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The Development of New Silver-Free Brazing Alloys for Steel Tubular Assembly

A new cost-efficient, silver-free alloy meets tensile and fatigue strength requirements for tubular joints on bicycle frames

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ABSTRACT. Alloys based on copper-manganese have been examined as cheaper alternatives to brazing alloys of silver-copper-zinc and for joining mild steel tubular structures for applications such as bicycle and furniture frames. The highest brazing temperature limit compatible with high-tensile-strength steel tubes is 900°C. Other essential requirements are the compatibility of the brazing alloys with torch brazing in air and with conventional fluxes, and their ability to consistently bridge joint clearances of up to 0.5 mm, so as to remove the need for lugs. Furthermore, the brazed joints have to satisfy the requisite tensile and fatigue strengths for the intended applications.

Two brazing alloys have been developed that meet these requirements, 70Cu-20Zn-10Mn (wt-%; melting range, 799–925°C) and 54Cu-35Zn-6Ni-4Mn-1Si (wt-%; melting range, 850–930°C). They produced well-filled joints in steel tubular structures, conferring adequate tensile strength (>260 MPa) and fatigue strength (bending moment to failure >150 N.m at 10^5 cycles), so as to comply with the DIN 79100-2000-04 Standard for bicycles. Both brazing alloys have been found to be more easily capable of rework than the 44Ag-30Cu-26Zn reference alloy.

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Introduction

Silver-based brazing alloys, which usually contain more than 40 wt-% of the precious metal, have been playing a major role in metal joining. Their relatively low melting points (600–800°C) and wide metallurgical compatibility with base alloys have led to their use in joining copper alloy and steel components. However, silver-containing brazing alloys are expensive, silver being more than 75 times the price of copper and approximately 150 times that of zinc, on a weight basis. In the increasingly competitive consumer markets where brazing is used, including the bicycle and office furniture industry, there is a growing demand for cheaper filler metals to replace the silver brazes for joining mild steel tube.

In the furniture and bicycle industries, there is a further requirement for new brazes. For tubular assembly where brazing is used, lugs are normally required for connecting the steel tubes. Lugs, which fit over the ends of the tubes, help to ensure the joints are close fitting, but they also fix the angles of the frame and so limit the options on frame geometry available to customers. Brazing tubes together without lugs increases the flexibility in frame configuration but reduces the precision to which the joint clearances can be fixed, so the new brazes should possess good joint-filling properties for this purpose. From extensive discussions with furniture and bicycle manufacturers associated with this project, it was ascertained joint clearances between tubes, even in a lugless configuration, seldom exceed 0.5 mm. This provided a realistic target to achieve.

KEY WORDS

Brazing
Silver-Free
Tubular Joints
Brazed Joints
Bicycles
High-Strength Tube

This paper describes the successful development of two new silver-free brazes suitable for producing tube-to-tube joints without lugs at temperatures of 800–900°C, compatible for high-tensile-strength steel tubing. The new brazes produce joints that meet the tensile and fatigue strengths required of the assemblies.

This project was carried out by the authors on behalf of their organizations (TNO Institute of Technological Research, Astrium Ltd., and Berkenhoff GmbH), as appropriate under the European CRAFT Program (Project BE-S2-2565). It enjoyed the support of the European Union and the active collaboration of two furniture manufacturers (CAR Projectmeubelen BV and Ahrend Productiebedrijven Zwanenburg BV), a bicycle manufacturer (Van Raam Aalten BV), a steel tube manufacturer (Corus Tubes BV), a manufacturer of

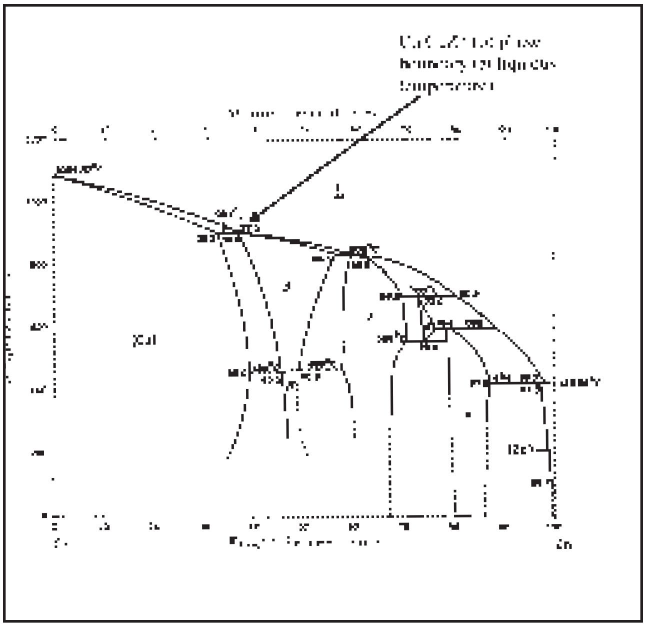

Fig. 1 — The copper-zinc binary alloy phase diagram (Ref. 1).

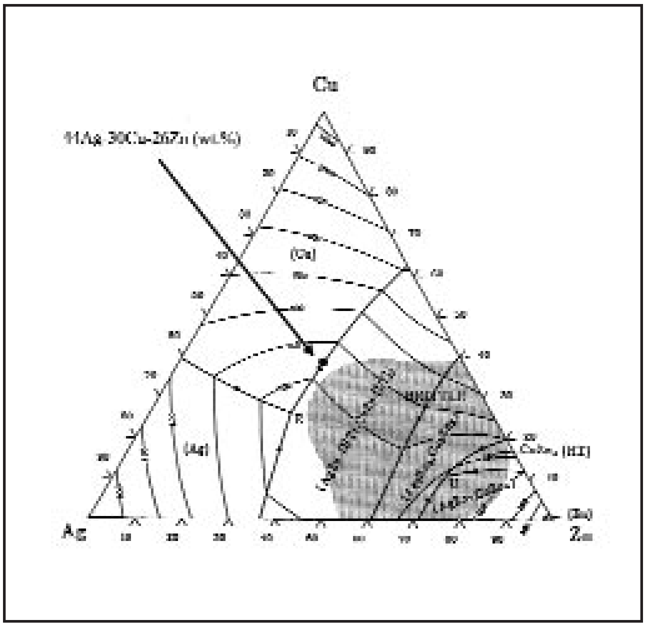

Fig. 2 — Liquidus projection of the copper-silver-zinc ternary alloy phase diagram (scaled in atomic percent), with the composition of the 44Ag-30Cu-26Zn alloy shown (Ref. 2).

Table 1 — New Alloy Compositions Examined in this Project, Together with the Reference Braze, and Some of Their Characteristics

Alloy Composition (wt-%)	Approx. Melting Range (°C)	Phases Present	Tensile Strength of Brazed Joint (MPa) 0.5-mm Joint Clearance	Hardness (Hv 0.01)
70Cu-20Zn-10Mn	799–925	(**Cu**, Mn) + CuZn (minor)	270	160
54Cu-35Zn-6Ni-4Mn-1Si	850–930 (approx.)	(**Cu**, Mn, Ni, Si) + CuZn	285	>180
70Cu-25Mn-5Ag	830–880 (approx.)	(**Cu**, Mn, Ag)	200	130
44Ag-30Cu-26Zn (reference braze)	665–730	(**Cu**, Ag, Zn) + (**Ag**, Cu, Zn) +ß”	280	190

brazing alloys (Berkenhoff GmbH), a manufacturer of brazing equipment and fixtures (Everwand & Fell GmbH), a supplier of dedicated milling equipment (A. P. van den Berg BV), and a manufacturer of notching machines (Franz Diekmann GmbH).

Selection of Silver-Free Alloys

Selection of candidate silver-free brazing alloys was arrived at following a reexamination of metallurgical fundamentals. All compositions referred to are in weight percent, unless otherwise stated.

Conventional low-melting-point brazing alloys are based on copper, with additions of zinc, silver, and other metals. The zinc addition lowers the melting point of copper. However, above ~46 wt-% Zn hard phases, starting with ß (the CuZn intermetallic compound), become dominant and the braze will be brittle. Furthermore, volatility of the alloy, on account of a significant zinc fraction, also becomes a problem (generation of bubbles and blisters in the joint). These issues place a practical limit on the amount of zinc that can be added and also the maximum melting point reduction that can be achieved by adding zinc alone to 903°C — Fig. 1.

The addition of silver further lowers the melting point of copper-zinc alloys. The melting point reduction obtainable from a silver addition is considerable, down to 665°C for a silver content of 56%, as shown by the ternary eutectic point E in Fig. 2.

A commercially supplied silver alloy recommended for brazing mild steel or copper has the composition of 44Ag-30Cu-26Zn. This alloy was selected in the project as a reference braze that has a melting range of 665–730°C and contains the following phases:

(**Cu**, Ag, Zn) + (**Ag**, Cu, Zn) + ß"

where ß" represents a mixture of copper-zinc and silver-zinc intermetallic compounds, while (**Cu**, Ag, Zn) and (**Ag**, Cu, Zn) denote solid solutions of copper, silver, and zinc, with the element shown in bold constituting the major constituent.

Silver is a relatively expensive brazing alloy constituent costing ~$140/kg, compared with $1–10/kg for most other engineering metals. A principal objective is to replace silver with other cheaper metals as melting point depressants.

The window of requirements that had to be met included the following:

- Brazing temperatures ≤ 900°C so the melting point of the brazing alloys must be even lower.
- Ability to carry out brazing operations in air (*i.e.,* the brazing alloys have to be compatible with conventional fluxes).
- Achieving a degree of bridging of joint clearances by the braze. This would be done by exploiting the “pasty” two-phase (liquid + solid) region below the liquidus temperature in performing the brazing operations. An assessment of the literature on wide joint clearance brazes indicated an alternative approach, namely the use of fillers (powder fractions that remain solid during the brazing operation, which

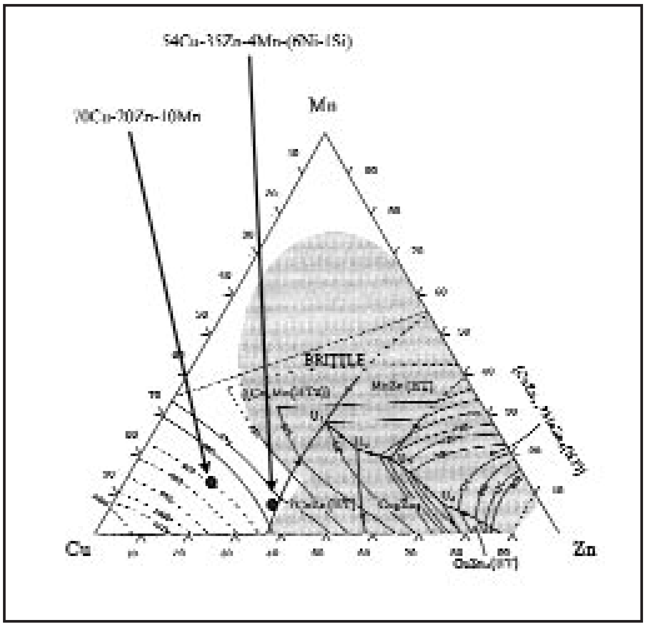

Fig. 3 — Liquidus projection of the copper-manganese-zinc ternary alloy phase diagram (scaled in atomic percent) with the compositions of the 70Cu-20Zn-10Mn and 54Cu-35Zn-6Ni-4Mn-1Si alloys (in weight percent) shown (Ref. 6).

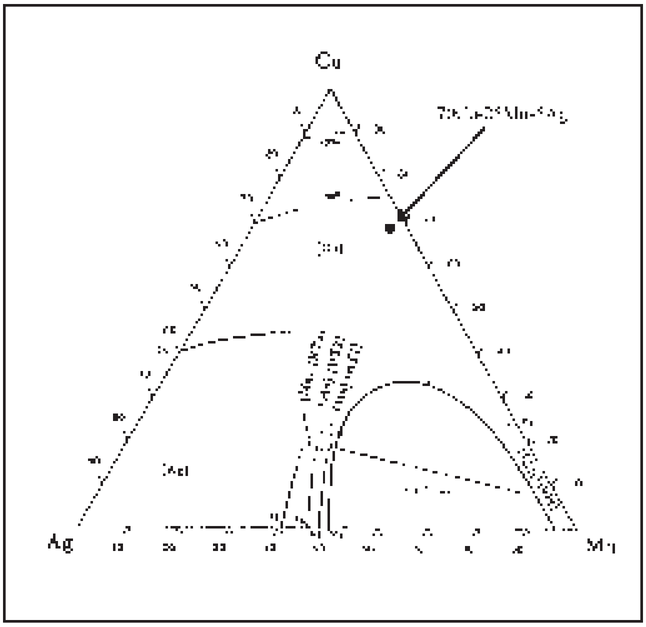

Fig. 4 — Liquidus projection of the copper-manganese-silver ternary alloy phase diagram (scaled in atomic percent) with the composition of the 70Cu-25Mn-5Ag alloy (in weight percent) shown (Ref. 7).

help plug the clearance), was impractical and costly for this application.

- Confining consideration to brazing alloys of satisfactory mechanical strength for the intended application, which can help achieve acceptable mechanical strength of the joints for the target applications.
- The brazing alloys must not contain toxic constituents such as cadmium.

A search of the literature suggested a promising candidate braze might be found among copper-zinc-manganese ternary alloys. Manganese has the particular advantage of being even cheaper than zinc. A particular composition referred to was 60Cu-30Sn-9Mn-1Ce, melting at 640–700°C (Ref. 3). While this alloy was judged satisfactory for producing joints for beryllium-copper assemblies suitable for divertor plates in nuclear fusion reactors, this and other relatively low-melting-point alloy compositions in the Cu-Sn-Mn system have proved to be too brittle for steel assemblies (Refs. 4–5).

A more fruitful alternative alloy system proved to be copper-zinc-manganese. Manganese lowers the melting temperature of high copper Cu-Zn-Mn alloys. The constituents are very cheap in relation to silver-containing brazes. However, for a wide range of compositions, these ternary alloys are brittle — Fig. 3.

Based on the required properties of the brazing alloys (ductility, melting range, etc.), the most promising alloy compositions were selected. One of these was the 70Cu-20Zn-10Mn alloy. A second candidate was provided, having 6 wt-% nickel and 1 wt-% silicon. Both elements are known to promote wetting of the braze, especially on oxidized steel surfaces. Silicon also confers fluidity. However, these additions raised the melting point of the alloy and needed to be offset by increasing the zinc content to bring the alloy composition as close as possible to the brittle region, which, at low manganese contents, was essentially the low-temperature CuZn compound. Nickel entered into solid solution with copper and manganese and the small silicon fraction was also expected to enter into solution in the other phases.

The constituent phases of these two alloys, together with their melting points and selected mechanical properties, are shown in Table 1.

A Cu-Mn-Ag alloy of composition 70Cu-25Mn-5Ag was also prepared and evaluated in this project for comparison. This alloy composition is represented on the relevant ternary phase diagram in Fig. 4. The cited melting ranges were measured by differential thermal analysis (DTA).

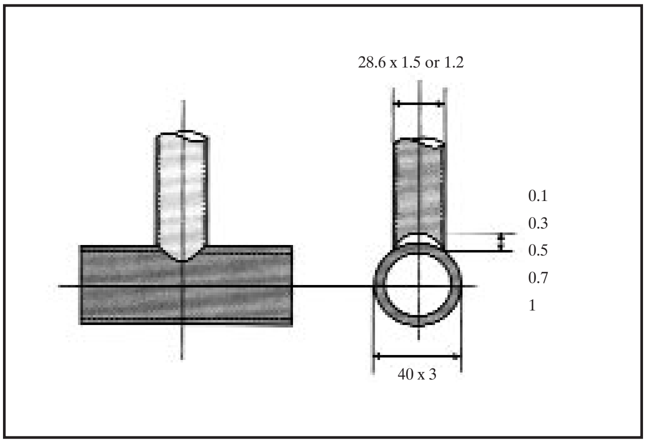

Fig. 5 — Schematic drawing of test specimens for the laboratory brazing trials.

Table 2 — Dimensions of the Test Specimens

Tube Diameter mm	Wall Thickness mm	Length mm
28.6	1.5	300
40.0	3.0	40

This alloy consists entirely of a copper-rich Cu-Mn-Ag solid solution. There are no hard phases present, but this characteristic limits the mechanical strength of the alloy and of joints made with this braze, as determined in this study (Table 1). Consequently, this alloy was eliminated from the short list prior to the assembly trials on complete bicycle frames.

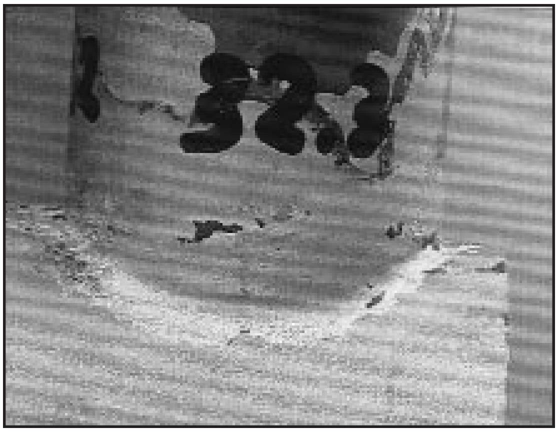

Fig. 6 — Joint made to mild steel tubes using 54Cu-35Zn-6Ni-4Mn-1Si brazing alloy.

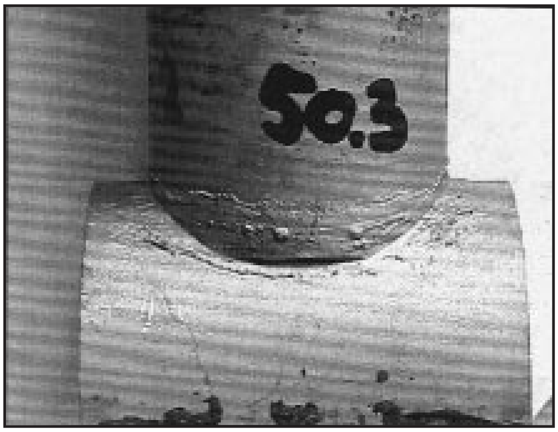

Fig. 7 — Joint made to mild steel tubes using 70Cu-25Mn-5Ag brazing alloy.

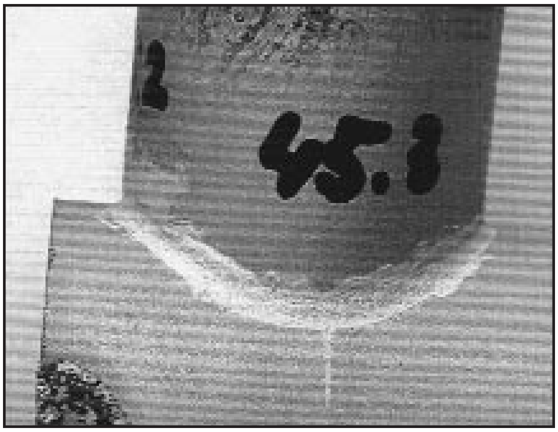

Fig. 8 — Joint made to mild steel tubes using 44Ag-30Cu-26Zn brazing alloy.

Brazing Trials

T-shaped test pieces of simplified geometries were used in this study, comprising an end-profiled tube set vertically against a wider horizontal tube, as shown in Fig. 5.

The dimensions of the mild steel tubes used are shown in Table 2. The tube ends were prepared with different radii, to produce the required maximum clearances at the saddles of the joints, as shown in Fig. 5. The profiles were produced by notching with a special tool on the equipment of Franz Diekmann GmbH.

The initial series of brazing trials made use of induction heating and were carried out at a laboratory facility at Astrium. The brazing alloy wire was used in the form of ring preforms, fitted around the base of the upper tube. Flux paste was then applied to the joints. These were heated from room temperature to peak joining temperature within two minutes, by radio-frequency power from an induction coil wrapped around the lower end of the vertical tube. A pause of a few seconds at ~100°C was introduced to enable the water in the flux to boil off and so prevent excessive spitting and frothing of the flux. The optimum peak heating temperature was judged to have been reached when wetting and filleting was observed by eye to have taken place around the joint. The temperature indicated by the thermocouple placed inside the test piece and close to the joint was used only as a rough guide and as a reference. Further intermediate temperature dwells were deemed unnecessary because both components were being heated evenly, as evidenced by the uniform glow around the joint, following passage through the Curie temperature transition (~700°C), which provides a natural slowing down of the heating rate.

In subsequent brazing trials, heating cycles for the brazing process were accomplished in production facilities using air-propane torches. In two of these facilities, brazing was carried out by hand using a single torch. A third facility (Everwand and Fell) used automated ring burners, which provided more uniform heating of the circular joint and superior reproducibility of process conditions. Once again, a pause of a few seconds was introduced in the heating cycle to dry the flux while minimizing spitting. The optimum peak heating temperature was judged by eye to correspond to the moment when wetting and complete filleting had taken place.

The trials involved the brazing alloys in combination with the fluxes shown in Table 3. The higher melting points of the three experimental brazing alloys necessitated the use of a different brazing flux (Degussa S paste, containing a fluoroaluminate) than the lower-melting-point reference braze, for which a fluoroborate flux paste (Degussa H 28) was appropriate.

The tube ends were profiled so a maximum joint clearance of 0.5 mm in the saddle of the joint was provided. As reflected in Figs. 6–8, all the brazed joints were filled and there were no holes in the joints. However, the filleting produced using the Cu-25Mn-5Ag braze was poorer than for the other brazes (compare Fig. 7 with Figs. 6 and 8). This indicated the 54Cu-35Zn-6Ni-4Mn-1Si and 44Ag-30Cu-26Zn brazes possessed superior spreading and filling characteristics. This matched visual observations made during brazing, namely that 70Cu-20Zn-10Mn braze appeared more sluggish when molten.

A final series of tube assemblies was brazed on the facilities at Everwand and Fell to ascertain whether the 0.5-mm joint clearance compromised the mechanical properties of the joints. For this purpose, tubes with end profiles that gave 0- and 0.5-mm clearances were brazed according to the configuration in Fig. 5 and then mechanically tested.

Tensile Testing

Tensile strength was calculated from measurements of tensile load to fracture made at TNO based upon the maximum load value and area of the joint contour between the profiled end of the vertical tube and the cylindrical surface of the horizontal tube. Calculations were made with the help of a modeling and drawing program called Unigraphix and was based on the dimensions of the prepared tube ends.

Results of the tensile tests carried out on brazed tubes in the first series of trials are represented on the bar chart in Fig. 9. The joints made with the 54Cu-35Zn-6Ni-4Mn-1Si, 70Cu-20Zn-10Mn, and the 44Ag-30Cu-26Zn reference braze all exhibited tensile strengths between 250 and 300 MPa. The joints made with the 70Cu-25Mn-5Ag exhibited significantly lower tensile strengths (150 to 230 MPa).

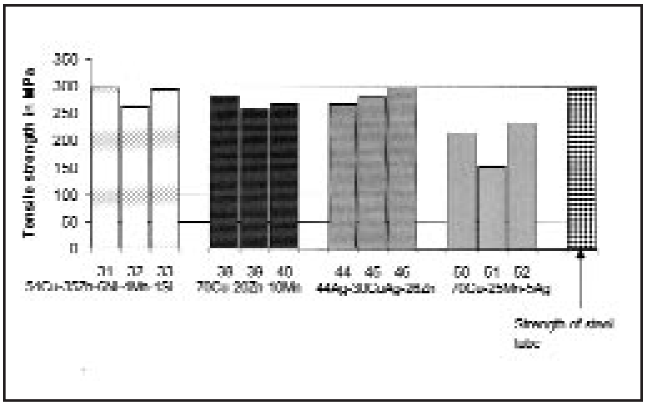

Fig. 9 — Tensile strength of the joints in tubular assemblies with a maximum joint clearance of 0.5 mm, made with the four different brazes and induction heating.

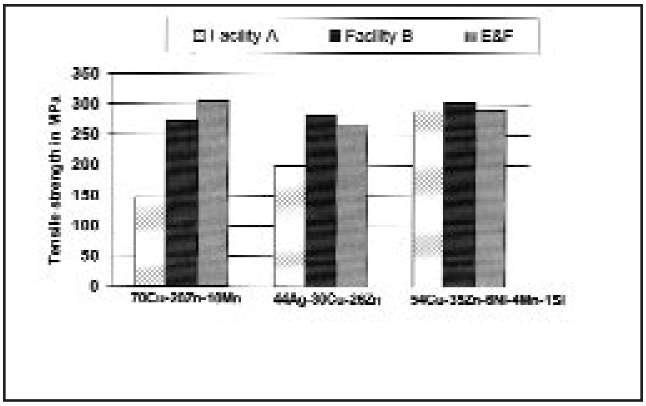

Fig. 10 — Tensile strengths (0.5-mm clearance) of tubular assemblies joined with three brazes at different industrial facilities.

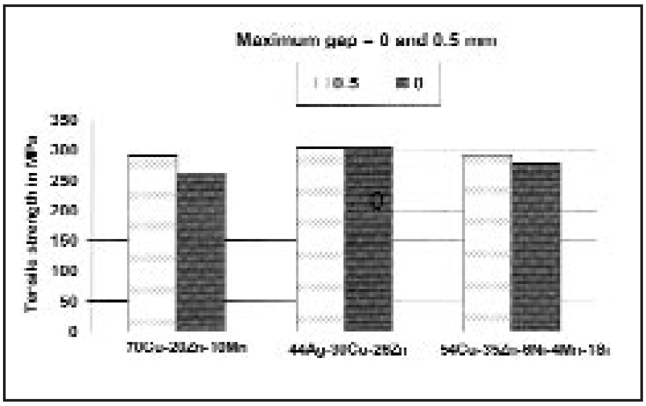

Fig. 11 — Tensile strengths of tubular assemblies with a 0- and 0.5-mm maximum joint clearance, brazed at Everwand and Fell.

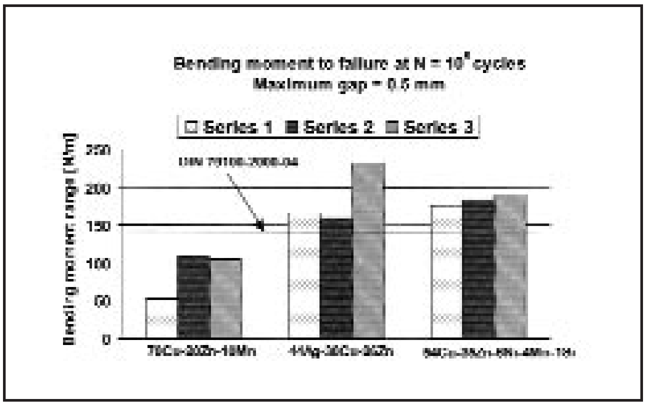

Fig. 12 — Fatigue test results for assemblies torch brazed by hand at facility A.

For most of the tube assemblies, failure was observed in the joint. However, two of the three assemblies joined with the 54Cu-35Zn-6Ni-4Mn-1Si braze and one of the three joined with the 70Cu-20Zn-10Mn braze failed in the smaller-diameter steel tube, 30–40 mm from the joint. This is consistent with the fact that the measured joint strengths for joints made with these two brazes was close to the measured strength of the base metal tube (of Fe 360) of 300 MPa. Notwithstanding the controlled conditions used for the brazing operations, there was ~15% scatter in the tensile test results.

It should also be noted, the tensile strengths obtained with the two silver-free brazes compared favorably with that of the conventional 44Ag-30Cu-26Zn braze.

Duplicate tube assemblies brazed at three production facilities using gas torches were similarly tensile tested at TNO. On this occasion, the 70Cu-25Mn-5Ag braze was dropped from the work-program, owing to its inferior strength. The silver content in this alloy offered no evident advantages. This left two experimental brazes, the 70Cu-20Zn-10Mn and 54Cu-35Zn-6Ni-4Mn-1Si alloys. The average of the two strength values obtained for joints made with each of the three brazes is represented in the bar chart in Fig. 10.

The averages showed considerable variation between the different facilities in which the joints were brazed. The widest variation was found for joints made with the 70Cu-20Zn-10Mn braze and the least with the second experimental brazing alloy of composition 54Cu-35Zn-6Ni-4Mn-1Si. The greater tolerance to the process conditions of the latter braze is consistent with its enhanced filleting and spreading characteristics.

The superior joints obtained at Everwand and Fell, as judged by their consistently higher strengths, can be accounted for by the following differences in brazing practice at the three facilities:

Table 3 — Selected Brazes Involved in the Third Series of Brazing Trials

Brazing Alloy Composition	Flux
70Cu-20Zn-10Mn	Degussa S
54Cu-35Zn-6Ni-4Mn-1Si	Degussa S
70Cu-25Mn-5Ag	Degussa S
44Ag-30Cu-26Zn (reference)	Degussa H 28

1) More precise alignment of the tubes at Everwand and Fell with the aid of more sophisticated jigging. At the other facilities, the clamping arrangements were cruder and alignment geometries less reproducible.

2) Use of ring burners with eight flames, which gave uniform heating of the joints. At the two other facilities, hand torches with single flames were used that were

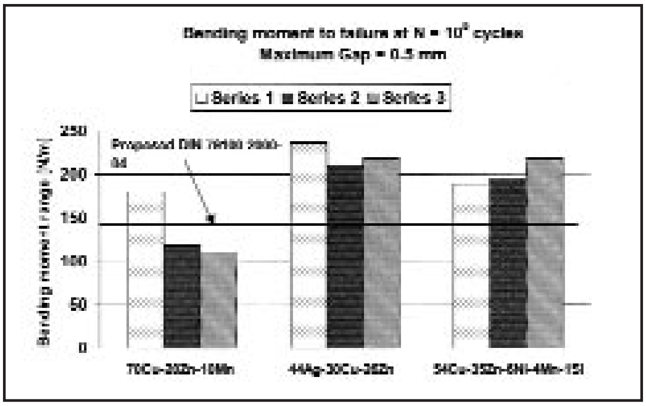

Fig. 13 — Fatigue test results for assemblies torch brazed by hand at facility B.

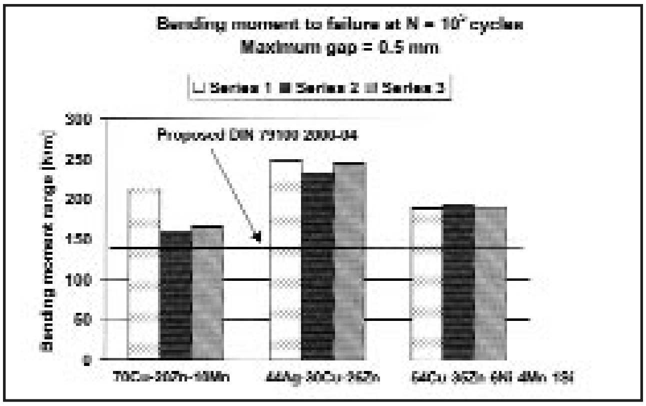

Fig. 14 — Fatigue test results for assemblies brazed using an automated ring burner system at Everwand and Fell.

Fig. 15 — Fifteen bicycle frames prepared at Van Raam Aalten BV with five joined using each of the three brazing alloys: 70Cu-20Zn-10Mn, 54Cu-35Zn-6Ni-4Mn-1Si, and 44Ag-30Cu-26Zn.

more likely to produce uneven heating.

3) Only Everwand and Fell used a gas flux in their burners.

The tensile strength of the pairs of assemblies brazed at Everwand and Fell with maximum joint clearances of 0 and 0.5 mm are shown in Fig. 11.

Fatigue Testing

Whereas quantified standards of tensile strength do not appear to exist in the bicycle and metal furniture industries, there exists a new European DIN 79100-2000-04 Standard for the fatigue testing of bicycles. In this DIN Standard, the load during fatigue testing is alternately applied to the left and right pedal, while the crank makes an angle of 45 deg to the horizontal. The bicycle frame is accepted if it withstands 100,000 cycles under an applied load of 850 N.

In this study, a simpler configuration was used whereby a cyclic load was applied at a fixed distance of 100 mm from the joint of a T-shaped brazed assembly. Calculations established the DIN standard corresponds to a bending moment of 145 N.m at 100,000 cycles.

For the fatigue tests, triplicate assemblies were joined using the two experimental brazes and the silver-based reference braze. The same three industrial facilities where the tensile test assemblies took place were used. Figures 12–14 show the test results in terms of the bending moment to failure at N = 10^5 cycles. It can be seen the highest fatigue strengths were obtained for the tubular test pieces brazed by Everwand and Fell. These also show the least scatter. These last set of measurements indicated all three brazes, the two experimental alloys and the reference silver-based alloy, all complied with the DIN 79100-2000-04 Standard. By contrast, the assemblies torch brazed by hand at the two other facilities (denoted as A and B) failed to satisfy the same standard when the 70Cu-20Zn-10Mn braze was used. Clearly, the automated Everwand and Fell procedure, with its close control of temperature, heating rate, and uniformity, demonstrated its capability of producing consistent joints of superior quality as compared with manual operations used elsewhere. This exercise highlighted the importance of adhering to highly controlled brazing conditions, especially for the 70Cu-20Zn-10Mn braze because of its relatively sluggish flow characteristics.

Evaluation Trials

Further brazing trials were carried out as a prelude to assembly of complete bicycle and furniture frames using the new silver-free alloys. Following the successful completion of the experimental trials, work proceeded toward trials involving complete frames.

As part of this stage of the work, it was decided to undertake a short program to establish optimum brazing conditions for a production environment, in view of the variability experienced using different industrial facilities. Much of this work was carried out in conjunction with Van Raam Aalten BV. This company uses ring burners in brazing bicycle frames, for which they currently use a higher melting point 60Cu-40Zn braze together with a compatible higher temperature flux.

Brazing trials were carried out using mild steel tubing jointed in two configurations, representative of sections of bicycle frames as follows:

1) A single tube, 28 mm in diameter, with a suitably profiled termination, produced by notching, positioned at an angle of 60 deg to a horizontal tube of the same diameter (single-angled joint).

2) Two single tubes, one 25 mm in diameter and the other 28 mm in diameter, with suitably profiled terminations 15 cm apart, positioned symmetrically at 60 deg to a horizontal tube 28 mm in diameter (double-angled joint).

The ring burners were set up and tested prior to the trials. Four torches were directed at each joint and maintained at a distance of 6.5 cm from the joints.

Key Findings

Quantity and Form of the Brazing Alloy Used

In the procedure used at Van Raam Aalten, the brazing alloy wire was introduced inside the upper steel tube and, when molten, flowed outward to fill the joint clearance and form fillets. The two candidate brazing alloys were supplied as 2-mm-diameter wire. The optimum volume of brazing alloy to form a satisfactory joint to a 25-to 28-mm-diameter steel tube was determined to be 250 mm^3. Using the ring burners and this method of introducing the wire preform, the joint was heated indirectly via the tube and good thermal contact was necessary. Accordingly, considerably faster joint formation occurred when the length of brazing wire was cut into small lengths. These came into more intimate contact with the heated horizontal tube and melted more quickly.

Outgassing from the Braze

The 70Cu-20Zn-10Mn braze tended to outgas, largely through Zn volatilization, and formed bubbles and blind holes (collapsed bubbles). This phenomenon became more marked as heating was prolonged. With the induction heating used at Astrium, this effect was not noticed. This volatilization phenomenon will be the subject of a future study. It is hoped this will resolve the paradox that the higher zinc-containing braze shows a reduced propensity to volatilize. This characteristic makes the ternary alloy (70Cu-20Zn-10Mn) less attractive than the quinary alloy (54Cu-35Zn-6Ni-4Mn-1Si) for brazing using torches and ring burners.

Heating Time

For the ring burner configuration, two minutes was judged to be the optimum heating time. This included a 15-second extension beyond the time taken for the braze to melt and emerge around the entire outer perimeter of the joint, which was found to improve fillet formation. It was noted the heating time was identical to that used when an induction source was employed in the initial trials.

Use of a Gas Flux

Van Raam Aalten used a gas flux, which was introduced directly into the flames of its ring burners. This was a simple and economical method of introducing the flux since it removed the need for an additional procedure for applying the flux such as dipping the tube ends into flux paste. Experiments showed the 54Cu-35Zn-6Ni-4Mn-1Si braze could be used with the gas flux alone, which means it lends itself to automated brazing. On the other hand, the 70Cu-20Zn-10Mn braze required the use of flux paste either alone or in addition to the gas flux.

Fifteen complete bicycle frames were successfully assembled, five using each of the three brazes. Each was subjected to fatigue testing. The frames are shown in Fig. 15. In this preproduction phase, it was inevitable some of the joints had to be reworked. It was discovered the two new silver-free brazes endured reheating and rework better than the Ag-Cu-Zn reference braze.

Conclusions

Two silver-free brazing alloys have been developed that are suitable for use with mild steel tubing. These are of composition 70Cu-20Zn-10Mn (melting range: 799–925°C) and 54Cu-35Zn-6Ni-4Mn-1Si (melting range: approximately 850–930°C).

These brazes are capable of consistently filling joint clearances up to 0.5 mm. The resulting joints have the requisite tensile strength (>260 MPa) and fatigue strength (measured as a bending moment to failure >150 N.m at 10^5 cycles) when brazing is carried under well-controlled conditions. Such joints meet the DIN 79100-2000-04 fatigue strength standard for bicycles.

In their brazing characteristics and mechanical properties, the two new brazes compare favorably with the 44Ag-30Cu-26Zn reference braze, which is considerably more expensive because of its silver content.

Of the two new brazes, the 54Cu-35Zn-6Ni-4Mn-1Si alloy confers slightly improved mechanical properties than the other alloy. More importantly from a manufacturing point of view, its superior spreading and filleting characteristics make it more tolerant to the brazing conditions employed. It is also capable of being used with a gas flux alone, so it is better suited to automated brazing operations.

Both new brazes are better suited to rework than the reference braze.

The brazes have been successfully employed in the pilot production of bicycle frames.

Acknowledgments

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