Material specifications for copper boilers.

General.

This note is concerned with the material specifications for 'pure' copper, as commonly used in model engineering for making 'small' steam boilers. It is not concerned with the vast range of copper alloys, such as 'brasses' or 'bronzes', for which there is an almost endless list of specifications and applications.

Except for the small commercial boilers sold primarily as 'toys' and working at low pressures (typically < 0.5 bar), model steam boilers are not fabricated from any materials other than 'pure' copper or steel. The current Boiler Test Code (2018), Vol. 2 contains special provisions for small, brass, low-pressure steam boilers.

This note is also not about materials for ferrous (steel) boilers. That is a separate subject entirely.

The two commonly-available material designations for 'nearly pure' copper are CW004A (formerly C101) and CW024A (formerly C106).

CW004A

C101/CW004A is the designation for the 99.9% pure copper used in a range of engineering applications, primarily electrical. It is also known as high conductivity (HC) copper or 'electrolytic tough pitch' (ETP) copper.

A level of 0.02% to 0.04% oxygen is maintained in ETP copper to oxidise any remaining impurities to oxides which would otherwise dissolve in the copper forming solid solutions and thereby reducing conductivity. Oxides have little effect on conductivity [Ref. 1].

C101 has a nominal conductivity of 100% IACS (International Annealed Copper Standard). It also has high thermal conductivity. This is therefore the material of choice for use in conductors and electrical components.

However, the oxygen content may have an adverse effect on the fatigue strength of the material when components are fabricated by heating or used in a reducing atmosphere [Ref. 2, Note A]. Accordingly, CW004A should not be used when the fabrication or service environment is in a reducing atmosphere and the part is designed to carry significant stress loading [Note B].

Model steam boilers, by their nature, are regularly cycled from low or zero stress up to perhaps 20% of their maximum yield stress or elongation. Clearly, compromise of their fatigue resistance MUST be avoided.

CW004A is not suitable for the construction of steam boilers.

CW024A

C106/CW024A (DHP; phosphorus deoxidised copper) is a grade of copper from which oxygen has been removed by the controlled addition of phosphorus during the production cycle [Ref. 5].

It is the material normally used for the manufacture of copper tubes as it can be readily formed and brazed. C106 has deep drawing characteristics superior even to those of C101 and can easily be made in tube form.

The presence of phosphorus acts as a deoxidant by reducing the copper oxide that would otherwise react with hydrogen (as above). The residual phosphorus remains alloyed with the copper within the specified range 0.013-0.050%. It has the effect of slightly reducing the electrical conductivity. The copper content is 99.85% minimum and the grade should be specified for all non-electrical applications, especially those involving assembly by welding or brazing.

Phosphorus deoxidised copper is not susceptible to hydrogen embrittlement, which is a serious risk with non-deoxidised grades.

Commonly-available plumbing tubing is also made from C106/CW024A [Note C].

Welded boilers

The material specifications for welded copper boilers are best left to the coded welder, who may well have specific requirements.

Boiler testing and certification.

The MELG scheme for boiler testing will not identify the presence of embrittlement and/or fatigue failure until the boiler is in a very dangerous condition indeed. Model steam boilers are designed with a safety margin in the region of 8 - 10.

Both the $2 \times P_w$ initial hydraulic test and the $1.5 \times P_w$ repeat hydraulic test do not get anywhere near testing the ultimate strength of a boiler. To do a proof test would require a test at 6 or $8 \times P_w$, which would carry a serious risk other damage being caused to the boiler, by distortion if not outright failure.

A boiler that had, in fact, been reduced by embrittlement and/or fatigue to only just surviving a $2 \times P_w$ test would be hazardous. A feature of fatigue failure is that the part remains apparently sound until it suddenly fails. The next time pressure is applied, or the one after that, could result in abrupt failure.

Conclusions

The appropriate material for the construction of copper steam boilers is CW024A (C106) - so called "oxygen-free" or phosphorous-deoxidised copper. Electrical grades containing oxygen intended to control impurities that would otherwise adversely affect the electrical conductivity must not be used.

This note is informative only. There are no proposals, at present, to mandate the certification of copper used for steam boiler construction.

Commercial boiler manufacturers will use the appropriate material and will, most likely, state that on the documentation.

Persons making boilers for their own use ('hobby use') are encouraged to make sure that the material used is appropriate. That is especially true for using 'any old stock material' and especially old water plumbing tube dating from 30 - 40 years ago!

Users of 'old' boilers that have been in service "for years", made of unspecified material, have been warned. However, it is true that most plumbing tube and 'engineering' copper supplied over many years will have been of the 'oxygen-free' variety.

The reader might be tempted to ask "why have we got away with it for so long?". It is certainly true that there have been very few, if any, failures attributed to failure of the bulk material in copper boilers. Most have been inadequate design or failures of joints. The answer to that might be that all engineering copper materials supplied to boiler makers over the years has been of the appropriate grade or that the safety margins are large enough to accommodate the weakening or that the combination of maximum working stress and the number of stress cycles is not sufficient to cause a problem.

This note is simply intended as a guide to the use of the correct material. Then, the potential problems of embrittlement disappear.

Notes

A - redox reactions in reducing atmospheres.

CW004A contains a (very) small amount of residual oxygen in the form of cuprous oxide, Cu_2O . During brazing or silver-soldering (i.e. at anything over 150 C but especially over 400 C) the Cu_2O may be reduced by any available reducing agents, e.g. from the heating gas, to form pure copper, together with by-products...

i) Hydrogen

 $Cu_2O+H_2 \ \ \rightarrow \ \ 2Cu+H_2O$

ii) Acetylene (from excess gas in the brazing torch $5Cu_2O + C_2H_2 \rightarrow 10Cu + 2CO_2 + H_2O$

iii) Propane (-do-)

 $10Cu_2O + C_3H_8 \rightarrow 20Cu + 3CO_2 + 4H_2O$

iv) Carbon monoxide (from oxygen-starved coal fire- those little blue flames dancing over the fire bed)

$$Cu_2O + CO \rightarrow 2Cu + CO_2$$

This is known as 'hydrogen embrittlement'. It does not seriously affect the tensile strength or elongation of ETP copper, but does affect its fatigue strength (Refs. 3 and 4). Therefore, it must be avoided in any structure that may be subject to cyclical stress or vibration.

In cases (i) - (iii), the reduction process will mainly occur during construction of the boiler as the necessary temperatures and gas supply will not be present in normal service. The hot water vapour produced (steam) can create very high pressures within the solid material. Above the critical temperature of 374 C the only form that the water can take is as steam. Pressures over 80,000 psi (5 x 10^2 MPa) may be generated, potentially causing fissures and cracks in the material [Ref. 2].

In case (iv), superheater tubes are very likely indeed to reach the temperatures necessary for the chemical reactions. Thus, the CO reaction is the only one likely to continue after the boiler construction has been completed and the boiler placed in service, and limited to the superheater tubes (if copper).

B - Fatigue failure

Fatigue in metals is caused by the progressive growth of initially small cracks and other defects. Small defects are characterised by sharp-radius boundaries that cause stress enhancement in a material subjected to stress. The local stress at the boundary of the defect may be high enough to cause localised failure of the material even when the stress in the bulk of the material is well below the level that would cause failure of the bulk material.

In a material subject to cyclical stress the repetitive failures at the defect boundaries cause the defect to grow progressively, without limit. Thus, the material will fail eventually if repeatedly subjected to the same levels of stress cycling. Almost invariably, the maximum stress increases as the section of material remaining to carry the load become smaller. The result is an apparently sudden and catastrophic failure of the whole component. Examination of the failure usually reveals the gradual progression of the failure line across the section, until the remaining section is incapable of carrying the overall load.

Model or miniature steam boilers are not usually stress cycled for the 10's or 100's of thousands of cycles usually encountered in engineering fatigue tests. However, they are cycled to a significant fraction of their ultimate strength (perhaps 15 - 20 %) and the presence of significant embitterment during their manufacture may still cause failure at stress levels much lower than the bulk material can support.

C - Plumbing tubing

Common plumbing tube intended for water supply or heating systems is almost always made from C106/CW024A material. However, it is not commonly used in boiler construction because it is usually too thin.

It is also usually supplied in a half-hard condition caused by the drawing process. The common copper tube designations (Table 'X', 'Y', etc) refer to the wall thicknesses and hardness characteristics and not to the actual material type.

In the past (1970's ?), some inferior tubing was supplied for plumbing applications. Although the material (probably) was C106 (or the equivalent at the time), it contained significant particulate inclusions that resulted in the large-scale incidence of leaks from plumbing systems. That was probably exaggerated by the very thin gauge of the tubing. Such weaknesses are clearly not acceptable for steam boilers.

References.

- 1. <u>https://copperalliance.org.uk/about-copper/conductivity-materials/electrolytic-tough-pitch-copper</u>
- 2. *Hydrogen Embrittlement of Tough Pitch Copper by Brazing*, E. Belkin and P.K. Nagata, Welding Research Supplement, p. 54-s, February 1975.
- 3. Harper, S., et al, ibid, p. 416. (from Ref. 2).
- 4. Morin, D. L., unpublished data (from Ref. 2).
- 5. https://www.columbiametals.com/products/copper/c106

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