Silver-Free Filler Metals Meet Strength Requirements in Brazed Joints

The results of wetting and shear strength testing along with metallurgical characterization of Cu-4Sn-6P and Cu-40Zn-1Sn-0.3Si silver-free filler metals designated for brazing copper and brass are detailed

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Two silver-free filler metals, TiBraze®P14 (Cu-6P-4Sn wt-%) and TiBraze®LOK59-03 (Cu-40Zn-1Sn-0.3Si wt-%), were experimentally evaluated to determine if these alloys are suitable to replace silver-based filler metals for brazing copper and brass.

Characteristics of the filler metals, such as spreading area, joint strength, and microstructure, were analyzed. These characteristics were compared to filler metals that are currently used in the industry, such as standard silver-based BAg-1, BCuP-5, and a silver-free BCuP-9.

Metallurgically compatible silver-free braze alloys used to join copper and brass-based materials were found to yield ultimate joint strengths rivaling those of silver-based filler materials. Data collected based upon computational models (Thermo-Calc™), optical microscopy, and shear tests provided substantiation of compatibility. The shear strength of brazed joints made with TiBraze®P14 is higher by 21–24% than that of low-silver standard BCuP-5 filler metal.

Although the shear strength of silver-free filler metals is between 72 and 85% of the shear strength in silver-based Alloy BAg-1, the high cost of silver-based joints can be significantly reduced by using silver-free filler metals. By increasing the overlap and using silver-free fillers, joint costs can be reduced while meeting strength requirements.

Materials and Procedure

The base materials used in this study were copper C110 and brass C260 alloy containing 70 wt-% of copper and 30 wt-% of zinc. These materials are machinable and widely used for manufacturing hydraulic and pneumatic pipes, cartridges, ammunition casing, radiators, hardware, and so on. They do not require heat treatment after welding, brazing, or soldering.

Two new silver-free filler metals, TiBraze®P14 in the form of a brazing paste using a rubber-based binder and TiBraze®LOK59-03 rods Ø2.4 mm, were evaluated to determine characteristics such as spreading area, joint strength, and microstructure.

Table 1 contains chemical compositions of each filler metal. Test results of the same silver-free filler metals in combination with low-carbon steel and stainless steel are reported elsewhere (Ref. 1).

Two standard silver-containing filler metals — BAg-1, BCuP-5 — and a silver-free BCuP-9 alloy were tested for comparison with new silver-free filler metals.

Brazing was performed in air by heating with a propane torch. The flux used during brazing was the boron-modified, black fluoroborate flux 601B/3411 (Superior Flux & Mfg. Co., Solon, Ohio).

Methods, materials, and sample designs applied for testing wetting and

Table 1 — Brazing Filler Metals, Their Compositions, and Melting Ranges

Brazing Filler Metal	Chemical Composition, wt-%	Melting Range, °C	°F
TiBraze®LOK59-03	Cu-39.7Zn-(0.9-1.1)Sn-(0.2-0.4)Si	880–905	1616–1662
TiBraze®P14	Cu-(5.3-6)P-(3.5-4)Sn	635–680	1175–1256
BCuP-9	Cu-(6-7)Sn-(6-7)P-(0.01-0.4)Si	637–674	1178–1274
BCuP-5	Cu-(14.5-15.5)Ag-(4.8-5.2)P	643–802	1190–1475
BAg-1	Ag-(14-16)Cu-(14-18)Zn-24Cd	607–618	1125–1145

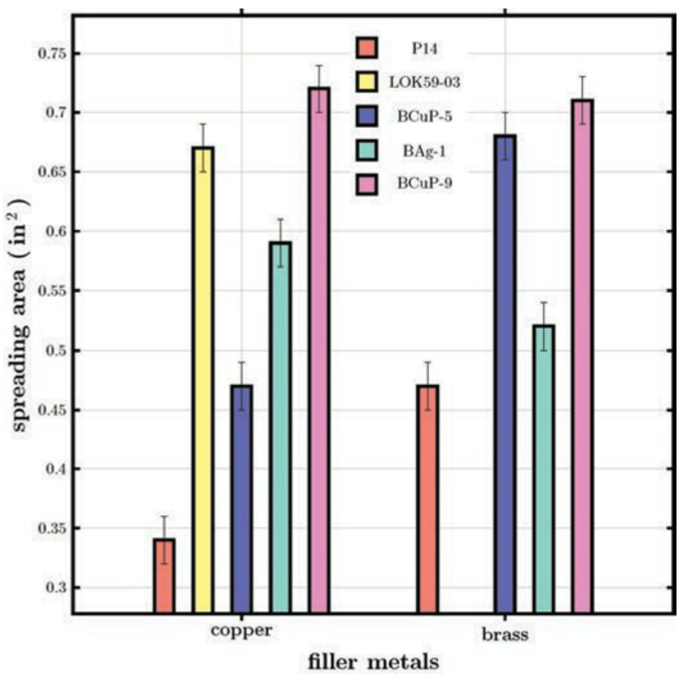


Fig. 1 — Average spreading areas of tested filler metals on copper and brass.

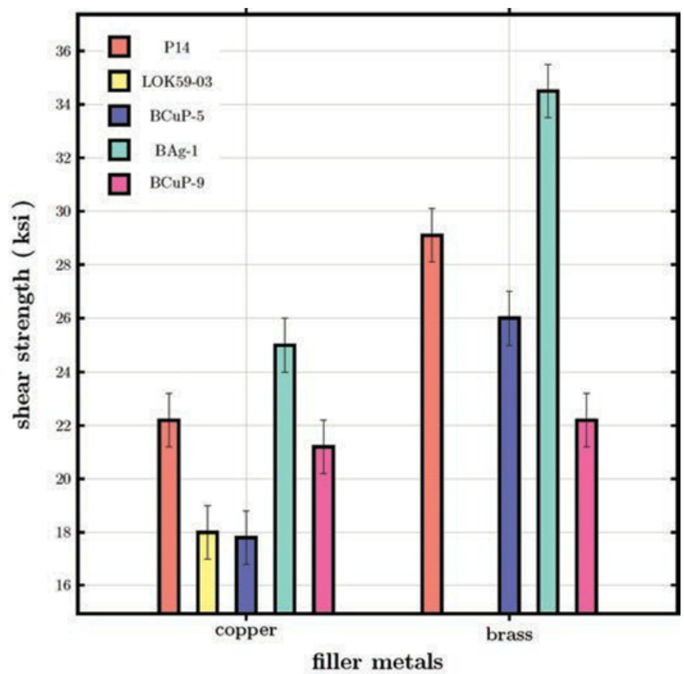


Fig. 2 — Average shear strength of tested filler metals on copper and brass.

Table 2 — Average Shear Strengths of Brazed Joints, for Each Filler Metal, ksi (MPa)

Braze Filler Metal	Copper	Brass
TiBraze®LOK59-03	18.0 (124.2)	–
TiBraze®P14	22.2 (153.2)	29.1 (200.8)
BAg-1	25.0 (172.5)	34.5 (238.1)
BCuP-5	17.8 (122.8)	26.0 (179.4)
BCuP-9	21.2 (146.3)	22.2 (153.2)

spreading, shear strength, and microstructure characterization are described elsewhere (Ref. 1).

Results and Discussion

Wetting Characteristics

The spreading area provides an indication of how the filler metal will spread and flow into the joint during brazing. Figure 1 shows the resulting average spreading area of each filler metal on different base metals.

The filler metals with low spreading area have difficulty spreading through the joint and creating fillets, thus decreasing the overall strength of the joint. Silver-free LOK59-03 exhibited better spreading on copper than a standard silver-based Alloy BAg-1, and silver-free filler metal P14 had almost the same wetting characteristics on brass as BAg-1. At the same time, P14 exhibited the worst spreading on copper among all tested brazing alloys.

Shear Strength

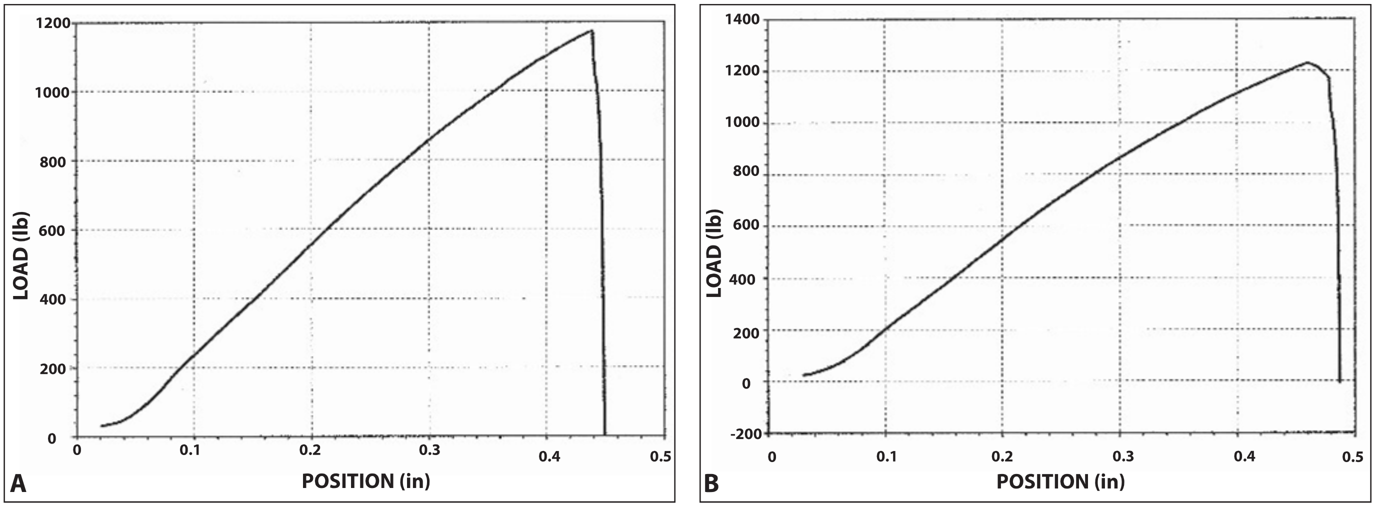
The results of the average shear strength testing for all filler metals are presented in Table 2 and Fig. 2.

Brazing with P14 resulted in sufficient shear strength with copper and, especially, brass — the second highest value after the standard silver-based Alloy BAg-1 that makes the silver-free P14 alloy a prospective substitute for silver. At least 15%-silver containing BCuP-5 can be completely substituted by P14 in such applications as the manufacture of copper tubing and brass faucet brazed joints.

As expected, LOK59-03 exhibited modest values of shear strength in copper brazed joints that can be explained by higher yield strength of the brazed joint metal than that of the base metal, which results in limited deformability of the joint metal.

The load-displacement diagram (Fig. 3A) shows low ductility of the LOK59-03 brazed joint, while the copper brazed joint made with P14 has mechanical behavior with some ductility of the joint metal (Fig. 3B).

Brass brazed joints made with the silver-free P14 alloy exhibited certain ductility and a yield point about 15.5 ksi (107 MPa). The load-displacement diagram (Fig. 3C) shows formation of several microcracks that, however, do not propagate through the joint metal but only release stresses, while the joint continues to resist higher shear loading. Shear strength of copper or brass brazed joints made with the silver-free P14 filler metal is greater than that of both phosphorus-containing standard braze Alloys BCuP-5 and BCuP-9. The strength of P14 joints is second only to the silver-based BAg-1 brazing filler metal.



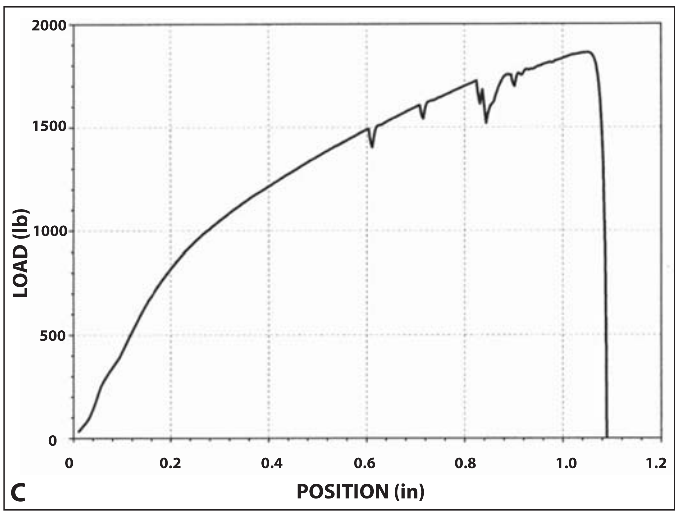


Fig. 3 — Load-displacement relationships of brazed joints. A — Low-ductile behavior of copper joints brazed with LOK59-03; B — moderate ductile behavior of copper joints brazed with P14; C — ductile behavior of brass joints brazed with P14 despite several microcracks, which appeared in the joint metal.

Macro- and Microstructures of Brazed Joints

Brazed joints were examined via optical and scanning electron microscopy to characterize the phase composition and solidification microstructure of each filler metal.

Figure 4A, B are images of a copper joint made with the P14 filler metal. The quality of this joint is characterized by dense joint metal and smooth, defect-free fillets. Phase composition of the joint metal and the amount of each phase as predicted by Thermo-Calc™ are represented elsewhere (Ref. 1).

Based on the calculations from this software, three phases are present in the P14 joint metal: the eutectic phase composed of Cu_3P and Cu_3Sn, and an FCC phase, which is copper-tin alloy with an insignificant amount of phosphorus. The eutectic phase dominates in the joint metal that provides moderate ductility and high shear strength of brazed joints 22.2 ksi (153.2 MPa).

No intermetallic layers were found at the interface with the base metal. The Cu-Sn alloy phase was solidifying first along the base metal interface, while the relatively low-melting eutectic system was ousted into the middle of the joint, where it crystallized at a lower temperature.

Apparently, the liquid reached a low enough temperature to begin to form the eutectic phase prior to the complete transformation of the FCC phase. Formation of the FCC phase predominantly occurs at the interface in the uniform eutectic microstructure of the joint metal.

Figure 5A and B are images of a joint made with brass (base metal) and P14 powder (filler metal). The phase composition of the joint metal is presented by an FCC phase of a ternary solid solution Cu-(8.5-11)Zn-2Sn wt-% and an eutectic system containing Cu_3P and Cu_3Sn components. The microstructure displays that the FCC phase grows along the joint interface with the base metal, similar to the copper-based metal joint. The eutectic phase dominates the middle of the joint.

Figure 5A portrays a smooth fillet and uniform microstructure of the

Table 3 — ThermoCalc™ Predicted Phases and Constituents in the LOK59-03 Joint Metal

Filler Metal	Phase	Percentage of Each Phase at 25°C	Composition (wt-%) Cu	Zn	Sn	Si
LOK59-03	BCC	5.1	50.4	40.4	8.6	0
	Cu_3Sn	1.2	61.6	0	38.4	0
	FCC	93.7	60.2	39.8	0	0

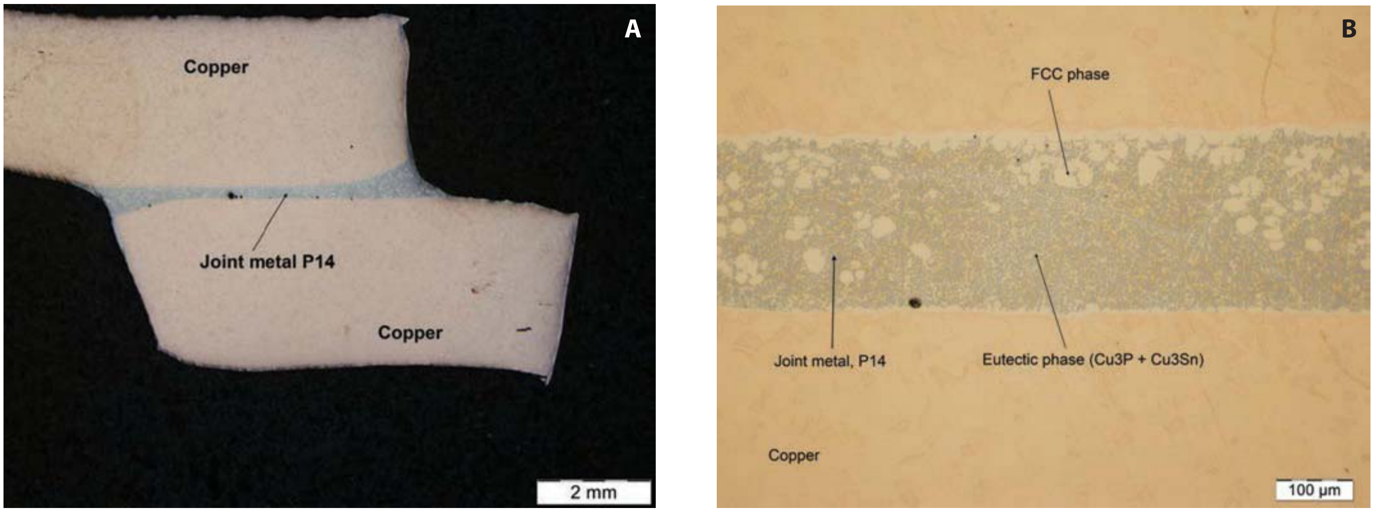


Fig. 4 — A — Macrostructure of copper + P14 brazed joint, ×12.5; B — microstructure of copper + P14 brazed joint, ×200.

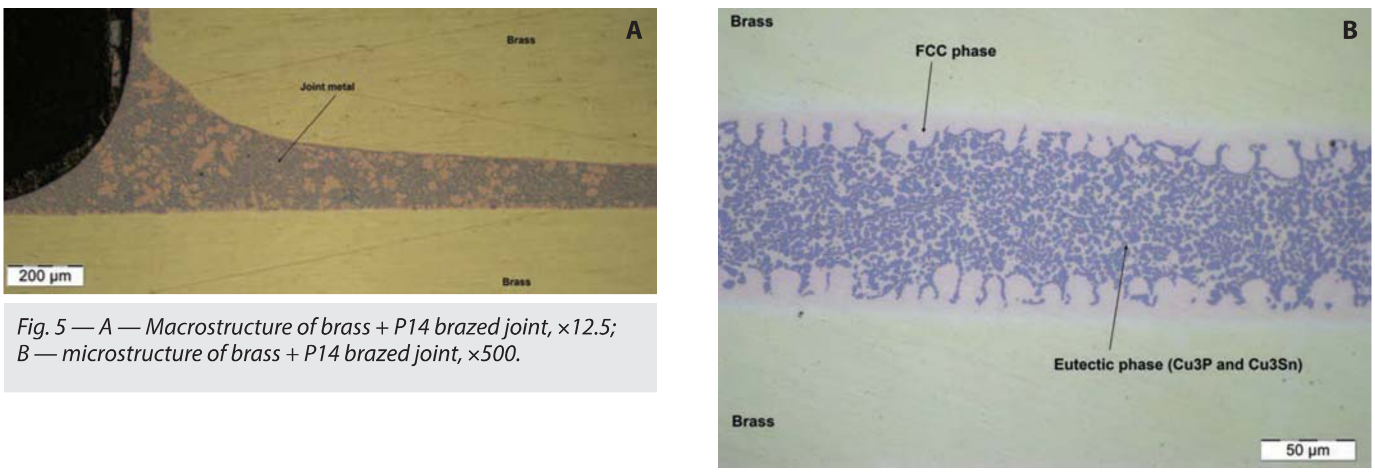


Fig. 5 — A — Macrostructure of brass + P14 brazed joint, ×12.5; B — microstructure of brass + P14 brazed joint, ×500.

joint metal. Some fillets contain few defects, particularly pores. It is likely that the pores appeared due to insufficient heating upon formation of the joint. Considering the relatively high strength of the brazed joints, as well as joint and fillet formation, this base metal and filler metal combination is good for brazing brass parts.

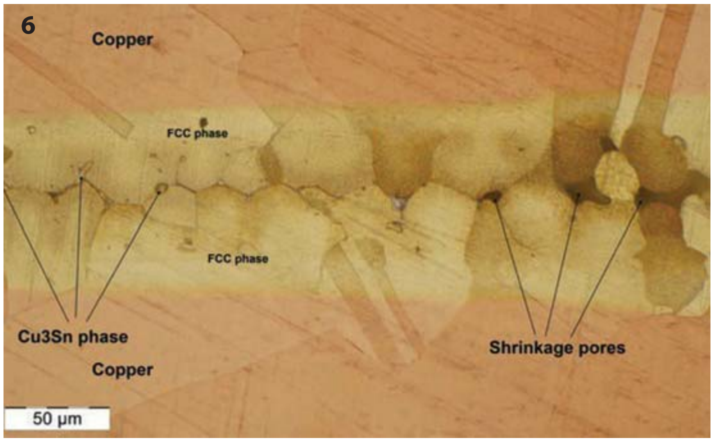
Figure 6 is an image of a joint made with copper (base metal) and LOK59-03 (filler metal). According to thermodynamic modeling with Thermo-Calc™, three phases should occur in the LOK59-03 joint metal (Table 3): FCC phase, BCC phase, and Cu_3Sn intermetallic compound. The BCC phase is the high-temperature phase that solidifies around 890°C. This means that the BCC phase will begin to form first. The entire liquid will transform into the BCC phase around 884°C, which is the solidus temperature. As the joint metal cools, the BCC phase begins to transform into the FCC phase at 689°C.

Upon cooling to room temperature, most (93%) of the microstructure will have transformed into the FCC phase. There should be very little Cu_3Sn phase because its transformation begins at a lower temperature, ~450°C. There is insufficient time for a significant amount of Cu_3Sn to form upon cooling from 450°C to room temperature.

However, after studying the microstructure of the joint metal (Fig. 6), we suggest that the FCC phase (which is simply yellow brass) is crystallized first on the solid copper and the FCC grains grow rapidly to the middle of the joint because the solidus of this brass phase concurs with the low limit of the brazing temperature range. Low-temperature phases, such as Cu_3Sn, are ousted to the central zone by said growing FCC grains.

Our point of view is supported by the multiple epitaxial crystal growth of the FCC phase on copper grains that is clearly seen in Fig. 6, because the copper (base metal) and the yellow brass component of the joint metal have the same FCC lattice. Rapid solidification of the FCC phase is evidenced by the appearance of shrinkage pores in the central zone of the joint. Such pores are typical for rapidly solidified cast structures. The same pores were also found between dendrites in the fillet area. Supposedly, these pores located along the central line cause a relatively low-strength copper joint brazed with LOK59 filler metal.

Hence, LOK59-03 is recommended



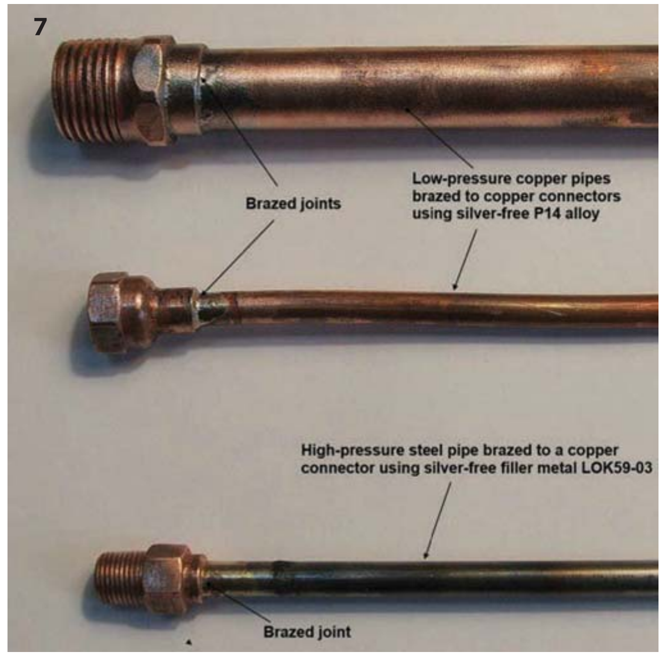


Fig. 6 — Microstructure of copper + LOK59-03 brazed joint, ×1000.

Fig. 7 — Copper-to-copper and copper-to-steel tubing brazed joints made with silver-free P14 and LOK59-03 filler metals.

Fig. 8 — Brass tube brazed joints made with silver-free P14 filler metal.

for brazing steels or copper to steel, while the P14 alloy is more suitable for brazing copper and brass structures. Silver-free brazing filler metals P14 and LOK59-03 are suitable to substitute silver-based alloys in joining hydraulic, pneumatic, and lubrication pipelines and can be widely used in the manufacture of automobiles, refrigerators, house water pipes, machinery equipment, electronics, and so on. Typical examples of brazed joints of copper, steel, and brass tubes made with these silver-free filler metals are presented in Figs. 7 and 8.

Conclusions

1. Silver-free brazing filler metals are capable of meeting strength requirements in copper and brass brazed joints. Brazing with the low-temperature silver-free filler metal TiBraze®P14 (Cu-4Sn-6P) resulted in sufficient shear strengths with copper and, especially, brass — the second highest value after the standard silver-based Alloy BAg-1. This makes the silver-free P14 alloy a very likely substitute for silver-based filler metals. At least 15%-silver containing BCuP-5 can be completely substituted by P14 in such applications as the manufacture of copper tubing and brass faucet brazed joints.

2. When used for joining copper or brass tubes with connectors, adapters, and faucets, both tested silver-free filler metals provided formation of quality, dense brazed joints with smooth fillets. Significant cost savings can be realized with silver-free brazing filler metals, warranted even in the case that joint overlap lengthening is required. WJ

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Reference

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