Furnace Brazing of Steel with Brass Filler Metal

Good results are obtained with filler metals containing a small amount of Ti or Zr in conjunction with a N_2 atmosphere to reduce dezincification without impairing spreadability

BY I. KAWAKATSU AND T. OSAWA

ABSTRACT. Evaporation of zinc (dezincification) from molten brass filler metals was investigated for the purpose of developing a brass filler metal having low dezincification and good spreadability during furnace brazing of steel in a protective atmosphere.

To minimize dezincification, the following approaches were attempted:

1. Addition of minor alloying elements to the brass filler metal.
2. Control of the dew point of the brazing atmosphere.
3. Selection of a suitable protective atmosphere for additive elements.
4. Surface treatment or plating of the filler metal.

The best results were obtained with filler metals containing a small amount of titanium or zirconium in conjunction with a nitrogen atmosphere. By using a nitrogen atmosphere and these filler metals, dezincification could be reduced to an acceptable level without impairing spreadability.

Introduction

Brass is obviously an important nonferrous material, and it is also important as a brazing filler metal. Brass filler metal has been widely used for brazing steels in many industrial fields. It is more economical than silver-base filler metals, it has a lower melting point than copper, and its mechanical properties are adequate (Ref. 1). Torch or dip brazing with brass and the aid of a flux is common practice. However, furnace brazing without a flux has rarely been considered suitable for this filler metal because of the high vapor pressure of zinc (Ref. 2).

For many years the benefits of furnace brazing steel with brass filler metal in hydrogen or nitrogen atmospheres have been recognized. Also, methods to prevent dezincification have been tried, but difficulties such as poor brazability, contamination of furnace and air have been solved. For this reason many fabricators have rejected the use of a brass filler metal for furnace brazing. On the other hand, the authors reasoned that, if dezincification from molten brass could be prevented during furnace brazing with a protective atmosphere, brass would be a suitable filler metal.

The purpose of this investigation was to clarify the phenomenon of dezincification from molten brass during furnace brazing and to obtain a suitable Cu-Zn base filler metal having lower dezincification and good brazability with steels. The reduction of dezincification during furnace brazing was attempted by the following steps:

1. Addition of minor alloying elements to the brass filler metal.
2. Control of the dew point of the brazing atmosphere.
3. Selection of a suitable atmosphere for the additive elements.
4. Surface treatment of the brass filler metal, e.g., plating.

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Table 1—Content of Additive Elements in Brass (40% Zn)

Element	Content, wt-%				
Al	0.05	0.1	0.3	0.5	
Si	0.1	0.2	0.3	0.5	1.0
Ti	0.05	0.1	0.3	0.5	
Zr	0.05	0.1	0.3	0.5	
Mn	0.3	0.5	1.0	2.0	
Sn	0.5	1.0			
Ag	0.5	1.0			
In	0.5	1.0			

Experimental Procedure

Cu-Zn base filler metals, which individually contained Al, Si, Ti, Zr, Mn, Ag, Sn and In as additional elements, were prepared. These were then investigated for their effect on the degree of dezincification, spreadability and brazability in several kinds of brazing atmospheres such as helium, hydrogen, nitrogen and argon. The content of the additive elements ranged from 0.05 to 1.0 wt-%, and each filler metal contained the same zinc content (40 wt-%). Each filler metal was cast into a rod 10 by 10 by 200 mm (0.394 by 0.394 by 7.87 in.) and drawn to a 1.5 mm (0.060 in.) diameter wire. Table 1 shows the contents of the additive elements.

If an oxide film which forms on the filler metal surface during brazing prevents evaporation of zinc, a higher oxidizing atmosphere could result in less dezincification. To prove this, the influence of the dew point of the brazing atmosphere on dezincification, spreadability and brazability was examined in relation to oxidation of additive elements. When nitrogen was used as the brazing atmosphere, the relationship between the degree of dezincification and additive element was investigated because the nitride film may also have a significant effect on dezincification. The degree of dezincification of the brass filler metals was measured by weight loss after heating in a hydrogen atmosphere. The dew point of the brazing atmosphere was regulated at −60, −40 and −20 C (−76, −40, −4 F) by a humidity controller as shown schematically in Fig. 1.

Experiments were also made with brass filler metal wires plated with copper, nickel and nickel-phosphorus for the purpose of preventing dezincification prior to melting of the filler metal.

Results and Discussion

When brass is used as the brazing filler metal in furnace brazing, the degree of dezincification of the molten brass is one of the most important factors that affect the success of the operation. Therefore, the relationship between dezincification and brazability must be understood.

Effects of Additive Elements on Dezincification

Figure 2 shows the effects of several additive elements on zinc evaporation from brass filler metals when brazed in a hydrogen atmosphere. It is obvious that additions of Al, Si, Ti or Zr to brass reduced dezincification effectively, whereas additions of Ag, Sn, Mn or In had little effect.

These results indicate that the additive element may be oxidized preferentially, forming an oxide film which covers the brass surface and prevents dezincification. The additive element must have a greater potential for oxidation than brass. Oxidation of the additive element may depend on properties of atmosphere, especially its dew point. Thus, the addition of an element which is more easily oxidized than brass is essential to prevent zinc evaporation.

Generally, the degree of oxidation of metal can be estimated by the free energy of formation of its oxide; a metal whose oxide is of lower free energy is more easily oxidized. Table 2 shows the free energy of formation of the oxides (Ref. 4) for the additive elements used in this experiment. The values of Al_2O_3, SiO_2, TiO_2 and ZrO_2 have greater negative values than the others—that is, Al, Si, Ti and Zr are oxidized very easily. On the other hand, it is more difficult to oxidize Ag, Sn and In. These relations coincide with the results shown in Fig. 2. Figure 3 is a schematic diagram which illustrates the mechanism whereby the zinc evaporation was prevented by the oxide film.

The degree of dezincification was affected by the type of gas used for the brazing atmosphere. Dezincification was lowest in argon and highest in hydrogen.

Effect of Dew Point on Dezincification

If the oxide film of the additive element prevented evaporation of zinc by covering the molten brass, then the dew point or humidity of the atmosphere is an important factor. It can be expected that, in a wet hydrogen atmosphere with a higher dew point, zinc evaporation may be prevented more effectively via the oxide film

Table 2—Free Energy of Formation of Various Oxides (at 900 C i.e., 1652 F)

Oxide	ΔF (Kcal/mol)
Al_2O_3	−204
SiO_2	−157
TiO_2	−173
ZrO_2	−205
MnO_2	−71
Ag_2O	+58
SnO_2	−77

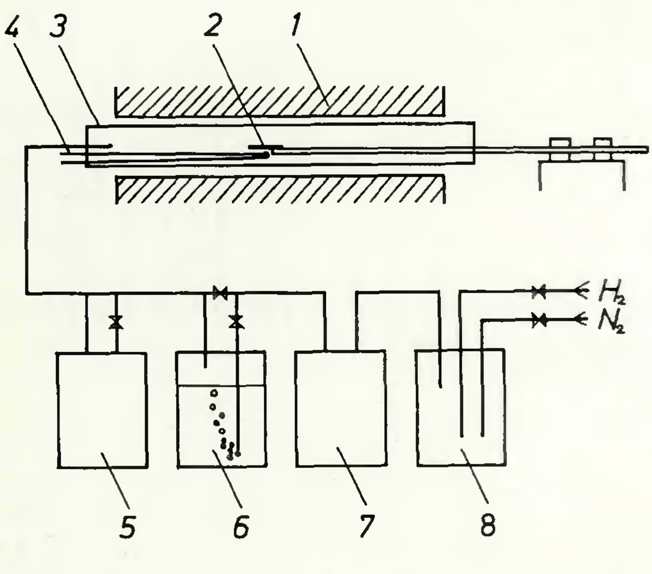
Table 3—Relation Between Dew Point and Water Vapor

Dew point	Amount of water mg/liter	%
−20 C (−4 F)	1.08	0.124
−40 C (−40 F)	0.18	0.018
−60 C (−76 F)	0.02	0.002

Table 4—Surface Color[a] of Various Brass Filler Metals After Heating in Hydrogen at 970 C (1778 F) for 5 Minutes

Dew point	Plain brass	0.1% Al	0.3% Si	0.3% Mn	1.0% Ag	0.5% Sn	0.5% In
	Additive element						
−20 C (−4 F)	D	A	A	B	D	D	D
−40 C (−40 F)	D	B	B	D	D	D	D
−60 C (−76 F)	D	C	B	D	D	D	D

(a) A—golden yellow; B—yellow; C—brown; D—dark red.



1. Furnace
2. Sample holder
3. Fused silica tube
4. Thermocouple
5. Dew point meter
6. Humidity generator
7. Dryer
8. Gas mixchamber

Fig. 1—Schematic diagram of experimental apparatus

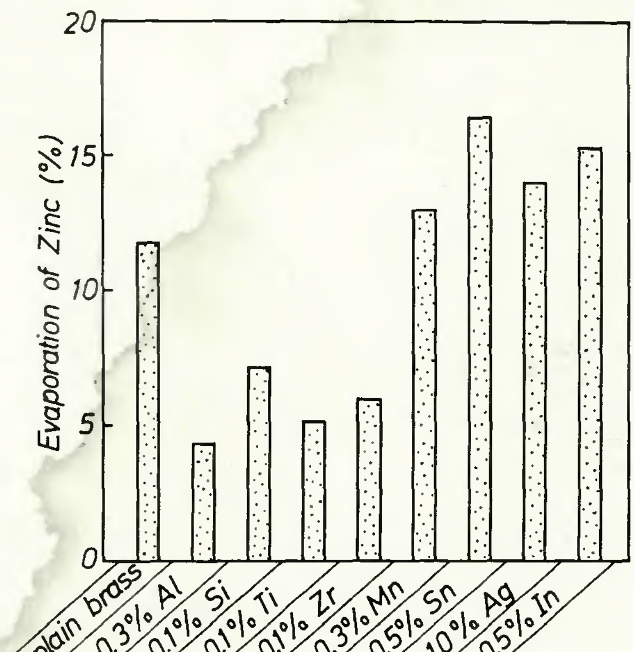


Fig. 2—Effect of additive elements in brass (40 wt-%) on zinc evaporation in hydrogen with dew point of −20 C (−4 F), heated at 970 C (1778 F) for 3 min.

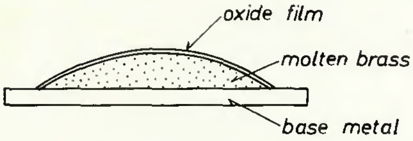


Fig. 3—Schematic illustration for prevention of zinc evaporation from molten brass filler metal

mechanism described. Table 3 shows the relation between the dew point and content of the water vapor.

Figure 4 shows the dependence of the degree of dezincification on heating time and dew point for various additive elements. It is obvious that dezincification increases with heating time. The effect of the dew point depended upon the additive elements present. The additive elements may be classified into two groups as follows:

1. Elements which enhance the effect of dew point on zinc evaporation—Al, Si, Ti, Zr.
2. Elements which have little effect on the relation between dew point and zinc evaporation—Ag, Sn, In.

Generally, in the first group, zinc evaporation is lower in wet hydrogen since the surface of molten brass filler metal is covered by the oxide of the additive element. In contrast, the additive elements of the second group do not form oxide films which prevent zinc evaporation; consequently, the degree of dezincification is influenced little by humidity of the brazing atmosphere.

Oxidation phenomena of the additive elements can be explained thermodynamically. Richardson and Jeffes (Ref. 5) published a convenient graphical representation of the free energy of formation of oxides. From their graph it can be seen that the ratio of H_2/H_2O for equilibrium formation of Al_2O_3 and TiO_2 is about $6 \times 10^{10}/1$ and $8 \times 10^{6}/1$ for these oxides, respectively.

From those values and data in Table 3, it is clear that Al and Ti form oxides easily even in hydrogen with a dew point of −60 C (−76 F). On the other hand, oxidation of Ag does not occur even in hydrogen with a dew point of −20 C (−4 F), since the H_2/H_2O ratio of Ag_2O is about $7 \times 10^{-4}/1$. These relationships clarify the mechanism for prevention of zinc evaporation represented in Fig. 3.

Table 4 shows the color change after zinc evaporation test. It is obvious that Al and Si were superior additive elements for preventing zinc evaporation.

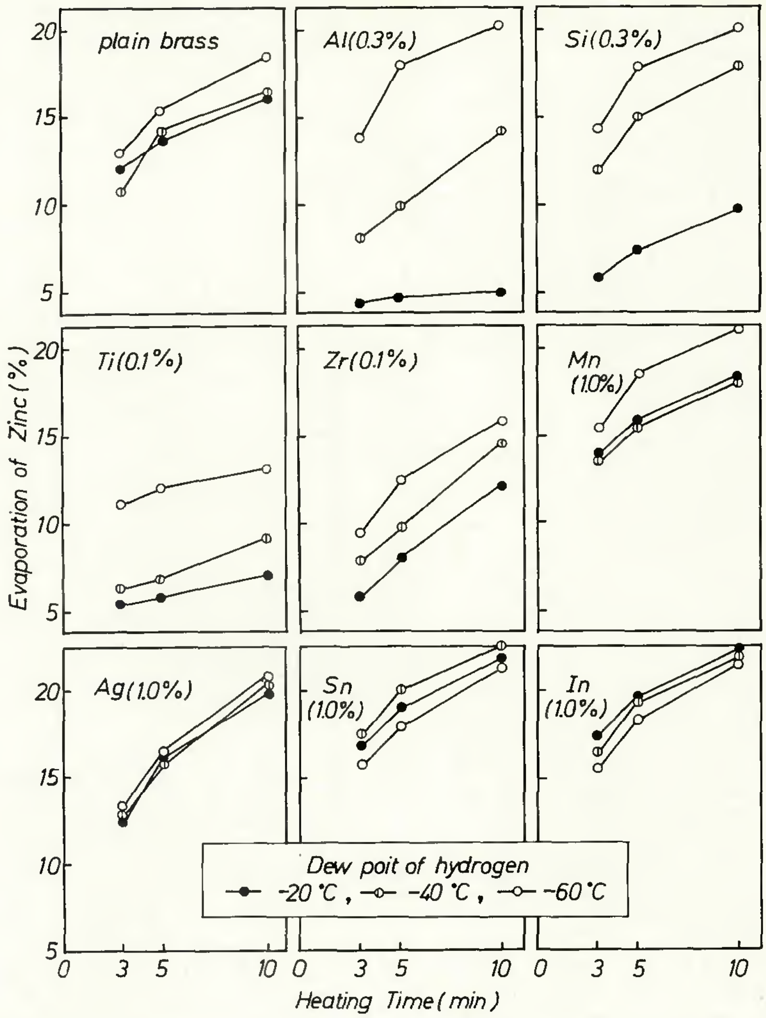


Fig. 4—Effects of heating time and dew point of brazing atmosphere on dezincification of brass filler metals containing various additive elements, heated at 970 C (1778 F) in hydrogen atmosphere

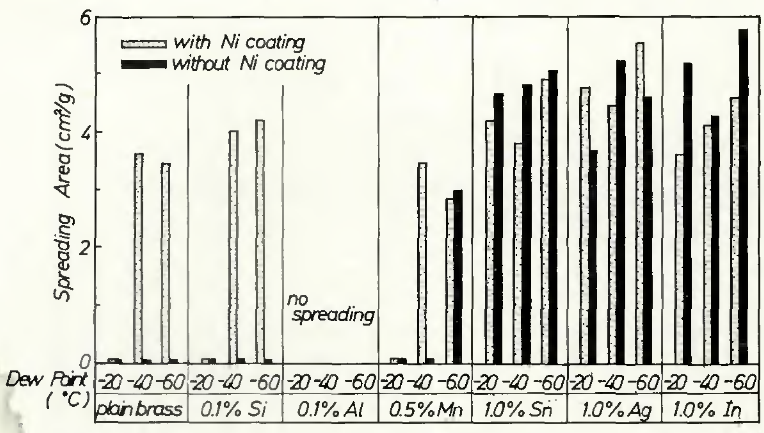


Fig. 5—Spreadability of the brass filler metals containing various additive elements and brazed at 970 C (1778 F) in hydrogen

Spreadability of Brass Filler Metal

The spreadability of brass filler metal on low carbon steel was also investigated. Figure 5 gives the results of these spreadability tests for brasses which contain various additive elements. The relationship of spreadability to the dew point of the atmosphere is also presented. The effect of coating the filler metal with nickel was also investigated in the test.

As shown in Fig. 5, the brass filler metals containing Al and Si were effective in preventing zinc evaporation but did little to improve spreadability. This trend is particularly noticeable in brasses that contained Al. On the other hand, brass filler metals which contained Ag, Sn and In did not effectively prevent zinc evaporation although they improved the spreadability.

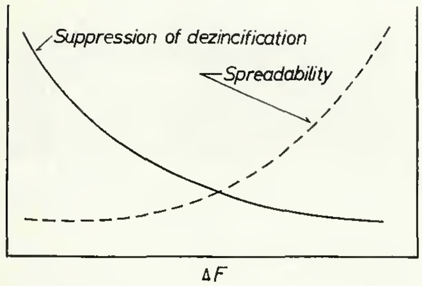


Fig. 6—Correlation between suppression of dezincification and spreadability of the brass filler metal containing additive elements (of which free energy of formation of oxides is ΔF)

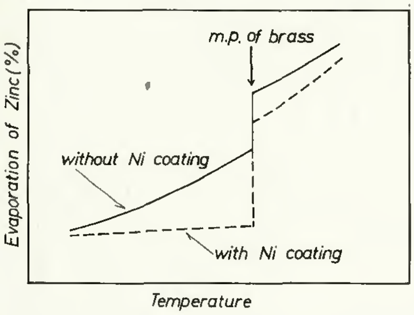


Fig. 7—Schematic illustration on relation between nickel coating on brass filler metal and zinc evaporation. Nickel coating prevents evaporation of zinc before the brass filler metal melts

There was an inverse correlation between the prevention of dezincification and the improvement of spreadability. This relationship is schematically illustrated in Fig. 6. Note that the spreadability of brass filler metal containing Ag, Sn and In was hardly affected by the dew point of atmosphere gas.

Nickel coating did not markedly improve spreadability but did tend to improve initial spreading. Some filler metals which did not spread in the absence of a nickel coating showed better spreading after coating. From this fact it is obvious that nickel coating may prevent zinc evaporation before melting of the brass. This relationship is shown schematically in Fig. 7. In this experiment the brass filler metals were coated by copper, nickel and nickel-phosphorus plating; the nickel-phosphorus coating gave excellent results.

Brazability

The brazability of molten brass filler metal was evaluated by brazing tee joints. The results are presented in Table 5.

Figure 8 shows cross sections of fillets in tee joints. The brass filler metal that contained Si formed good fillets, whereas the brass that contained Ag or Sn formed poor fillets which exhibited large voids or holes. These defects in the fillets may be assumed to have been caused by zinc evaporation.

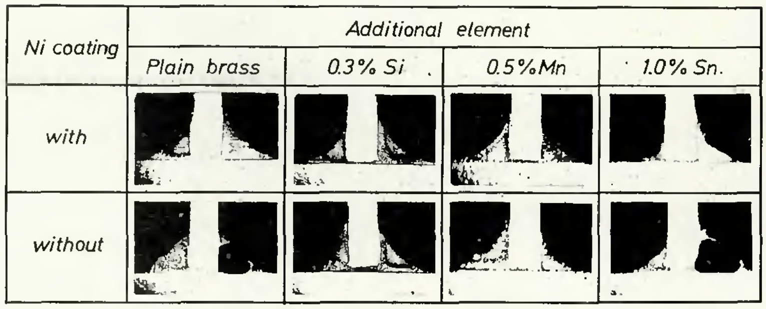


Fig. 8—Cross sections of fillets in tee joints brazed with various brass filler metals at 970 C (1778 F) in hydrogen

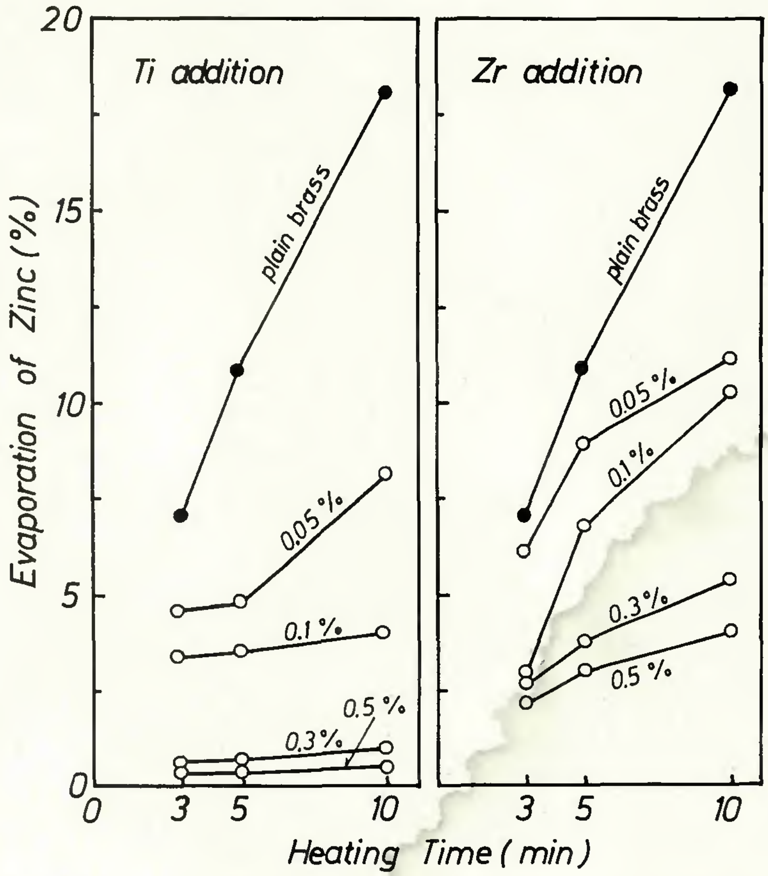


Fig. 9—Effect of titanium and zirconium addition to brass filler metal on zinc evaporation in nitrogen with dew point of −60 C (−76 F), heated at 970 C (1778 F)

Behavior of Ti and Zr in a Nitrogen Atmosphere

It is interesting to note that, when nitrogen was used as the brazing

Table 5—The Brazability[a] of Various Brass Filler Metals in Hydrogen at 970 C (1778 F)

	Additive element						
Ni coating	Plain brass	0.1% Al	0.3% Si	0.3% Mn	1.0% Ag	0.5% Sn	0.5% In
With	B	D	A	B	B	B	B
Without	C	D	A	B	C	C	B

(a) A—excellent; B—good; C—poor; D—no flow.

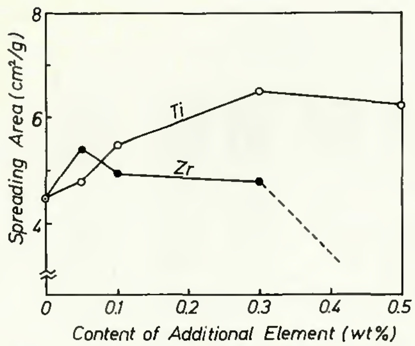


Fig. 10—Effect of titanium and zirconium additions on the spreadability of brass filler metal

atmosphere, the amount of zinc evaporation from plain brass decreased to approximately 60% of that when hydrogen was the brazing atmosphere. From this fact it can be expected that a brass filler metal which contains a strong nitride forming element may lower dezincification owing to the nitride formation on the surface. For this purpose Ti and Zr are selected as additive elements in this experiment.

Figure 9 shows the amount of zinc evaporation from various brass filler metals containing Ti or Zr when the brazing atmosphere was nitrogen. It is obvious that zinc evaporation was significantly low, i.e., approximately 30% of that when a hydrogen atmosphere was used. This phenomenon was probably caused by the titanium or zirconium nitride formation on the molten brass filler metal, which prevented evaporation of zinc. This mechanism is similar to the case of Si oxide formation in a wet hydrogen atmosphere.

The brass filler metals which contained Ti or Zr also exhibited better flow characteristics. The surface color of the flowed filler metal was a brilliant golden yellow—the same color as plain brass.

As illustrated in Fig. 10, the spreadability of the filler metals that contained Ti and Zr was superior in a nitrogen atmosphere to that of other filler metals in a hydrogen atmosphere (see Fig. 5). The brass filler metal which contained Zr exhibited a brownish yellow color after brazing, although its dezincification was lower. This color change may be due to the property of zirconium nitride, not to dezincification.

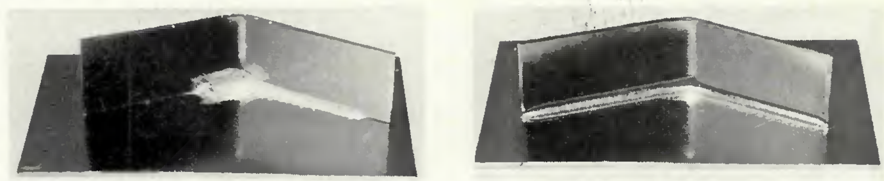


Fig. 11—Brazed joints: A (left)—with plain brass (40% Zn) in hydrogen; B (right)—with brass filler metal containing 0.1% Ti in nitrogen

As shown in Fig. 9, the amount of zinc evaporation decreases with an increase in Ti or Zr content. The addition of 0.5% Ti to the brass filler metal decreased its dezincification to about 5% of that exhibited by plain brass. The brass filler metal which contained Ti exhibited superior performance in a nitrogen atmosphere; consequently, furnace brazing with a brass filler metal is practical.

Figure 11 shows a specimen joined with a brass filler metal containing Ti in a nitrogen atmosphere. This joint is compared to one brazed with a plain brass filler metal in a hydrogen atmosphere. Figure 12 presents cross sections of fillets that were brazed in nitrogen atmosphere using the improved filler metals.

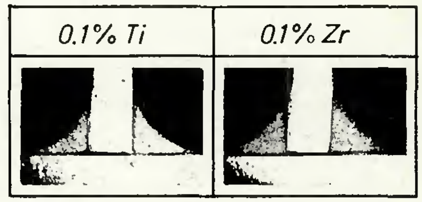


Fig. 12—Cross sections of fillets in tee joint brazed with two kinds of brass filler metals at 970 C (1778 F) in nitrogen

Conclusion

The results obtained in this investigation are summarized as follows:

1. Brass filler metals containing Al, Si, Ti or Zr proved effective for preventing dezincification, and those containing Ag, Sn or In did not inhibit dezincification.

2. The degree of dezincification of brass filler metals containing Al, Si, Ti or Zr was affected by the dew point of the brazing atmosphere; the lower the dew point the higher was the dezincification.

3. An oxide film which formed on the filler metal inhibited the evaporation of zinc, and filler metals which contained elements that were strongly oxidized exhibited less dezincification.

4. The addition of Ag, Sn and In to a brass filler metal improved the spreadability on low carbon steel in hydrogen atmosphere, but the addition of Al, Si, Ti and Zr results in rather poor spreadability. Additive elements which prevented dezincification generally reduced spreadability.

5. A filler metal containing either Ti or Zr exhibited superior performance such as lower dezincification and better spreadability in a nitrogen atmosphere.

6. Plating on brass filler metal improved the resistance to dezincification and increased spreadability, particularly brass filler metals containing 0.3% Si and coated by nickel plating.

7. The use of a Ti-containing filler metal and a nitrogen brazing atmosphere effectively eliminates dezincification and permits furnace brazing of steel with a brass filler metal.

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