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Copper-Manganese-Base Silverless Brazing Systems

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

° C	degree Celsius	min	minute
g	gram	µin	microinch
in	inch	pct	percent
in^2	square inch	sec	second
in/min	inch per minute	wt-pct	weight-percent
ksi	thousand pounds per square inch		

COPPER-MANGANESE-BASE SILVERLESS BRAZING SYSTEMS

By V. R. Miller [1] and W. L. Falke [2]

ABSTRACT

The Bureau of Mines conducted research on substitute brazing filler alloys with properties similar to those of silver filler alloys in an effort to conserve silver and reduce hazards from cadmium emissions. Experimental work was conducted first on the commercial silver brazing alloys BAg-1, BAg-1a, BAg-2, and BAg-3 to establish criteria for evaluating the substitute alloys. Properties investigated included the wettability of copper, brass, and steel substrates, and the strength of joints made with the filler alloys. A series of experimental alloys containing 50 to 60 pct Cu, 20 to 28 pct Mn, and 17 to 30 pct Zn was prepared and evaluated, together with Cu-Mn-Zn alloys with 5 pct Pb or 2 pct Ni. Wetting properties and joint strengths were not as good as those for silver filler alloys, and the high application temperatures reduced the copper and brass base metal strengths. However, experimental alloys containing 70 pct Cu, 15 to 20 pct Mn, and 10 to 16 pct Sn had wetting and strength properties approaching those of the silver filler alloys. The application temperatures for these alloys were higher than those for silver fillers, but not as high as those for the Cu-Mn-Zn alloys. With the Cu-Mn-Sn alloy fillers, copper alloy joint members are less deteriorated by recrystallization than when applying Cu-Mn-Zn alloys. The Cu-Mn-Sn system has potential for further development as a substitute brazing alloy system, particularly if the melting temperature can be reduced by the addition of other elements without decreasing the ductility and wetting.

[1]Supervisory research physicist, Rolla Research Center, Bureau of Mines, Rolla, Mo.
[2]Supervisory research chemist, Rolla Research Center, Bureau of Mines, Rolla, Mo.

INTRODUCTION

Inherent in the goals of Bureau of Mines Research in the minerals and materials area is a continuing endeavor to minimize the requirements for critical and scarce mineral commodities through substitution and conservation. Owing to the limited reserves and widening use of silver, its conservation is vital. This is especially true for silver brazing alloys because their use is largely dissipative. One means to conserve and efficiently utilize silver is to develop brazing filler alloys to substitute for silver brazing alloys, which consumed 8.5 million troy ounces in 1980.

The research described in this report was undertaken in an effort to obtain silverless filler alloys exhibiting properties similar to those of silver filler alloys as a means to conserve silver by substitution and to reduce hazards from cadmium emissions. As an initial step in developing silverless brazing alloys, some selected properties of silver brazing alloys were determined to establish criteria for evaluating possible substitutes. These properties were the wettability of copper, brass, and steel substrates by the filler alloys and the strength of joints made with the filler metals. Experimental filler alloys were prepared from ternary Cu-Mn-Zn and Cu-Mn-Sn systems, with or without additions of other metals, to evaluate the potential of these alloys as substitutes for silver filler alloys.

BACKGROUND

Brazing, like forge welding, is one of the oldest metal joining processes. A brazing process for the fabrication of gold jewelry was in use around 600 B.C. by the Etruscans of northwest Italy (14).[3] With the advent of the Iron Age and ferrous technology, copper-zinc filler metals, called spelter, were developed for joining iron and steel. Theophilus, writing in the 10th century A.D., makes reference to a metal joining process used by the Chinese, which probably used copper-zinc alloys (14).

Paralleling the development of low-melting-point gold filler metals was the discovery of silver-base filler alloys exhibiting low melting points. These were developed by silversmiths for use in their craft (2). The process seems to have been forgotten, as far as written records show, until 1865 when Cu-Zn-Ag alloys were used to braze joints in the transatlantic telegraph cable. In 1890, Cu-Zn-Ag alloys were used for brazing turbine blades in steam engines (14). The use of silver filler alloys expanded during the next 35 years, and in 1929 the American Society for Testing and Materials established specifictions for silver brazing alloys (1). The literature up till that date consisted largely of formulas which specified a certain portion of silver and brass to be used to make more malleable and lower melting alloys. Little definitive information regarding the physical properties of the silver filler alloys was given. The work on establishing standards for the silver-bearing fillers was to recommend a suitable number of compositions to meet the different trade requirements (11).

In the early 1930's, cadmium was added to the Cu-Zn-Ag filler alloys to produce lower melting and more ductile alloys (12). The alloy patented is now categorized under American Welding Society (AWS) classification BAg-1a. During the 1940's widespread industrial acceptance of the Ag-Cu-Zn-Cd alloys occurred as their employment became necessary in many military manufacturing processes (10). In the ensuing years, many complex forgings and stampings were redesigned to allow fabrication by brazing of parts produced by mass production techniques (13).

[3]Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

Beginning in the 1950's and continuing into recent years, brazing research turned toward the basics of metallurgical principles involved in metallic bonding (5-8). During this time, alloy development continued but in a different direction. The advent of jet aircraft, missiles, and the space age made it obvious that the early silver brazing alloys were no longer adequate to meet many of the special requirements of these advanced designs (10). Subsequently, research was directed toward ductile alloys for elevated-temperature service and included nickel-base alloys as well as precious metal alloys of gold or palladium or both (9).

In the 1970's, the introduction of a threshold limit value for cadmium in European countries resulted in the decision to switch to cadmium-free filler alloys rather than install fume-extraction equipment. However, there were no direct replacement alloys equal in physical properties and intrinsic costs. The Ag-Cu-Zn ternary alloys were available but required a 55-pct Ag content if solidus temperatures as low as 630° C were to be achieved (15). The research on cadmium-free filler alloys was spurred on by the rising cost of silver. In the United States, the rising silver cost was somewhat offset in the brazing industry by the use of filler alloys of somewhat reduced silver content. The decreased silver content did, however, result in higher brazing temperatures, longer brazing periods, and increased difficulty in flux removal, all of which increase production costs. Consequently, there is a practical limit to the reduction of silver in Ag-Cu-Zn-Cd filler alloys.

EXPERIMENTAL MATERIALS AND PROCEDURE

MATERIALS

The wetting experiments were performed on copper, brass, and steel plates which were 1.5-in squares of commercial 1/16-in-thick-rolled sheet. The copper alloy was type CA 110, which is electrolytic tough pitch copper containing 99.9 pct Cu. The brass alloy was type CA 260, which is cartridge brass containing 70 pct Cu, balance Zn. The steel was type AISI 1018. The joint strength experiments were performed on bars of similar alloys which were 6 by 1 by 1/8 in. in size.

The silver filler alloys used for the research consisted of AWS type BAg-1, BAg-1a, BAg-2, and BAg-3 alloys. Table 1 lists the chemical compositions and the thermal properties of these alloys, and table 2 lists the experimental alloy compositions and their thermal properties as determined by heating and cooling curves. For the wetting and joint tests, a quantity of each of the filler metals was melted and cast into bars which were rolled into plates 0.1 in thick. One-eighth-inch-diameter pellets were punched from each plate to obtain a constant volume of filler metal for each test. The fluoride-bearing commercial brazing flux used in the tests was dried and ground to a powder; 0.5 g was used for each test.

TABLE 1. - Silver filler alloy compositions and temperatures

Filler alloy	Composition, wt-pct					Temperature, ° C	
	Ag	Cu	Zn	Cd	Ni	Solidus	Liquidus
BAg-1	45.6	15.3	16.2	22.9	0	607	619
BAg-1a	50.7	15.5	16.5	17.3	0	627	635
BAg-2	35.4	25.3	21.1	18.2	0	607	702
BAg-3	50.1	15.4	16.1	15.5	2.9	632	688

TABLE 2. - Experimental filler alloy compositions and temperatures

Filler alloy	Composition, wt-pct						Temperature, ° C	
	Cu	Mn	Zn	Sn	Ni	Pb	Solidus	Liquidus
1.....	59.3	20.0	20.7	0	0	0	816	836
2.....	55.2	20.3	24.5	0	0	0	812	830
3.....	50.2	20.0	29.8	0	0	0	805	825
4.....	52.7	28.1	19.2	0	0	0	839	847
5.....	50.0	24.0	23.9	0	2.1	0	826	840
6.....	52.2	25.5	17.3	0	0	5.0	802	812
7.....	69.8	14.4	0	15.8	0	0	725	760
8.....	70.4	19.7	0	9.9	0	0	800	810

PROCEDURE

Prior to wetting and joint strength tests, the copper and brass plates and bars were degreased in a common solvent, pickled in a 5-pct-sulfuric-acid solution, and etched for 1 min in a 30-pct-nitric acid solution. Steel specimens were similarly degreased and pickled, but etching was conducted in a 10-pct-Nital solution for 5 min. The etching procedures were experimentally determined so that a surface roughness of 30 to 40 μin was obtained.

For wetting tests, the square plates were placed inside an induction coil and supported on three ceramic supports (1/8-in diameter) for heating. The bottom side of the plate was sprayed with a flat black, heat-resistant paint prior to insertion. This coating was used to obtain a constant emittance for the infrared sensor used to measure the temperature of the plates. The temperature sensor was focused on the bottom of the plate directly beneath the test sample of filler alloy. The temperature-measuring system was calibrated by noting the deviations in melting points of standards heated on various plates. Measured temperatures were within 2° C of the melting temperatures of the standards.

Wetting experiments were performed by placing the commercial flux on a plate and heating it to the desired temperature. The filler alloy was then placed on the plate and allowed to spread for a specified time after melting. Fumes from fluxes and metals were removed by an exhaust duct located above the specimens. The power to the induction coil was then turned off and the drop allowed to solidify before the plate was removed from the coil.

The solidified spread areas were measured to obtain quantitative data on the effect on wetting properties of the various parameters and alloy compositions. The area of spread was used as an indicator of the wettability of the filler metals. The spread areas were measured by photographing the plates along with a graduated scale. The negatives were placed in a modified microfilm reader, and the spread-area image was projected onto a flat white surface at a magnification of 36 times. A planimeter was then used to measure the area. Five plates were prepared and measured for each variable tested, and an average value for the spread area was calculated.

Lap-joint specimens for measuring shear strengths were prepared in accordance with AWS C3.2-63, Standard Method for Evaluating the Strength of Brazed Joints, with one exception. The exception was that the bars were riveted at the various overlaps rather than tungsten-inert-gas welded. Welding was tried, but for the copper bars the excessive heat caused severe oxidation in the joint and sound joints were difficult to obtain. For comparative purposes, all joints were assembled in the same manner.

Joint specimens were brazed by induction heating. The specimens were fluxed and heated to the desired temperature, and the filler alloy was applied to one side of the joint. To avoid excessive

fillets, the amount of filler alloy applied was slightly in excess of what was needed to fill the joint. The power to the induction coil was turned off a specified time after the filler alloy had melted and entered the joint. The Cu-Mn-Sn alloys were water-quenched when the temperature had dropped to 550° C. After cooling, the specimens were machined to produce the reduced gauge section, with the rivets being removed in the process. Fillets and burrs were removed by hand filing; and the overlap, width, and thickness of the gauge section were measured with a micrometer. Some of the very small overlap joints were broken in the machining process and were not remade for subsequent mechanical testing. The mechanical testing was conducted on an Instron Universal testing machine[4] using grips for flat bars and at a cross-head speed of 1 in/min.

RESULTS AND DISCUSSION

WETTING TESTS

The parameters of time and temperature were varied for the wetting experiments with silver filler alloys to establish criteria for evaluating the experimental alloys. Table 3 lists the results for tests at different temperatures, and table 4 lists those for different time periods.

The results presented in table 3 indicate that maximum spread occurs at about 60° C superheat in all but two cases. They also indicate that, for the majority of the alloys, the maximum spread occurs on brass, followed by copper, and then steel. The only exception at 60° C is the BAg-2 alloy which contains the most copper and zinc, both of which wet steel well.

The effect of time on area of spread, as seen in the results of table 4, is not quite as well defined as that of temperature. About 50 pct of the maximum spreads occurred in 30 sec and 50 pct in 60 sec. The only filler alloy that had maximum spread at 60 sec for all three substrates was BAg-1a. Except for this alloy, the trend of increased spread with time appeared to be controlled more by the substrate material than by the filler alloy. Maximum spread with increased time was noted to occur for three of the four alloys on brass, two of the four alloys on copper, and only one of the four alloys on steel.

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 3. - Silver filler alloy spread areas (in^2) formed in 30 sec at different temperatures above the liquidus

	Brass	Copper	Steel
BAg-1:			
30° C.....	0.485	0.329	0.111
60° C.....	.679	.339	.206
120° C.....	.481	.312	.175
BAg-1a:			
30° C.....	.363	.249	.108
60° C.....	.634	.292	.190
120° C.....	.336	.312	.183
BAg-2:			
30° C.....	.411	.358	.273
60° C.....	.665	.492	.607
120° C.....	.222	.450	.309
BAg-3:			
30° C.....	.284	.234	.144
60° C.....	.445	.288	.275
120° C.....	.291	.431	.201

TABLE 4. - Silver filler alloy spread areas (in^2) for different periods at 60° C above the liquidus

	Brass	Copper	Steel
BAg-1:			
15 sec.....	0.446	0.264	0.141
30 sec.....	.679	.339	.206
60 sec.....	.656	.392	.204
BAg-1a:			
15 sec.....	.453	.241	.143
30 sec.....	.634	.292	.190
60 sec.....	.730	.331	.206
BAG-2:			
15 sec.....	.439	.381	.400
30 sec.....	.665	.492	.607
60 sec.....	.668	.440	.461
BAg-3:			
15 sec.....	.325	.204	.158
30 sec.....	.445	.288	.275
60 sec.....	.526	.273	.258

For evaluating the experimental alloys, a spread time of 30 sec and a temperature of 60° C above the liquidus were selected. Using these conditions, the smallest silver alloy spread areas obtained on the substrates were selected as the basis for the evaluation. This resulted in area-of-spread criteria of ≥0.190 in^2 for steel, ≥0.288 in^2 for copper, and ≥0.445 in^2 for brass. The results of the wetting tests are listed in table 5.

TABLE 5. - Experimental filler alloy spread areas (in^2) formed in 30 sec at 60° C above the liquidus

Filler alloy[1]	Substrate		
	Steel	Copper	Brass
1.....	0.138	0.054	0.090
2.....	.135	.057	.080
3.....	.133	.059	.057
4.....	.097	.058	.070
5.....	.078	.058	.055
6.....	.168	.145	.160
7.....	.447	.265	.179
8.....	.356	.216	.147

[1]Compositions given in table 2.

It is readily seen in table 5 that the wettability of the experimental alloys is much less than that of the silver filler alloys. None of the alloys approach the criteria for brass and copper, and only the Cu-Mn-Sn alloys (7 and 8) meet the criteria for steel. The trend for the experimental alloys was for maximum spread to occur on steel, which is the opposite of that observed for silver alloys.

The causes of wetting and spreading are still controversial, but Bailey and Watkins (3) found that metal solubility or interfacial compound formation was a necessary condition for good wetting and subsequent bond strength. Wassink (17) has stated that the occurrence of intermetallics at the interface means that dissimilar atoms attract each other more than similar ones. As a result, wetting and bond strength are improved by the addition of an element that is mutually soluble or forms compounds with the base metal.

For the case of the Cu-Mn-Zn alloys, the solubilities may be too high on copper and brass substrates. Figure 1*A* is a cross section of a silver filler alloy on brass; figures 1*B*, 1*C*, and 1*D* show a Cu-Mn-Zn alloy on copper, brass, and steel, respectively. In figures 1*B* and 1*C*, migration of the boundary or interface down into the substrate is evident. The molten filler alloy appears to have dissolved and alloyed with the substrate rather than spread upon it. This is not the case in figure 1*D* (steel substrate), where the boundary layer remains uniform and substrate penetration is not evident.

Additional work was conducted on the Cu-Mn-Zn alloys despite their poor wettability. This was done because wetting-spreading is a dynamic occurrence with several factors active simultaneously. These include surface tensions of the liquid and solid phases as well as the interfacial tensions.

Blanc (4) has pointed out that fluxes are as important in brazing practice as the filler alloys themselves. The results of wetting tests on the experimental filler metals using a flux formulated in the laboratory are listed in table 6. This flux consisted of 50 pct $K_3Al_3F_6$, 30 pct KBF_4, 10 pct $BaCl_2$, 5 pct $LiCl_2$, and 5 pct KCl.

TABLE 6. - Experimental filler alloy spread areas (in^2) at 60° C above the liquidus for 30 sec using a laboratory-prepared flux

Filler alloy[1]	Substrate		
	Steel	Copper	Brass
1.....	0.450	0.167	0.076
2.....	.457	.197	.109
3.....	.500	.226	.120
4.....	.215	.202	.151
5.....	.191	.135	.160
6.....	.184	.111	.069
7.....	.528	.363	.276
8.....	.419	.373	.294

[1]Compositions given in table 2.

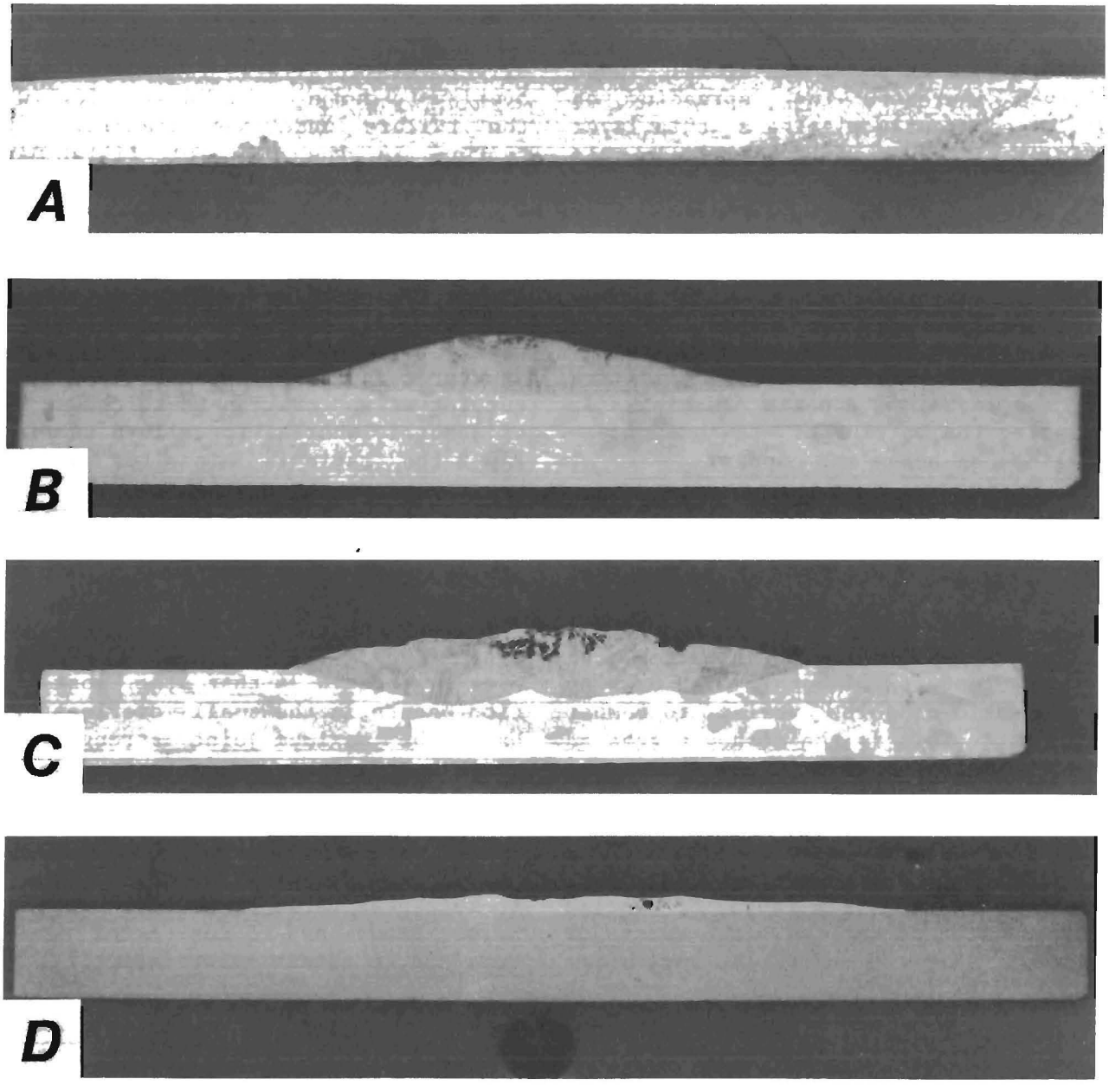

FIGURE 1. - Cross sections of filler alloys on various substrates (X 10). Panel *A* is silver alloy on brass, *B* is Cu-Mn-Zn on copper, *C* is Cu-Mn-Zn on brass, and *D* is Cu-Mn-Zn on steel.

All alloys exhibited increased wetting and spreading when using the laboratory flux, except alloy 6, which displayed decreased spreading on copper and brass. The increase was such that all alloys except 6 met or exceeded the criterion for steel. On copper, the Cu-Mn-Sn alloys (7 and 8) exceeded the criterion but the Cu-Mn-Zn-base alloys did not meet it. No alloy met the criterion for brass, even with the increased wetting. However, the increased wetting was encouraging, and

qualitative tests with experimental fluxes were started using active fluxes with additives such as $SnCl_2$ and $NiCl_2$. These additives increased the spreading on brass by apparently plating a thin layer of tin or nickel on which the filler alloys could spread more readily than on brass alone. This is similar to the technique developed by Schwaneke, Falke, and Crosser (16) in which an electroplated nickel coating was applied to copper-base alloys to promote spontaneous wetting and spreading of zinc-base solders. On the basis of this qualitative work, the technique appears feasible for increasing the wetting of the experimental alloys on brass and copper.

JOINT STRENGTH TESTS

The values of the joint shear strength for the silver and experimental filler alloys joining copper, brass, and steel joint members are plotted in figures 2 to 10 as a function of both joint overlap and the ratio of joint overlap to member thickness. This is the method suggested by the American Welding Society. The shear strength and overlap values are tabulated in appendix A for the silver alloys and appendix B for the experimental alloys. For comparison purposes, it is necessary to have a range of overlap distances because of the high values of "apparent joint strength" at very short overlap distances compared to those at long overlaps. The most sensitive portion of the curve is the low-overlap portion, where the apparent joint strength is the highest. In this same region of the curve, the most variation in test results will occur because the joints are very sensitive to all factors that affect the brazing operation. A design engineer, on the other hand, is looking for the load-carrying capacity of the joint and thus is most interested in portions of the curve representing less than maximum shear stress. Consequently, a good way to compare the experimental and silver filler alloys is to look at the overlap-to-member thickness for which the failure undergoes transition from rupture in the joint or filler alloy (open circles in the figures) to rupture in the joint member (filled circles in the figures).

The strengths of copper joints brazed with silver alloys are plotted in figure 2. For the BAg-1 and BAg-2 alloys, fractures in the joint members start occurring at an overlap-to-thickness ratio of about 1, whereas for alloys BAg-1a and BAg-3 the ratio is close to 1.6. For brass joints formed with the silver brazes (fig. 3), the ratios are about 1 for BAg-1 and BAg-1a and then jump to about 3 for BAg-2 and BAg-3. For steel joints made with the silver filler alloys (fig. 4), the ratio for all alloys approaches 5. It is also evident in figures 2 through 4 that the most variation occurs in the small overlaps, which have the maximum joint strength. The maximum strengths appear to be related to the joint member strength, with the highest maximum strength values occurring for steel, followed by brass and then copper. For design purposes, an overlap-to-thickness ratio of about 2 for copper, 3 for brass, and 5 for steel would be required to retain joint integrity.

For the joining of copper with experimental alloys 1 through 4 (fig. 5), the overlap-to-thickness ratio producing failure in the joint member is also about 2. For brass, the ratio is 1 to 2, as shown in figure 6. For the steel specimens, figure 7, the ratio is 5 for alloys 2 and 3 and greater than 5 for 1 and 4. Thus, the overlap-to-thickness ratios used for silver filler alloy design would also work for these alloys.

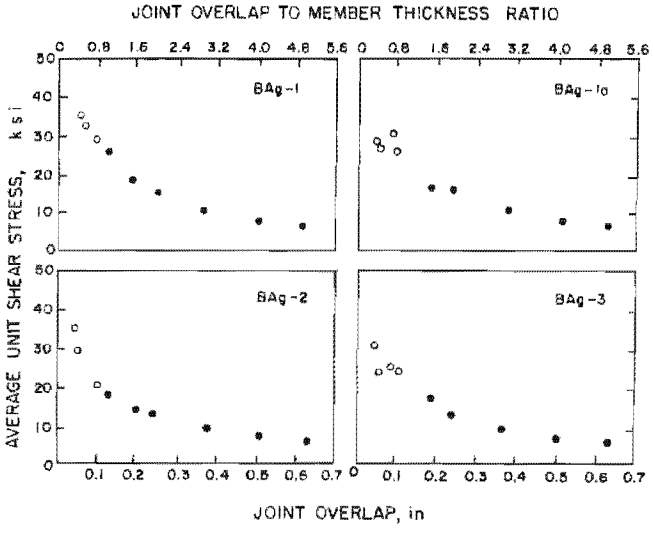

FIGURE 2. - Shear strength of copper joints brazed with silver filler alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy; filled circles designate fractures outside the joint in base members.

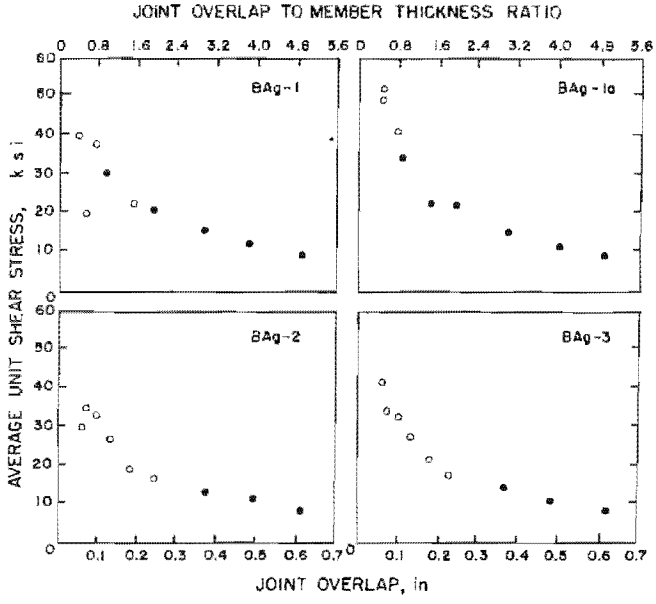

FIGURE 3. - Shear strength of brass joints brazed with silver filler alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy; filled circles designate fractures outside the joint in base members.

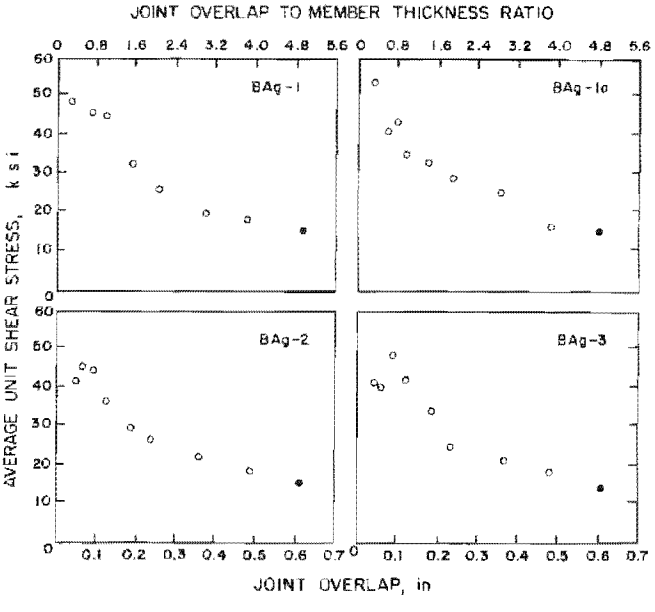

FIGURE 4. - Shear strength of steel joints brazed with silver filler alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy; filled circles designate fractures outside the joint in base members.

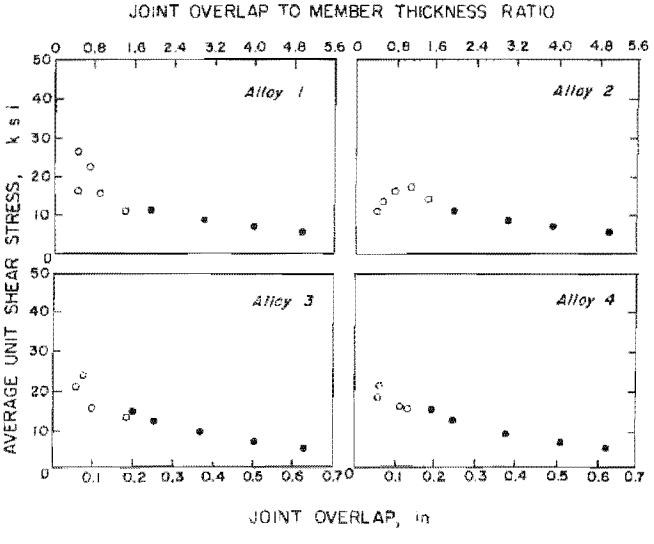

FIGURE 5. - Shear strength of copper joints brazed with experimental Cu-Mn-Zn alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy; filled circles designate fractures outside the joint in base members.

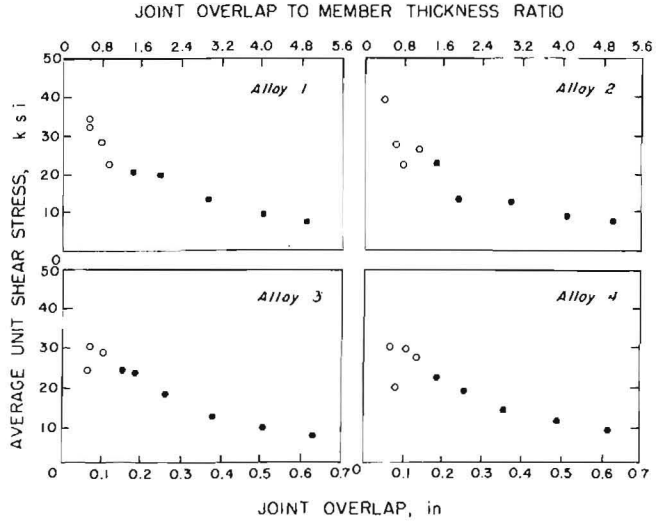

FIGURE 6. - Shear strength of brass joints brazed with experimental Cu-Mn-Zn alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy, filled circles designate fractures outside the joint in base members.

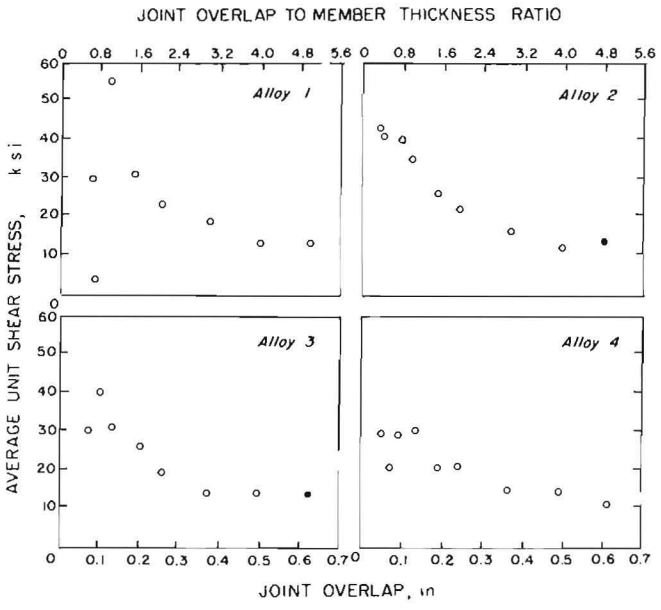

FIGURE 7. - Shear strength of steel joints brazed with experimental Cu-Mn-Zn alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy; filled circles designate fractures outside the joint in base members.

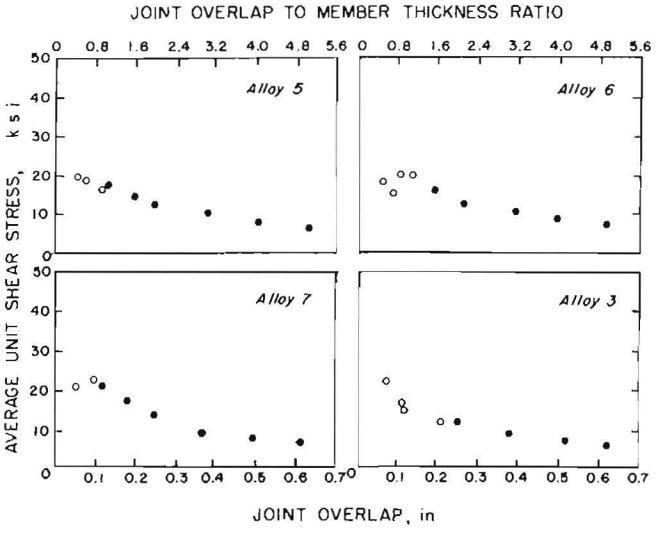

FIGURE 8. - Shear strength of copper joints brazed with experimental Cu-Mn-Zn-Ni, Cu-Mn-Zn-Pb, and Cu-Mn-Sn alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy; filled circles designate fractures outside the joint in base members.

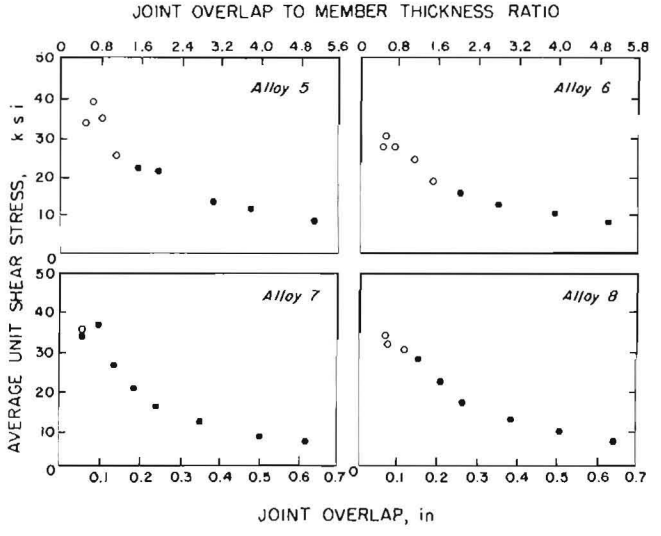

FIGURE 9. - Shear strength of brass joints brazed with experimental Cu-Mn-Zn-Ni, Cu-Mn-Zn-Pb, and Cu-Mn-Sn alloys as a function of joint overlap and the ratio of joint overlop to member thickness. Open circles designate specimens that fractured in the filler alloy; filled circles designate fractures outside the joint in base members.

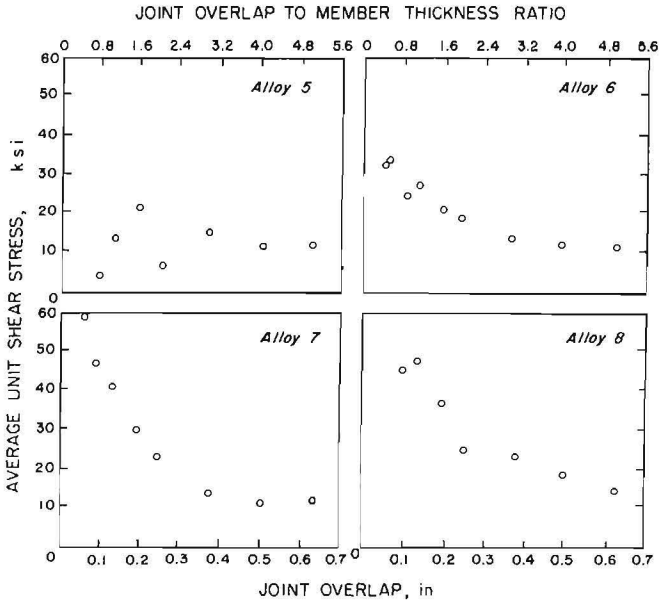

FIGURE 10. - Shear strength of steel joints brazed with experimental Cu-Mn-Zn-Ni, Cu-Mn-Zn-Pb, and Cu-Mn-Sn alloys as a function of joint overlap and the ratio of joint overlap to member thickness. Open circles designate specimens that fractured in the filler alloy.

As shown in figure 8, the overlap-to-thickness ratios for experimental alloys 5 to 8, when used to join copper, are in the range of 1 to 2. For the same alloys and brass (fig. 9), the ratios are about 1.5 to 2 for the Cu-Mn-Zn-base alloys 5 and 6. However, for the Cu-Mn-Sn alloys, 7 and 8, the ratios are about 0.5 to 1, which is less than that for brass brazed with silver alloys. As indicated in figure 10, the highest ratio of 5 did not result in fractures in the steel joint members, indicating a larger ratio was needed. These alloys would work satisfactorily for joining copper and brass joints designed for fabrication with silver filler alloys. For the steel joints, a ratio of 5 still resulted in fracture in the filler alloy rather than the steel. However, the strengths were as high as those for brass (fig. 9) at the higher ratio, and substantially higher for alloy 8. The absence of failure in the steel substrate is a result of the substantially higher strength of the steel relative to brass.

On the basis of this type of comparison, the experimental alloys would be similar to silver filler alloys as far as joint design was concerned; i.e., they would ensure failure in the copper and brass joint members and not in the joint. However, an additional factor should be considered when comparing the different alloys. That factor is the higher temperature needed to braze the materials with the experimental alloys. If one disregards the high joint strengths at small overlaps and looks at the values where failure occurs in the joint members in figures 2 and 5, the effect of the higher temperature can be seen. The values for failure in the copper member are 20 to 25 ksi for the silver filler alloys (fig. 2), and only 10 to 15 ksi for experimental alloys 1 to 4 (fig. 5).

Comparing the values in figures 3 and 6 for the brass joint members shows a similar trend. The values are about 30 ksi for BAg-1 and BAg-1a, and about 15 ksi for BAg-2 and BAg-3. For alloys 1 to 4, the values are about 20 to 25 ksi, which shows a reduction but not as large as for the copper members. For steel, the values are about 15 ksi for both the silver alloys and experimental alloys 1 to 4.

In figure 8, the values for copper range from about 15 to 20 ksi for alloys 5 to 8--values which are higher than for the first group of experimental alloys but still below those for the silver filler alloys. In figure 9 for the same alloys joining brass, the values range from 15 to 35 ksi. The two Cu-Mn-Sn alloys, 7 and 8, have the highest values of about 30 to 35 ksi, which are comparable to the values for the silver brazing alloys. These two alloys also have the lowest liquidus temperatures of the experimental alloys.

For steel, the comparison cannot be made because failure occurred in the joints for all the overlap-to-thickness ratios evaluated. The reduction in strength of the copper and brass joint members is due to the annealing effects of the higher temperatures than those required with the silver brazes; heavier

structural members would be required for comparable design strengths.

Some reduction in joint strength using the experimental alloys is also probably due to the formation of manganese oxides and their entrapment in the joint. These oxides were noted in the interior of small voids exposed upon fracturing. More active fluxes to prevent oxide formation would help to strengthen the joints.

Of the fillers fabricated and tested, the Cu-Mn-Sn alloys exhibited the best properties of combined wetting-spreading, strength, and relatively low application temperature. The problem encountered with the Cu-Mn-Sn alloys is that they are brittle if allowed to cool slowly. When they are water-quenched from above 550° C, they are ductile and can be cold-worked.

Additional alloys were prepared with additions of Pb, Zn, Bi, Cd, and Ag to determine if lower melting alloys could be produced. The addition of fourth elements was found to enhance embrittlement except for the silver addition (5 pct). The silver addition reduced the melting point of the alloy into the 680° to 700° C range. However, a combination of 5 pct Ag and 3 pct Cd was found to be more effective in reducing the melting point with some sacrifice in ductility. A similar effect was also noted when cadmium and silver were added to the Cu-Mn-Zn base alloys. These alloy additions have not been investigated further.

CONCLUSIONS

On the basis of the results obtained in this work, Cu-Mn-Zn-base alloys do not possess the wettability or temperature range to qualify as direct substitutes for silver filler alloys. Although additional flux development might increase the wetting and spreading of the experimental alloys, the annealing effects on the strength of copper and brass joint members can only be reduced by lowering the filler alloy melting point. Additional flux development, particularly to retard manganese oxidation, might permit the use of these alloys to join steel members in certain applications.

The Cu-Mn-Sn alloys hold more promise as a base for developing substitute alloys for silver brazing alloys. The melting points and wetting and strength properties are closer to those of the silver filler alloys than are the corresponding properties of the Cu-Mn-Zn base alloys. However, additional research is needed to determine if elements other than Pb, Bi, Cd, Zn, or Ag can lower the melting point without decreasing the wetting and the joint ductility. Decreased silver prices may allow the use of perhaps 5 pct Ag in the alloys, which results in melting temperatures similar to those of conventional silver filler alloys.

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APPENDIX A.--SILVER FILLER METAL JOINT STRENGTHS

TABLE A-1. - Strength of joints brazed with silver alloys

	Copper joints		Brass joints		Steel joints	
	Overlap, in	Shear stress, ksi	Overlap, in	Shear stress, ksi	Overlap, in	Shear stress, ksi
BAg-1.....	0.053	35.1	0.049	40.0	0.048	48.5
	.062	32.3	.055	19.4	.061	63.3
	.098	28.5	.090	38.1	.087	45.1
	.124	25.9	.118	30.5	.120	44.6
	.185	18.4	.177	22.6	.190	31.8
	.249	15.3	.239	21.2	.252	25.0
	.366	10.7	.369	15.4	.371	18.9
	.506	7.9	.481	12.1	.482	17.4
	.618	6.3	.613	9.1	.619	14.3
BAg-1a.....	.046	28.5	.053	52.7	.044	54.5
	.061	26.7	.059	50.0	.080	41.7
	.092	30.7	.092	41.8	.101	44.1
	.105	25.7	.108	34.3	.125	35.6
	.188	16.2	.177	22.5	.185	33.5
	.239	16.0	.243	22.7	.249	29.7
	.375	10.5	.374	15.1	.365	28.5
	.503	7.6	.506	11.5	.490	16.6
	.617	6.6	.619	9.2	.612	15.7
BAg-2.....	.049	32.5	.056	30.3	.047	41.5
	.059	29.0	.065	35.6	.062	45.9
	.103	20.6	.092	33.2	.087	44.3
	.132	18.1	.127	27.6	.123	36.3
	.202	14.3	.178	19.7	.186	29.6
	.243	13.8	.243	17.1	.234	26.2
	.369	10.0	.368	13.6	.362	22.1
	.497	7.7	.491	11.3	.491	18.0
	.618	5.9	.618	8.6	.612	14.8
BAg-3.....	.046	31.5	.053	41.6	.048	41.0
	.062	24.2	.065	34.2	.063	40.0
	.093	25.5	.093	32.7	.090	47.6
	.111	24.8	.121	27.8	.125	42.5
	.186	17.4	.174	21.7	.187	33.9
	.234	13.9	.224	17.5	.240	24.7
	.364	10.1	.364	14.3	.375	21.2
	.496	7.6	.481	10.9	.492	18.1
	.618	6.1	.622	8.7	.617	14.3

APPENDIX B.--EXPERIMENTAL ALLOY JOINT STRENGTHS

TABLE B-1. - Strength of joints brazed with experimental Cu-Mn-Zn alloys

	Copper joints		Brass joints		Steel joints	
	Overlap, in	Shear stress, ksi	Overlap, in	Shear stress, ksi	Overlap, in	Shear stress, ksi
Alloy 1.....	0.058	16.1	0.062	34.5	([1])	([1])
	.061	26.5	.064	32.7	0.072	29.7
	.087	22.9	.095	28.4	.097	3.8
	.116	15.5	.117	22.5	.119	55.2
	.179	11.1	.177	20.3	.172	31.6
	.246	11.8	.241	19.8	.242	23.3
	.379	9.0	.364	13.1	.366	18.7
	.501	6.8	.506	9.8	.498	13.9
	.630	5.9	.612	7.9	.619	13.3
Alloy 2.....	.051	11.5	.048	39.9	.047	43.6
	.067	13.8	.071	27.4	.051	41.1
	.100	16.8	.094	22.5	.095	40.0
	.133	18.0	.134	26.8	.125	35.5
	.180	14.9	.179	22.9	.191	26.7
	.245	11.1	.234	13.1	.250	22.2
	.380	8.9	.366	12.7	.377	16.9
	.490	7.6	.510	9.1	.503	12.6
	.631	6.0	.623	7.7	.619	14.1
Alloy 3.....	.054	21.0	.058	24.3	([1])	([1])
	.074	23.8	.071	30.6	.067	30.0
	.098	15.7	.096	29.0	.094	40.6
	.181	13.3	.149	24.3	.123	31.0
	.196	14.9	.182	23.8	.192	25.9
	.253	12.4	.255	17.9	.250	19.3
	.371	9.5	.377	12.4	.368	16.1
	.503	7.5	.505	9.4	.491	13.9
	.627	6.0	.627	7.4	.619	13.9
Alloy 4.....	.055	17.9	.064	29.4	.050	30.0
	.059	20.7	.078	18.4	.075	21.0
	.109	16.0	.101	29.1	.092	29.1
	.130	15.3	.139	26.1	.138	30.7
	.190	15.0	.181	21.5	.192	20.9
	.247	12.2	.256	17.5	.240	21.6
	.381	9.3	.358	13.5	.368	15.1
	.513	6.9	.488	10.1	.495	14.7
	.632	6.0	.620	8.1	.618	10.3

[1]Specimen broke and could not be tested; no comparable overlap made.

TABLE B-2. - Strength of joints brazed with experimental Cu-Mn-Zn-base and Cu-Mn-Sn alloys

	Copper joints		Brass joints		Steel joints	
	Overlap, in	Shear stress, ksi	Overlap, in	Shear stress, ksi	Overlap, in	Shear stress, ksi
Alloy 5.....	0.053	19.2	0.060	32.9	([1])	([1])
	.076	18.9	.080	38.5	([1])	([1])
	.117	16.0	.108	34.5	0.095	4.0
	.129	17.1	.141	24.3	.135	12.7
	.194	14.5	.196	21.1	.195	21.2
	.243	12.4	.249	20.2	.249	7.1
	.380	9.7	.385	12.5	.369	15.7
	.502	7.5	.481	10.4	.498	10.6
	.628	5.9	.637	7.3	.625	10.9
Alloy 6.....	.050	17.2	.052	26.7	.045	32.6
	.077	14.4	.058	29.6	.058	33.1
	.093	19.6	.089	26.7	.100	24.0
	.127	19.3	.138	24.1	.133	26.8
	.180	15.7	.179	18.7	.191	20.9
	.252	12.0	.247	15.3	.240	18.7
	.382	9.7	.349	12.8	.364	13.7
	.488	7.7	.490	9.8	.490	12.2
	.611	6.3	.624	8.0	.630	11.6
Alloy 7.....	.051	20.8	.055	35.1	([1])	([1])
	([1])	([1])	.057	33.8	.059	59.3
	.093	22.0	.091	36.3	.086	47.2
	.114	20.7	.132	27.3	.123	41.1
	.179	17.0	.181	21.3	.191	30.0
	.249	13.4	.241	17.1	.243	23.1
	.376	10.0	.351	13.2	.368	13.9
	.493	7.7	.498	9.7	.498	11.3
	.617	6.3	.619	8.0	.624	10.5
Alloy 8.....	([1])	([1])	.050	34.7	([1])	([1])
	.066	22.0	.056	32.2	([1])	([1])
	.101	16.5	.092	30.3	.088	45.6
	.111	14.3	.129	28.3	.124	47.6
	.202	11.4	.184	22.9	.190	37.2
	.248	11.5	.242	17.2	.245	25.1
	.372	9.0	.360	13.3	.372	23.8
	.511	7.1	.491	10.0	.494	18.4
	.619	5.9	.625	7.6	.628	14.4

[1]Specimen broke and could not be tested; no comparable overlap made.

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