

# Sulfide-Induced Corrosion of Copper-Silver-Phosphorus Brazed Joints in Welding Transformers

*A source of moisture was traced to leaking brazed joints within the transformer's secondary winding*

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**ABSTRACT.** Failures of welding transformers were traced back to leaking brazed joints on the secondary winding within the transformer case. The leaks were caused by extensive corrosion of both the Cu-Ag-P braze metal and the adjoining copper tube and/or casting that formed the secondary winding. The corrosion consisted of selective attack of copper within the braze metal as well as the adjoining copper tube and casting. The existence of extensive copper sulfide scale in the winding and particularly at the brazed joint along with the presence of high phosphorus levels within the corrosion products suggests that the corrosion mechanism was sulfide-induced corrosion that led to formation of phosphoric acid within the joint. This acid selectively attacked copper either within the joint or adjacent to it. This mechanism was reproduced in the laboratory by exposing brazed joints to sulfide-contaminated deionized water at elevated temperature. A long-term solution to the corrosion problem was identified: replacement of the Cu-Ag-P braze with a phosphorus-free Ag-Cu-Zn-Sn braze.

## Introduction

Transformers used for resistance spot welding of vehicle structures can fail for a variety of reasons. Since the transformers are water cooled, water entering the transformer case from any number of sources can provide a low-resistance current path or short between the transformer secondary and primary windings. In this work, a source of moisture was traced to leaking brazed joints contained within the transformer case as part of the construction of the transformer's secondary winding.

The secondary winding is typically con-

structed from both wrought and cast parts fabricated from electronic-grade copper. The components are joined during assembly with a torch brazing process and a filler metal from the copper-phosphorus-silver braze metal family. These alloys have been used extensively for more than 30 years in welding transformers. They are economical and can be self fluxing when used to braze copper. The copper phosphide family of braze metals is widely recommended for joining copper and high-copper alloys in a variety of applications (Refs. 1–6), particularly copper-to-copper tube including copper piping in cooling systems. Although similar brazed transformers have shown good durability, the occurrence of failed transformers from water leaks has been observed often enough to warrant further investigation. Ultimately, more durable braze joints may be required to survive specific operating conditions.

## Experimental

Damaged transformers were examined to determine the root cause of failure for the brazed joints. Failure analyses consisted of visual examination, optical examination, and scanning electron microscopy (SEM) examination with energy-dispersive spectroscopy (EDS). SEM EDS analyses were performed using a Zeiss EVO SEM with a Noran EDS system adapted to the microscope. In addition, personnel in the Chemical Analysis group

at the GM R&D Center examined brazed joints with a field emission scanning electron microscope (FESEM) and x-ray photoelectron spectroscopy (XPS).

## Results and Discussion

### Failure Analyses

#### Secondary Winding Design: Components and Braze Filler Metal

Figure 1 shows a portion of a typical winding of a transformer removed from an assembly plant. The winding consists of a thick-walled copper tube with cast copper pads brazed to the ends of the tube. The tube and pads are both pure copper conforming to the Copper Development Association Specification C11000, which is an electrolytic tough pitch copper alloy consisting of 99.9% copper with some residual oxygen. While the C11000 specification refers to wrought material, the same alloy was used to cast the winding pads. The brazing alloys used to join the transformer winding components are from a family of high-phosphorus-content alloys that require no fluxing to wet the copper substrate. The alloys used were either a Cu-18Ag-6.25P alloy (all values in wt-%) or a Cu-6Ag-6.1P alloy.

A cross section through a brazed joint made from the Cu-6Ag-6.1P alloy is shown in Fig. 2A. The left side of the joint is the side exposed to the atmosphere while the right side of the joint has cooling water running through it during use. Figure 2B shows the as-polished microstructure of the joint. Several phases are visible including primary pro-eutectic copper, which appears as light-gray particles, dark-gray copper-phosphide ( $\text{Cu}_3\text{P}$ ) particles, and a eutectic consisting of lamellae of copper and  $\text{Cu}_3\text{P}$ .

A typical microstructure for the Cu-18Ag-6.25P alloy is shown in Fig. 2C. In addition to the microstructural constituents found in the Cu-6Ag-6.1P alloy,

### KEYWORDS

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Secondary Winding  
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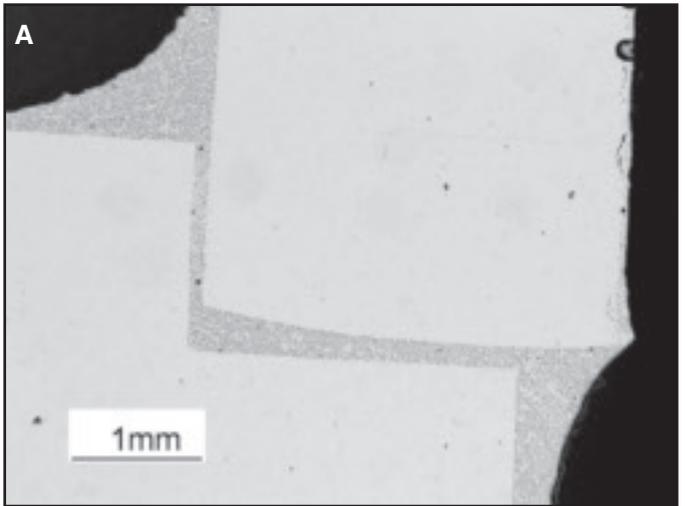
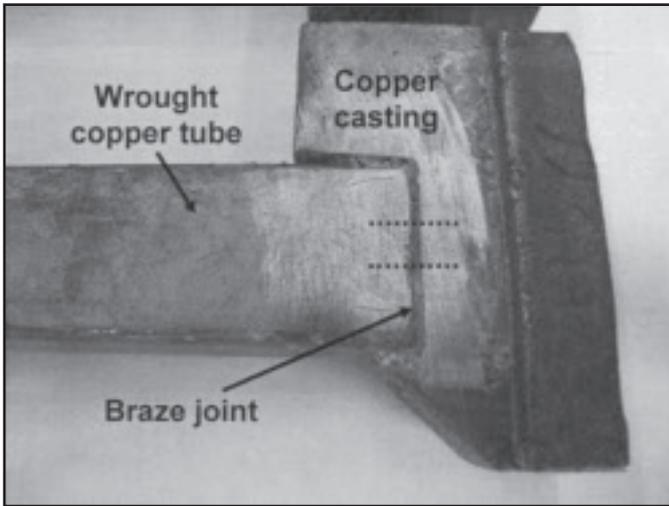


Fig. 1 — A portion of a secondary winding removed from a failed transformer. Dotted lines indicate section taken for braze joint evaluation.

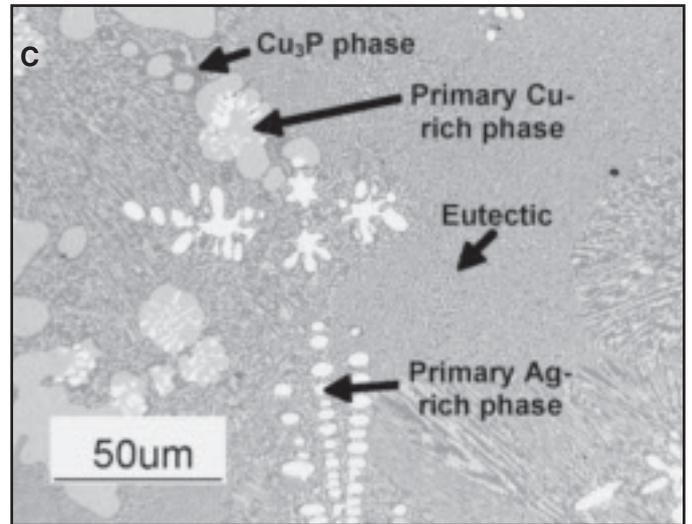
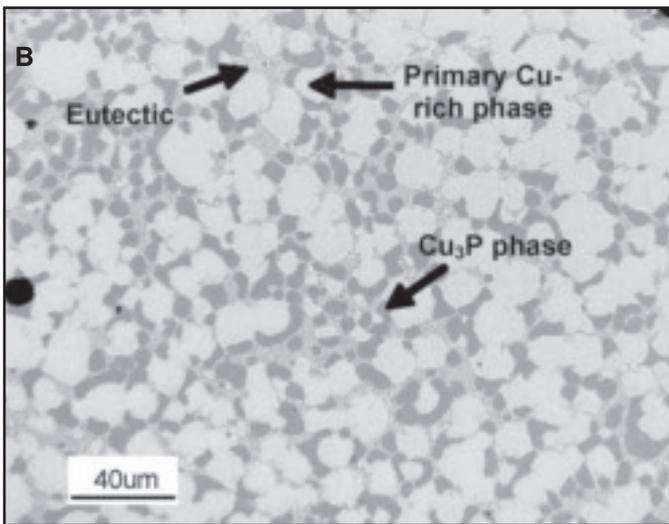


Fig. 2 — Cross sections of typical undamaged braze joints. A — An overview of a Cu-6Ag-6.1P braze metal joint; B — microstructure of brazed joint; C — microstructure of a higher-Ag filler metal, Cu-18Ag-6.25P, that contains globular primary Ag particles in addition to the constituents of the 6Ag alloy.

the higher-Ag braze metal contains primary Ag-rich particles deposited early in the solidification process. Those Ag-rich regions have the lightest color in Fig. 2C. The composition of this high-Ag alloy is close to the ternary eutectic so that the greatest volume fraction of the microstructure consists of copper and  $\text{Cu}_3\text{P}$  lamellae in eutectic form. Some  $\text{Cu}_3\text{P}$  particles are also visible.

### Selective Copper Attack

Numerous braze joints from corroded windings were evaluated in metallographic cross section. Figure 3 shows a butt joint brazed with the Cu-18Ag-6.25P alloy. The water side and air side of the joint are indicated. The braze metal itself appears dark toward the water side of the joint. In addition, dark areas define much of the

braze/tube and braze/casting interfaces.

Figure 3B illustrates a typical joint microstructure near the undamaged “air-side” of the braze filler metal adjacent to the winding’s cast pad. Features of the braze microstructure include a large volume fraction of Cu/ $\text{Cu}_3\text{P}$  eutectic as well as Cu-rich and Ag-rich particles. The casting shows a large grain size of  $\sim 50\ \mu\text{m}$  with Cu-oxide particles outlining the grain boundaries. Toward the center of the braze joint is an area with significant damage — Fig. 3C. The two very large, round pores are likely gas porosity carried over from the brazing operation. Degradation of the joint has produced a large gap between the braze filler metal and the copper tube. Also, selective attack of copper lamellae in the braze has occurred and turned the eutectic dark in color. Finally, the primary copper particles were also at-

tacked as shown by some dark areas surrounding some of the particles and other particles missing completely (see arrows).

Figure 3D shows an area located closer to the water passage. In this micrograph, attack of both the copper tube and copper casting is apparent. In addition, extensive attack of copper particles as well as copper lamellae in the braze filler metal has occurred. Figure 3E shows a microstructure of the brazement adjacent to the water flow passage. With a few exceptions, the microstructure is nearly devoid of Cu-rich phases.

These micrographs illustrate a form of selective Cu attack that leaves the Cu phosphide phase intact, while dissolving/reacting/damaging any copper metal in contact with the copper-phosphide. The at-risk copper constituents include the copper eutectic lamellae, primary Cu-rich

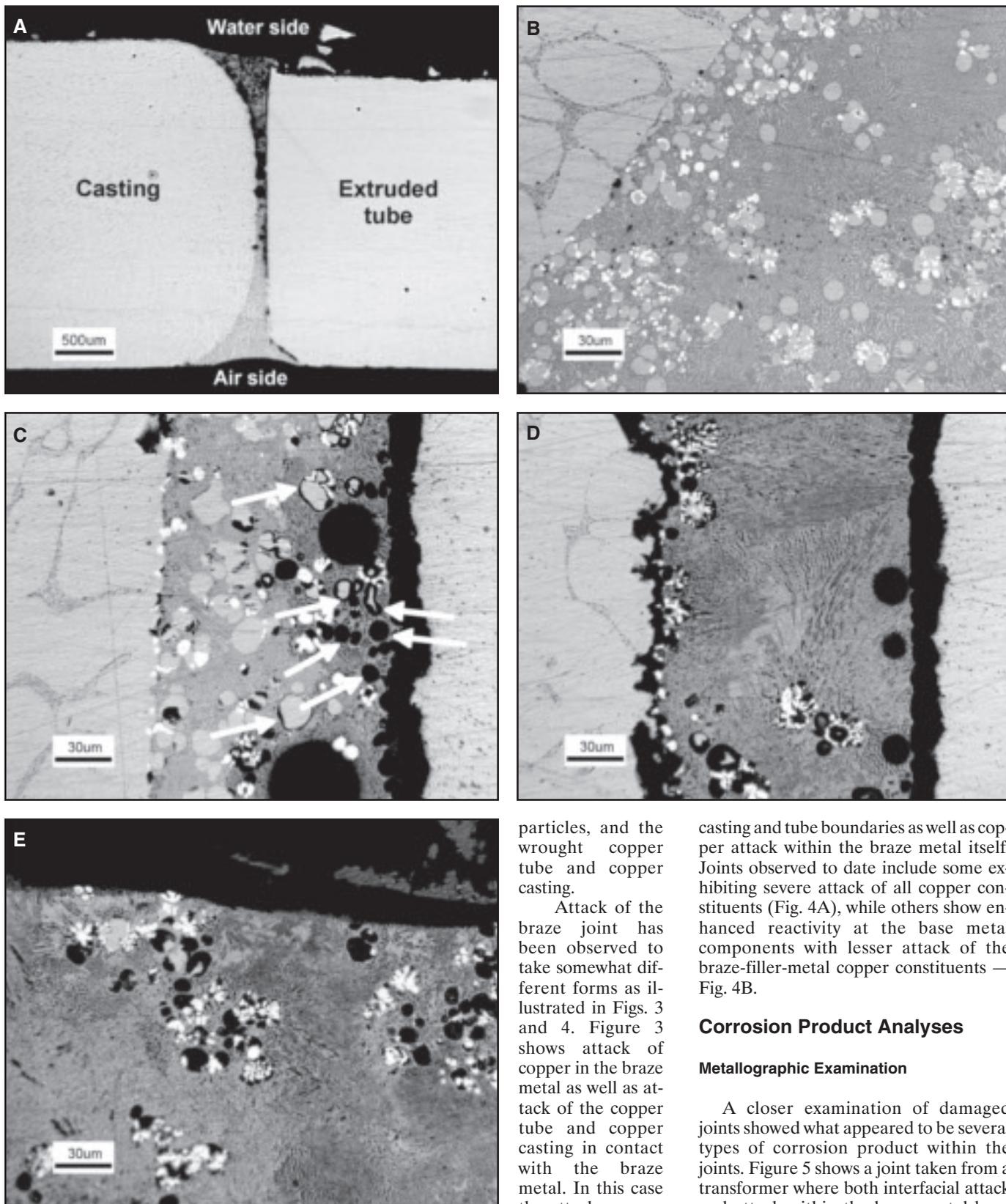


Fig. 3 — Cross-sectional views of a damaged brazed joint. A — An overview; B — a location with no damage near the air side of the joint; C-E — locations with progressively more severe damage approaching the water side of the joint.

particles, and the wrought copper tube and copper casting.

Attack of the braze joint has been observed to take somewhat different forms as illustrated in Figs. 3 and 4. Figure 3 shows attack of copper in the braze metal as well as attack of the copper tube and copper casting in contact with the braze metal. In this case the attack appears to progress inward from the water flow passage. Figure 4A shows an excellent example of interfacial attack occurring along both the

casting and tube boundaries as well as copper attack within the braze metal itself. Joints observed to date include some exhibiting severe attack of all copper constituents (Fig. 4A), while others show enhanced reactivity at the base metal components with lesser attack of the braze-filler-metal copper constituents — Fig. 4B.

### Corrosion Product Analyses

#### Metallographic Examination

A closer examination of damaged joints showed what appeared to be several types of corrosion product within the joints. Figure 5 shows a joint taken from a transformer where both interfacial attack and attack within the braze metal have progressed from the water-flow side of the joint toward the air side of the joint.

Corrosion products in both Fig. 5B and 5C were analyzed with SEM energy-dispersive spectroscopy (EDS). Figure 5B shows analyses for a light-gray corrosion product that typically forms during the

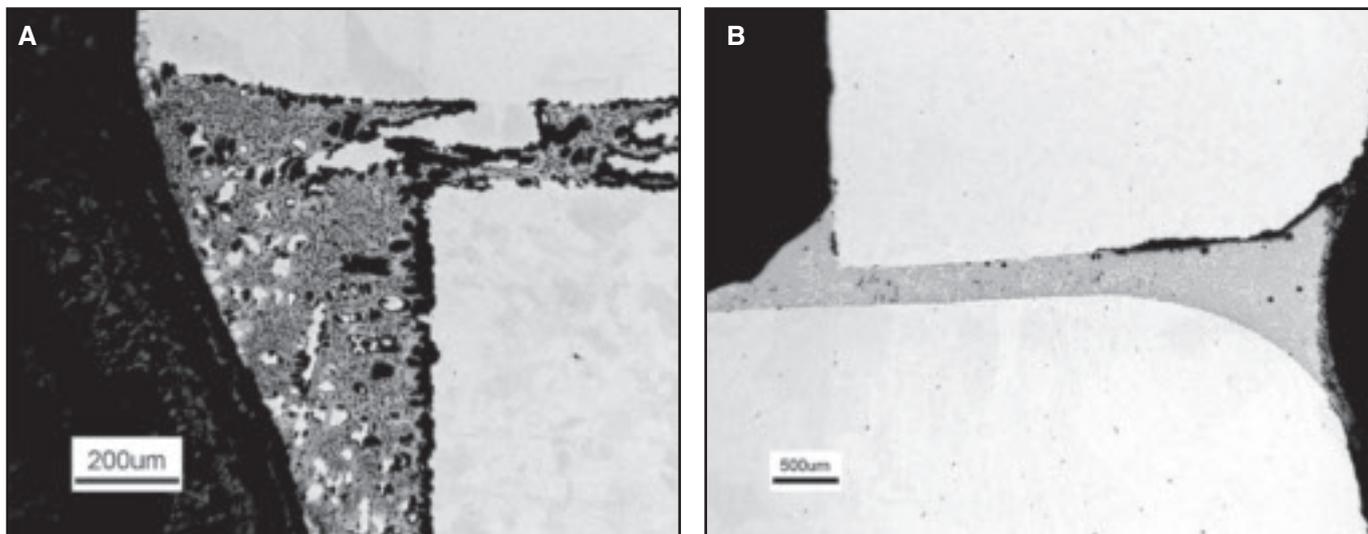
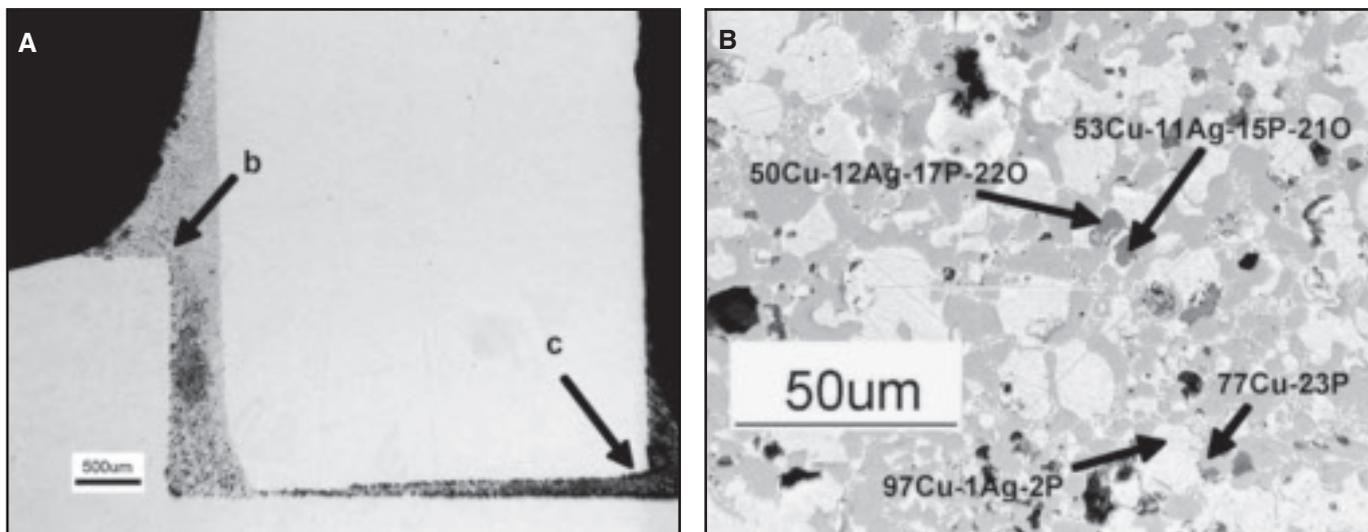


Fig. 4 — Cross-sectional views of damaged brazed joints. A — Severe interfacial attack and attack within the braze; B — severe interfacial attack from the air side with limited interfacial and braze metal attack from the water passage.



early stage of joint degradation. Also shown for comparison are compositions of the primary copper and  $\text{Cu}_3\text{P}$  phases. The primary copper phase contained approximately 1 at-% Ag and 2 at-% P, while the phosphide phase showed no Ag. Compositions of the corrosion products displayed the expected high levels of O, but also contained (unexpected) high levels of both Ag and P: ~12 at-% Ag and ~16 at-% P. Hence, although the microstructural evidence most clearly showed attack of the copper, elemental analyses indicate that both Ag and P are involved in the corrosion process. Cu is also clearly removed from the joint area since the primary copper, which was once 97 at-% Cu, is replaced with a corrosion product containing only ~50 at-% Cu.

Figure 5C shows compositions of corrosion products located in a more severely damaged area of the joint. Several types of morphologies are evident. These include a

smooth dark-gray product (A), a porous dark-gray product (B), and a granular product (C) that is red in color. Relative to that found for the light-grey corrosion product in Fig. 5B, analyses of the dark-gray corrosion products revealed lower Ag and P levels, higher Cu levels, and the presence of about 2 at-% S. The granular red corrosion product (C) had higher oxygen levels as well as sulfur and is suspected of

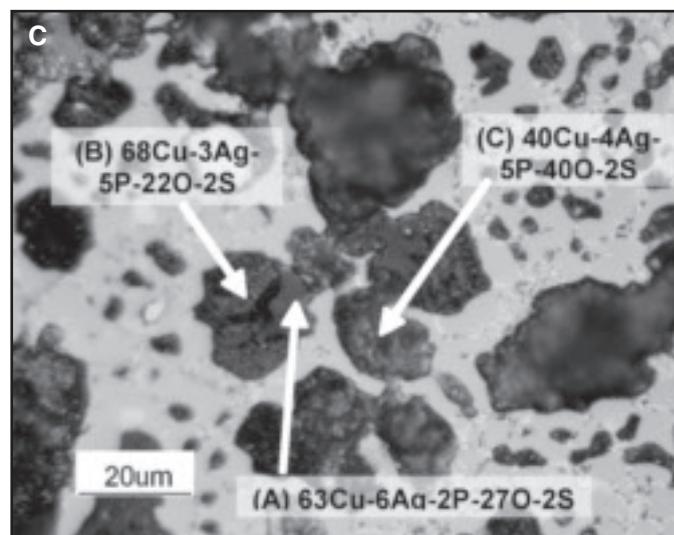


Fig. 5 — Cross-sectional views of a damaged brazed joint. A — Low magnification; B — high magnification in an area with less severe attack; C — high magnification in an area with more severe attack. Compositional analyses done by SEM EDS with results expressed in at.-%.

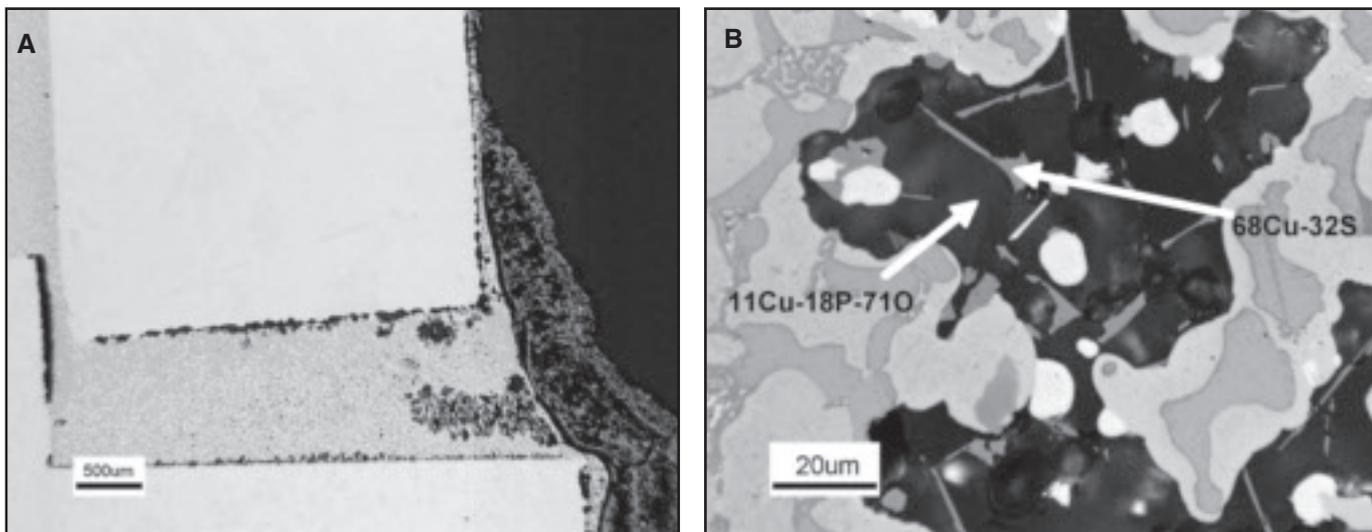


Fig. 6 — Cross-sectional views of a severely damaged brazed joint. A — Low magnification; B — high magnification. Compositional analyses were done by SEM EDS and expressed in at.-%.

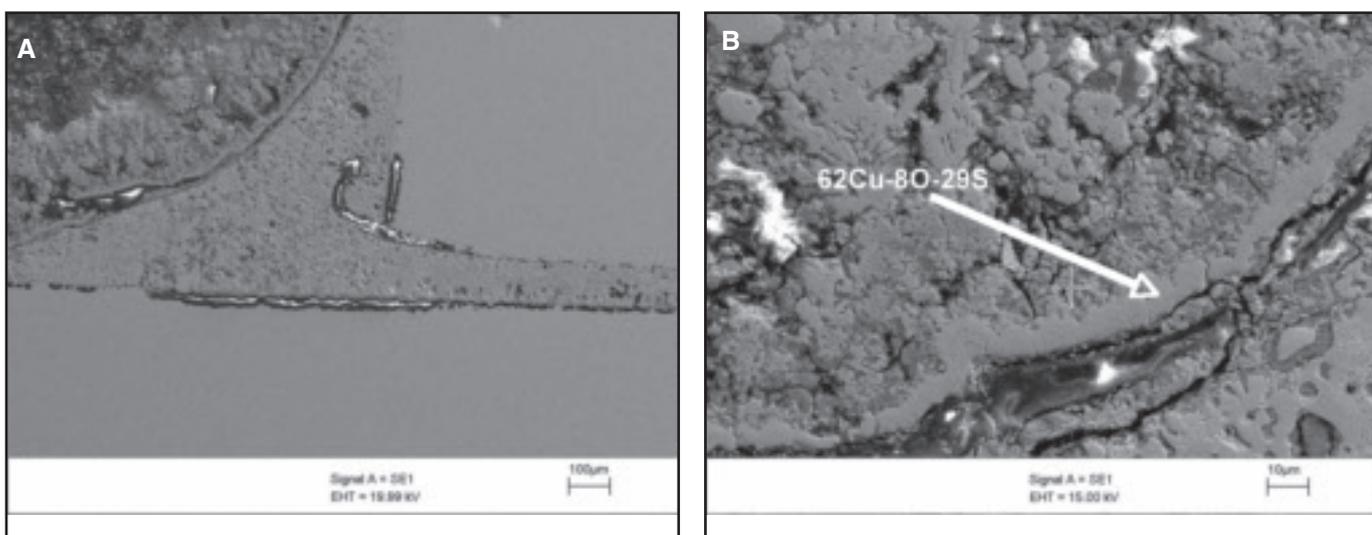


Fig. 7 — Cross-sectional views of a damaged brazed joint showing a heavy layer of copper sulfide on the braze metal surface in contact with the water passage. A — Low magnification; B — high magnification. Compositional analyses were done by SEM EDS and expressed in at.-%.

being predominantly CuO.

An even more severe form of attack was found in one winding joint. Figure 6A shows a metallographic overview of the joint while Fig. 6B shows a high-magnification view along with results of EDS analyses. The joint cross section reveals angular particles that were identified as copper sulfide,  $\text{Cu}_2\text{S}$ . The dark phase surrounding the particles contained Cu and P with very high levels of O, and was thought to be a copper phosphate compound.

Another characteristic feature of the attacked brazed joints is that they all showed a thick layer of copper sulfide,  $\text{Cu}_2\text{S}$ , on the braze surface exposed to the water flow passage. Figure 7 shows an SEM image of braze metal area in contact with the water passage for a joint removed from a failed transformer. An EDS analy-

sis determined that it was copper sulfide.

### Fracture Surface Examination

To further understand the corrosion mechanism, joints were deliberately fractured and examined. Joint integrity was so poor that sections of the joints approximately 6 mm wide could easily be fractured manually. The exposed surface of the braze metal was typically found to be covered by a blue film or coating. EDS analyses of these coatings found that they consisted of Cu, P, and O, which suggests that it is a form of copper phosphate similar to that shown in Fig. 5. XPS analysis performed on one of the joints identified the film on the braze metal as copper phosphate with a composition containing up to 5 at.-% sulfur.

In many instances there was no residue on the surface of the adjacent copper component. Figure 8 shows an example of this for a cast copper pad removed from the adjacent tube. Braze metal had covered the cast pad within the water flow passage. Severe attack of the pad had occurred beneath the braze metal. Because of the extent of the damage, the braze metal was weakly attached and easily removed by hand. The figure reveals a strongly etched structure with the grain boundaries clearly revealed. No residue was obvious in this area.

### Literature Descriptions of Similar Copper Corrosion Phenomena

While literature data concerning the corrosion of Cu-P brazed joints are some-

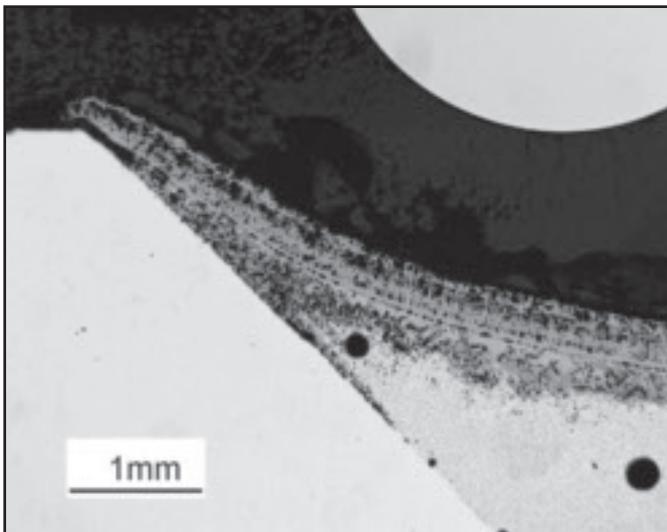
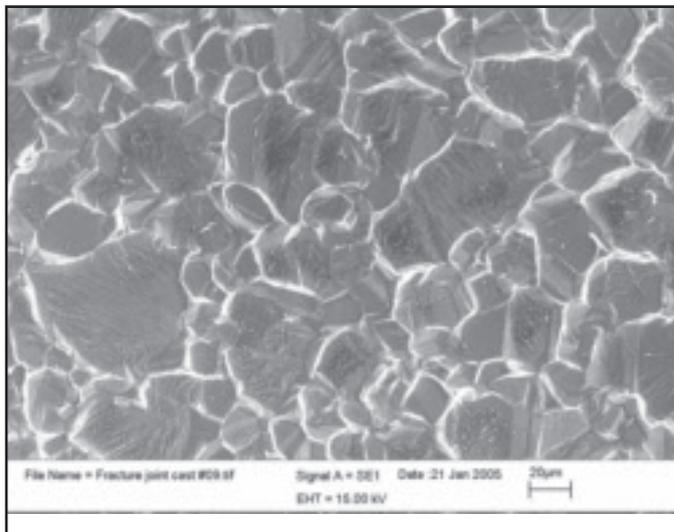


Fig. 8 — SEM micrograph of the brazed joint showing the surface of the cast pad beneath corroded braze metal clearly revealing the grain structure.

Fig. 9 — Simulated transformer brazed joint fabricated by torch brazing electronic-grade C11000 copper plate and Cu-6Ag-6.1P braze alloy after exposure to water at 60°C containing 160 ppm sulfide for three weeks. Joint damage, including penetration into the braze and interfacial attack, mirror that from damaged plant transformers.

what limited, the type of corrosion that selectively attacks copper both within the braze joint as well as adjacent to the braze material has been documented previously in a variety of environments. B. Upton found extensive interfacial corrosion of copper phosphide and corrosion of the copper-rich phase for joints exposed to seawater in Langstone Harbor, U.K. (Ref. 7). K. Nielsen found extensive interfacial corrosion of copper adjacent to the copper phosphide braze for copper tubes that contained hot (60°C) drinking water obtained from Copenhagen, Denmark (Ref. 8). A British Engine failure analysis showed both interfacial corrosion at the joint and selective copper attack within the braze joint that was located within a heating system (Ref. 9).

The above examples exhibited the same failure mode seen in the brazed weld transformers. However, the critical issues leading to the failures were not clearly identified. It is known that the copper phosphide phase is more noble than the copper phase in Cu-P filler metals. Hence the more active copper will always tend to be attacked preferentially during galvanic corrosion. However, the AWS brazing manual specifically notes that copper-phosphorus filler metals have excellent corrosion resistance except when “exposed to sulfurous gases, compounds or solutions (Ref. 3).” The Brazetec GmbH Web site provides documentation of a copper phosphide corrosion failure where copper within the braze is selectively attacked and converted to copper sulfide and copper oxide (Ref. 10). The reason for the attack was given as exposure of the braze joint to media containing sulfur

and/or sulfur compounds.

There is additional literature data to support the role of sulfur in the degradation of Cu-P brazements, although most of it is related to corrosion in atmospheres containing H<sub>2</sub>S gas. T. Takemoto et al. found that copper joined with copper phosphide braze metal experienced selective corrosion of copper, particularly at the braze/copper interface when exposed to moist air containing H<sub>2</sub>S gas (Ref. 11). P. C. Wingert investigated the corrosion of copper connectors brazed with a copper phosphide alloy and found that high-temperature, high-humidity atmospheres containing sulfur attacked copper within the braze as well as adjacent to it (Ref. 12). In this case, however, the primary corrosion product was copper sulfide.

H. Matsuoka et al. described selective copper attack for copper phosphide joints that appears more closely related to that found in the weld transformers (Ref. 13). Attack included both interfacial corrosion between the joint and braze as well as selective copper attack in the braze metal. Those joints were exposed to a moist atmosphere containing H<sub>2</sub>S gas that produced phosphoric acid from the copper phosphide braze metal. This acid then attacked the copper phases within and adjacent to the braze metal in a galvanic corrosion reaction. Copper sulfide was present, but only on the surface of the braze metal. This description closely matches the transformer winding failure mode wherein copper sulfide is found along interior water passages covering the braze metal (Fig. 7) and copper phosphate compounds are found in the corrosion product within the braze joint (Figs. 5 and

6). The production of phosphoric acid has also been postulated to occur in copper-phosphide braze joints exposed to water at room temperature, but in this case sulfide was not introduced into the system and the phosphoric acid resulted in the formation of protective scales (Ref. 14). In addition, during electropolishing, phosphoric acid is known to produce both the faceted grain structure found on some brazements (Fig. 8) (Ref. 15) as well as copper phosphate residue (Refs. 16, 17).

## Weld Transformer Winding Corrosion Mechanism

The selective attack of copper within and adjacent to copper phosphide joints is postulated to be caused by sulfide-containing species in the water that form a sulfide scale on the braze and copper component surfaces. Beneath the sulfide scale, the local solute environment changes, which catalyzes the formation of phosphoric acid in the braze joint. Phosphoric acid then begins to selectively attack copper either in the joint or adjacent to it. Corrosion products consist primarily of copper-phosphate-related compounds, with evidence of sulfur within much of the corrosion product. Copper within the corrosion product is transported away from the joint out to the water passage where it encounters sulfide within the weld water and adds to the sulfide deposit on top of the braze metal. As corrosion along the interfaces advances, the attack reveals the grain structure of the adjacent copper tube or casting and eventually produces a large gap between the braze metal and the copper component.

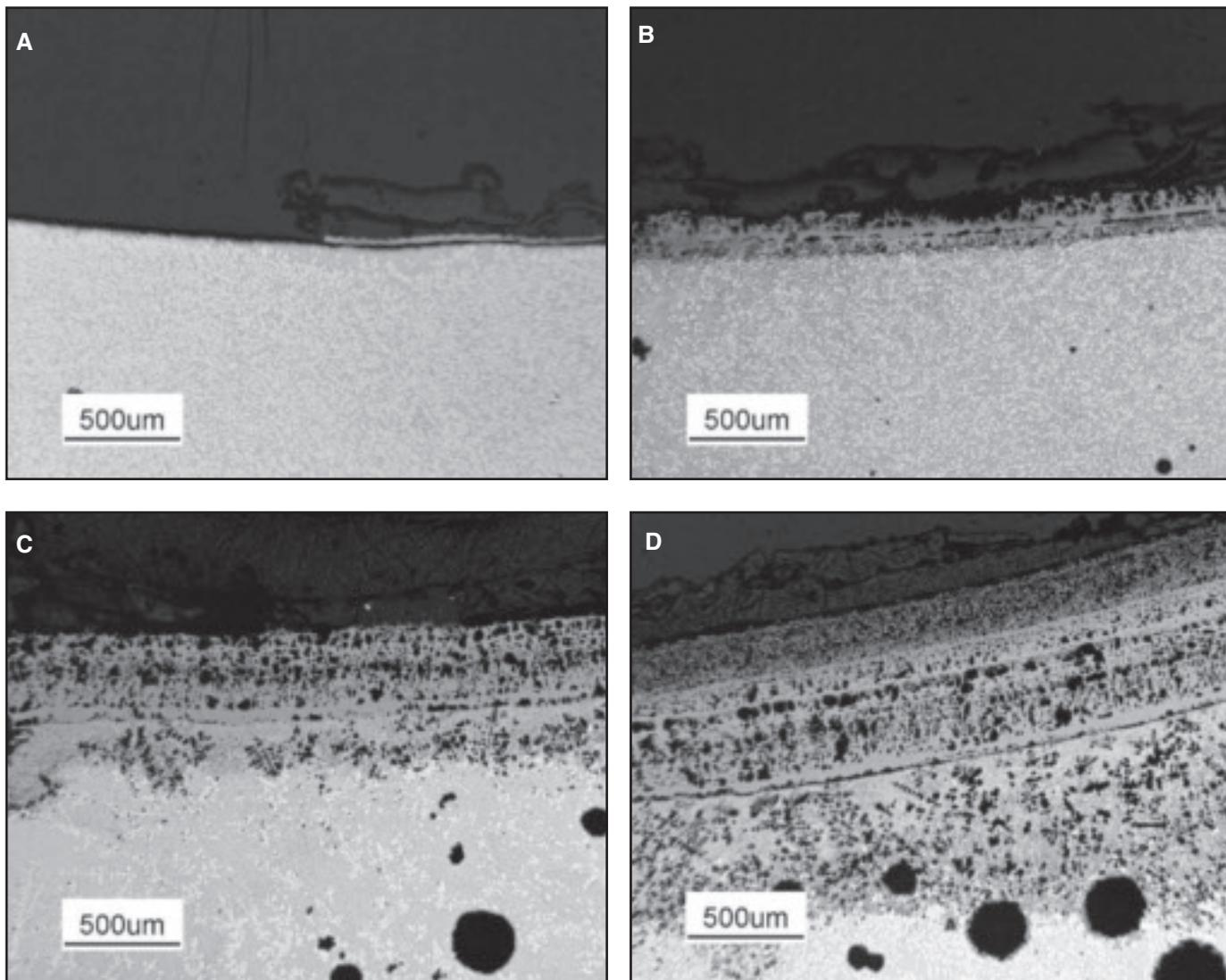


Fig. 10 — Simulated brazed transformer joint fabricated by torch brazing electronic-grade C11000 copper plate with Cu-6Ag-6.1P braze alloy after exposure to water containing 160 ppm sulfide at 60°C. A — 1 week; B — 2 weeks; C — 3 weeks; D — 5 weeks.

To verify the corrosion mechanism and gain an understanding of the corrosion kinetics, corrosion tests on specially prepared brazed samples were performed in water containing a high sulfide level. The Cu-6Ag-6.1P braze alloy was deposited in grooves machined into a 9.53-mm-thick C11000 plate by torch brazing. The geometry of the groove and plate thickness were designed to provide both a similar joint geometry to that found in the transformer joints and a similar as-brazed microstructure. Samples ~10 mm wide cut from the plate were exposed to specially prepared deionized water. The deionized water was treated with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  to give a sulfide level of 160 ppm. The sulfide level was monitored daily and sulfide additions were made to the water each day to maintain a level of 160 ppm. Temperature was controlled to 60°C with a hot plate with thermocouple control. To simulate the high water velocity in a welding trans-

former, the solution was stirred magnetically at a high rev/min using digitally controlled stirrers. The test was carried out for seven weeks with samples removed at 1, 2, 3, 5, and 7 weeks.

After exposure, samples were sectioned metallographically for assessment of the corrosion damage. Figure 9 shows an example of the sulfide-induced corrosion damage. Its appearance replicates damage observed in transformer joints. Figure 10A–D shows cross sections taken at 1, 2, 3, 5, and 7 weeks, respectively. The sulfide scale thickness, depth of attack into the braze metal, and depth of attack along the copper/braze metal interface were all measured from micrographs of joint damage. Figure 11 gives the measurement data as a function of time exposed to the sulfide-containing water. It is apparent from the micrographs in Fig. 10 and the measurement data in Fig. 11 that the corrosion reaction begins slowly, but

once underway, proceeds at an exceptional rate.

Sources for sulfide contamination of weld water systems have been under investigation. Closed-loop weld water systems are uniquely vulnerable to the action of sulfate-reducing bacteria (SRBs) that can grow in anaerobic environments. These bacteria can act to reduce innocuous sulfate ions into aggressive sulfide species that could promote the corrosion observed in transformers. Measured levels of sulfate in more than one of the affected systems indicated levels much below those of the make-up water used to refill the system after a water-loss event. This is indirect evidence that the sulfate present had been converted to another species.

While little is known regarding the mechanism of sulfide-induced corrosion specifically for the braze alloys under discussion, considerable work has been done

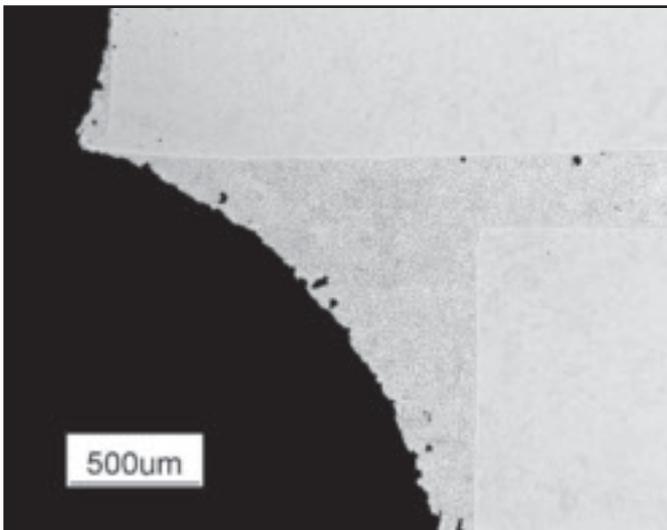
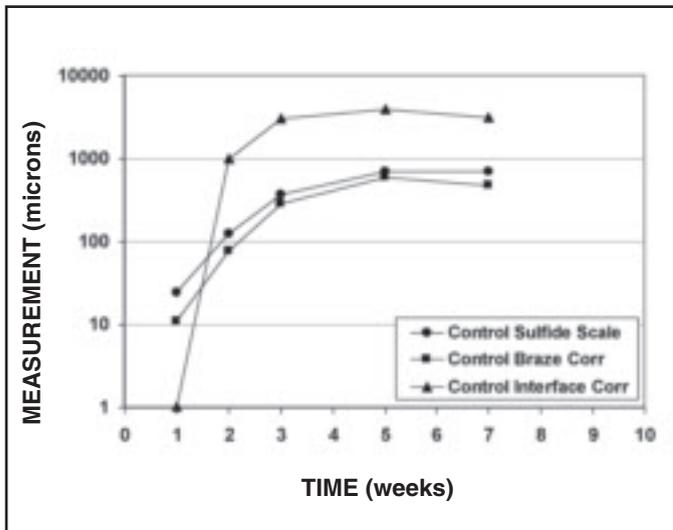


Fig. 11 — Corrosion penetration into the brazed joint after exposure to simulated weld water at 60°C containing 160 ppm sulfide.

Fig. 12 — Brazed joint taken from a transformer that utilized a high-silver, phosphorus-free braze alloy. The joint shows no discernible corrosion after five months of exposure in a plant whose weld water system suffered from sulfide contamination.

to study the effects of sulfide on copper and copper-nickel alloys (Refs. 18–22). These studies all report that sulfide in the water, most likely as hydro-sulfide ions (HS<sup>-</sup>), greatly accelerates the corrosion of copper by acting as a catalyst for both the anodic and cathodic reactions. Very little sulfide is needed in the water: as little as 10 ppb can accelerate corrosion (Ref. 18). Also, once the sulfide scale is established on the metal surface, removing sulfide from the water does not return the corrosion rate back to that of sulfide-free metal in clean water, but rather the accelerated corrosion rate will remain. Thus, if the sulfide scale found on certain transformer braze joints is acting as a catalyst as it does for ordinary copper corrosion, its removal may be necessary to stop the accelerated attack. However, once phosphoric acid is formed deep inside the joint along the crevices and within the phosphide braze metal itself, corrosion may possibly continue at a rapid rate despite correcting the water composition and removing the sulfide scale. In view of this possibility, more work is needed to assess the effectiveness of possible treatments to arrest sulfide-induced corrosion once a significant amount of corrosion product has already formed in an existing manufacturing system.

### Corrective Actions

Solutions to controlling the sulfide-initiated corrosion problem have taken multiple forms. First, steps have been taken to minimize the presence of sulfide ions in cooling water, i.e., limiting sulfate-reducing bacteria through the addition of biocides effective against these bacteria.

Second, water treatments to limit such corrosion have taken the form of changes in recommended practices to increase levels of copper corrosion inhibitors. Third, a long-term solution has been implemented whereby transformers are not put at risk for this type of corrosion by replacing the Cu-Ag-P braze by a sulfide-resistant braze filler metal.

At this time, a replacement braze metal has been identified and implemented. The Ag-Cu-Zn-Sn braze family was developed in response to the need for low-melting-point filler alloys that have low solidus temperatures, narrow melting ranges, and good corrosion resistance, but do not contain Cd. These alloys, though more expensive than the Cu-Ag-P family, have shown excellent corrosion resistance in practice. Because they are P-free, the catalytic presence of copper phosphide within the braze metal is removed. The specific alloy recommended is BAg-7, which is nominally 56% Ag, 22% Cu, 17% Zn, and 5% Sn, and is close to the eutectic composition. Figure 12 shows a joint from a transformer installed for five months in a plant with a history of sulfide contamination and corrosion. The joint shows no sulfide buildup and no corrosion whatsoever.

The Ag-Cu-Zn-Sn family of alloys is compatible with the torch brazing process when the proper flux is used. Braze filler metals of appropriate melting points are also available to manufacture complex assemblies that require successive processing with filler metals of decreasing melting point. These alloys all have compositions close to the ternary eutectic of Ag-Cu-Zn, and thus all have low melting points. Tin acts as a melting point depressant and improves flow (Ref. 23). The alloy is typically

recommended for brazing steel, copper, and nickel alloys and has good corrosion resistance, good flow characteristics, high ductility, and a low melting point (Refs. 5, 24, 25). We recommend use of these and similar alloys as a solution to sulfide-induced corrosion. Their use in weld transformers should protect the transformers against accelerated corrosion in the presence of sulfide ions. Until additional work is done, it is further suggested that alloys of this family with high Zn contents (>20–25%) be avoided to maximize corrosion resistance.

### Conclusions

1) Failure analyses of numerous joints brazed with Cu-Ag-P braze alloys revealed that joint leaks were caused by the selective attack of the copper within the brazed joint as well as the copper components in contact with the joint. Within the braze deposit, copper subject to corrosion is distributed as primary copper particles and copper lamellae in a eutectic structure. The copper components attacked by the corrosion process included the wrought copper tubes and castings that were used to fabricate the transformer winding.

2) Scale formed in the internal water passages of the secondary winding at the braze metal location was found to contain large amounts of copper sulfide. The presence of copper sulfide indicates that sulfur previously existed within the water cooling system in the form of sulfide S<sup>2-</sup> or hydro-sulfide HS<sup>-</sup> ions, or H<sub>2</sub>S gas (rather than as innocuous sulfate SO<sub>4</sub><sup>2-</sup>). This hypothesis has been anecdotally corroborated by plant personnel, who reported “black water” and sulfurous odors, two signs of

sulfide contamination.

3) Corrosion products were found both within the braze metal and at the interfaces between the braze filler and the copper components. These products contained high levels of oxygen and phosphorus. Analyses of corrosion product by XPS found phosphorus to be in the form of a phosphate. This is evidence that sulfide in the water promoted the formation of phosphoric acid that, in turn, caused the joint corrosion.

4) Preliminary laboratory tests exposed coupons of Cu-Ag-P braze metal deposited on copper plate to sulfide-containing deionized water at elevated temperature. This procedure successfully reproduced the corrosion mechanism, i.e., formation of a thick sulfide scale under which selective copper attack resulted in interfacial corrosion and corrosion products containing phosphorus. Depth of corrosion penetration within the braze and along the braze metal/copper interfaces showed that the corrosion begins slowly and rapidly accelerates to consume millimeters of metal within several weeks.

5) Brazed joints fabricated from a high-Ag, Ag-Cu-Zn-Sn braze that contained no phosphorus exhibited no corrosion when exposed to the same plant environment that produced extensive corrosion of Cu-Ag-P joints. This observed behavior is supported by literature data and indicates that a long-term solution to sulfide-induced corrosion will be the replacement of the phosphide braze in new transformers with an Ag-Cu-Zn-Sn alloy.

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