NEW AMORPHOUS BRAZING FOILS FOR EXHAUST GAS APPLICATION

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Abstract

Environmental regulations for engine emissions are becoming increasingly stringent. The use of brazed exhaust gas recirculation coolers (EGRC) is considered to be an effective approach to reduce NO_x emissions in order to meet the current and future EU, JP and US emissions targets. EGRC's are made from stainless steel to withstand high temperatures of the exhaust gas and the corrosive environment within these coolers. Due to the better efficiency and weight-to-performance ratio compared to conventional tube and shell EGRC's, the plate type cooler is becoming increasingly important for this application.

Amorphous brazing foils (ABF's) are commonly used to join the plate type structures of heat exchangers as they allow the possibility to install fully automated assembly lines with a higher degree of process reliability compared to brazing paste. In order to meet the technical and economical requirements of the EGRC industry it was essential to develop new ABF's with aligned compositions. The properties of these new alloys are discussed and compared to standard BNi brazing filler materials.

Introduction

Amorphous Brazing Foils (ABF's)

Nickel based brazing filler materials have been used since the middle of the last century where high strength and good corrosion and oxidation resistance even at high temperature was required. In the conventional crystalline state the brazing filler materials (BFM´s) are inherently brittle and cannot be produced in continuous forms such as foil, wire, etc. As a result, they were available only as powders or their derivatives. During the last 30 years, developments in rapid solidification technology also known as melt-spinning, has made possible the production of amorphous brazing foils (ABF) with compositions that could previously only be utilized in powder form [1].

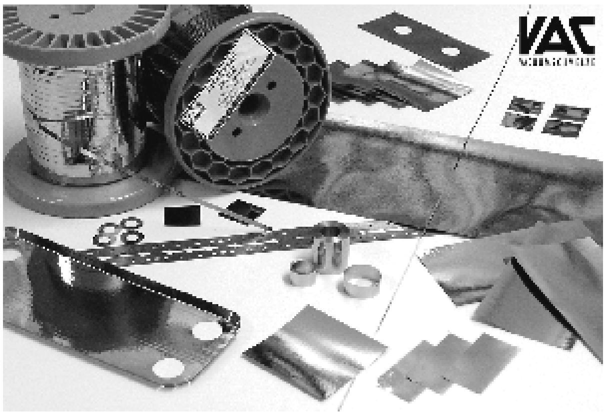

Figure 1: *A variety of different type's amorphous brazing foils and stamped or cut preforms*

Due to continuous improvements of the melt spinning technology over the last few years, significant cost reduction has been realized to allow use of these foils even in cost sensitive mass production applications. Vacuumschmelze (VAC) located in Hanau, Germany produces these foils and preforms (Figure 1) under the designation VITROBRAZE®. Based on the unique properties of ABF's, a wide and increasing application base has evolved. Most notably, the heat exchanger and metallic catalyst markets benefit from the unique properties of these foils. With amorphous brazing foils high volume manufacturers can realize fully automated, high speed production lines with the lowest reject rate. Overall, the production process with ABF's becomes economically advantageous compared to a brazing paste process.

EGR Coolers

Cooled EGR (Exhaust Gas Recirculation) systems have been used since end of the 1990's by engine manufacturers to reduce emissions from diesel truck engines. Depending on engine operating conditions, these systems divert up to 30 percent of an engine's exhaust stream through the system cooler, then back into the combustion chambers where the cooled exhaust gases reduce the oxygen content of the air/fuel mix. This limits peak temperature of the combustion and thus, reduces NO_x formation. The EGR cooler is the key component of the system. The vast majority of these coolers use engine coolant to reduce gas temperature from around 600°C to 150°C. High cooling efficiency, low pressure drop, ruggedness and compactness are chief requirements for an EGR cooler. EGR coolers are made out of stainless steel to withstand high temperatures of the exhaust gas and the corrosive environment within these coolers. The design differs among engine and cooler manufacturers, but there seems to be no doubt that flat plate designs will dominate the market very soon.

Recently developed new ABF compositions

The technical and commercial interest in Ni-based ABF's was affected by the good corrosion resistance and the low material costs of this alloy system. Due to the continuous pressure for cost reduction in mass production products, primarily in the Automobile industry, a broad interest in new ABF compositions with further cost reduction potentials can be seen.

Vacuumschmelze has succeeded in developing new ABF's with aligned compositions for both vacuum brazing and continuous style, controlled atmosphere brazing furnaces. Benchmark tests were compared to brazing joints made with the standard Ni-based amorphous brazing foils BNi-1a (VZ2111), BNi-2 (VZ2120), BNi-5a (VZ2150) and BNi-9 (see table 1).

New Iron containing brazing foils for vacuum furnace brazing of stainless steels

Vacuum brazing with Nickel-base BFM's is a common process for fluxless joining of stainless steel parts. This high temperature vacuum process offers several advantages, i.e. best purity level of atmosphere (oxygen), reduced distortion of parts to be brazed, combination of brazing with further heat treatments, etc. Vacuum brazed parts for exhaust gas applications are mainly made of austenitic stainless steels and joined with BNi-5 type brazing alloys if a high level of corrosion and oxidation resistance is required. To reduce costs, there is an obvious tendency to switch over to materials with reduced Nickel content, like ferrite stainless steels as base material and Iron based brazing alloys.

Several investigations dealing with Fe-containing BFM´s in powder or paste form were published in the last years [2-5]. Some commercial products already use these new kinds of filler metals [2,3]. So far amorphous brazing foils are only available in the group of Ni-, Co- or Cu-alloys with an Iron content well below 10 %. The target of substituting Nickel for Iron is to reduce the raw material costs of BFM´s. These new alloys should have a melting range well below 1200°C in combination with a good corrosion resistance and sufficient mechanical strength to fulfil the requirements of the EGRC market.

If we compare the ternary Ni-Si-B and Fe-Si-B systems, it becomes clear that an adequately low melting point BFM is not possible in the Fe-Si-B system. Pure Iron shows a melting point 80°C higher than Nickel. Both ternary systems with Silicon and Boron exhibit deep eutectics. The Fe-system reaches a melting point of 1155°C at a composition Fe-Si_{10}-B_{12} at. %. This is app. 145°C higher than Ni-system where a melting point of 1010°C will be reached at a composition of Ni-Si_{11}-B_{11} at .%.

Table 1: *Commercialized chromium containing Nickel ABF's along international standards*

	Composition [wt.%]					Melting range [°C]	
Alloy*	**Ni**	**Fe**	**Cr**	**Si**	**B**	**Ts**	**Tl**
BNi-1a	(75)	4,5	13-14	4,5	3	970	1100
BNi-2	(82)	3	7	4,5	3,2	970	1025
BNi-5a	(75)	-	18-19	7-8	1-1,5	1040	1140
BNi-9	(81)	-	15	-	3,5-4	1050	1070

(*) = VITROBRAZE designations for these foils are:
VZ2111 for BNi-1a
VZ2120 for BNi-2
VZ2150 for BNi-5a

For a basic analysis in the complex (Ni, Fe)-Cr-Si-B system, amorphous foils in a width of 80 mm and a thickness of 35 µm with different Iron and Chromium contents were produced. The melting range, casting and mechanical properties of the foils were analyzed in a previous work [6]. Through these casting tests it became clear that compositions with a high Iron content in combination with a high Chromium content can be difficult to process as amorphous foil, thus reduction in raw material costs will be compensated by much more complex processing. Furthermore these alloys have a melting point well above 1200°C. Therefore, they do not meet the target of the conducted development. By using moderate Nickel/Iron ratios, reasonable Chromium contents are possible in combination with good processing properties. These compositions show liquidus temperatures in the range of 1150°C similar to BNi-5 and could be brazed well below 1200°C.

Based on this previous investigation, the alloy design for a new ABF with 35% Fe content was fixed with VITROBRAZE VZ2106 (see table 2). To improve the corrosion resistance of the alloy, Molybdenum and Copper were added (see chapter "corrosion resistance").

To reach ABF compositions with an even higher Iron content and comparable corrosion resistance, it is necessary to add Phosphorous to achieve adequate depression of the liquidus temperature. The power to decrease liquidus temperature upon addition is very strong for Phosphorous in Iron. In binary systems the effect is about 28,8 °K/at.% for Fe-P, whereas Boron shows 21,4 °K/at.% for the Fe-B system and Silicon only 10,5 °K/at.% for Fe-Si alloys. The presence of Phosphorous in a brazing alloy used for joining of stainless steel, results in the formation of brittle phosphoric compounds in the brazed joint. These brittle phases can decrease mechanical strength of the brazed article as well as corrosion resistance. Due to this fact the Phosphorous content should be kept within certain limits [7]. This development work was the basis for VITROBRAZE VZ2099 alloy with 51% Iron (Tab. 2). This alloy is the worldwide first commercialized Iron based ABF.

Table 2: *Composition and melting range of novel iron containing ABF's*

	Composition [wt.%]				Melting range [°C]	
Alloy	**Ni**	**Fe**	**Cr/Mo/Cu**	**Si/B/P**	**Ts**	**Tl**
VZ2106	44	35	13,5	7,5	1045	1155
VZ2099	29	51	13	7	935	1145

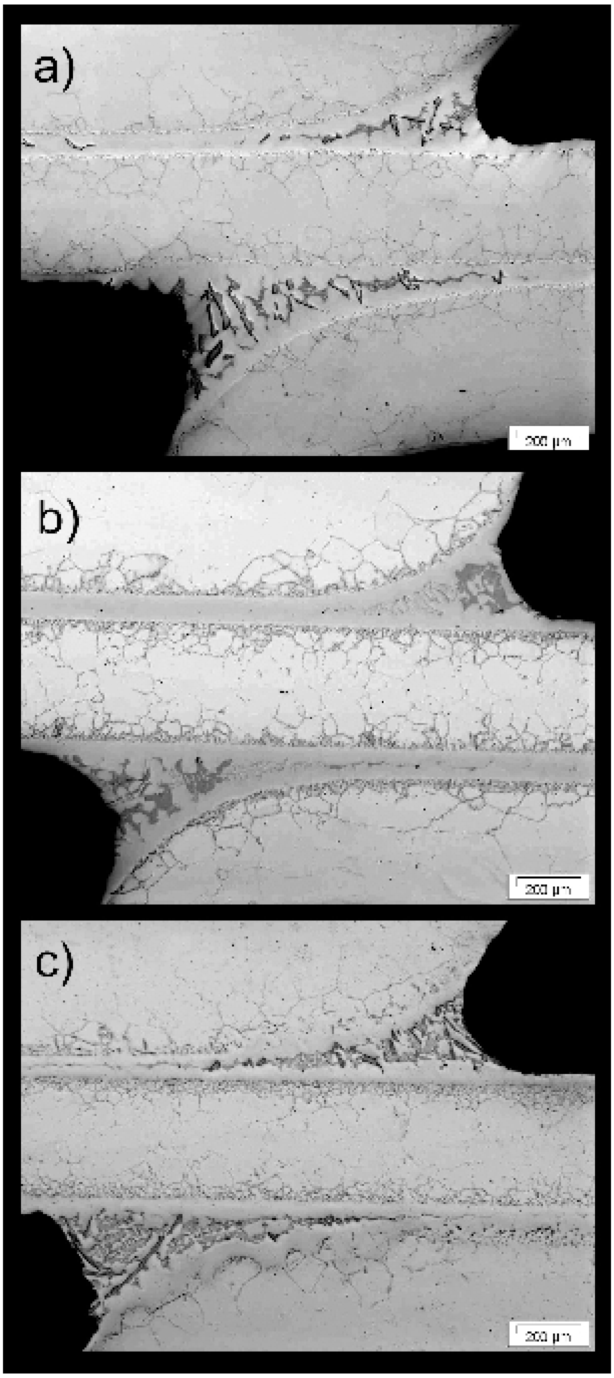

Figure 2: Microstructure of 304 stainless steel/ABF brazed joints taken from industrial plate type heat exchangers. Brazed with 35 µm thick brazing foils at 1195°C for 20 min under vacuum. /a/ BNi-5a (VZ2150) /b/ VZ2106 /c/ VZ2099

To test the strength property of VZ2099 on as brazed stainless steel articles in industrial applications, burst pressure tests on fully brazed industrial plate type heat exchangers were performed. The required burst pressure of these mid size 90 mm x 45 mm x 310 mm heat exchanger is 8 MPa. Brazing was carried out with a short brazing cycle of 20 minutes at 1195°C under vacuum. Foil thickness of the ABF was 0,035 mm. No heat treatment for diffusion of the elements B, Si, P to increase the strength and ductility, was conducted. The heat exchangers brazed with the Phosphorous containing Iron based VZ2099 foil could be pressurized up to 19 MPa before failure, i.e. more than 2 times the required value. The heat exchangers brazed with the phosphorous free ABF's reached 38 MPa in the best cases. Further improvements in strength and corrosion behaviour are achievable by using extended brazing cycles [13] and other special brazing techniques [8].

On micrographs taken from the middle section of these heat exchangers (Fig. 2) we can see that VZ2106 and VZ2099 (Fig. 2b and 2c) have formed sound fillets which are comparable with these formed by a standard BNi-5a alloy (Fig. 2a). A general observation on stainless steel brazed joints made with this new Iron containing ABF's is a greatly reduced tendency to base metal erosion. The cause of this effect could be the Iron/Nickel ratio of these filler metals, which seems to be close to saturation compared to a pure Nickel brazing alloy. Negligible dissolution of Iron from the base metal has occurred to form a Fe/Ni solid solution. These effects could be of interest in case of very lightweight brazed steel structures with very thin base material (BM). Further investigation of this issue is currently in progress.

New Nickel brazing foils for controlled atmosphere brazing of stainless steels

The use of a continuous style, controlled atmosphere brazing (CAB) or 'humpback' furnace to braze stainless steels is becoming more common as the automotive producers increasingly employ brazed stainless steel components. To improve competitiveness, a clear tendency to use such continuous style CAB furnaces instead of vacuum furnaces for high volume production can be seen. These furnaces are capable of producing components at lower capital and operating costs. However, the use of this furnace type to braze oxidation or corrosion resistant stainless steel parts has two associated challenges:

Issue one: This is especially associated with the development of modern, plate type coolers. These coolers, an EGR cooler for example, have a very high efficiency because of their very compact and complex designs. These extremely complex designs result in a lot of internal braze joints. The gas exchange within these very convoluted, internal areas of the cooler is very limited by using a continuous style CAB furnace. This can result in a low quality atmosphere around these joints during brazing. Due to the very limited gas flow around the internal areas of these brazed articles, it is often unsuccessful to use a brazing paste which may form residues during decomposition of the organic components they contain. These residues will be deposited on the walls of the internal structures of the brazed cooler and can cause early life failure due to corrosion problems. This results in a strong need for an organic free, bulk material which acts as filler metal. Amorphous brazing foils do not contain any organics and thus eliminate the corrosion risk.

Issue two: The maximum service temperature of this type of furnace is typically limited to well below 1150°C. A service temperature above the limit would result in massive problems with the belt and the isolation materials of the furnace. Due to this temperature limitation it is not possible to use a high chromium BNi-5a alloy with a typical brazing temperature of 1190°C. But the high corrosion resistance achieved with a BNi-5a alloy is a precondition for some types of EGR coolers. In some cases a BNi-7 alloy (Ni-Cr14-P10 wt.%) with a melting temperature below 950°C can meet the brazing requirements, but there is no industrial source for an ABF of this alloy. This results in a strong need for a novel high chromium and low melting point ABF. For this application Vacuumschmelze developed its new VITROBRAZE VZ2170 (see Table 3). This new ABF having a Ni-Cr-Si-B-P composition containing 21% Chromium. This is the highest Chromium content so far realized on a commercialized Nickel based ABF. Phosphorous containing Nickel brazing alloys are highly suited to brazing jobs carried out under nitrogen containing “low cost” atmospheres like cracked ammonia or forming gas. This fact in combination with the high level of corrosion resistance and the low melting temperature of 925°C makes the VZ2170 brazing foil very unique and well suited for this brazing environment.

Table 3: *Composition and melting range of novel nickel ABF*

	Composition [wt.%]				Melting range [°C]	
Alloy	**Ni**	**Fe**	**Cr/Mo/Cu**	**Si/B/P**	**Ts**	**Tl**
VZ2170	70	-	21	9	880	925

VITROBRAZE VZ2170 has already been used successfully in brazing of many thousands of large EGR coolers where a high level of corrosion resistance is required. Figure 3 shows microstructures of joints taken from those EGR coolers. Smooth fillet formation with no cracks or pores can be observed. Sufficient joint strength for this application was obtained. The ultimate tensile strength of brazed joints was analyzed using a static tensile test. The sample geometry, similar to [13], was a butt brazed

SS316L tensile specimen according to DIN EN 12797:2000. The samples were brazed by using 25 µm and 50 µm thick brazing foils and provides ultimate tensile strength values well above the yield strength of the base metal. Although the filler metal contains Boron, we could not find any noticeable segregation of Chromium borides in the base metal adjoining braze area (white arrows on Fig. 3b and 3c). This is very beneficial for the corrosion resistance of the brazed parts.

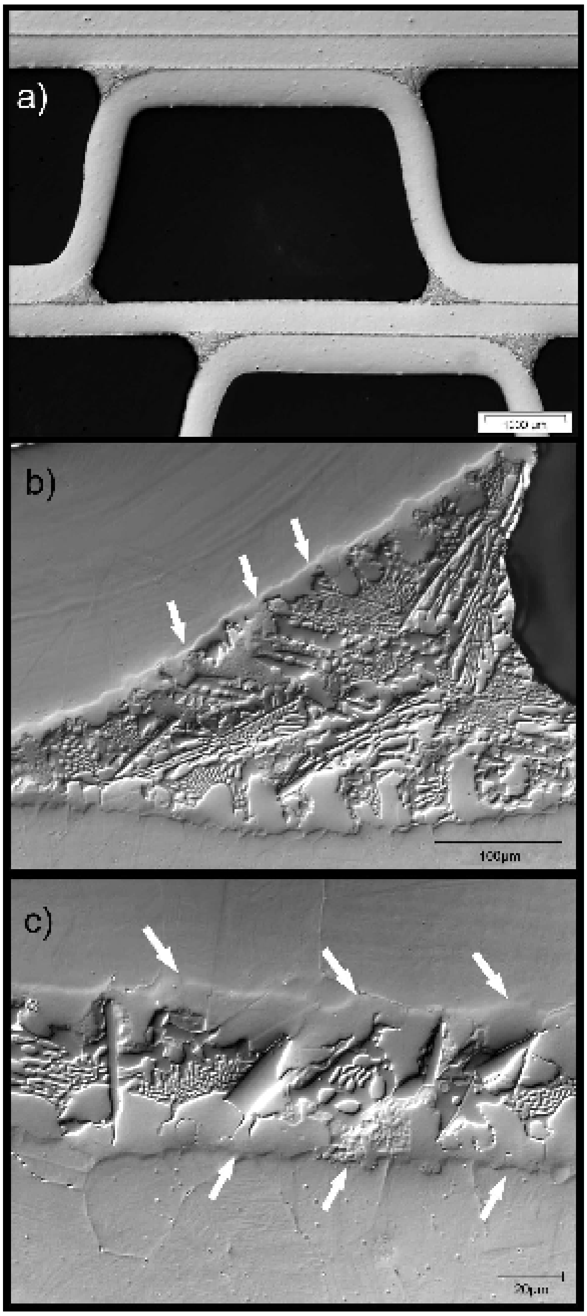

Figure 3: Microstructure of a 316L stainless steel/VZ2170 brazed joint taken from an EGR cooler, brazed with 35 µm thick brazing foil in a conveyer belt furnace. 1050°C for 10 min under pure, dry H_2 atmosphere. /a/ joint overview /b/ central segment /c/ meniscus of the brazed seam. *Note that no excessive boride segregation at the interface and the BM grain boundaries will occur (white arrows).*

Corrosion resistance of these novel ABF's

Only a few investigations relating to the corrosion resistance of joints made with Ni-based brazing filler materials can be found in the literature [9,10]. Basic analysis of the corrosion resistance of such brazing joints will typically be conducted electrochemically using current density-potential-measurements [4,5]. However, practical conditions should generally be favoured, because the corrosion behaviour of a component will be affected from a complex interaction of different conditions between the component and its environment [14]. Within our investigations, samples of the base material 316L (1.4404) joined with different brazing foils were conducted in a quantitative corrosion test. By using this testing procedure the corrosion resistance will be affected not only by the composition of the base material and the BFM´s but also by the quantity of the BFM applied, the size of the area wetted from the BFM, as well as the temperature and time profile of the brazing cycle. The enclosed parameters were kept constant, and the brazing temperature being adapted to the selected BFM. The corrosion media was a synthetic exhaust condensate with a pH-value of 1,6 and sulphate-, nitrate- and chloride ions. The samples were carried out at a temperature of 70°C. After exposure, the weight loss of the brazed samples was measured.

The newly developed brazing foils show a very good corrosion resistance (figure 4b), superior to most of the Standardized Nickel ABF's (figure 4a) and comparable with the values reached with BNi-5a.

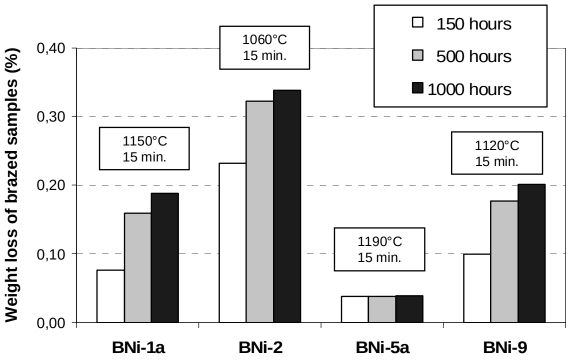

Figure 4a: *Weight loss of brazed 316L / Standard Nickel ABF's samples in artificial exhaust gas condensate.*

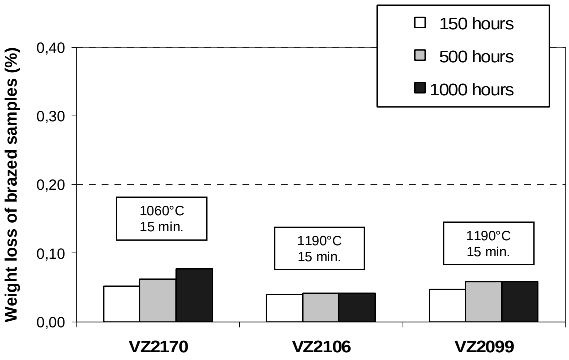

Figure 4b: *Weight loss of brazed 316L / novel ABF's samples in artificial exhaust gas condensate.*

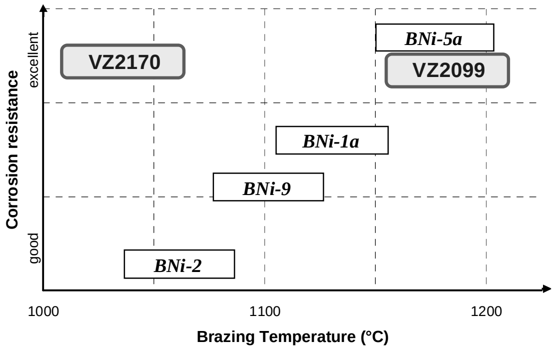

Figure 5 Comparison of corrosion resistance of SS 316 L / ABF brazed joints versus brazing temperature

Despite the new Iron containing alloys VZ2106 and VZ2099 having a lower Chromium content compared to BNi-1a and BNi-9, the corrosion resistance reaches a much better level. This was mainly achieved due to the Iron, Molybdenum and Copper content. Another benefit of these elements is the quite rapid passivation in the corrosion test. These results were confirmed by several test runs. Explanations for the results can be found in the literature dealing with corrosion [11,12].

If Chromium is present in Nickel alloys, additions of Iron have a positive effect on the corrosion resistance of these alloys. Investigation using current density – potential - measurements found a better corrosion resistance in ternary Ni-Cr-Fe alloys compared to binary Ni-Cr-alloys even at far lower Cr contents. Commercial Ni-Cr-Fe alloys have a good resistance to Hydroxides, especially if Sulphur and Chloride ions are present. Furthermore a good corrosion resistance in gaseous halogen compounds, good oxidation resistance, as well as resistance against carburisation and nitrogen absorption are observed. Molybdenum and Copper improve significantly the corrosion resistance of Ni-Fe-Cr alloys. Molybdenum, even in moderate amounts, assists the formation of a stable oxide film in Fe-Cr alloys. It improves the resistance against Chloride ions, sulphur containing media, crevice and pitting corrosion. Additions of Copper in the range of 1-3% lower the active and passive current density and support the effect of Chromium in the described alloys. By lowering of the active current density, an improvement in the corrosion resistance can be expected in oxide and reducing type media. Compared to Ni-Cr-Fe alloys, Ni-Cr-Fe-Mo-Cu alloys are beneficial if mixed-acids like Sulphur and Nitric acids are present [11,12].

The low melting Nickel ABF VZ2170 reached a sufficient resistance towards mixed acids even without additions of Molybdenum, Copper and Iron. Due to this high level of corrosion resistance in combination with the low melting point we can place this unique ABF on the upper left section of a “Brazing Temperature vs. Corrosion Resistance” chart (Fig. 5). VZ2170 is the worldwide first ABF placed in this sector.

Summary

A) New types of ABF’s have been introduced for production of corrosion resistant stainless steel parts like heat exchangers, metallic catalysts and other apparatus. These foils offer unique improvements and advantages over so far standardized amorphous brazing foils.

B) Economical benefits resulting in the use of these novel filler metal foils can be achieved by using (a) the ABF filler metals VZ2106 or VZ2099 with reduced raw material costs or (b) using VZ2170 ABF on “low cost” conveyer belt furnace brazing operations.

C) The corrosion resistance of stainless steel joints brazed with the new alloys is high compared with that of joints brazed with BNi-5a filler metal.

D) A sufficient joint strength for practical application was obtained in the case of stainless steel and these new filler metals.

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