Interfacial Compositions of Silver Filler Metals on Copper, Brass, and Steel

A silverless filler metal should contain elements that are mutually soluble or form interfacial compounds with copper, brass and steel base metals, and interface reactions should be time and temperature dependent.

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ABSTRACT. The U.S. Department of the Interior, Bureau of Mines conducted research on silver (Ag) filler metals to establish criteria for the development and evaluation of substitute silverless filler metals. Metallography and X-ray microprobe scans have been used to show the interfacial phases obtained with Ag filler metals on copper, brass, and steel. Wetting tests on plates of copper, brass, and steel were made using four commercial Ag filler metals with a flux.

Cross sections of the filler metal-base metal interface were examined to determine the reaction products. The results show that formation of interfacial compounds is dependent upon time, temperature, and composition of filler and base metals. Interfacial regions of fractured AWS-type brazed joints were examined also to determine the location of the fracture. Although the compounds formed between filler and base metal may be brittle, they do not detract from the strength of Ag-brazed joints. In fact, the compounds increase bond strength at the interface for filler-metal and steel combinations.

The research included an investigation of the interfaces between filler and base metals to determine the compounds and the factors affecting compound formation and subsequent bond strength. Knowledge of the interfacial reactions and the elements entering into them was considered important to an understanding of the wetting and strength properties of Ag filler metals and how similar properties might be obtained with silverless filler metals.

A series of spread tests on copper, brass, and low-carbon steel was made with silver brazing filler metals. The resulting area of spread was used as an indicator of the wettability of the filler metal. Sectioned spread plates were subjected to optical metallography and X-ray microprobe analysis to show the location and distribution of the various elements in the interfacial phases. While optical metallography has allowed definition of some features of the interfacial reactions, the X-ray microprobe analyzer has been used in recent years to reveal the multiple reactions that occur.

Experimental Procedure

The experiments were performed using four commercial silver filler metals, the compositions of which are given in Table 1, and a commercial AWS-type 3A flux. The copper, brass, and steel plates were 1.5 in. (38.1 mm) squares of commercial 3/8 in. (1.6 mm) thick rolled sheet. The copper alloy was type CA 110, the brass alloy was...
were experimentally determined so was conducted in a 10% Nital solution dried and ground to a powder, and 0.5 each bar to obtain a constant volume.

Type CA 260 (70 Cu-30 zinc), and the steel was type AISI 1018.

The copper and brass plates were prepared for the spread tests by degreasing in solvent, pickling in a 5% sulfuric acid solution and then etching for 10 min in a 30% nitric acid solution. The steel plates were similarly degreased and pickled, but etching was conducted in a 10% Nital solution for 5 min. The etching procedures were experimentally determined so that a surface roughness of 30 to 40 in. was obtained on the plates.

A quantity of each of the silver filler metals was melted and cast into bars which were rolled into plates 0.1 in. (2.5 mm) thick. Pellets, each 1/8 in. (3.2 mm) in diameter, were punched from each bar to obtain a constant volume of filler metal for each test. The commercial flux used in the tests was dried and ground to a powder, and 0.5 g was used for each test.

The square plates were placed inside an induction coil and supported on three ceramic supports 6 in. (3.2 mm) in diameter for heating. The bottom side of the plate was sprayed with a flat black, heat-resistant paint prior to insertion. The coating was used to obtain a constant emissivity 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 metal. The temperature-measuring system was calibrated using melting point standards applied to various plates which were then heated. Measured temperatures were within ±1°C (±1.8°F) of the melting standards.

Wetting experiments were performed by placing the flux on a plate and heating it to the desired temperature. The filler metal was then placed on the plate and allowed to spread for the specified time after melting. The parameters of time and temperature varied to determine their effect on the wetting and interfacial characteristics of the four alloys and three substrates. The temperatures used were 30, 60, and 120°C (86, 140 and 212°F) above the liquidus (superheat) of the filler metals, and the spread times were 15, 30, and 60 s.

The solidified spread areas were measured to obtain quantitative data on the effect of the various parameters on the wetting properties. 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 drop image was projected onto a flat white surface. A planimeter was then used to measure the area of the enlarged drop image, which was magnified 36 times.

Five plates were prepared and measured for each variable tested, and an average value was calculated. Spread area data for the two filler metals BAg-1a and BAg-3 are given in Tables 2 and 3. The trends exhibited for the other two filler metals parallel the results listed. The data have been limited to these two filler metals because the emphasis is to be placed on the products resulting from the interfacial reactions between filler and base metal. The fact that Ag filler metals exhibit good wettability is well known, and the complete data are to be published in a later report. Representative plates for each variable were then sectioned through the center of the spread area, mounted in plastic, polished, etched, and subjected to optical metallography and X-ray microprobe analysis.

Brazed joints were prepared to determine the joint strengths of the four filler metals and three substrates used in the wetting experiments. The joint specimens were prepared in accordance with AWS C3.2-63, Standard Method for Evaluating the Strength of Brazed Joints. Joint specimens were brazed by induction heating at a temperature of 60°C (140°F) above the liquidus of each brazing filler metal. The specimens were fluxed and heated to the desired temperature, and the filler metal was applied to one side of the joint. The power to the coil was turned off 30 s after the filler metal had melted and entered the joint.

Strength data are given in Table 4 for joints brazed with filler metals BAg-1a and BAg-3. The data are listed for only these two filler metals for the same reason as given for the spread area data. The data listed are for joints with 1/8 in. (3.2 mm) overlap. After mechanical testing, sections were cut through the center of joints, mounted in plast-
tic, polished, etched, and examined by optical metallography. The specimens sectioned were those that fractured through the filler metal and not through the base metal.

**Results**

Results of the experiments are presented as a series of photomicrographs on which the interfacial and dispersed phases have been labeled for identification and discussion. The distribution of each element was determined from scanning electron microprobe composites made from X-ray scans for each element of interest. The microprobe pictures were color composites with each element represented by a different color. Line profile scans also were made for each of the areas to help determine the distribution of the individual elements.

Resolution of detail in the microprobe pictures is not as clear as in the photomicrographs for reasons associated with the generation of X-rays. In addition, the reproduction in black and white of color composites results in loss of detail provided by the color. The labeled photomicrograph format was therefore used for publication purposes.

Figure 1 shows the typical microstructure and microprobe analyses obtained.

**Filler Metals Without Ni on Brass and Copper**

A photomicrograph of the cross section of a BAg-2 filler metal that was spread on a brass substrate is shown in Fig. 1a; Fig. 1b is the black and white reproduction of the color composite from the microprobe. Figure 1c shows the line scan profiles across the area for the individual elements. The lack of detail in Fig. 1b and 1c is readily evident.

When Ag filler metals without Ni spread on copper and brass, a Cu-Zn phase forms at the interface and a similar phase is noted in the matrix. This is shown in Fig. 1a where the brass substrate is labeled I and the Cu-Zn interfacial and dispersed phases are labeled 2. The matrix, area 3, is a nonhomogeneous mixture of Ag-Cd. The matrix appears to also contain some Cu and Zn in the microprobe scans. This is probably the small Cu-Zn particles that are not resolved in the X-ray area scans.

In general, the interfacial and the Cu-Zn phases in the matrix increase in size with time of contact between molten filler metal and solid base metal. Figure 2 shows this for a BAg-1a filler metal spread on brass at a 60 C (140 F) superheat for different periods of time. In Fig. 2a the time of spread was 15 s, in Fig. 2b it was 30 s, and in Fig. 2c it was 60 s. Note the increase in the Cu-Zn interfacial phase as well as the Cu-Zn phase in the matrix. In Fig. 2a area 1 is the brass substrate; area 2 is the Cu-Zn interfacial phase and the phase in the matrix. The small dark areas are also Cu-Zn particles, and the white background, area 3, is the Ag-Cd matrix.

A similar type of increase in the amount of interfacial phase and in the size of the dispersed Cu-Zn phases is obtained by increasing the temperature at which the filler metal is spread. This is illustrated in Fig. 3 by a BAg-1a filler metal spread on brass substrates at three superheat temperatures for 30 s. In Fig. 3a the superheat was 30 C (86 F), in Fig. 3b it was 60 C (140 F), and in Fig. 3c it was 120 C (248 F). The thickness of the interfacial Cu-Zn phase increases with temperature, as does the size of the Cu-Zn phases in the matrix of the filler metal. Labeled areas are the same as in Fig. 2. In examining Figs. 2 and 3, it would appear that the temperature effect is more prominent than the time effect.

**Ni-Bearing Filler Metal on Brass and Copper**

Ni-bearing filler metal (BAg-3) on copper and brass exhibits more penetration into the base metal, primarily at the grain boundaries, than the filler metals without Ni. This is shown in Fig. 4 where the substrate, labeled area 1, is copper in Fig. 4a and brass in Fig. 4b.
As a result of the penetration, the interface is no longer uniform next to the substrate but is irregular.

In the case of this filler metal the interfacial phases, labeled 2, contain Ni in addition to Cu and Zn, as does the phase in the matrix. The matrix, labeled 3, consists of Ag-Cd with some Cu and Zn present which is probably the small Cu-Zn phases (small dark areas in Fig. 4) that are not resolved in the X-ray scans.

The results of varying the spread time are shown in Fig. 5 where a BAg-3 filler metal was spread on Cu substrates, area 1, at a 60 C (140 F) superheat for 15 s in Fig. 5a, 30 s in Fig. 5b, and 60 s in Fig. 5c. The effect on the formation of interfacial phases, area 2, is similar to that of the non-Ni-bearing filler metals in that it increases with time. The difference is that the Ni-bearing filler metals penetrate into the substrate more, rather than forming compounds at the interface. As a result of the penetration, the Cu-Zn-Ni interfacial phase is not in a layer but is separated into small phases in a Ag-Cd matrix, area 3.

The results of varying the temperature are shown in Fig. 6 for the Ni-bearing filler metal on brass substrates, which are labeled area 1. In Fig. 6a the superheat temperature was 30 C (86 F), in Fig. 6b it was 60 C (140 F), and in Fig. 6c it was 120 C (248 F). Note the penetration into the substrate and the separation of the Cu-Zn-Ni phase, area 2, from the interface. In Fig. 6c the Cu-Zn-Ni phase extends up from the interface zone into the matrix, area 3, a considerable distance.

**Filler Metals Without Ni on Steel**

Silver filler metals without Ni do not form interfacial compounds with steel base metal. This is shown in Fig. 7, which consists of micrographs of the interfacial region of BAg-1a, BAg-1, and BAg-2 filler metals spread on steel.

The interfaces between base metal at the bottom and the filler metal at the top are sharply delineated. The only difference is in the dispersed phases of Cu-Zn in the filler metals. The BAg-2 filler metal—Fig. 7c—contains Cu-Zn phases of larger size, which is to be expected since it contains more Cu and Zn, and less Ag.

Microprobe analyses showed no formation of interfacial compounds, with the color composites and elemental line scans showing a sharp distinction between steel base metal and Ag filler metal. The filler metal was found to have Cu-Zn phases dispersed in a Ag-Cd matrix.
Fig. 6—Effect of temperature on interfacial compound formation of Ni-bearing filler metal BAg-3 on brass; superheats as follows: a-30 C (86 F); b-60 C (140 F); c-120 C (248 F). X500

Varying the spread time produced little effect upon the interfaces or the matrix of the filler metal, as shown in Fig. 8. In Fig. 8a the spread time was 15 s, in Fig. 8b it was 30 s, and in Fig. 8c it was 60 s. The filler metal was a BAg-1a alloy, and the spread time was 30 s.

A considerable difference in structure of the same filler metal, BAg-1a, is seen when Fig. 9 is compared with Fig. 3. In both cases the filler metal, times, and temperatures of the tests were the same, but the base metal was different. The Cu-Zn phases are seen to increase in size with time and temperature in brass and Cu, but not for steel. The Cu-Zn interfacial phase appears to grow up into the filler metal matrix, and then detach.

This formation, growth, and separation of the Cu-Zn phase would partially explain the difference in structure noted between Ag filler metals on Cu and brass, and on steel. A more plausible explanation is that the BAg-1a filler metal, with its near eutectic composition, solidifies at essentially a constant temperature. The higher superheats and longer time to solidification has allowed dissolution of Cu and Zn from the base metal. This permits the solidification of Cu-Zn rich dendrites prior to solidification of the eutectic matrix. On steel the filler metal dissolves only minute amounts so the composition is virtually unchanged, and the filler metal solidifies as the original near eutectic composition.

Ni-bearing Filler Metal on Steel

The Ni-bearing filler metal, BAg-3, does form interfacial compounds on steel as evidenced in Fig. 10, which shows the effect of time on the thickness of the interfacial phases. The spread time was 15 s in Fig. 10a, 30 s in Fig. 10b, and 60 s in Fig. 10c, and all were at a superheat temperature of 60 C (140 F).

The interfacial phase, area 2, does not form to the same extent on brass as on copper. There appears to be a
Fig. 9—Effect of temperature on interfacial reactions between BAg-la filler metal and steel; superheats as follows: a—30 C (86 F); b—60 C (140 F); c—120 C (248 F). X500

Fig. 10—Effect of time on interfacial compound formation of Ni-bearing filler metal BAg-3 on steel; spread times as follows: a—15 s; b—30 s; c—60 s. X500

Fig. 11—Effect of temperature on interfacial compound formation of Ni-bearing filler metal BAg-3 on steel; superheats as follows: a—30 C (86 F); b—60 C (140 F); c—120 C (248 F). X500

There is little difference in the effect of time and temperature on the formation of the interfacial and dispersed phases, which are labeled area 2. The interfacial phase is a mixture of Cu-Zn-Ni, as are the dispersed phases, which are in a matrix, area 3, of Ag-Cd. There is also some Fe in the interfacial compound, which would be expected in the case of alloying at the interface.

Microprobe color composites show that the Fe is in a thin region of the alloyed layer next to the steel substrate. As mentioned previously, features such as those just described are readily visible in color but not in black and white.

Location of Fractures in Joints Made With Ag Filler Metal

Cross sections of fractured AWS standard brazed joint specimens were prepared for optical examination. The sections were taken from specimens which broke through the filler metal and not through the base metal in order to determine the weakest area in the brazed joint. For the filler metal combinations with copper and brass base metals, the failures were found to occur in general through the filler metal. They did not occur through the interfacial phases or at the boundary between the base metal and interfacial phases.

Typical failures are shown in Fig. 12. Figure 12a is a fractured brass joint brazed with a BAg-1 filler metal. The dark area in the center of the micrograph is the mounting material in the space between the two fractured surfaces. The interfacial phase can be seen next to the top of the dark area; note how it has been deformed during testing.

The fractured joint in Fig. 12b is brass brazed with BAg-1a filler metal. The fracture occurred here through the filler metal, and the deformation of the interfacial phase at the top of the dark area is also visible. The joint in
Fig. 12c is copper brazed with a BAg-2 filler metal. The fracture here is also through the filler metal and not the interfacial phase. Again the deformation of the interfacial phase can be seen. The joint in Fig. 12d is copper brazed with BAg-3 filler metal. The same type of fracture has occurred in this joint as in the previous ones.

For combinations of filler metals without Ni and steel, failure was found to occur along the interface, indicating that this is the weakest area. The fact that the Ag filler metals without Ni do not form interfacial compounds or alloy at the interface with steel was discussed previously and also shown in Figs. 7, 8, and 9. The sharp interface without alloying represents more of a mechanical than a metallurgical bond and therefore would be expected to be the weakest area.

The fractures along the interfacial area and the lack of alloying and compound formation are shown in Fig. 13 for the Ag filler metals and steel combinations. Fig. 13a is a micrograph of a fractured steel joint brazed with BAg-1 filler metal, the joint in Fig. 13b was made with BAg-1a filler metal, and the joint in Fig. 13c was made with BAg-2 filler metal.

The combinations of steel base metal and Ni-bearing Ag filler metal exhibited a fracture different from the other Ag filler metal-steel combinations. This is due to the formation of an interfacial phase of Cu-Zn-Ni with the Fe in the base metal. The alloying produces a bond that is stronger than that obtained without alloying, and the fracture occurs through the filler metal and not along the interface. This is illustrated in Fig. 14, where the alloying appears as a thin, dark line between the steel and the filler.
Discussion of Results

Several general observations can be made on the basis of the evidence shown. In every case there is alloying and interfacial phase formation between Ag filler metals and the copper and brass base metals. The interfacial phases consist of a Cu-Zn mixture, except for the Ni-bearing alloy, in which case the phase is Cu-Zn-Ni. The Ag andCd constituents do not appear to enter into the interfacial reactions but instead make up the matrix of the filler metal.

The reactions occurring at the interfaces are largely the dissolution of the base metal by the liquid filler metal and the formation of the enriched phases upon cooling. Formation of the phases begins at the solid-liquid interface, which tends to seed the precipitation of the enriched phases from the liquid. Nickel in the filler metal produces intergranular penetration of the base metal, and the interfacial region becomes very irregular.

Ag filler metals without Ni do not alloy or form interfacial compounds on steel base metals. The interface between the filler and base metals is sharp. The presence of Ni in the filler results in alloying and an interfacial phase consisting of Cu-Zn-Ni and Fe.

The quantity of interfacial phases formed depends upon time, temperature, and composition of filler and base metals. The compounds formed as a result of the reactions between filler and base metals are usually brittle. The subsequent effect of the compounds upon the joint strength depends upon the quantity and distribution in the joint. In the case of Ag filler metals used to join copper and brass, the Cu-Zn phase at the interface shows evidence of plastic deformation with the fracture occurring through the filler metal.

Copper and brass joints made with Ag filler metals exhibit good strength, as shown by the representative data in Table 4. The typical dependence of joint strength on base metal is apparent, brass joints being stronger than copper. The data also display the increase in joint strength obtained with the addition of Ni. The compounds consequently do not appear to be extremely brittle when present in a thin layer as they were here. Excessive alloying and compound formation, due to extreme temperature and prolonged time of contact, would result in poor joint strength.

A marked similarity has been noted in the interfacial regions of Ag filler and Pb-Sn soldered joints on copper and brass base metals. The Pb is like the Ag in that it does not appear in reaction products at the interface but is in the matrix of the filler metal. Some alloying is required for the Pb-Sn solders so that the interfacial regions become transition zones where the compositions of the different phases blend gradually into the compositions of the adjacent phases.

The overlapping of phase boundaries is evidently important to the formation of a strong solder joint. When a sharp boundary is formed, the solder joint is usually weak because it is more of a mechanical than a metal-lurgical bond.

In the case of the combinations of Ag filler metals without Ni and steel base metal, there is no alloying or formation of interfacial compounds. Instead, there is a sharp boundary between filler and base metal. The failures in brazed joints of this combination occur along and adjacent to the interface, indicating that this is the weakest area.

When Ni is present in the Ag filler metal, alloying and interfacial compound formation occur. Fractures for the combination occur in the filler metal adjacent to the compounds, indicating that the interfacial bond is stronger than in the previous case. The values in Table 4 show the increase in the strength of steel joints when Ni is present in the filler metal. Consequently, alloying and interfacial compound formation do not detract from the strength of joints brazed with Ag filler metals when present in controlled amounts.

Bailey and Watkins found that metal solubility or interfacial compound formation was a necessary condition for good wetting and subsequent bond strength. Wassink 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 can be improved by the addition of an element that is mutually soluble or that forms compounds with the base metal.

The spread area data in Tables 2 and 3 for the steel base metals show a similar result. The spread areas, and consequently the wettability, are larger for the Ni-bearing filler metal, which forms compounds with the steel base metal.

Conclusion

Based on the information obtained on the interfacial characteristics of Ag filler metals on copper, brass, and steel base metals, several properties are seen to be important to the development of a silverless filler metal. A substitute filler metal should contain elements that are mutually soluble or form interfacial compounds with the copper, brass, and steel base metals to promote good wetting and bond strength. The interface reactions should be time and temperature dependent to allow control of the amount of compound formed.

The usual means of control is by varying the time and temperature of the brazing cycle. The amount of interfacial compound needs to controlled because it is usually brittle. When present in too large a quantity, such compounds reduce the joint strength.

All of the individual elements comprising the filler metal do not have to be soluble or enter into reactions with the base metal. One element appears to be sufficient, even when present in small amounts, as shown by the Ag filler metal with 3% Ni on steel.

References