Invited Lecture: Recent Developments in Amorphous Brazing Foil

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Abstract: Amorphous brazing foils are an attractive alternative to atomized powders because the foil does not require a binding paste which is burned off during the metal joining process that can lead to oxide formation and a porous joint. Metglas currently offers a series of Ni-Cr-B-Si based foils that have a recommended braze cycles that reach final temperatures in the range of 1050 – 1200 ℃. Often the brazing cycle is done using a batch process with a vacuum type oven. Recent industrial trends have shifted away from the batch ovens in favor of continuous belt furnaces to increase throughput. However, the operation temperatures are often below 1100 ℃ and require new foils to meet this. We have developed a new series of Ni-Cr-P based alloys with lower melting points to meet this demand. The braze joint often requires high corrosion resistance so the Cr levels in the new alloys has been increased. We will highlight the different braze joint characteristics between the Ni-Cr-B and the Ni-Cr-P series of alloyEmail: eric.theisen@metglas.coms

Keywords: Amorphous foil, brazing, low melting point, high corrosion resistance

1. Introduction

Amorphous brazing foils are an attractive alternative to atomized powders because the foil does not require a binding paste, which is burned off during the metal joining process that can lead to oxide formation and a porous joint. Metglas currently offers a series of Ni-Cr-B-Si based foils that have recommended braze cycles that reach final temperatures in the range of 1050 - 1200 ℃. Often the brazing cycle is done using a batch process with a vacuum type oven. Recent industrial trends have shifted away from the batch ovens in favor of continuous belt furnaces to increase throughput. However, the operation temperatures are often below 1100 ℃ and require new foils to meet this. Further details on automotive applications for braze foils can be found elsewhere [1]. Metglas has developed a new series of Ni-Cr-P-Si based alloys with lower melting points to meet this demand. The braze joint often requires high corrosion resistance so the Cr levels in the new alloys has been increased. There are significant differences in the braze joint characteristics between the Ni-Cr-B-Si and the Ni-Cr-P-Si series of alloys.

Table 1 shows the chemistry and melting characteristics of the most common Metglas brazing foils. The new series of P containing alloys are MBF62, MBF67 and MBF601 and are all commercially available in foil form. The MBF62 alloy is designed to be a low melting point, high corrosion resistant alloy for application such as exhaust gas recirculation coolers. The MBF67 has a similar application with additional Cr and Mo levels for extremely corrosive environments. The MBF601 has higher Fe levels and is a lower cost material which is also suitable for potable water heat exchanger applications.

Table 1 Metglas Brazing Foils nominal chemistries and melting characteristics

MBF Alloy	Nominal Composition, wt%							Melting Temp °C	
	Cr	Fe	Si	B	P	Mo	Ni	Solidus	Liquidus
15	13	4.2	4.5	2.8	--	--	Bal	965	1103
20	7	3	4.5	3.2	--	--	Bal	969	1024
30	--	--	4.5	3.2	--	--	Bal	984	1054
50	19	--	7.3	1.5	--	--	Bal	1052	1144
51	15	--	7.3	1.4	--	--	Bal	1030	1126
62	21	<1	0.5	0.5	8	1	Bal	878	940
67	25	<1	1.5	0.5	6	1.5	Bal	890	970
601	16	32	1.5	0.5	6	1.5	Bal	960	1035

Table 2 shows the same compositional data in atomic percentages rather than weight percent. It is notable that the atomic ratio of B to Cr in these new alloys is on the order of 0.1 where as the ratio for MBF20 and MBF51 are ~2 and ~0.5 respectively. It has been shown elsewhere that the corrosion performance of the alloys becomes much worse as the B to Cr ratio increases [2]. High levels of B in the braze filler metal results in chromium boride precipitation. This pulls the Cr from the solid solution state of the base material reducing the corrosion resistance in the braze interface. It has been observed that completely B free braze foils are difficult to cast in a ductile form is not necessary to remove all of the B for corrosion resistance provided the B/Cr ratio is low [3].

Table 2 Metglas Brazing Foils nominal atomic chemistries and B to Cr atomic ratios

Element At %	MBF20	MBF51	MBF62	MBF67	MBF68	MBF601
Cr	**6.6**	**14.6**	**20.8**	**24.7**	**28.8**	**15.8**
P	**--**	**--**	**13.3**	**10.0**	**10.0**	**9.9**
Mo	**--**	**--**	**1.8**	**2.8**	**--**	**2.7**
B	**14.5**	**6.5**	**2.4**	**2.3**	**--**	**2.4**
Si	**7.8**	**13.1**	**0.9**	**2.7**	**7.4**	**2.7**
Fe	**3.9**	**--**	**--**	**--**	**--**	**29.4**
Ni	**67.2**	**65.7**	**60.7**	**57.4**	**53.8**	**37.1**
B/Cr Ratio	**2.199**	**0.449**	**0.114**	**0.095**	**0.000**	**0.150**

2. Experiments

Initial developments of these new alloys focused on the ability to cast the foil in amorphous form using the planar flow melt spinning process. The desired goal was to produce MBF68 (Ni 29Cr 4Si 6P) foil. However, the MBF68 foil has been too difficult to cast in a ductile foil form at thickness suitable for brazing. The MBF62, MBF67 and MBF601 alloys were found to be able to cast in an amorphous form with good ductility by modifying the chemical composition slightly. Fig. 1 shows x-ray diffraction scans of the MBF67 and MBF68 as-cast foil. The offset in the axes between the three scans is for clarity. The broad diffraction peak for the MBF67 foil scan indicates that it is fully amorphous whereas the sharp peak for the MBF68 foil scan indicates some amount of crystalline phase in the as-cast state. This corresponds to ribbon that is mechanically brittle. To compare these diffraction scans with a fully crystallized material an MBF67 ribbon sample was heat treated above its crystallization temperature and the multiple sharp crystalline peaks are observed. The MBF68 as-cast ribbon is clearly not entirely crystalline but also not amorphous enough to show good ductility.

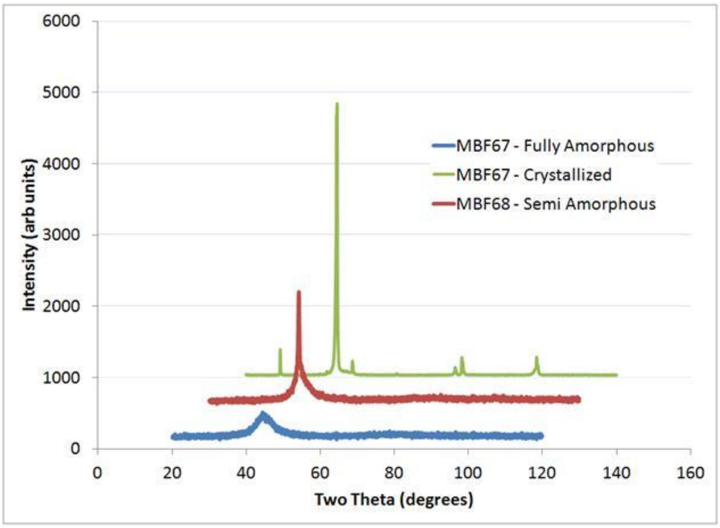

Fig. 1 X-ray diffraction scans show as-cast amorphous MBF67 ribbon to be fully amorphous. The MBF68 ribbon is partially crystallize in the as-cast state. An intentionally crystallized MBF67 ribbon is also show for comparison

The ability to cast into ductile amorphous foils allows for the braze evaluation to take place. Brazement samples joining two 316 stainless steel sample plates were carried out in a vacuum brazing oven using MBF51, MBF62, MBF67 and MBF601 foil and the samples were studied. The plates were nominally 4” by 1” as shown in Fig. 2 (a). The brazing procedure was to place samples flat with approximately 4 lbs of dead weight placed on the top plate. The vacuum in the furnace was held at 10^-4 torr minimum during the brazing cycle. The oven temperature was ramped up and held for 20-45 minutes at dwell temperature 1 (260 ℃) and then ramped to dwell temperature 2 and held for another 20-45 minutes to ensure temperature and pressure stabilization. The temperature was then ramped to required brazing temperature for each alloy and held for 15-20 minutes. Table 3 lists the dwell and brazing temperatures for each alloy. The furnace was then allowed to cool under vacuum to a temperature about 200-300 ℃ below which oxidation of joints would occur. After the brazing cycles were completed the samples were sectioned to analyze the joint morphologies, as shown in Fig. 2 (b).

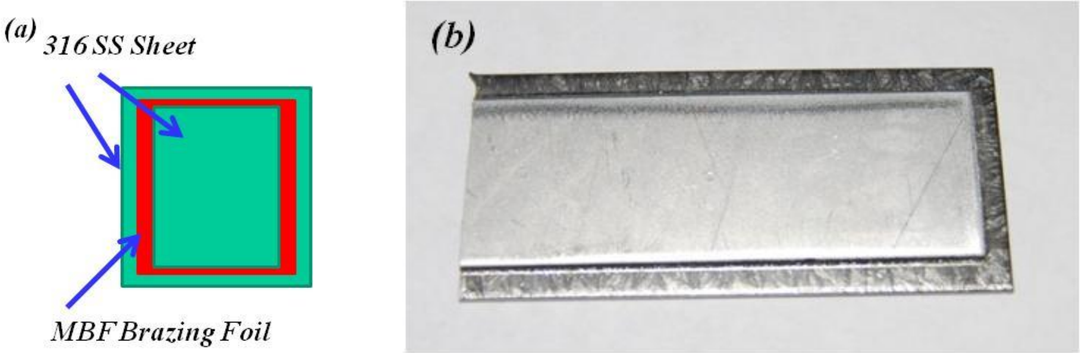

Fig. 2 (a) Schematic of the braze sample. (b) Brazement after the joining showing the sample after a piece has been sectioned for analysis

Table 3 Dwell temperatures and brazing temperature for each of the MBF alloys.

Alloy	Dwell Temperature 1	Dwell Temperature 2	Brazing Temperature
MBF 51	260 ℃	1075 ℃	1175 ℃
MBF 62	260 ℃	920 ℃	1020 ℃
MBF 67	260 ℃	900 ℃	1000 ℃
MBF 601	260 ℃	960 ℃	1060 ℃

Three brazements of each alloy were corrosion tested following Method B of JASO (Japan Automotive Standards Organization) M611-92E Standard for internal corrosion test method for automotive muffler and three brazements were left unexposed as control specimens. The Method B is a cyclic test and one cycle consists of 5 and 24 hour immersions in an oven at 80 ℃ followed by a cool down to room temperature and reagent change. After these five immersions, a 6th immersion was completed in an oven at 250 ℃ for 24 hours. The total cycles completed were four which equate to exposure at 80 ℃ for 480 hours and 250 ℃ for 96 hours. Once the required cycles were completed the brazements were removed and photographed. Loose deposits were removed according to the JASO M611, Section 7.2.2, using a solution of 60% nitric acid at 80 ℃ for 2 hours, rinsed with d-ionized water and dried. The samples then were weighed on the same analytical balance and overall measurements of length, width and thickness were repeated. Fig. 3a shows the front face of a brazed specimen before the test and Fig. 3b shows the specimen surface after exposure to solution reagent and after the surface being cleaned. Table 4 shows the mass loss of each sample during the test and all of the samples passed the JASO M611 standard.

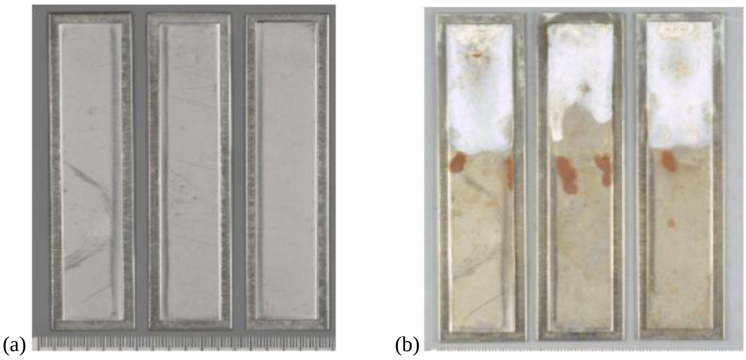

Fig. 3 (a) Braze sample before the corrosion test and (b) the same samples after the test was completed.

Table 4 Percent mass loss and change in thickness of each brazement after the corrosion test.

Alloy	Percent Mass Loss (Average)	Change in Thickness (mm)
MBF51	0.02	Less than -0.01
MBF62	0.016	Less than -0.01
MBF67	0.02	Less than -0.01
MBF601	0.03	Less than -0.01

3. Results and discussion

This study focuses on the characteristics of the new Ni-Cr-P-Si based amorphous foils. However, MBF51 was included in this analysis to contrast the effects of the Ni-Cr-B-Si based foils in the final brazement with that of the Ni-Cr-P-Si foils in the final brazement. A comprehensive study of the brazements of all of the Ni-Cr-B-Si based Metglas brazing foils can be found elsewhere [4].

Immediately following the initial vacuum braze cycle, the brazement samples were sectioned and then progressively polished to a 1 micron diamond solution using standard metallographic techniques. The samples where then analyzed on an SEM. Fig. 4a shows the braze joint for the MBF51 sample. The dashed white line is added for clarity to distinguish the initial base metal from the braze layer. Here the B diffuses into the base metal leaving a solid solution of Ni and Cr in the braze joint. Fig. 4b shows the braze joint for the MBF62 sample. Again, the dashed white line is added for clarity to distinguish the initial base metal from the braze layer. Here small amounts of B diffuses into the base metal along the grain boundaries leaving a solid solution of Ni and Cr in the braze joint, and the remaining B stays in the joint area forming chromium borides. The SEM samples of MBF67 and MBF601 showed similar features.

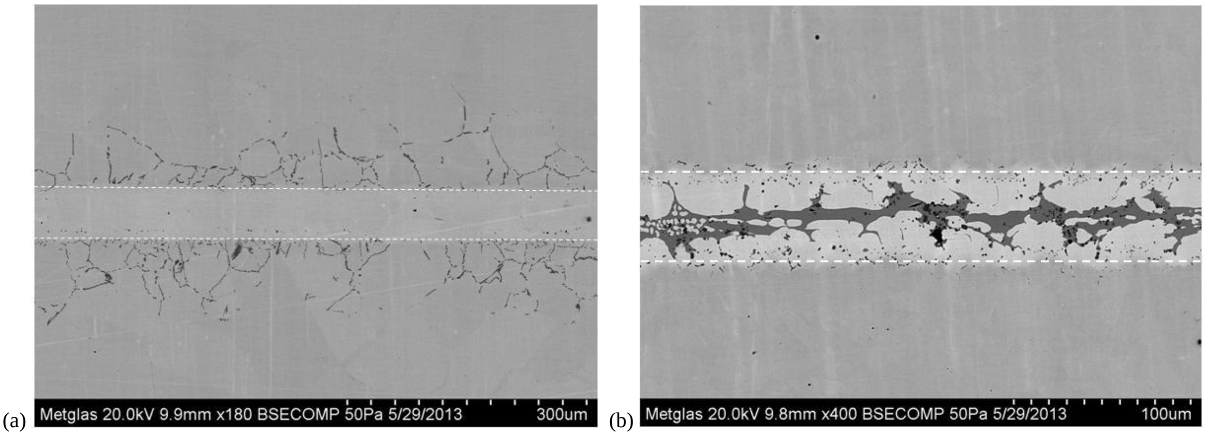

Fig. 4 (a) SEM image of braze joint after braze cycle for MBF51. (b) Similar SEM image for MBF 62 braze joint after braze cycle.

The results of the JASO M611 corrosion test indicate that all of the samples would meet this specification for mass loss. This particular corrosion method was selected to meet the demands of some Asian automotive manufactures. Other studies have looked into test procedures focused for European automotive manufactures [2, 5]. Similar trails are currently ongoing for the new Ni-Cr-P-Si based Metglas braze foils.

After the corrosion test was completed the brazement samples were sectioned and polished to examine the fillet surface of the exposed interface. Fig. 5 shows the SEM images of the sample where very little corrosion is observed along the fillet surface. Similar to Fig. 4, there appears to be very little diffusion into the base metals and the eutectic phases are contained within the braze layer. An x-ray elemental analysis is shown in Figure 6 and indicates the relative concentrations of Fe, Ni, Cr and P.

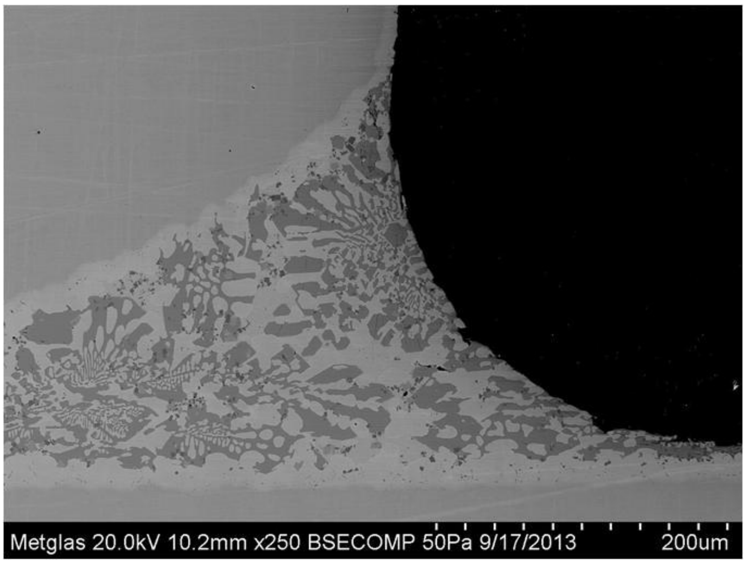

Fig. 5 SEM image of the fillet edge after the corrosion test for the MBF67 braze joint

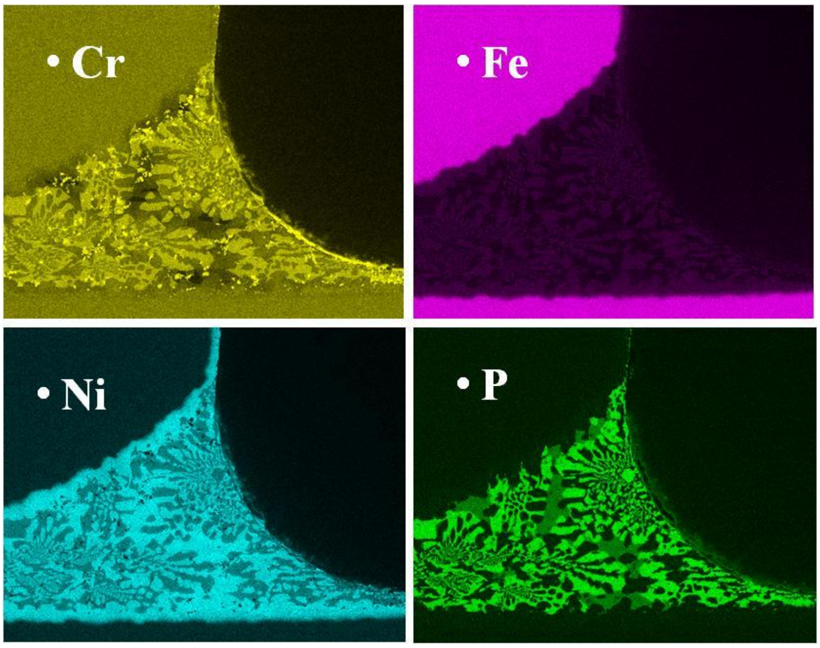

Fig. 6 Elemental analysis of the braze layer and fillet edge after the corrosion test for the MBF67 braze joint

4. Conclusions

Metglas has developed a new series of Ni-Cr-P-Si and Ni-Fe-Cr-P-Si based foils that can be cast with good ductility. They all offer high corrosion resistance and low melting points. The B to Cr ratio for these alloys is on the order of 0.1 which enhances corrosion resistance. There are significant differences in the braze joint characteristics when comparing the Ni-Cr-B-Si based brazements to that of the Ni-Cr-P-Si based brazements. The P containing foils contain small amounts of B, which reduces B diffusing into the grain boundaries of the base metals. This prevents the corrosion of the base metal. There also tends to be more eutectic phases contained within the braze layer for the P containing foils whereas the B containing alloys tend to show a solid solution of Ni and Cr in the braze layer.

References

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