaned from any foreign objects and/or particles which may be found during fabrication either within the bundle or in the water boxes. When cathodic protection means are provided for (both impressed current or via sacrificial anodes made of zinc or of pure, ARMCO-type, iron), these should be disconnected to enhance the rate of initial corrosion, thus leading to a more uniform film formation. After start-up, if service operation does not immediately follow, the heat exchanger should be drained, rinsed, thoroughly dried and conditioned in the most appropriate way as a function of the duration of shut-down.

g) Periodic Maintenance, Tube Replacement and Salvage: Ship-borne heat exchangers should be subjected to periodic maintenance during vessel overhauls. Preferably on the basis of programmed (i.e.pre-set) interventions, involving bundle water box/tube plate inspection, clean u[and re-conditioning. Should some tubes be found leaking or excessively thinned down (inner-probe eddy-current testing, such as by Probolog, etc., may be useful in tracing these), they should be replaced with good-quality tube spares kept on board under adequate storage conditions; their direct roller expansion into worn tube plate holes should be avoided. Because such holes need to be brought back to shape by reaming and pre-rolling: generally, the consequent increase in hole diameter expansion, which should bowever never become more than about 10% in terms of tube wall thinning. The newly installed tubes should also undergo some start-up procedure. I A badly corroded heat exchanger due to localized attacks such as pitting, deposits and even impingement, can often be salvaged and operated satisfactorily for a considerable time, if subjected to good acid cleaning (e.g, with an HCI solution) to remove all surface films down to bare metal, immediately followed by pre-passivation (see"Pretreatment") and appropriate start-up procedures.

Heat Exchanger Design

This is the realm of the thermo-hydraulic engineer, and metal manufacturers and metallurgists should just limit themselves to pointing out the particular weakens or strong points of their materials.

Mention has already been made, albeit in rather general terms, of materials selection and water flow limitations (at the lower and upper levels) ; here, we would like to draw attention to some facts which may be of practical assistance in good design practice:

- Water Inlets: the cooling water should arrive as smoothely and evenly as possible all over the tube plate surface: side inlets are thus strongly recommended, combined with a water box shape appropriate to ensure about the same water velocity in all tubes; entrained air/gas bubbles and water turbulence can lead to tube-end impingement attack: thus regulating valves should be placed downstream of the heat exchanger rather than in front of it, while it is advisable to provide sufficient water trucking length for the circulation pump in order to achieve a reasonably laminar flow.

- Tube End Shaping : again to avoid impingement, the tube ends on the inlets side should be belled at about 45 for their first 3-4 mm; it has also been suggested that these tube ends should be left protruding from the tube plate surface by about 15-20 mm (whether belled or not), to ensure smoother water entry and concentrate any possible impingement outside of their critical rolled-in part;

finally, it has been shown that plain bores, duly pre-rolled and sized, will ensure better tightness than grooved ones, albeit with a little sacrifice in pull-out strength; but tightness should be considered much important than the other factor, which can be controlled by mechanical means (tie-rods,etc)

- Avoidance of Vibration: the heat exchanger should be insulated, via dampers, elastic joints, etc., from the main external sources of vibration (engines, motors, pumps, etc.) ; the natural vibration of bundle tubes, or "whistling", shall be prevented by appropriately spacing the tube supports (remember that thinner-wall and/or lower modulus tubes like titanium and stainless steel, will require about 50 pct more supports than the copper alloys).

- Cathodic protection : Cathodic protection has been shown to yield some benefit in reducing impingement attack on tube ends, as well as water box or tube plate corrosion due to galvanic coupling in sea waters; in self-contained apparatus like ship-borne heat exchangers, sacrificial anodes should be preferred to impressed current systems, but periodical inspection/replacement of the anodes should of course be ensured Zinc anodes are most common (especially in those parts of the water box where mude formation can cause passivation or screening), but in many instances pure iron anodes will give better service, being less "active" and thus interfering also less with the formation of protective films, while at the same time releasing significant amounts of ferrous ions to act as further Protestants of the tube surface (especially in the case of brasses). Of course, the water boxes should be so designed as to avoid stagnation of water around anodes, with consequent passivation or reduction of effectiveness.

- Ammonia Attack: even a few ppm of NH+ ions in the condensate, especially if some CO is also present, can lead to corrosion of tubes from the steam side, and brasses are most susceptible to this phenomenon, when used in the incodensable removal section of a condenser; it has been found very effective, apart from having recourse to 70/30 or 90/10 cupro-nickels in this section, also to design it with an "open" (as opposed to "shrouded") arrangement, whereby the continuous, unimpeded percolation of the condensate will avoid local rises in ammonia concentration, such as those found near supports and tube plates in the form of "channel" or groove-like attack.

- Selection of Materials Specifications: fortunately enough, the copper alloys used in heat exchangers are world; but national standard specifications often vary from one another in several details, while forgetting to take account of some operation requirements, as they tend to be manufacturing-oriented. Renouncing to national (and supra-national) pride, the Author would suggest that only USA (ASTM/ANSI/ASME), British (BSI) or Federal German (DIN) standards be chosen when specifying copper alloys for heat exchangers; attention is also drawn to the recent establishment of a more restricted, better suited specification for copper alloy seamless tubes for desalination, which takes account of much practical experience earned over 20 years (and 120,000 MT of tubes) in the very critical field of sea water desalination plant world-wide.

The Short-and Long-Term Economics of Copper Alloys

The economics of materials selection must be based on a variety of factors, such as satisfactory and proven performance records, easy availability (including spares), competitive cost-effectiveness, retrieval value at the end of apparatus, and the like.

All these criteria are well met by copper alloys in water-cooled tube-and-shell heat exchangers, and competitive materials liked stainless steels and titanium have therefore had to concentrate their promotional efforts purely in trying to push through the idea of "trouble-free apparatus" as a disguise for a "fool-proof" approach. Now, it is the Author's conviction, and of a vast majority of corrosion, and of a vast majority of corrosion experts and service operators, that this approach and concept is wrong in itself: firstly, because stainless steels and titanium, too, have their drawbacks (pitting, stress-corrosion, intergranular and crevice attack, for the former; leaking ends, hydrogen embrittlement for the latter; and fatigue, biofouling and difficult re-rolling of spare tubes for both)/ and, secondly, because it is extremely unwise to leave any sort of apparatus unattended, even more so when it is of a critical nature (the condenser of a steam turbine, the distiller of a ship desalinator, etc.)

As has already been said, in this paper and in many others,(ss) all problems encountered with copper alloys have found an easy and practicable solution; furthermore, copper alloys are the most economic in both the short-and long-term, as shown in Table III. This table was prepared in late 1985, using metal and currency rates prevailing at that time; while no really significant change has virtually occurred since it has not been thought worth while up-dating the figures in the Table, as

experience has shown that continuous variations can occur (e.g. between the preparation and the reading of this paper), which do not however obscure the very fact that copper alloys are from 2 to 3 times cheaper, and even more so when their recycling value is taken account of.

Conclusions

Copper alloys in shipbuilding heat exchangers have almost a half-centennial experience of good service, having in fact been initially developed for this end-use. Metallurgical and operational expertise earned over so many years has identified practical solutions to all kinds of problems likely to be encountered in operation, and high quality copper alloy semis (tube, plate,sheet) can now be obtained readily from a plurality of specialized manufactures in the mark-economy countries of the world.

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TABLE 111- Comparative costs (In US dollars m^3 of heat exchange surface).

Tube Material	Size OD × wall	Present Price US \$/m^3	25 years Cost US \$/m^3	Over Final Cost US \$/m^3
All-brass tube Scrap value	31.75 OD × 18BWG (1.245)	33.4 (100) 10.0	100.2 20.0	{ 80.2 (100)
90/10 Cn Ni Scrap value	31.75 OD × 18 BWG (1.245)	41.4 (124) 15.3	124.2 30.6	{ 93.6 (117)
66/30/2/2 Cu Ni Scrap value	31.75 OD × 22 BWG (0.711)	56.0 21.5	168.0 43.0	{ 125.0 (228)
Titanium Scrap value	31.75 OD × 22 BWG (0.711)	71.0 (213) 15.0	213.0 30.0	{ 183.0 (228)
Scrap ferritic steel Scrap value	31.75 OD × 22 BWG (0.711)	63.8 3.0	191.4 6.0	{ 185.4 (231)
Super Qustonitic steel Scrap value		91.9 (275) 5.0	275.7 10.0	{ 265.7 (331)