New Brazing Development In The Automotive Industry

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Abstract

This paper is a short review of a recent progress in development and applications - particularly in the automotive industry - of amorphous alloys used as advantageous brazing filler metals (BFM). First, a short compendium will be made of newly developed brazed parts of the modern diesel engine. These parts clean exhaust gases and improve engine efficiency. Then, specifics of these amorphous alloys will be provided. The major emphasis will be given to very recent and successful applications of amorphous BFM in joining of stainless steels and high temperature/high corrosion resistant alloys used as parts component materials. Most of these automotive applications are related to joining of thin-walled 3dimensional, 3D multi-channeled structures located within parts' bodies. Here the issues of base metal erosion during brazing operations are of major concern. Microstructure and properties of various base metal joints are described underlying their uniqueness due to a small amount of BFM containing in preplaced preforms made of amorphous foil. Brazement locations in automotive parts and specific grades of amorphous brazing filler metals which are predominantly used in each case will also be described.

Introduction

The growing and urgent efforts to improve efficiency of practically all machinery producing and consuming energy in the World has resulted in explosive manufacturing expansion in many areas associated with energy conservation. A specific area where brazing flourishes is in the production of 3-dimensional (3D) thin-walled honeycomb-like structures. These remarkable, light-weighted, temperature and corrosion resistant structures require a precise placement of thin preforms thus avoiding potential part erosion by molten brazing filler metals (BFM). The list of applications with brazed energy-efficient 3D structures includes - or is in a planning stage to be included - such products as heat exchangers, boilers, co-generators, heat recovery units, intercoolers, condensers in dryers, stationary jet turbines, and many others.

The same intensity efforts are now applied to pollution elimination efforts and efficiency increase for cars, motorbikes and working vehicles in construction, mining, etc. Figure 1 is a schematic that shows the very last and widely used auxiliary parts of a modern diesel engine. These parts or units such as Metal Catalyst Substrates (MCS), Exhaust Gas Recirculator Coolers (EGRC), and Diesel Particulate Filters (DPF) decrease the environmental impact of diesel and gas engines; regulate the fuel/air gas mixture temperature and thus, increase their total efficiency. Figure 1 has also small real pictures of these remarkable parts.



Figure 1 Schematic of a modern diesel engine equipped with brazed parts that clean exhaust gas and increase engine efficiency.

To understand better specifics of the manufacturing, described below it is worth to give a short description of their generic functionalities and typical designs.

MCS units (Figure 2 and 3) have been in use for many years as a part of Catalytic Supports and their role is to convert harmful, poisonous exhaust gas components such as CO and NO into $CO_{2 and}$ NO₂. The vast majority of them, particularly in the USA is made from ceramics and can be called CCS (Ceramic Catalytic Substrate). An example of CCS is shown in Figure 3b. In the case of both CCS and MCS, there is a plurality of many channels positioned along the exhaust pipe. These channels have rectangular or sinusoidal crosssections and are covered by Pt/Pd catalyst film. The catalysts initiate reactions of oxygen with CO and NO thus yielding the exhaust gas with completely oxidized CO₂ and NO₂. CCS and the catalysts attached to them take nearly one full minute after start-up before being heated enough to effectively burn harmful gas emissions. Metallic substrates are made of flat and corrugated thin ribbons. They are wrapped together with BFM foil strips preplaced between them and inserted in a metallic cans to keep them in strongly bonded state upon brazing. Sometimes BFM powders are used in stead of foil.



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completely along with freshly supplied fuel and air oxygen. The EGR Coolers with compact design are in essence a plurality of alternating channels made of thin stainless steel strips cold-pressed into cores with complicated forms or thinwalled tubes. In both of these designs, parts are brazed together and to the EGRC bodies using either preplaced BFM foils or powders. Cooling of the in-coming exhaust gas in EGRC by the circulating water (Fig. 3) results improves engine efficiency.





Figure 2 (a) Broken view of a modern brazed metal catalyse support; (b) Compare MCS and Ceramic Support cross-sections.

The brazed MCS (Fig. 2a, blown up insert) heat up much more quickly and efficiently and, therefore, burn these emissions almost immediately upon engine start-up. **MCS** also have a smaller cross-section than CCS which provides improved flow rate (less engine back-pressure). Their higher cell density/lower wall thickness allow for overall reduced substrate size. No wonder that all race cars are equipped with **MCS**.

The main role of **EGRC** (Fig. 3) units is to cool part of the exhaust gas which is returned back to diesel cylinders. The returning gas contains partially unburned fuel, contaminant impurities, and oxygen. These gas contaminants are burned

Coolant goes thru the channels at each layer and runs in the opposite direction of the air flow



Figure 3 Plate/Fin EGR Cooler Anatomy :

Each channel must be brazed in order to assure bonding of fins to the layer (maximizing effectiveness of heat transfer) & engine coolant channels must be fully joined to avoid leakage – therefore continuous brazing must happen along each channel at each layer.

DPF units (see Figure 1) entrap and burn graphite particles which form as a result of incomplete diesel fuel burning. There are different DPF designs based on the mesh filtering principle. Practically all of them have metallic parts; joining of which is frequently made via brazing. The most advanced design is a DPF in which the filter body is made from metallic foam cloth. The cells of these foams have wall thickness about 5-10 μ m. Evidently, if brazing is used for joining parts together, then low eroding filler metals is required for these parts.

Summarizing the specific issues for brazing these diesel units one should emphasize that all of them are made of 300-series stainless steels or high chromium containing, iron-based alloys such as Fecrallov as the base metals (BM). Of particular importance is the fact that all these BM have very thin, 50 to maximum 200 µm, cross-sections. Therefore, BFM to be used should guarantee a long service time with high joint oxidation and corrosion resistance combined with very low part erosion during manufacturing processing. The latter requires using very thin and uniformly applied BFM. The need for thin BFM is now well satisfied by using amorphous brazing filler metal foil which is mostly known as Metglas® Brazing Foil (MBF). Their MBF acronym has become a generic term similar to Inconel, etc. MBF is produced with the thickness in the range 20-75 µm. It is now used as a filler metal of choice in manufacturing of the majority of the above mentioned units.

It is worth herewith to provide more details as to why MBF amorphous brazing foil dominates brazing of 3D structures particularly in automotive industry. Concrete industrial examples will be also provided elucidating the advantage of the foil vs. powder forms of filler metals.

2 MBF AMORPHOUS BRAZING FOIL AS A FILLER METAL OF CHOICE IN AUTOMOTIVE BRAZING [1]

Rapid solidification (RS) technology essential in the manufacturing of flexible amorphous brazing foil as a new class of filler metals has found numerous applications during more than two decades. The most important advantages of RS amorphous and microcrystalline BFM alloys vs. BFM powder forms are their flexibility and ductility even for compositions that are exceedingly brittle when produced by conventional metallurgical methods. Because a ductile amorphous alloy brazing foil such as MBF may be used as a preplaced preform, there is no need for large brazement gaps, as those used with power pastes, to achieve a complete filling of the braze cross section. More, MBF, for example, has a particular advantage over powder, and polymer-bonded tape forms because of its superior flow characteristics. Indeed, gas-atomized powder has a very large total surface area with subsequently large amounts of surface oxides. These oxides prevent, to a certain degree, fusion of individual powder particles into a uniform liquid pool. The MBF flows more freely upon melting than any powder form [2]. A smaller clearance also promotes improved retention of BM properties because of curtailed BM erosion by the use of a smaller volume of FM in the MBF form. From an economical point of view, only about one third of the filler metal weight is needed per joint square area when using MBF as a filler metal vs. that of a sprayed or pasted powder. For all these reasons, a preplaced self-fluxing thin MBF preform is superior to the powder-containing paste.

2.1 MBF compositions

MBF alloys have mostly Ni/Cr-based compositions with boron and silicon as melting point depressors and eutectic forming

components. That makes them not only compatible with stainless steel BM but also provides superior joint corrosion and oxidation resistance needed in automotive applications. In general, fractions of boron and silicon are present to convert the alloys in the amorphous state upon rapid solidification and to decrease their melting temperatures. So far, no iron-based MBF is widely used in foil form because of poor amorphability and castability of high iron/chromium alloys.

Silicon alone cannot provide even a limited amorphability to Ni-based alloys. An addition of a minimum of 1.4 wt. % of boron is needed to produce amorphous foil. It also plays a very beneficial role in the improvement of filler metal wetting and flow.

The selection of boron and silicon concentrations during brazing filler metal development was performed primarily to achieve some balance between the melting temperatures and wettability and the adverse effect that boron may have upon joint mechanical properties.

Chromium and some refractory elements such as molybdenum and tungsten, when added as replacements of nickel, increase MBF alloy melting temperatures. They also improve joint corrosion and oxidation resistance. For example, an addition of only 5 wt. % molybdenum substantially decreases the pitting corrosion [3, 4]. Chromium, at levels above about 14-16 wt. % decreases the amorphability of these alloys noticeably to a degree that Ni-19.0Cr-7.3Si-1.5B (wt. %) MBF-50 alloy with 19 wt. % Cr can be cast in a ductile amorphous foil form to a maximum thickness of only 37 µm. Still, the maximum thickness and foil widths that can be achieved with high Cr-containing alloys don't present any barrier for wide use in the industry because their dimensions are sufficient for most automotive applications.

The choice of the brazing temperature is strongly associated with the amount of chromium in MBF. The minimum brazing temperature of about 1050°C can be employed when using Ni-7.0Cr-3.0Fe-4.5Si-3.2B MBF-20 alloy. Unfortunately, MBF-20 contains a rather low Cr percentage of only 7 wt. %. Recently, a couple of new compositions containing 10 wt. % Cr were introduced for industrial trials. These alloys conditionally designated as MBF-24 and MBF-25 have melting temperature below 1100°C. All alloys with 15 and higher Cr concentration, for example Ni-15Cr-1.4B-7.25Si MBF-51 and others have to be brazed at about 1150 °C or even higher temperatures. On the other hand, these brazing temperatures are not critical in automotive applications: base metals for these applications operate at high temperatures. Therefore, their structure and mechanical properties are not adversely affected by brazing operations as many industrial examples have proven.

2.2 Performance of joints made of MBF alloys

The general description of joint performance of various classes of stainless steels and superalloys base metals is given in a comprehensive review of Ni/Co-based MBF alloys [1]. Specific details of the optimization of the brazing process and

joint properties can be found for such combinations of BM/BFM as: 316L/MBF-51/316L [5], 430/MBF-20/430 [1, 3], 436/MBF-20/436 [1,3], 304L/MBF-51/304L[6], Fecralloy/MBF-50/Fecralloy [6], PM2000/MBF-50, -51/PM2000 [3], and X30 and X40/MBF-51 and -53 [7].

MBF joint mechanical properties are rather high, and in some cases may approach that of the virgin base metals. For example, mechanical properties of 316L/MBF-51/316L joints after optimal heat treating are given in [5].

It is obvious that joint strength close to that of the virgin base metals can be achieved via a proper selection of MBF grade, foil thickness, and the heat treating cycle parameters.

2.3 Corrosion and oxidation resistance of MBF joints

Joints manufactured from MBF alloys have good-to-excellent corrosion and oxidation resistance. The major positive factor is the presence of Ni as the alloy compositional base. The resistance is improved even more with increased Cr and particularly Mo and W concentration(s). The data on corrosion resistance of widely used 316 stainless steel joints produced with MBF-51 in sea water and standard water solutions of NH₄OH, H₃PO₄ and HCl are given in [5, Table 5]. Good corrosion resistance in sea water and the ammonia water solution is very beneficial for heat exchangers that use sea water as coolant, and for refrigeration equipment. Results of corrosion testing in a simulated diesel exhaust gas environment for 316 and 321 stainless steel joints manufactured with MBF-51 and MBF-53 can be found in Table 4 [3].

The similar favorable effect of molybdenum additions was achieved when brazed exhaust gas coolers were corrosion tested under real conditions. In addition, the erosion of stainless steel tubes by the alloy containing molybdenum is very limited [8].

2.4 Microstructure of some MBF joints

MBF joint structure-properties relationships have been under constant attention in series of work reviewed in [1]. An augmenting work was completed recently revealing the structure of practically important joints manufactured of 304LN and Fecralloy materials as BM and (Ni-15Cr-7.3Si-1.4B) MBF-51 and (Ni-19Cr-7.3Si-1.5B) MBF-50 as FM, correspondingly [6]. The first combination is applied in heat exchanger manufacturing whereas the second one has been used in MCS for automotive exhaust systems. Both types of joints were manufactured using brazing cycles with a short, 10-15 min, exposure to 1175°C in vacuum.

Microstructure of MBF joints was studied in some base metal cases encompassing austenitic steels 316 [5] and 304 [3], ferritic steel 430 [3] and superalloys [1, 7].

These brazed components are made mostly of 300- and 400series stainless steels or Fecralloy. The most important factors affecting joint specifics are the amount of the filler metal per

the joint cross-section and the temperature and time of the brazing cycle. These factors determine the completion of the liquid FM and solid BM interaction; the shorter this interaction, the more chances for formation of the joint eutectic central line due to presence of boron and silicon still retained in the joint. The line consists of brittle intermetallic borides and silicides crystallized but segregated from each other within the ductile matrix phase. The joints which have a continuous eutectic microstructure across the complete joint cross-section are brittle and weak. MBF foil has an advantage vs. powders with similar compositions because a smaller amount of the filler metal per cross-section unit is needed to form a joint. The smaller boron amount per cm^2 yields a larger degree of joint depletion from boron and thus a lesser amount of chromium borides in the joints. At the same time, the difference in the steel crystal structure, particularly its density, determines the mechanism and degree of boron diffusion in the base metal. It also affects how it segregates in the base metal, i.e., trans- or inter-granularly. Because austenitic steel have dense γ -phase crystal structure, the chromium boride segregation happens at the grain boundaries. Therefore, its effect on the base metal strength occurs due to potential base metal grain boundary embrittleness. Still, in many cases the selective grain boundary segregation can be negated via the post-brazing heat treating. In ferritic steels the boride phases may segregate within the grains as well and, therefore, the potential negative effect of the chromium boride segregation is less pronounced.

Thus, the choice of the foil thickness to be used, optimization of the joint dimensions, and heat treating conditions should be specific for each type of the base metal. Figure 4 shows three examples of microstructure of strong joints which processing was carefully optimized.





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Fig /?? Microstructure of three types of stainless steel joints brazed with MBF-51 and MBF-50 amorphous brazing foils: Fecralloy/MBF-50; b, c)316L/MBF-51.

Obviously, all of them have vastly different phase composition and morphology. The first, Fecralloy/MBF-50, joint (Figure 7 a, uppermost micrograph) has multiphase structure in which a noticeable strengthening of the Fecralloy base metal occurs.

This

strengthening is due to a newly discovered metallurgical reaction between b.c.c. Fe-20Cr-5Al BM and nickel and boron which diffuse from Ni-19Cr-1.5B-7.25Si MBF-50 [6]. This reaction results in precipitation of fine, regularly distributed $Ni_x(Al)_y$ particles in the BM matrix phase (see cut off d in Fig. ????).

The mechanism of strengthening is similar to that in superalloys in which γ' phase precipitates. The chromium borides (black particles in Figure ??a, b, c) are segregated within the ductile braze matrix without forming a continuous eutectic line. Therefore, the brazements have both high ductility and considerable total strength.



The second example is a thick 304L/MBF/51 joint (Fig. 4, middle micrograph). Here, the eutectic boride and silicide phases are present but without extensive detrimental effects because they are encapsulated in a ductile matrix phase as in the previous case [6].

The third case is 316L/MBF-51 joints (Fig. 4, lowest micrograph) with a single-phased strong and ductile structure similar to that of the virgin 316L steel obtained via long post-brazing annealing [5]. Here chromium borides have practically disappeared entirely and the brazement mechnical properties have not been detrimentally affected. The strength of the joint is equal to the yield strength of the 316L base metal.

These, and similar, microstructures guarantee rather long and reliable service time for components described herewith.

3. TYPICAL BRAZEMENT LOCATIONS OF DIESEL AUXILARY PARTS AND THEIR SERVICE LIFE TIME

In some MCS, the Fecralloy joints are made using two very narrow, 5 mm wide, 25 μ m thick MBF-50 strips which are preplaced in symmetrical positions on opposite sites of MCS core. They easily withstand up to a 3 t load before failure after long term exposure to exhaust gases at 650°C. Fig. ??? shows a standard MCS tested after such conditions.



Figure ??? MCS after push-out testing in the shear mode at 650°C: Force to Failure is >3 tons

As one can see the failure occurred in the base metal, not in the joint area. The MCS joints made of Fecralloy as BM and brazed with MBF-50 have been in use for at least 3 decades in a small number of applications. Today much larger MCS production has widely expanded MBF application. According to previous experience one may firmly expect 10 years of service without replacement or failure in cars and heavy tracks.

300-series stainless steel joints are mostly used in EGRC which usually have rather low service load. The most critical factor in determining their longevity is corrosion and fatigue resistance. So far, many EGRC units have been made using Ni-13Cr-4.2Fe-4.5Si-2.8B MBF-15 and Ni-15Cr-5Mo-7.25Si-1.4B MBF-53 which contain about 15 wt. % Cr. Their joints are located in specific areas shown in Fig. 1. This BM/BFM combination has been deployed for at least 5 years without replacement or failure according to service statistics.

Europe recently approved DPFs which are built up from metallic foams. They are produced from Inconel with MBF-50 applied for component joining. The accelerated tests made at high temperatures promise a rather long service time with graphite particulate elimination close to 60%. Some newly designed DPF also provide 98 % CO and 95% of hydrocarbon elimination in addition to particulate filtering.

Conclusions

Today amorphous brazing foil is an important and wellestablished brand of filler metals due to advances in the rapid solidification technology and development of new commercial products and applications. Amorphous brazing foils are produced in multi-tonnage quantities which can be cut, stamped, or shaped into millions of precise preforms ranging in weight from a few dozen milligrams to a few hundred grams.

Current efforts are directed toward development of new applications finely attuned to the specific needs of each individual brazed product. In this respect, automotive applications have proven to be the area of particular growth with an even more promising rate in the near future. The amorphous brazing foil manufacturing efficiency and ease of automation help to demonstrate their economical competitiveness vs. gas-atomized powders. There are no doubts that amorphous brazing foil will dominate the high temperature brazing area very soon, if not already.

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