Back to the future with COPPER BRAZING

Anneal-resistant copper alloys and a dedicated brazing process could bring copper's high strength and heat conductivity back to air conditioning.

Remember when copper was commonly used in mobile air conditioning? Hans Fernqvist does. He's a leading technical expert on climate AC systems at **Volvo Car Corp.** and has been actively involved in the development and writing of SAE and ISO standards on mobile air conditioning (MAC) for nearly 20 years. According to him, old Volvos had air conditioners made from mechanically expanded copper tubing that kept away bad odors from bacteria and fungi.

"A cooling core of copper-brass could finally solve the problem of foul-smelling air conditioning," he remarked in a recent article.

Anneal-resistant copper alloys and new brazing techniques are leading the way for innovative copper heat-exchanger designs, like this prototype, that could streamline manufacturing and cut costs while boosting efficiency. Photo courtesy CuproBraze Alliance.

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Key points

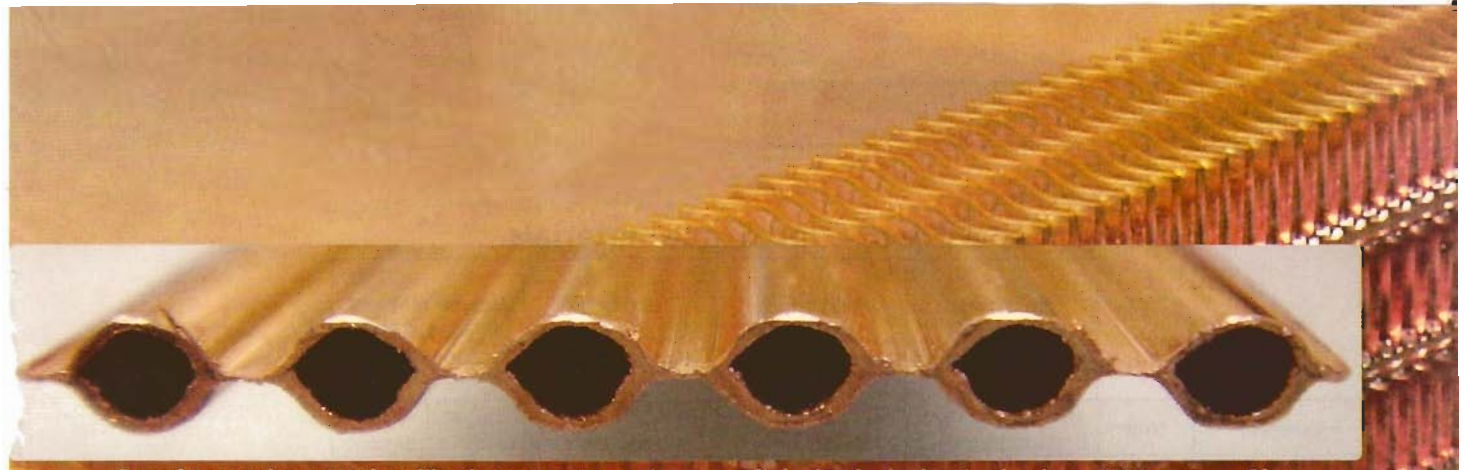
- Engineered copper alloys don't lose strength after brazing.
- Brazing pastes and foils alloy with base metals to form joints.
- 650°C brazing in nitrogen forms strong, reliable heat-exchanger cores.

Resources

International Copper Association (ICA), *copper.org*

CuproBraze Alliance, *cuprobraze.com*, has a CuproBrazing Handbook, video explanation, and supplier listing.

Copper Development Association, *copperinfo.com*



Brass heat-exchanger tubes, like these prototypes, have antimicrobial properties that kill the bacteria and fungi linked to foul odors in aluminum MAC systems. Photo courtesy CuproBraze Alliance.

In addition to being odor-prone, aluminum has lower thermal conductivity and strength than copper. Which begs the question: Why was it phased out over the past 30 years?

A copper comeback?

Early air conditioners, starting with AC's passenger-car debut in 1939, were made from copper and brass. Copper's high thermal conductivity made it a natural choice for the fins and heat exchangers. However, most of these systems were soldered with tin-lead alloys.

Although by 1969 more than half of all new cars sold were AC-equipped, the 1970s saw manufacturers seeking to eliminate lead from their products and switching to aluminum components that could be brazed using then-new processes. Aluminum brazing does not require a separate filler material. Instead, highly reactive fluorine compounds at high temperatures remove passivating Al_2O_3 before brazing.

For copper alloys, both soldering and brazing call for melting a filler metal, flowing it into the joint, and binding it with the base metal. However, solders melt below 450°C while brazing, by definition, uses filler metals with higher melting points. At brazing temperatures, the filler metal alloys with the base metal, but the base metal does not melt as it would in welding.

Copper alloys at that time were significantly weakened by exposure to the brazing temperature. Aluminum was weaker overall, but could withstand higher temperatures without degradation.

Groundbreaking designs in aluminum heat exchangers allowed the lower-strength, lower-thermal-conductivity material to outperform the previous generation of copper designs. Aluminum also had a reputation as a wonder metal which manufacturers claimed would eliminate toxic materials from manufacturing.

A decade after ditching the lead, the MAC industry had more chemical trouble: chlorofluorocarbon (CFC) refrigerants eating away at the ozone layer. As the ozone hole shrank, regulators turned their attention to the global-warming potential (GWP) of the hydrofluorocarbon refrigerants that replaced CFCs. Low-GWP refrigerants, including high-pressure CO_2, require some reengineering of MAC systems. For example, CO_2 coolant, also known as R744, requires pressures of 133 bars compared to 30 bars with common hydrofluorocarbons.

The quest for lower energy consumption is another driving force behind MAC redesigns. Manufacturers want compact, lightweight heat-exchanger designs that pack the same cooling power with less load on car engines or batteries. Lightweight means thin gauges and materials with high specific strength. Thin-gauge materials' lower cross-sectional area also lets air pass more freely through heat-exchanger cores. The resulting lower pressure drop boosts efficiency and fuel savings.

Efficient MAC designs often run hotter than those of the previous generation. The alloys now being considered for brass tubes and copper fins in heat exchangers have ultimate tensile strengths of 340 to 400 MPa at 25°C and retain 70 to 75% of their strength at 250°C. Aluminum alloys for the same application have 25°C strengths of 150 to 180 MPa and only retain 25 to 50% of their properties at 250°C.

Drivers are spending more time in their cars, too. While MAC has become a necessity for comfort and resale value, the foul odors that can emanate from aluminum MAC systems detract from customer perceptions of quality and cause worry about bacteria or mold spores in the car's air.

In March 2008, the U.S. Environmental Protection Agency acknowledged a growing body of research, funded in part by the International Copper Association and the Copper Development Association, showing copper surfaces slow or eliminate bacterial and fungal activity. The agency now lets merchants market copper and some of its alloys based on their antimicrobial properties, the first solid material permitted such a claim.

Finally, the original drawback to copper, the need for lead-based soldering, has been put to rest in recent years with the development of an environmentally friendly process for brazing copper-brass components. The CuproBraze process was specifically developed for the manufacture of automotive, heavy-duty truck, and industrial heat exchangers in a low-cost, environmentally friendly process. The International Copper Association licenses CuproBraze technology free of charge to manufacturers.

Advanced heat exchangers use flat tubes to carry hot working fluid from the engine or turbocompressor. The geometry maximizes contact between the fluid and the tube walls. Those walls, in turn, contact fins that remove

Nominal properties of CuproBraze materials

Properties	Unit	Fin copper SM 0502 (standard temper)		Fin copper SM 0502 (soft temper)		Tube brass SM 2385, C66420 (CuZn14Fe0.9)		Header material SM 2464, C74400 (Cu64ZnNi3)	
		Before brazing	After brazing	Before brazing	After brazing	Before brazing	After brazing	Before brazing	After brazing
Conductivity	% IACS	60	90	60	90	35	30		
Yield strength	N/mm²	340	260	122	160	340	270	115	105
Tensile strength	N/mm²	400	330	264	297	420	400	350	340
Young's Modulus	**N/mm²**		**118,000**				122,000		103,400
Hardness	HV	120	100	69	77	130	115	70	67
Elongation A50	%	1	10	35	28 to 30	25	30	70	75
Density	kg/m³		8,900				8,750		8,500
Melting temperature	**°C**		**1,083**				1,000 to 1,025		910 to 930
Specific heat	kJ/kg-°C		0.385				0.380		0.377
Thermal expansion 20 to 300°C	**°C⁻¹**		17.7 × 10^{-6}				19 × 10^{-6}		19 × 10^{-6}

heat from the working fluid. Copper fins' high thermal conductivity and good strength let designers thin out the fins while getting the same performance as aluminum. Side supports, headers, and tanks complete the system's core.

To build a typical heat exchanger, high-frequency induction heating (or HF welding) creates tubes from brass strip. HF welding works on wall thicknesses 110 μm and above and leaves no seam irregularities to hinder core assembly. The tube former also cuts the tubes to length before a tube sprayer applies the brazing alloy to the tubes' OD. New multichannel tube designs made from copper-alloy strips are also being evaluated for use in air-conditioning components.

A corrugation machine converts copper strips into fins which are then cut to length and collected for transfer to the assembly area. There, workers or semiautomated equipment insert the folded fins between the tubes.

Next, side supports are attached, and specialized machinery inserts the tube ends of the tube-fin assemblies into holes in the header plates that hold the assembly together. Header slurry application machines coat the holes with brazing paste. Uniform paste application contributes to the system's reliability. Finally, the entire assembly goes into the brazing furnace at 600 to 650°C.

The alloys used in conventional copper and brass radiators are designed for soldering below 450°C. Extended exposure to high temperatures effectively anneals the metals, compromising their room-temperature yield strength. Standard brass yields at about 310 N/mm² at 25°C, but that drops to about 80 N/mm² after a 2-min anneal at 650°C.

The properties drop because during the temperature exposure metal atoms move through their lattice via solid-state diffusion. The movement heals lattice dislocations and other defects that are cold-worked into the metal to strengthen it.

Annealing is time and temperature-dependent. The effect is much more pronounced as temperatures approach the metals' melting point, although they can lose significant strength at lower temperatures, too. So despite brazing's promise of strong joints, heat-exchanger designers could not take advantage of it until anneal-resistant copper alloys were developed. The new brass alloys, for example start out with 350-N/mm² yield strengths at 25°C and only lose about 50 N/mm² after the 650°C anneal.

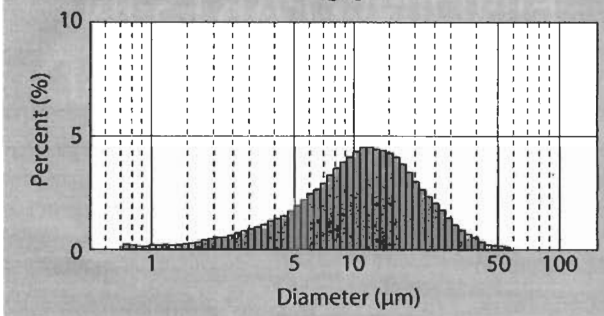
Engineered alloys

Anneal-resistant copper for MAC fins relies on chromium additions that form copper-chromium intermetallic compounds. The alloy is cast and rolled. Rolling deforms the metal and forces the chromium into coherent precipitates, meaning chromium islands are still linked into the copper's crystal structure although they strain the lattice.

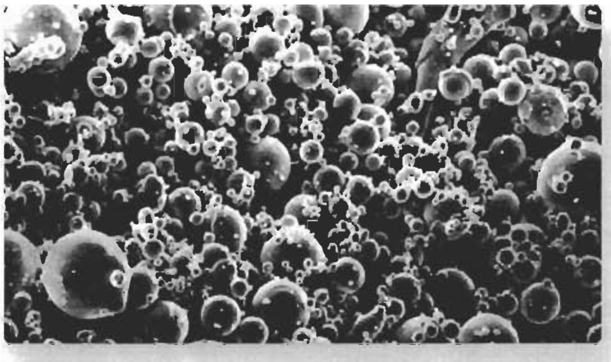
In this form, the chromium cuts the as-shipped alloy's electrical conductivity to about 60% of what it would be for unalloyed, annealed copper, 3.48 × 10^7 S/m compared to 5.80 × 10^7 S/m or 100% IACS for the pure metal. The thermal conductivity drops proportionately.

The islands of chromium nucleate larger, noncoherent precipitates, averaging 3 nm in diameter, during brazing at 640 to 650°C. The precipitates prevent softening of the alloy at those temperatures. After precipitation, the alloy's electrical conductivity rebounds to 92% IACS (5.34 × 10^7 S/m). Thermal conductivity reaches 377 W/m-K after brazing, compared to 222 W/m-K for aluminum fin alloys.

The conventional brass used for radiator tubes is 65 to 70% copper and 30 to 35% zinc. It melts between 920 and 960°C. Higher-temperature-joined CuproBraze brass


Particle-size distribution in brazing powder

OKC 600 brazing alloy is gas-atomized to form a filler powder. Particle sizes center on 15 to 30 µm; particles larger than 90 µm are sieved out.



tubes use alloy C66420 which contains 85% copper and 14% zinc and melts at 1,010 to 1,025°C. The high copper content defends against stress-corrosion cracking and dezincification. The addition of about 0.9% iron introduces 200-nm precipitates that resist recrystallization and help the alloy retain fine grains on the order of 3 µm in diameter.

The material for headers, side supports, and tanks is a Cu64ZnNi3 brass designated C74400. Solution hardening from the nickel addition retains mechanical properties after the brazing operation. The material has good strength, even at elevated temperatures. It also forms well, so it is ideal for the stamping and piercing operations involved in header manufacture.

Though the alloys discussed here resist higher temperature brazing, most of the filler alloys commonly used for brazing melt at too high a temperature to be used in MAC applications. Only the CuSnNiP-family of fillers melt at sufficiently low temperatures, 590 to 650°C, to successfully braze tubes and fins using the CuproBraze process. Two of these alloys are designated OKC 600 and VZ 2255.

The OKC 600 alloy is patented (U.S. Patent Number 5,378,294) but is licensed free of charge to manufacturers of high-quality powder for automotive and heavy-duty industrial heat-exchanger applications. It is made up of 4.2% nickel, 15.6% tin, 5.3% phosphorous, and 74.9% copper. It melts between 600 and 610°C.

VZ 2255 has 7% nickel, 9.3% tin, 6.5% phosphorous, and 77.2% copper. Its melting point is between 600 and 630°C.

These alloys do not permit cold forming, so cladding the tube or fin to be joined with the filler metal is not possible. Instead, the fillers may be supplied as powders produced by gas-atomizing the molten material into fine-grained spheres in a nitrogen atmosphere. The average particle size is 15 to 30 µm with particles over 90 µm sieved out. OKC600 is only available as powder, which can be mixed into brazing-pastes.

VZ 2255 is normally supplied as an organic-free, 20 to 40-µm-thick foil made in one-step rapid solidification. The speed of the process gives the alloy an amorphous structure with high ductility.

To ease application of the brazing powder, it is shipped premixed with a solvent-based binder to form a paste. Binders decompose or evaporate cleanly below the brazing temperature without leaving residues on the brazed samples. Tube-to-fin, tube-to header, and tank-to header joints do well with brazing pastes.

Workers can apply the pastes by spraying, pouring, dipping, roll-coating, and other methods. Solvent-based pastes have to be dried before firing, usually in air between 50 and 130°C. Higher temperatures can compromise the brazing properties of the paste. After the paste dries, tubes or other coated components can store in a clean environment for up to several months.

The mixing of brazing powders with binders means that users should determine metal coverage by weight as opposed to thickness. The tube coating should add 150 to 250 gm/m^2 after drying. Although tight-tolerance tubes and fins join well with thinner layers, it may be useful to start with a thicker coating and scale back as appropriate.

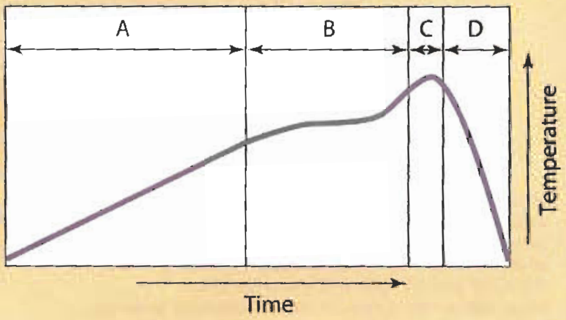
The paste that joins tubes to headers is a looser slurry applied to the air side of the header. Filler metal makes up about half the volume of the slurry, so 0.5 to 1.8 gm should be applied depending on tube width. Users may also choose to add a small amount of flux to this kind of paste to compensate for slightly oxidized components.

Brazing foils can replace or complement brazing pastes; the two types of fillers can be brazed together and produce the same joint properties. The binder-free foils are especially useful for brazing internal connections where fumes from the binder burnoff can become trapped and compromise the brazed joints.

Brazing away

Batch, semicontinuous, or continuous furnace setups can braze parts equally well. Brazing furnaces must

CuproBraze temperature cycle



The typical CuproBraze temperature cycle calls for a slow heatup to let binder in the brazing paste burn off (A). The heat-exchanger core and fixture are allowed to equalize at around 550°C before brazing begins (B). The brazing period begins when the brazing powder reaches 600°C. Here, the filler metal wets and alloys with the base metal (C). Cooldown should be 1°C/sec or slower to 550°C to prevent thermal distortion (D).

be able to reach 700°C, control their temperature ramps, and conduct nitrogen purges. Aside from these basic factors, the choice of furnace is largely determined by part size, production volume, and whether all joints in the part will be brazed in a one-shot process.

Heat-expansion length increase (Δl) from 25 to 650°C for 1-m-long object

Material	Heat expansion coeff. (μm/m°C)	Δl for 25°–650°C (mm)
Copper fin (SM 0502)	17	10.6
Tube brass (SM 2385)	19	11.9
Header brass (SM 2464)	20	12.5
Steel	11	6.7
Stainless steel	15	9.4

A single-chamber batch furnace meets the needs of a small production line. A three-chamber furnace with a double in-out operating mode permits more efficient use of the middle (brazing) chamber, where the holding time is the shortest. For high-volume production, the best choice is a continuous furnace which loads parts on a moving belt.

Typically, such a furnace is sized for brazing 1,500 kg/hr with a maximum height of 350 mm on a 1,200-mm-wide belt. An automated control system allows for flexibility when brazing parts of different configuration and mass. The furnace's four zones of temperature control are preset to heat the core to 650°C.

During the ramp from room temperature to 650°C, the fixtures and different sections of the part can undergo differing degrees of thermal expansion. To minimize these differences, brazing fixtures should have a low mass that lets their temperature equilibrate to that of the radiator core during the heat cycle. Designers also prefer stainless steel over plain steel for tooling because stainless' thermal expansion coefficient is closer to that of brass. They may also choose slightly flexible fixtures that respond mechanically to the part's expansion and contraction.

Brazers should also be alert for oxidation during and after the heat cycle. Because CuproBrazing uses little or no flux, furnaces for the process must purge the atmosphere with nitrogen until there is less than 20 ppm of oxygen present. More oxygen lets the brazing powder oxidize at elevated temperatures after the protective binder has burned off. Oxidized powders can't fully alloy with the base part and will compromise final joint strength.

An efficient nitrogen purge during the slow burnoff of the binders lets gas composition equalize throughout the part. A slow heatup also helps parts, filler, and fixtures thermally expand at the same rate to minimize distortion.

The binder burnoff creates process emissions, and the constant flow of nitrogen expels them from the brazing atmosphere. Local regulations and the type of binder will dictate whether these emissions need to be burned in an oxygen atmosphere outside the furnace or diluted with ambient atmosphere.

Once the part temperature approaches the filler metal's melting point, experts recommend a steeper temperature ramp. Many process engineers set their proportional control furnaces to overshoot the brazing temperature at this point so the part can heat at more than 30°C/min. The base metal melts over 300°C higher than the filler metal, so there's little worry that a slight temperature overshoot will damage the adherends.

The alloying reaction kicks off as soon as the filler is molten, but some joints may need to reach 650 to 670°C to fully wet out. In addition, the brazing time should be just long enough to alloy the filler and parts without letting filler atoms diffuse too far into the base metal. Long exposures to brazing temperatures can compromise the joint's high-temperature properties. Small MAC units can be fully brazed in 2 to 4 min.

Parts should cool slowly, at about 1°C/sec, at least until the maximum temperature reaches 550°C and the filler metal has resolidified. Keeping parts in the inert atmosphere until they've cooled to 150°C, or less if the ambient air is humid, prevents discoloration. CuproBraze brazing furnaces can join with nitrogen convection sections to cool the parts while keeping the furnace short or freeing it for the next cycle. Any discoloration that does occur is only a cosmetic effect and not an indication of a weak joint. **MD**