Overview: Brazing With (NiCoCr)-B-Si Amorphous Brazing Filler Metals: Alloys, Processing, Joint Structure, Properties, Applications*

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CONTENT

ABSTRACT

This paper is a detailed and updated review of METGLAS® amorphous brazing foil (MBF) properties and specifics as well as the advantageous experience in its multifaceted applications accumulated in the last two decades. The major emphasis is to provide a practical guidance for their intelligent usage that will contain, in the first part, description of these materials in the virgin as-cast state. This state has a unique combination of physical properties. The metallurgical background will also be given in this part to the existing range of available chemical compositions and their potential compatibility with various base metals. The amorphous alloy mechanical properties and thermal stability, wettability over various metals and its dependence on the brazing atmosphere and preform preparation will be described as well. The second part presents properties of MBF joints manufactured from various classes of base metals and obtained under optimized brazing conditions for each concrete class of the base metals. Particular attention is given to the joint microstructure/properties relationships yielding brazements with high strength, ductility and corrosion and fatigue resistance. Finally, MBF versatile technical and manufacturing features are underlined. These MBF advantageous features are the driving forces behind rapid expansion of their applications in various important modern industries. Concrete examples of these applications are also given.

1. INTRODUCTION

One of the first practical applications of rapidly solidified (RS) technology was in the production of ductile amorphous brazing foil from alloys with compositions that could previously only be utilized in powder form or as powder-filled pastes. [1-4] Indeed, most of the filler metal (FM) alloys used in high-temperature brazing are eutectic compositions formed by transition metals (TM) such as nickel, iron, chromium, etc., in combination with metalloids, such as silicon, boron, and phosphorus. In the conventional crystalline state all these materials are inherently brittle and cannot be produced in continuous forms such as foil, wire, etc. Therefore, they were available only as powders or their derivatives.

On the other hand, the very presence of metalloids at or near the eutectic concentration promotes RS conversion of such alloys into a ductile amorphous foil. Starting from Sexton and DeCristofaro's[1] discovery of RS potential in manufacturing of flexible amorphous brazing foil, this new class of filler metals has found numerous applications during the last two decades. These amorphous filler metals are known as METGLAS® Brazing Foil (MBF) alloys.

The most important advantage of RS amorphous and microcrystalline FM alloys is their flexibility and ductility. 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 pastes, to achieve a complete filling of the braze cross section. MBF, for example, has a particular advantage over powder, and polymer-bonded strip 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.[5] A smaller clearance also promotes improved retention of base metal (BM) properties because of curtailed BM erosion by the use of a smaller volume of FM in the MBF form. For these reasons, a preplaced self-fluxing thin MBF used as preform is superior to the powder-containing paste. The paste requires larger clearances for filling joint cross sections and results in deleterious effects on properties owing to a coarser joint grain size, more fully developed intermetallic compounds and the presence of substantial amounts of contaminants.

Most METGLAS® alloys being produced via RS technology have an amorphous structure, with a random, spatially uniform arrangement of the constituent atoms. Because RS amorphous materials are compositionally much more uniform even after crystallization, their melting occurs over a narrower temperature range under transient heating that exists in practice. This is a consequence of the shorter distances over which atoms of different elements have to diffuse in order to form a uniform liquid phase. The resulting "instant melting" of RS materials is one of their important features. This property can facilitate a short brazing time when needed. This is particularly important when brazing fine-gauge honeycomb cores that have to be protected from erosion by molten filler metals during joining. The absence of contaminating organic solvent bases that powder pastes/tapes contain eliminates soot formation and furnace fouling. The low level of gaseous impurities in MBF that is due to the specific characteristics of its production technology, is an attractive feature for vacuum furnace brazing. MBF brazing temperatures cover a wide range from 830ºC (1526ºF) to 1200ºC (2192ºF). They are well compatible with materials of various nature and, therefore, have been very successfully used in joining of many classes of base metals such as stainless steels, superalloys, hard cemented carbides, low carbon steels, etc. Today, because of these unique properties, MBF occupy an important and growing role as the most advanced filler metals used in applications related to aerospace industry, precise machinery and tools, modem medical equipment, etc.

Since the publication of the first review of these materials[3] extensive new experience was accumulated in the development and production of new alloy compositions and a better understanding of metallurgical nature of specific joining processes involving these alloys was attained. Industrial manufacturing involving MBF alloys has also advanced resulting in today's production of multi million-dollar product lines. It is therefore worthwhile to summarize the current status of brazing using (NiCo)-based MBF alloys, specifically compositions produced and applied in large volumes. The (NiPd)-based MBF-l000-series alloys[6, 7] and (TiZr)-based MBF-5000-series alloys[8-10] have some unique but small applications are left out of this overview. Most results presented in this paper including those that are previously unpublished were obtained in collaboration that included this paper's author, however some data obtained by other groups that used alloy samples and products produced and given for testing by Honeywell Int., METGLAS® Solutions will be given as well. First, the compositions and description of basic properties of (NiCo)-based alloys will be provided together with the metallurgical background behind their selections. The list of currently available products and their dimensions will be given followed by the general outlines for choosing optimal brazing procedures. Next, joint structures and properties will be given in relationship with individual classes of base metals such as ferritic and austenitic stainless steels, heat resistant alloys, and superalloys. Finally, the alloy applications and case histories will also be presented in a short and generic way. Such a format may aid potential users with identification of related application cases and selection of certain alloys for specific cases.

2. METGLAS® BRAZING FOIL (MBF)

2.1 MBF Compositions

Over the years of alloy development, the composition selection has been made mostly in the vicinity of ternary and pseudo ternary eutectic concentrations given in the paternal Ni-B-Si and Co-B-Si alloy phase diagrams shown in Figs. 1a and 1b in at.%.[11] The proximity to the eutectic compositions yields a double benefit: first, good alloy brazability because of an associated narrow alloy melting range and, second, the ability to form the amorphous state upon rapid solidification (RS). Table 1 presents compositions and some properties of MBF alloys developed so far. Among those only two industrial alloys, MBF-30 and -35, are ternary. The MBF-35 composition is located precisely in $Ni_{.77}$ $B_{.10}$ $Si_{.13}$, ternary eutectic point and the MBF-30 ($Ni_{.77}B_{.15}Si_{.79}$) composition is located on a pseudobinary eutectic line as can be seen in Fig la. So far, no complete quaternary diagram, even such as the all-important Ni-Cr-B-Si composition, has been constructed. Thus one does not have an option to properly select an optimal alloy composition with the lowest melting temperature. To avoid this data deficiency, all other alloys that have four or more elemental components may be regarded as pseudo ternary (Ni/TM)-B-Si and (Co/TM)-B-Si compositions. Here, the TM fractions of such elements as chromium, molybdenum, etc, added for performance improvement, are considered as parts of the single (Ni/Co+TM) fraction. In such a form their compositions can now be considered in relationship with ternary phase diagram specifics. The appearance of alloy melting troughs and crystallization peaks determined using differential thermal analysis (DTA) shows how close a tested alloy composition is to the multi component eutectic. If an alloy has a single DTA trough/peak that appears in a narrow range, then its composition is rather close to a eutectic one, and vise versa. Fig. 2 shows a few examples of MBF alloy melting characteristics obtained by DTA. Table 1 contains data on the alloy melting range spans.

2.2 Effect of Alloying

Because nickel and/or cobalt alloy bases provide higher joint corrosion and oxidation resistance than iron, no iron-based MBF is used in practice. In the early RS implementation the pioneers of MBF development decided to produce alloys in foil form with compositions that are similar to those of the standard powder AWS BNi-classifications.[12] It instantly "closed a void" that existed at that time in the available forms of FM. In general, the fractions of boron and silicon added to convert either cobalt- and/or nickel-based alloys in the amorphous state are similar. So far, cobalt-based alloys without or with a small amount of nickel were not used on a large scale in spite of their better corrosion resistance. The sole reason for that is the significantly higher cost of these alloys relative to their Ni-based counterparts. However, recent work has shown that their superior performance would definitely expand their application scope (see below).

Silicon alone cannot provide even limited amorphability to Ni- and/or Co- based alloys. An addition of a minimum of 1.4 wt.% of boron is needed to produce amorphous foil. This is an important deficiency of the MBF-series because boron, although it plays a very beneficial role in the improvement of filler metal wetting and flow, is poorly tolerated in some application cases. In general both boron and silicon are similar in their power to decrease liquidus upon addition: in binary systems the effect is about 23°C/at.% for Ni-Si and about 22.3°C/at.% for Ni-B alloys. Therefore, the selection of boron and silicon concentrations during brazing filler metal development is performed primarily to achieve some balance between its melting temperatures and wettability and an adverse effect that boron may cause on joint mechanical properties. Chromium and other refractory elements such as molybdenum and tungsten when added as a replacement of nickel and cobalt 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.[13, 14] Chromium when present at about 10-12 wt.% in Ni-based compositions does not change substantially alloy castability. However, at levels above about 14-16 wt.% the amorphability of these alloys decreases noticeably to a degree that MBF-50 alloy with 19 wt.% Cr can be cast in a ductile amorphous foil form to a thickness no thicker than 37 μm. Other refractory metals similarly affect the alloy amorphability.

In cobalt-based MBF-l00-series alloys chromium can be added up to 21 wt. % without decreasing amorphability while providing superior joint oxidation resistance and strength.[13, 15] Palladium, when added in up to 5 wt.% also substantially increases joint oxidation resistance by causing the formation of a protective layer made of high temperature intermetallic aluminum-palladium phase at the interface between the braze and the base metal. However, these joints have rather low strength.[13, 16]

2.3 Thermal Stability of MBF Amorphous State

It is well known that amorphous metallic alloys have a limited temperature range in which the amorphous state may be preserved without crystallization. MBF is not excluded from this rule: it is stable to about 400°C when heated at a moderate rate. Above this temperature the crystallization process initiates and completes at about 600°C at moderate heating rates. These temperature parameters do not vary significantly with changes of MBF compositions. Our experiment also showed that MBF foils could be kept for 30-40 min at about 250-300°C without traces of crystallization. This affords an opportunity to subject MBF foils to a rather strong plastic deformation in the 200-250°C range. Amorphous alloy ductility is substantially higher in this temperature range than at 25°C. The crystallization, if it occurs during the heating stage of the brazing cycle, normally yields a microstructure with phases that have very small dimension.

Such microstructure melts very rapidly and provides an advantageous melting pattern under transient heating conditions. In a crystallized state MBF are very brittle. Therefore, parts assembled with MBF preforms can be heated above 400°C but below brazing temperature only once without the danger of preform embrittlement and potential distorting positions of parts to be brazed.

2.4 Mechanical Properties of the As-cast MBF Ribbons

2.4.1 Strength and Ductility

All amorphous alloys including MBF have a unique combination of mechanical properties caused by the specific nature of their amorphous structure. Fig. 3 depicts a typical load-elongation graph of an MBF-51 46-μm thick foil specimen determined using an Instron testing machine in the tensile testing mode at a 2.5 mm/min loading rate. Table 2 shows average mechanical properties of this alloy.[17] As is evident from Fig. 3, the foil displays a typical brittle material behavior. On the other hand, the same foil specimen can be bent onto itself 180° several times without failure demonstrating a high degree of ductility in a small (about 50-μm) deformation zone. Variations in MBF ribbon composition produce moderate changes in its mechanical properties. The mechanical properties of MBF-51 ribbons presented in Table 3 can be considered as an example of what may be expected of other alloys as well. The explanation of such unusual duality in mechanical properties is given eloquently by L. Davis and V. Ramanan[18]: “Due to the absence of work hardening, metallic glasses behave as elastic-perfectly plastic materials. As such, in tensile tests, failure occurs coincident with yielding and the macroscopic ductility is equivalent to the elastic strain to failure. In the engineering sense, this is classified as “brittle” behavior. However, when such plastic instability is avoided, as in bending, rolling or compression, macroscopic deformation can be achieved with astonishing ductility”. In other words, large MBF ribbon samples have a very high elastic limit and very low ductility when they are subjected to tensile mode testing. On the other hand, such ribbon can be readily bent on itself 180°. It can be stamped and cut in different configurations that have very clean edges and without shuttering.

2.4.2 Microhardness

MBF ribbon are very hard, their microhardness is in the range of 800 kg/mm^2 and higher on the Vickers (diamond pyramid) VHN scale. For example, the microhardness of 50 and 70-80 μm thick MBF-30 ribbons is 900 (+/-30) and 950 (+/- 40) kg/mm^2, respectively, whereas that of MBF-50 37 μm-thick is 810 (+/-12) kg/mm^2. The microhardness level of MBF is similar to or even higher than that of the quenched martensitic high carbon steels. Because MBF ribbon thickness is about 25-100 μm, special precautions were taken during measurements: namely, MBF ribbons under testing were placed on a hard plate and stretched. Its backside was fully mechanically supported whereas the indentation load was set as low as about 15-20 g, to avoid excessively deep penetration.

2.5 Alloy Wettability and the Effect of the Brazing Atmosphere

As was described above, amorphous foils have much higher flow and wettability than powder forms of BNi-classification.[5] When brazed under vacuum conditions they wet a majority of steels and alloys with very low contact angles (10-15° and lower). A recent author's paper[19] gives a few examples of superior gap filling and explains its cause. For example, in the case of gaps in which the foil is only partially preplaced, the lateral advancement of MBF liquid into the empty gap space can be by as much as 8-10 mm. Therefore, parts with large cross-sections may be brazed in a vacuum or inert gas environment using relatively narrow multiple preforms made of MBF ribbons that are placed side-by-side and separated by gaps. The joints in such large parts have no leaks and posses a high overall integrity and strength.

Brazing with MBF can also be readily accomplished in furnaces with protected atmospheres where water and oxygen levels are kept below certain rigorous limits. Brazing of ferritic 409 steel under hydrogen, argon, and nitrogen, both pure and in mixture, was studied in[20, 21] using MBF-20 alloy and BNi-2 and -3 powders with similar compositions. It was shown that the contact angle varied from values as small as 6° in the case of pure argon and to higher but still "wetting" values, depending on amount of water vapor (Fig. 4). Most importantly, a pure nitrogen atmosphere (inexpensive relative to a vacuum environment) has been used in industry even with MBF alloys containing a substantial amount of chromium. Fig. 5 demonstrates the superior flow of MBF-20 and -

30 foils relative to BNi-2 and BNi-3 pastes over 409 steel in a furnace filled with 50:50 N_2 :H_2 mixture of industrial purity, i.e. -40°C FP. The integrity and tensile strength of joints made of foils were practically the same regardless of wetting angles but were still better than the integrity and tensile strength of joints made of paste.

A low concentration of oxygen and the presence of boron and silicon in the as-cast MBF ribbon also help to wet superalloy parts that are normally coated by a strong but thin intrinsic layer of complex Al/Ti/Cr oxides. Interestingly, from a thermodynamics point of view, all these oxides cannot be directly reduced, dissociated by boron and silicon contained in the liquid MBF alloys thus exposing clean metallic surfaces for successful wetting because boron and silicon have a comparatively low affinity to oxygen. In fact, such surface cleaning and exposure does occur but it is caused by a different effect. This effect relates to the thickness of the intrinsic superalloy oxide layers that are usually on the order of a few dozen nanometers. On the other hand, the liquid MBF film still has a rather high activity relative to oxygen while its thickness in the gaps is 3-4 orders of magnitude larger than that of oxides. Therefore, liquid MBF alloys can practically dissolve and dissociate thin oxide films when they come in contact with them under a vacuum environment because they have a substantial capacity to accept oxygen before reaching saturation. Fig. 6 shows the schematics of a wetting experiment in which MBF-100 alloy was tested for wettability of a solid piece of alumina and Fe-Cr-Al-based PM2000 alloy that has an intrinsic dense alumina oxide film under identical vacuum brazing conditions. While MBF-100 formed a ball- shaped solidified drop on the pure alumina surface, a PM2000 T-joint sample had excellent joints with very good fillets (Fig. 7). In this respect, one can call MBF a self- fluxing material. Similarly good wetting results were achieved when MBF-100 series alloys were used in joining and repair of vanes and blades made of superalloys.[16, 22] The tested superalloys were (Ni/Cr/Co)-based MSRR 7248 (CMSX-4), MSRR 7150, MSRR 7046, and Inconel 738, all covered a strong intrinsic protective alumina scale. The filet contact angles in all these cases were below 45°.

2.6 Effect of Joint Loading During Brazing with MBF

Moderate loading applied at a normal to the joint surface can strongly improve joint mechanical properties. Filler metal should be preplaced between base metal parts in a position such that upon melting the liquid metal layer will be perpendicular to the load direction. Because MBF preforms are always preplaced and completely cover the brazing gaps, it is particularly convenient and effective to apply joint load in this case. The explanation of this effect was given by A. Rabinkin and S. Pounds after carrying out brazing experiments under load. In these experiments they were using copper as the base metal and Cu-P-based MBF-2000-series alloys as the filler metal. [23] These experiments yielded an impressive 100% increase in strength and a tenfold increase in joint ductility due to formation of joints mostly consisting of the solid solution ductile matrix phase with a small fraction of intermetallics. The proposed "ejection model" explains the positive effects for joints produced using eutectic filler metals in general and MBF specifically. Accordingly, there is substantial rectification of the joints under load from metalloid elements that are constituents of brittle intermetallic eutectic phases. The rectification occurs via direct ejection of a part of the MBF liquid phase enriched in these metalloids and thus decreasing the fraction of the intermetallic phases in the joint microstructure. An interesting and practically beneficial confirmation of this effect and the validity of the "ejection model" was also reported in cases where lnconel 718 joints were brazed with Ni-P-based MBF-60 and Ni-Cr-P-based MBF-65 alloys.[24] Loading to 5-6 MPa resulted in a very dramatic, >100%, increase of joint strength and ductility and 50% decrease in joint microhardness. The same positive loading effect is observed in the case of the joining of plate/plate and plate/fin heat exchangers. These products are, essentially, stacks made of multiple alternating base metal plates (fins) and MBF preforms that may move in an unrestrained fashion in the loading direction during brazing.[13] Here, the total height of the brazed stack is kept constant regardless of the preform thickness yielding products with accurate dimensions (see below). The effective loads applied in these applications were selected from a practical range (a few MPa). The results illustrate the benefit of utilizing joint loading when using other MBF alloys containing boron and silicon.

2.7 Stamping and Etching of MBF Preforms

Not the least among economical and manufacturing factors in application expansion of Ni- and Co-based MBF has been an advancement in production of very intricately shaped and fine-detailed flat and three-dimensional preforms (Fig.8). In spite of their very high microhardness, MBF ribbons can be readily stamped and bent substantially using tools and conditions applied for stamping conventional carbon and stainless steels and Cu- and Ag-based alloys. Fig. 8 (white arrows) shows, for example, fine flat parts and rings made of one of MBF alloys 25-50 μm thick ribbon using conventional tools made of D2 grade tool steel. The steel was heat-treated to 60-62 HRC hardness. The stamping stroke speed of about 3 m/min was normally used. Because MBF ribbons are thin, the free tolerance between “female” and “male” tool parts should be kept close to 5 μm (0.0002"). Also, the natural tool edge radii should be close to or less then, 1 μm and not be “killed” after each sharpening cycle. Under these conditions, the stamped parts do not have any burrs or defects regardless of ribbon thickness in the as-cast and/or annealed, in the moderate, 150-200°C temperature range, states. Normally, die resharpening is required after about 10,000 stamping cycles when processing MBF ribbon. Preforms with very intricate forms are also produced using photo-etching technology that has been developed earlier for manufacturing of electron beam metallic filters as parts of color TV tubes (Fig.8, black arrows). In many cases an inexpensive high-pressure water jet method has also been applied. This method enables simultaneous manufacture of hundreds of similar preforms from a stack of foils.

2.8 Currently Available Amorphous Brazing Foil Products and Cross-reference of MBF Specifications

To the best of our knowledge the vast majority of MBF products is produced as a result of more than two-decades of development accomplished by METGLAS® Solutions, a division of AlliedSignal and, afterwards, of Honeywell Int. WESGO has also been producing these alloys on METGLAS® Solutions licenses. Several Russian groups advertised some products but so far these did not receive wide application in the West. Table 3 presents a list of the various MBF ribbons and their available dimensions that are currently produced on the industrial scale. It is well known that addition of chromium decrease amorphability of the Ni/Co-based alloys. Accordingly, the data given in Table 3 indicates that both the maximum thickness and the width of produced ribbons decrease with increase of their chromium concentration. So far, the industrial rapid solidification technology is capable of producing 200 mm (8") wide ribbon, however some MBF-20 samples as wide as 300 mm were shown at exhibitions. There are no doubts that wider of Ni/Co-based MBF ribbons will be produced soon.

Over the years many MBF alloys were approved as standard AWS classifications. Some major aerospace companies such as GE, Pratt & Whitney and others employ them but under their own classifications. Unfortunately this creates a degree of confusion when an MBF alloy must be selected as a filler metal based on customer specifications. To address this issue all classifications of MBF alloys known to us are collected in Table 4 for easy cross-reference.

3. PROPERTIES AND SPECIFICS OF MBF JOINTS PRODUCED WITH VARIOUS STEELS AND ALLOYS

As was mentioned above, MBF alloys are mostly used for joining high performance structural steels and alloys in applications that require high strength joints which exhibit high corrosion/oxidation resistance under high temperatures and in hard environmental conditions. The application of MBF alloys encompasses a wide range of high performance structural materials. Groups of the base metals will be considered here in a sequence of increasing number of base metal elemental components and metallurgical complexity: namely, ferritic 400 AISI series Fe-Cr steels, austenitic 300 AISI series stainless steels, then multicomponent superalloys, and, finally, single crystal superalloys. The joint mechanical properties/structure relationships will be described with a primary emphasis on the brazing cycle thermal conditions.

3.1 400 AISI Series Fe-Cr-based Ferritic Stainless Steels

3.1.1 AISI 409 joints brazed with MBF-20 and -30

Mechanical strength and microstructure of the joints made using MBF-20 and -30 alloys and BNi-2 and BNi-3 pastes for comparison was studied in.[20, 21] Standard AWS C3.2M specimens and procedure were utilized when measuring mechanical properties.

Brazing was performed at 1055°C for 10 min using 5 different furnace atmospheres such as 100% hydrogen, 50:50 H_2:N_2, 25:75 H_2:N_2, 50:50 H_2:Ar, and 100% Ar. Brazability and wetting of all samples was best when the atmospheres had a low (about -40°C) freezing point. Joint strength from these experiments exceeded the 409 steel yield limit, $\sigma_{0.2:}$ namely, 263 MPa (38.2 ksi) for MBF-20 and 221 MPa (32 ksi) for MBF-30. The joints made with powder pastes with similar BNi-2 and BNi-3 compositions had lower values of shear strengths, 221 and 197 MPa, respectively. The MBF-20 and -30 joint quality and strength were close to those of joints made under vacuum conditions. The most important practical consequence demonstrated by these results is an ability to use MBF in highly productive and very economical (relative to vacuum furnaces) belt and semi-continuos batch furnaces.

Microstructure of all MBF brazements both inside and adjacent to joint interfaces was unaffected by the atmosphere composition. The joint microstructure was comprised mostly of (NiCrFe) solid solution phase and a fine eutectic mixture of $(NiCr)_{1-x}S_x$ and Cr_3B crystals (Fig. 9). Boron strongly diffused in the base metal forming a perlite-like structure in spite of the short brazing time. Brazements with the same width as the MBF but made of powder pastes contained substantially more Cr_3B phase. This was probably the reason for their lower strength.

3.1.2 AISI 430 and 436 Joints Brazed With MBF-20

Brazed plates/sinusoidal fin specimens with design similar to that of industrial turbine heat exchanger were extensively studied by this author.[13] Plate and fins were UNS436 stainless steel sheets with 100-μm and 50-μm thickness, respectively. MBF-20 foil, from which flat preforms were made, had 25 μm, 37 μm, and 50 μm thickness. These thicknesses were selected to find the optimal combination of base and filer metals. Each sample had 16 identical plate/foil/fin/foil members and was assembled using a special holder and placed between vertical guides attached to a thick backing plate. This configuration permitted all stacked parts to move freely in the vertical direction during a complete brazing cycle. A load was placed on the top of each sample in the form of a metal or graphite block. The samples were placed in a vacuum furnace with the loading aligned in the direction of gravitational pull. The samples for mechanical tensile testing were cut afterwards and then machined by the electrical discharge method into specimens with I-beam shapes as depicted in Figs. 10a and b.

Optical observations of the tested failed samples were made under a moderate 20X magnification. They showed that in samples brazed using 25-μm and 37-μm average thickness foils, the failure occurred in the brazements (Figs. 11 a and b). Also, in some samples brazed using 25-μm foil, large unbrazed spots were observed (Fig. 12 a). These spots were formed because an insufficient amount of brazed filler metal needed to fill occasional dents or other defects existed in the fins. In the case of the 50-μm foil sample, the failure occurred in the middle of the fins, as depicted in Fig. 11 b, and no unbrazed spots were observed (Fig. 12 b). Therefore, the strength of the brazed structure in this case was ideally determined by the strength of the base metal. Metallography observations showed that the joint thickness in the middle portion of all brazes is the same regardless of the thickness of the virgin amorphous foil, even when comparing samples manufactured using 25-μm and 50-μm foils as Figs. 13a and b demonstrate. This effect was observed because gaps between parts were not constrained during brazing. Indeed, the excess liquid MBF-20 alloy was partially expelled from the capillary gaps into the fillet areas upon melting. The liquid flow out of the gap occurred until the surface tension forces at all gap surfaces became equal to the total load applied to the specimen. The total load was comprised of the parts weight and the weight of the external block. The excessive molten MBF-20 metal, particularly in the case of 50-μm thick foil, flowed out of the initial gaps forming large fillets and partially climbed up on the vertical walls of the fins. The initially thicker filler metal formed larger joint fillets with larger joint cross-sections as depicted in Fig. 13b. These larger fillets had advantageous shapes without a narrow cavity-like crystallization shrinkage pattern seen in Fig. 13a. As in the cases of 409/MBF-20 and –30 joints the joint integrity was high. The total mechanical performance of units brazed with 50-μm thick foil was determined by the strength of the base metal fins unaffected by brazing.

The microstructure and mechanical properties of 430 and 436 steel joints brazed using MBF-20 were also studied in.[25] It was shown that the joint shear strength is the same (about 200 MPa) regardless of the base metal grade and if the brazing temperature is in the range of 1050-1150°C and the brazing time is kept to about 10 min. Here there is some analogy with results on 409 and 439 joint properties and structure obtained in.[13] The chain of brittle chromium borides was segregated in the central zone of the joint (NiSi)-solid solution matrix phase. An extensive network of elongated borides was also observed in the areas adjoining the braze. Some chromium carbides were also present together with $Cr_x B_y$ crystals. Joint failure observed in this work occurred in the brittle mode in the joint central area containing a substantial amount of the brittle eutectic phases because of the short brazing time.

3.2 AISI 316L Joints brazed with MBF-51

Rabinkin et al.[17] carried out a comprehensive study of 316L joint mechanical properties, corrosion and brazement microstructure via brazing cycle optimization (see also section 3.5 below). MBF-51 foils were 25 and 50-μm thick and brazing cycles had various temperature/time parameters. Brazing with MBF-51 was carried out at a relatively high temperature (about 1175°C) because MBF-51 contains low boron and high chromium concentrations. The measured mechanical properties included the tensile strength, determined using a standard AWS C3.M procedure and specimens, and fatigue resistance. It was found that a joint tensile strength greater than 300 MPa (43.7 ksi) was achieved when a thin, 25-um thick foil and a rather short brazing time were used. The thicker, 50-μm foil needed longer brazing time to achieve the same level of the strength and joint ductility. It should be underlined that in both cases the joint strength was higher than the yield strength of the virgin 316L. Joint fracture started in appearance of cracks in the fillet area where an excessive amount of brittle eutectic phases was found. These cracks proceeded through the base metal area adjoining the interface where chromium borides were formed as a result of boron diffusion into the base metal. In addition, separate data were obtained on the burst pressure of some industrial heat exchangers manufactured using 316L and MBF-51. Here again the pressure could be increased 2-3-fold via proper brazing cycle choice. Today, in the best cases, heat exchangers made of 316L can be pressurized up to 12 MPa (120-140 atm) before failure.

Interaction of 316L austenitic steel with MBF-51 yields brazements in which a (NiFeCrSi) solid solution phase constitutes a large part of the joint area microstructure. The joint also contained well-faceted chromium boride crystals. These crystals were absent if the amount of filler metal per joint area was small, i.e., a thin foil, or, when the foil is thick, after long term brazing or brazing combined with post-brazing annealing are applied (Figs. 14a and c). This is due to the practically complete diffusion of boron into the base metal. On the other hand, these brazements are characterized by retention of almost all silicon within the joint area as a component of the (NiFeCr) solid solution phase (Fig. 15). Chromium borides formed in the 316L base metal segregated at grain boundaries in the 30-50-μm deep zone and coagulated into particles with a rounded shape if the time at the high temperature exposure was kept long. Again, a relatively low MBF-51 boron concentration contributes to a favorable 316L/MBF-51 joint microstructure and provides a good joint ductility and strength.

3.3 AISI Superalloy Joints

3.3.1 Inconel 625 Joints

In spite of the fact that MBF foils have been used for Inconel 625 for years, so far there is no direct data on Inconel 625 joint mechanical properties. Joining procedure optimization of the plate/fin heat exchangers used in aerospace applications was made by Hughes-Treitler Co. with the author's participation. Such plate/fin heat exchangers have a rigid frame that provides the total unit strength which by far exceeding the service pressure. Therefore, the only developmental goal was to obtain plate/fin sound joints that would be ductile and free from voids and cracks. The joints were manufactured of 1- and 0.2-mm thick plates and 125-μm thick fins using 37-μm thick MBF-51. BNi-2 and BNi-5 powder-based pastes which are similar in composition were also used as possible alternative filler metals. The brazing cycle applied to both kinds of filler metals consisted of slow heating and cooling stages and a long term (up to 90 min) brazing stage at 1155°C temperature. Such parameters were specifically chosen to avoid part cracking that results from high thermal stresses. The thermal stresses are created because the parts are big and their structural elements have different dimensions. The described thermal cycle yielded brazes which had mostly a single-phase joint microstructure similar to that of the AISI 300-series joints, and no cracks (Fig. 16). Only a small volume of eutectic phase mixture was present in the fillets (Fig. 16, white arrows) and, sometimes, in the fillet vicinity (Fig.16, black arrows). Moreover, the observed chromium borides, segregated at the braze interfaces, had a favorable round morphology after such long exposure. Joints made of the powder paste had a very pronounced porosity and poor integrity.

3.3.2 X40, X45, IN 738 and IN 939 Joints Brazed with MBF-100-series and MBF-53

These base metals are mostly used in the critical locations of aerospace and land based turbines and are required to withstand ultimate temperature and stress conditions over a long service time. Therefore, it is imperative to choose brazing conditions and the MBF-compositions in such a way as to preserve in aftermath of the brazing operation the complex microstructures and high performance properties of superalloys. Here one should preserve the following microstructures: namely, a γ^{-}-prime strengthened matrix phase in the Ni-based superalloys case, and solid-solution strengthened phase in Co-based superalloys. It is particularly important to keep the amount of boron in filler metals to a minimum because boron may induce brittleness by causing potential chromium boride segregation in the base metal grain boundaries. The properties of these joints, obtained under variety of brazing conditions, were measured and their corresponding structures were studied comprehensively and described in detail in a series of recent papers.[13, 16, 26-28] The resulting processing optimization conditions, which are described below, yield joints that have excellent mechanical properties, equal to or approaching those of the virgin superalloys. It should be noted that the composition of majority of MBF chosen for testing in these papers contain a minimal amount (1.4 wt.%) of boron. This amount is at the threshold of the alloy amorphability concentration limit.

Mechanical strength of the superalloy joints

L. Heikinheimo et al. studied joints manufactured from Co-based (X40 and X45) superalloys and Ni-based (IN738 and IN939) superalloys that are commonly used in the land based power turbines.[16, 26] MBF-100-series alloys and MBF-53 and MBF-80 alloys were used as the filler metals. Table 5 and 6 contains the base and the filler metal compositions studied in their works. Table 7 presents materials combinations in the joints, the brazing cycle parameters, and the type of the samples mechanical testing. Brazing was carried out under a high vacuum, typically 10^{-6} mbar, at 1170-1200°C and for various times. A part of the samples was also annealed after brazing according to the regimes shown in Table 7.

The joint strength was measured using both tensile and shear mode loading. Some results for the X40 joints, for example, are presented in Fig. 17. The strength of X40 joints is 725 MPa at room temperature (RT) and 496 MPa at 650°C. The elongation of the joints is 5-6.5 % at RT (7 % for X40 joint) and 7.5-11 % at 650°C (10 % for X40 joint). (More details may be found in [16, 26].)

Superalloy Joint Microstructure

X45/MBF-53 joints have a narrow (~25-µm) molten zone. They are characterized by the presence of a broken eutectic central line formed mostly by (NiCrMo) silicides and $W_x(SiC)_y$ silicocarbides, which are segregated inside the (NiCrWSi) solid solution matrix phase. Most of the boron has diffused into the base metal and formed rather large unfavorable $(CrW)_xB_y$ borides at grain boundaries in close proximity to the braze. Small borides are observed at BM grain boundaries some distance away from joints together with the intrinsic $(CrW)_xC_y$ carbides, but the latter have segregated inside of the base metal grains. Applied long term annealing did not yield a decrease in size of borides (Fig. 18).

Inconel 738 and 939 Joints Brazed with MBF-53

IN-738/MBF-53 joints have rather uniform and very favorable microstructure consisting mostly of the (NiCr)-based solid solution phase, in which small separate $(Cr,W)_xB_y$ borides are embedded (Fig.19). This phase is comprised of all metallic elements from both base and filler metals. Small, separated, and rounded borides together with intrinsic $(TiTa)_xC_y$ carbides are segregated at the base metal grain boundaries in a rather narrow region. This region is adjacent to the interface.

IN-939/MBF-53 joints are barely visible. Specimens display a complete recrystallization pattern through the entire joint area (Fig. 20). Isolated occasional binary Cr_xB_y borides that have narrow plate structure are observed in the center of the joint area. Nickel, chromium and probably silicon are very evenly distributed across the brazement. Very small borides are segregated at grain boundaries in the 60-70 μm-wide base metal zone adjacent to the joint. Small complex $(TiTaNb)_xC_y$ carbides are present inside of the base metal grains as well.

3.3.3 Single Crystal CMSX-2 and –4/MBF-80 Joints

K. Nishimoto et al. obtained excellent results in the transient liquid-phase bonding (TLP) joining of single crystal CMSX-2 (Ni-8.0Cr-4.6Co-0.6Mo-8.0W-1.0Ti-5.6Al-6.0Ta) and CMSX-4 (Ni-6.5Cr-9.0Co-0.6Mo-6.0W-1.0Ti-5.6Al6.5Ta-3.0Re-0.1Hf) superalloys.[27, 28] MBF-80 40-μm thick foil was used as a filler metal in brazing at 1100-1275°C temperatures for up to 5.5 h in vacuum under a slight load. Tensile tests of CMSX-2 joints bonded at ~ 1250°C in vacuum were carried out in the 650-900°C range. The tensile strength of all joints was equal to or greater than that of the base metal. The elongation and reduction of the joint area were observed to be either equal to or slightly lower than those of the virgin base metal. Most importantly, the K. Nashimoto et al. group was able to produce single-crystal continuity of both base metal single crystalline parts with virtually no traces of the braze and with a complete dissolution of MBF-80 components in CMX-2 base metal parts.

3.4 General Metallurgical Paths of MBF Joint Formation

Well-developed general metallurgical principles and knowledge attributed to the nature of stainless steels and superalloys are useful in understanding the formation of joints that have been described so far. During the brazing cycle, base metal dissolution starts as soon as the liquid phase of the FM is formed at eutectic concentration levels. . This dissolution completes in no longer than a few dozen seconds because the liquid phase becomes saturated with metallic components such as Co, Ni, Cr, W, etc. For example, in the case of CMSX- 2 superalloy brazed with MBF-80 alloy at 1250°C, this process completed in 10 s.[27, 28] The saturation process completes even more rapidly in MBF alloys that have much lower boron concentrations than MBF-80, in spite of the lower brazing temperature (1170°C). The next concentration equilibration stage involving the entire brazement area encompasses isothermal crystallization and extends well into the post-brazing annealing part of the brazing cycle when it is applied. In this stage the mass transfer proceed with the elemental rates that are characteristic of diffusion processes in solid metals. The boron diffusion rate is unique among all involved metallic elements and silicon as well; it is three orders of magnitude faster than that of chromium, silicon, etc. due to the relatively small boron atomic radius.[29, 30] On the other hand, boron has extremely low intergranular solubility in all highly alloyed materials because it has a large misfit with both interstitial and substitutional sites of metal crystal lattices. For example, in 316 steel it is about 90 ppm at 1125°C and 30 ppm at 900°C.[31] As a result, boron diffusion proceeds effectively via grain[34] and twin boundaries[33] where it decreases the interfacial free energy of loosely packed interfacial regions and reacts with iron, chromium, and molybdenum.[32] The products of these reaction are multimetal borides and carboborides, if the alloys that are being brazed contain carbon, such as $(CrFeMo)_xBy$ and $M_{23}(B,C)_6$, correspondingly.[30] The strong driving force behind the segregation of these borides is the high Gibbs free energy of their formation that for Cr_3B_4 and Cr_3B_5 is 295.9 and 242.7 kJ/mol, respectively.[34] Chromium depletion of grain areas adjacent to grain boundaries accompanies this boride segregation process and results in a well-known decrease in brazement corrosion resistance. The much slower rate of silicon diffusion results in delayed formation of silicides, if any, in the base metal interfacial areas. Sometimes, there is a complete retention of silicon as a substitutional component of the (NiCoCr)-based solid solution phase comprising the final joint.[17] When long brazing and/or annealing are applied, boron diffuses deeper in the base metal and the number of borides in the interface area decreases. Simultaneously, boride phases acquire rounded shape and coagulate resulting in improvement of mechanical properties. The joints are barely visible and similar in appearance of TLP bonded joints when a sufficiently long annealing time is applied to IN739 joints[26] (Fig. 20) and in the 316 stainless steel joints (Fig. 15).[17] Resulting mechanical properties, particularly ductility, increase substantially.[16, 26]

5. JOINT CORROSION AND OXIDATION BEHAVIOR

5.1 Corrosion Resistance

Only a few joint corrosion tests have been performed so far. Rabinkin et al.[17] tested the corrosion resistance of joints manufactured from 316L steel and high chromium containing MBF-50 and –51. Four different corrosive mediums such as a standard sea water solution, a 30% NH_4 (OH) solution, a 25 % phosphoric acid solution, and 0.5 % NaCI and 0.3% $(NH_4)_2$ S solution were applied in the case of MBF-51 joints. Only two mediums, the standard seawater solution and 25% phosphoric acid water solution were used for testing MBF-50. The results are shown in Table 8 and Fig.21.

MBF-50 joints: As seen in Table 8, the weight losses of the test specimens in both sea water and 25% phosphoric acid solution mediums were low. Only sea water produced some visual sign of a corrosive pitting attack seen mostly at the joint fillet “beach line” separating the wetted and unwetted areas of the base metal part. This pitting occurred on all of the specimens tested in seawater, with some large pockets of attack on specimens after 648 and 864 h of exposure.

MBF-51 joints: In the case of joints brazed with MBF-51 foil under conditions giving the highest strength, the weight losses of the test specimens were also low (Table 8). Some corrosion byproducts were seen in specimens immersed in seawater and 25% phosphoric acid but amounted to little, if any, corrosion attack. Scanning electron microscope examination of specimen surfaces and cross sections showed little if any corrosion or pitting attack after corrosion exposure. Some traces of attack were also seen in the base metal on the specimens subjected to the phosphoric acid solution, but generally, all the specimens had excellent visual appearance after the corrosion testing.

In general, the corrosion resistance of joints brazed with MBF-51 and MBF-50 alloys is high. In both cases, the test results showed that it was as great as the 316L base metal corrosion resistance. It is interesting to note that there was more pronounced pitting corrosion in the MBF-50 joints, in spite of the fact that chromium concentration in MBF-50 foil is 19 wt. Cr vs. 15 wt. in MBF-51. A short conventional brazing cycle time for MBF-50 is a possible cause of the increased corrosion.

MBF-53 and MBF-100: In the last two decades there has been a dramatic increase in demands for the reduction of potential environmental impact of car engines, particularly diesels. Concurrently, a new generation of jet engines working at 1200°C was developed using new materials. In both these cases, new brazing filler metals capable of withstanding severe service conditions were needed. The MBF-53 containing 5% molybdenum and MBF-100-series Co-based alloys were developed to address these needs by improving the joint performance in highly oxidized and corrosive environments.

A decrease of environmental impact of diesel engines and substantial engine fuel consumption improvements may be achieved by cooling diesel exhaust gases before they enter atmosphere in special gas coolers, which have thin fin/plate-type stainless steel cores. Brazing of these coolers demands base and filler metals with low rates of corrosion and oxidation. Corrosion testing of AISI 316 and 321 stainless steel thin coupons brazed with these alloys was carried out in a water solution simulating real conditions existing in diesel exhaust pipes.[13] These tests validated the improved performance of these alloys relative to MBF-50 and -51, as the data in Table 9 demonstrates.

The similarly favorable effect of molybdenum additions in MBF-53 on corrosion decrease was observed when brazed gas coolers were corrosion tested under conditions close to that existing in real engines. In addition, the erosion of stainless steel fins and plates by the MBF-53 was very limited. Still, the best results were achieved with an MBF-101 Co-based alloy.

5.2 Oxidation Resistance

Very large power plant steam generators have been manufactured using energy efficient systems based on a multi-mile long pipe/fin design. These steam generators work at about 500°C in the exhaust atmosphere of the oil burners, frequently under humid tropical conditions. Their life span should exceed 5-10 years. MBF-20 foil has been used to joint stainless steel pipes and low carbon steel strip fins. Recently, there appeared a need to improve steam generator efficacy by increasing lifetime of their hottest parts. MBF-53 alloys containing enhanced chromium content, -15 % vs. 7 % Cr in MBF-20, - and 5% molybdenum was proposed and tested as a beneficial replacement.[35] The accelerated corrosion test in strong acid solution showed remarkable MBF-53 joint performance as shown in Fig. 22.

MBF-100-series Co-based alloys were tested as potential prototypes in manufacturing of the cell-type and feltmetal seals made of dispersion hardened PM2000 (FeCrAlTiY)-based alloy[13]. MBF-100-series was also tested for use in joining and repair of vane and blades made of superalloys.[13, 16, 26] The results of the brazability and oxidation resistance testing in open air at 1165°C/65 hours made by D. Sporer are shown in Table 10.[13] These results demonstrate the high tenaciousness of MBF-100 series alloys and obvious superiority of joints made with these materials over joints made of the Ni-based MBF.

6. MAJOR APPLICATIONS [3, 21, 36-39]

At first, the prime application area of Ni-based MBF was confined to aerospace industry where for years MBF was used in brazing of aircraft structural parts, acoustical tail pipes (J-pipes), thrust reversers, turbine blades and seals (Fig. 23). MBF is also suitable for use in many other aerospace applications such as manufacturing honeycomb parts of space vehicles, firewalls, torpedo hulls, missile fins, and engine tail feathers. Ancillary engine components such as nacelles, heat exchangers, honeycomb seals, wear pads, seal shroud segments, diffusers, discs, corrugated interior hollow vanes, doublers, stiffeners, and struts for frames are also widely produced using this foil. All these components have rigid dimensional tolerances and high strength/stiffness-to-weight ratio requirements which are needed to handle the stresses inherent in aerospace applications. MBF as thin as 18 μm (0.7 mil) has been produced by METGLAS Solutions to satisfy the low erosion requirements for joining structural aerospace honeycombs. It gives consistently reliable and strong joints because of accurately metered brazing filler metal amount supplied in the joint area.

In recent years growing attention to the energy conservation and pollution elimination has spurred a substantial growth in MBF applications. MBF technology has been utilized in the production of plate heat exchangers for many industrial and utility functions such as fuel cells, heat pumps and catalytic converters for both gas and diesel internal combustion engines. A standard brazed plate-and-frame heat exchanger consists of a large number of alternating corrugated/flat metal plates stacked in tight, sealed contact with each other. These plates form an elaborate system of channels that comprise two separated liquid transport subsystems - one hot and one cool. Liquid and/or gas media flow through these subsystems exchanging heat and thus saving energy (Fig.24). Generally, brazed plate heat exchangers are very compact, energy efficient, stronger and well suited to operate under high temperature/high pressure conditions. Because of a very large number of contact areas to be brazed, uniform clean MBF provides much more uniform joints in comparison with powder filler metals. The most impressive example of the improved performance of foil versus powder can be observed in the manufacture of small heat exchangers for cooling human blood in artificial heart/lung machines during surgery. MBF forms smoother fillets than powder FM due to its better wettability and these fillets do not break blood cells. Consequently, only the foil form of BNi-type of brazing filler metals has been approved for this critical application.

Additional advantages of MBF vs. FM powders may be gained using robotic operation to assemble in one package multiple plates and preforms. MBF materials enable the assembly of complex heat exchangers before the brazing process with no environmental contamination associated with powder organic binders. The size of heat exchanger units brazed with MBF has been growing rapidly as Figs. 25 a and b demonstrate. These figures depict the latest WTT heat exchanger model and Ballard Unit for fuel cell engines. These developments, combined with an improved brazing technology created a rapid growth in usage of Ni-based MBF in new applications where there is a need for brazes with high corrosion resistance. New high-chromium containing

MBF-51 and –53 alloys also provide an opportunity to replace much more expensive assembled plate/gasket heat exchangers with brazed heat exchangers that posses a combination of high strength and superior corrosion resistance.

Stainless steel heat exchangers are produced currently in quantities of hundreds of thousands of pieces per year for chemical, pharmaceutical, food processing and medical industries, fuel cells, and refrigerators. In the latter case, a ban on the production of CFC's, a result of their depleting effect on the atmospheric ozone layer, caused a great need for development of non-corrosive stainless steel brazes containing no copper and capable of withstanding alternative heat exchanger mediums such as ammonia. In this respect, MBF-51, because of its superior performance, was approved by the German TUV as a standard brazing filler metal for high-pressure stainless steel apparatuses.

MBF-50 foil is also used in joining high temperature resistant (FeCrAlTiY) honeycomb cores to the (FeCr)-based steel cartridges of catalytic converters in cars and motorcycles (Fig. 26) with increasing frequency. In spite of a presence of a strong alumina scale on the surface of the Fe-Cr-Al core material, MBF wets and joins the core to the stainless steel cartridge due to the above mentioned effect of the oxide dissolution in liquid MBF-50.

A new fast growing and very large application is evolving in the production of so-called heat recuperators that clean the exhaust gases of diesel engines and in the same time preheat the air incoming in the diesel cylinders. Today diesel engines are fast displacing gas auto engines in Europe and the same trend is expected soon in the USA as well. MBF-15, -80, -50, -51, and –53 alloys containing high chromium concentration have all been tested and used successfully in various types of car and truck diesels.

7. THE FUTURE

Today MBF is an important and well-established brand of filler metals due to advances in the rapid solidification technology and development of new commercial products and their applications. They are produced in multi-tonnage quantities and are cut, stamped, or shaped into millions of precise preforms ranging in weight from a few dozen milligrams to a few hundred grams. The total cost of the final products in which MBF are the critical elements of a sophisticated manufacturing technology is measured in billions dollars if one takes into account the extremely costly aerospace, engines. Current efforts are directed toward development of new amorphous filler metal compositions finely compatible and attuned to specific needs of each of many various metallic material groups. These groups include many base metals such as advanced heat and corrosion resistant alloys, monocrystal superalloys, cemented carbides with various cobalt binder concentration, high chromium/aluminum heat resistant steels, and etc. In order to insure the industrial success of new and existing compositions, this work has to be complemented by the study and perfection of brazing conditions for each new individual joining case. The application of new MBF compositions can also be augmented by a further advancement of RS casting technology in order to decrease MBF production costs. Such cost decreasing will alleviate their partial cost disadvantage and make better 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 now because it's current production growth rate is very high.

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Tables

Tables

Table 1 Composition, Melting Temperatures and Density of Nickel- and Cobalt-based MBF-series Alloys

MBF	AWS & AMS Classifications	Nominal Composition, wt. %									Melting Temp. °C (°F)		Braze Temp. (Approx.) °C (°F)	Density, g/cm^3 (lb m/in^3)
		Cr	Fe	Si	C*	B	P	W	Co	Ni	Solidus	Liquidus		
15		13.0	4.2	4.5	0.03	2.8	-	-	1.0*	Bal	965 (1769)	1103 (2017)	1135 (2075)	7.82 (0.283)
20	AWS BNi2/AMS 4777	7.0	3.0	4.5	0.06	3.2	-	-	-	Bal	969 (1776)	1024 (1875)	1055 (1931)	7.88 (0.285)
30	AWS BNi3/AMS 4778	-	-	4.5	0.06	3.2	-	-	-	Ba	984 (1803)	1054 (1929)	1085 (1985)	8.07 (0.291)
50	AWS BNi5a	19.0	-	7.3	0.08	1.5	-	-	-	Bal	1052 (1924)	1144 (2091)	1170 (2138)	7.70 (0.278)
51		15.0		7.25	0.06	1.4	-	-		Bal	1030 (1886)	1126 (2058)	1195 (2183)	7.73 (0.278)
55		5.3	-	7.3	0.08	1.4	-	-	-	Bal	950 (1742)	1040 (1904)	1070 (1958)	7.72 (0.279)
60	AWS BNi6	-	-	-	0.10	-	11.0	-		Bal	883 (1621)	921 (1688)	950 (1742)	8.14 (0.294)
80		15.2	-	-	0.06	4.0	-	-	-	Bal	1048 (1918)	1091 (1996)	1120 (2045)	7.94 (0.278)
100		21.0	-	1.60	0.06	2.15	-	4.50	bal.	-	1136 (2077)	1163 (2125)	1170 (2138)	8.13 (0.294)
101*		21.0	-	4.40	0.06	1.55	-	4.50	bal.	-	1091 (1996)	1143 (2089)	1170 (2138)	8.10 (0.292)
102*		21.0	-	4.20	0.06	1.50	-	4.50	bal.	15.0	1078 (1972)	1139 (2082)	1170 (2138)	8.10 (0.294)

*Commercial availability pending.

Table 2 Mechanical Properties Of The As-Cast MBF-51 Brazing Foil [17]

Foil Thickness, μm (mil)	Stress at Maximum Load, MPa (ksi)	Strain at Peak, %	Young's Modulus GPa (psi)
28.2 (1.11)	1660 (241)	≈2.0	125 (18 x 10^6)
46.5 (1.83)	1900 (276)	≈2.0	113 (16 x 10^6)

Table 3 Currently Available Commercial MBF-series Alloys and Product Dimensions

Alloy	**Maximum Width of the Ribbon, mm (inches) at Thickness, μm (inches)**				
	25 μm (0.001)	**37 μm (0.0015)**	**50 μm (0.002)**	**62.5 μm (0.0025)**	**76 μm (0.003)**
MBF-15	**101.6 (4)**	**101.6 (4)**	**(2)**		
MBF-20	**101.6 (4)**	**212.5 (8.5)**	**212.5 (8.5)**	**212.5 (8.5)**	**212.5 (8.5)**
MBF-30	**101.6 (4)**	**207 (8.14)**	**207 (8.14)**	**101.6 (4)**	**50.8 (2)**
MBF-50	**101.6 (4)**	**50.8 (2)**			
MBF-51	**101.6 (4)**	**212.5 (8.5)**			
MBF-55		**50.8 (2)**			
MBF-60	**101.6 (4)**	**50.8 (2)**			
MBF-80		**50.8 (2)**			

Table 4 Cross Reference Chart of MBF Designations and Specifications

MBF	AWS	AMS	Pratt & Whitney	General Electric	Garrett Engine Division EMS 54752	Rolls Royce MSRR 9500	Snecma DMR 35	Textron Lycoming
15			PWA996 CPW494		-XIII	-705		M3876
20	BNi-2	4777		B50TF204	-II	-97	.302	
30	BNi-3	4778		B50TF205	-I	-114	.304	
50	BNi-5a*			B50TF217*		-722		
51	BNi-5b							
60	BNi-6		WA3610		-XI			
80				B50TF207	VIII	-719	.307	

* Alternative to GEB50TF81 powder and AMS 4782

Table 5 Base Metals (BM) Composition, Wt. % Studied in [16, 26]

Alloy	C	Co	Cr	Ni	Mo	Al	W	Ta	Nb	Ti	Fe	Si	Mn	Zr	B
X40	0.5	Bal.	25.5	10.5			7.5					0.75	0.75		
X45	0.18	Bal.	26.1	10.6	0.38	0.01	6.7				0.93	0.95	0.37		
IN738	0.17	8.5	16	Bal.	1.7	3.4	2.6	1.7	0.9	3.4				0.1	0.01
IN939	0.15	19.0	22.5	Bal.		1.9	2.0	1.4		3.7		<0.2	<0.2	0.1	0.01

Table 6 Compositions, Wt. %, Thickness, And Melting Characteristics Of The MBF Filler Metals Used In [16, 26]

Alloy	Thickness, μm	Composition, wt.%							T_{sol}, °C	T_{liq}, °C
		Ni	Co	Cr	Si	B	W	Mo		
MBF-100	37	-	Bal.	21	1.6	2.15	4.5	-	1136	1163
MBF-101	46	-	Bal.	20	4.5	1.70	4.5		1091	1143
MBF-53	25*	Bal.	-	15	6.5	1.35	-	5	1038	1127
MBF-80	25*	Bal.	-	15.2	-	4.0	-	-	1048	1091

*The foil was applied in two layers as a 50-μm thick preform.

Table 7 Material Combinations In Joints, Brazing Cycle Parameters And Joint Characterisation Methods [16, 26]

Alloy	Specimen type	Thermal cycle	Characterisation and testing methods
	rectangular bars in butt joint	**T/°C - time/h***	
MBF-100	X40	1200 - 16	SEM+EDX, AES, tensile testing at RT and 650 °C
MBF-101	X40	1200 - 16	
MBF-80	IN738, IN939	1170-15	
	plates in butt joint	**T/°C - time/min****	
MBF-101	X45*	1170 - 5	SEM+EDX, AES, shear testing at RT
MBF-53	X45*; IN738***; IN939***	1170 - 15	
MBF-80	IN738***	1170 - 15	

* All of the joints were post-brazing aged at 760°C for 48 h.
** One joint of each batch of six samples was post-brazing annealed at 1070°C for 2 h.
*** Post-brazing annealing at 1070°C for 6 h.

Table 8 Total Weight Loss and Appearance of 316L/MBF-51 and MBF-50/316L Joints Subjected to Corrosion Testing [17]

Corrosion medium	Percent weight losses after exposure for 864 hours		Visual appearance of traces of joint corrosion	
	MBF-51	MBF-50	MBF-51	MBF-50
Standard sea water solution (ASTM-D114Standard Procedure)	0.21	0.019	minor pitting	yes
30% NH_4OH water solution	none	N/A	none	N/A
25% H_3PO_4 water solution	0.62	0.088	minor pitting	none
0.5% NaCl&0.3% $(NH_4)_2S$ water solution	none	N/A	none	N/A

*Tested samples were comprised of two overlapping 2.5 x 3.75 x 0.317 cm 316L plates brazed with MBF-51 brazing foil with 50 µm (2 mil) thickness. The brazed overlap is 1.25 cm. Samples were completely immersed in corrosive solutions at 50˚C (120˚F) under 1 atm for up to 864 hours.

Table 9 Corrosion Weight Losses Of Some Brazed Samples In A Solution* Simulating The Environment In Car Exhaust Pipes [13]

Brazing filler metals used in tested samples	Weight change, %, after 258 h exposure		Weight change, %, relative to the initial weight after 524 h exposure		Weight Change, %, relative to the initial weight after 781 h exposure	
	316 SS	321SS	316 SS	321 SS	316 SS	321 SS
MBF-51 (Ni-15Cr-7.3Si-1.4B)	-2.4748	-21.375	-4.89	-22.3	-6.14	-22.3
MBF-51+5% Mo (Ni-15Cr-7.3Si-1.4B-5Mo)	-0.4888	-11.132	-1.13	-11.23	-1.74	-11.23
MBF-101 (Co-21Cr-4.5W-4.4Si-1.55B)	-0.5912	-0.1025	-0.59	-0.1	-0.59	-0.1
Unbrazed base metal 316SS and 321SS coupons having the same weight as the tested samples and used for comparison	-0.314	-0.0505	-0.31	-0.05	-0.31	-0.05

*The composition of the solution used is 10% water solution of a mixture of nitric, sulfuric, and hydrochloric acids.

Table 10 Brazability And Oxidation Resistance In Open Air At 1165°C/65 Hours Of PM2000 Honeycombs Brazed Using Ni- And Co-Based Amorphous Alloys [13]

MBF Alloy And Its Composition, Wt.	**Honeycomb Cell Size And Height, mm**	**Wicking (M1), %**	**Brazing/Oxidation Quality (BQN)**, %**
MBF-50 (BNi-50a) (Ni-19Cr-7.3Si-1.25B	**5 x 6.4**	**95*****	**6**
MBF-100 (Co-21Cr-4.5W-1.6Si-2.15B)	**1.6 x 10**	**100**	**61**
MBF-101 (Co-21Cr-4.5W-4.4Si-1.55B	**2.5 x 6.6**	**100**	**44**
MBF-102 (Co-15Ni 21Cr-4.5W-4.4Si-1.55B)	**2.5 x 6.8**	**65**	**61**
MBF-103 (Co-15Ni-21Cr-4.5W-3Pd-4.4Si-1.55B)	**1.6 x 10**	**59**	**65**
MBF-104 (Co-15Ni-21Cr-4.5W-5Pd-4.4Si-1.55B	**1.6 x 10**	**71**	**62**

*- Brazing was made at about 1200°C for 2-5 min in high vacuum, <1x10(E-5) mbar.

**- BQN [%]=(10xM1xH)/(10+N_b)x$H_{n,}$ where M1 is braze flow in %, H-honeycomb height, mm; N_b –number of double cell walls showing "through" or breakaway oxidation; H-normalized honeycomb height.

***-Three 25 mkm thick foils were preplaced from each of both sides of the honeycomb.