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Further Developments in Boron Free Nickel-Chromium-Phosphorus-Silicon Brazing Filler Metals

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Further Developments in Boron Free Nickel-Chromium-Phosphorus-Silicon Brazing Filler Metals

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Abstract

Ni-Cr-Si-P brazing filler metals are widely used and are of particular importance in the manufacture of Exhaust Gas Recirculation (EGR) units, Heat Exchangers and Catalytic Converters. Succeeding generations of EGR coolers have trended towards operation at higher temperatures. It is expected that evolving designs will require improved performance from the Brazing Filler Metal (BFM) including high temperature strength. Modern EGR designs employ thinner wall sections and more variable gap tolerances than previous models. Consequently, it is essential that the braze filler metal provides good flow, gap filling performance with minimal erosion in addition to adequate high temperature performance characteristics. Corrosion resistance and mechanical strength are fundamental requirements of the braze filler metal. The current work investigates the influence of solid solution strengthening additions such as molybdenum, tungsten and cobalt within boron-free BFMs and assesses the wetting properties, gap filling ability, corrosion resistance and tensile strength at elevated temperatures. Comparisons will be made against traditional and recently developed BFMs such as Nicrobraz[®] LM (AWS BNi-2) and Nicrobraz[®] 33.

Introduction

The use of boron as a major melting point depressant in high temperature brazing filler metals is well known as is its impact in terms of base metal erosion. Replacing boron with other melting point depressants can reduce the level of erosion experienced when brazing components of thin sections [1]. Ni-Cr-P-Si BFMs are known to exhibit good wetting and flow characteristics in both vacuum and protective atmosphere brazing processes [2].

The current work considers the addition of solid solution strengthening elements such as cobalt as a single element addition and molybdenum, tungsten, and cobalt as a multi-element addition to the braze filler metal. This work assesses the impact of these alloying additions on the brazing action and the properties of the brazed joint.

This paper compares in detail the brazing characteristics, mechanical and corrosion properties of two modified brazing filler metals with Nicrobraz[®] 33 and AWS BNi-2 (Nicrobraz[®] LM). The effectiveness of the solid solution strengthening agents will be assessed and the properties observed explained.

Four brazing filler metals with the nominal compositions shown in the Table I have been evaluated.

Table I: Brazing filler metal alloy nominal chemical compositions.

BFM	Ni	Cr	B	Si	P	Mo	W	Co	Cu	Fe
AWS BNi-2	bal	7	3.1	4.5						3
Nicrobraz [®] 33	bal	29		6.5	6					
EXP 390	bal	30		6.5	6	2	4	10	2	5
EXP 391	bal	35		5.0	6			13		5

The powders were manufactured by induction melting and gas atomization, and screened to AMS/AWS 140F (-106 μ m) particle size distribution.

The following tests were carried out:

1. Melting ranges were determined by Differential Thermal Analysis (DTA) and Cooling Curve.
2. Furnace brazing trials including gap filling performance tests were completed.
3. Tensile testing of butt brazed joints at room temperature and elevated temperature of 910°C was completed.
4. Corrosion resistance comparison in accordance with VDA 230-214 was performed.
5. Filler metal aggression testing was completed.
6. Metallographic examination was performed on all samples.

Results

Melting Characterization and Brazing Temperature Determination

Differential Thermal Analysis (DTA) testing involves the heating or cooling of a test sample and a known reference sample under identical conditions while recording any temperature difference between the sample and the reference. Differential temperature rises that occur during the thermal cycle between the test and reference samples allows determination of the solidus and liquidus temperatures.

In the case of the BFM under investigation, DTA testing and direct cooling curve plots produced a solidus and liquidus temperature estimate for each alloy.

These values are presented in Table II while Figures 1 and 2 show the test data for specific lots of the EXP 391 and EXP 390 BFM's.

Table II: DTA analysis from the brazing filler metal powders showing the solidus and liquidus estimations.

BFM	Solidus Heating / Cooling	Liquidus Heating / Cooling	Solidus Heating / Cooling	Liquidus Heating / Cooling
	°F		°C	
AWS BNi-2	1780	1830	970	1000
Nicrobraz [®] 33	1815/1779	1879/1862	991/971	1026/1017
EXP 390	1814/1769	2152/2070	990/965	1178/1132
EXP 391	1895/1859	1972/1924	1035/1015	1078/1069

The solidus temperatures on heating and cooling for AWS BNi-2, Nicrobraz[®] 33 and EXP 391 are broadly similar whilst the EXP 390 has a higher value. The liquidus temperatures of the EXP alloys 390 and 391 are much higher than those of AWS BNi-2 and Nicrobraz[®] 33.

DTA has shown marked differences between the EXP 390 and 391 alloys in terms of both the melting range and also the melting / freezing events observed. The EXP 390 alloy has an extended melting range while the EXP 391 alloy exhibits a relatively narrow melting range (Figures 1 and 2).

While solidus temperature is considered the minimum temperature for liquid-solid diffusion interactions to occur, the liquidus represents the point at which good capillary flow can take place with wide solidus/liquidus ranges often indicating the ability to fill larger joint clearances.

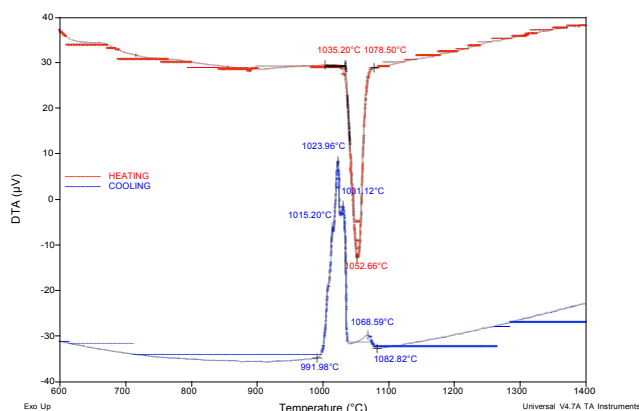


Figure 1: Differential Micro Volts versus Temperature DTA for alloy EXP 391

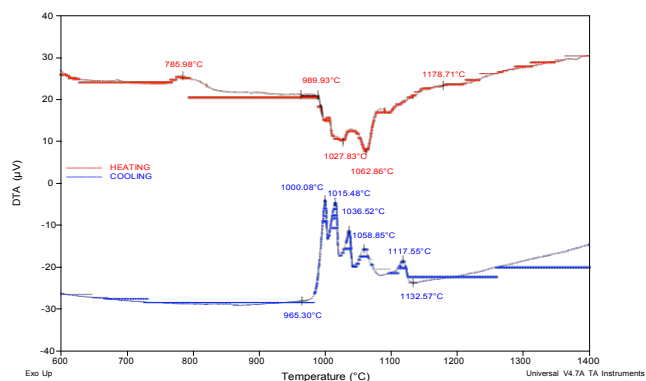


Figure 2: Differential Micro Volts versus Temperature DTA for alloy EXP 390

The brazing temperatures were determined from the DTA data and visual examination of brazed T-Specimens [3]. The temperature ranges for brazing these alloys are shown in Table III.

Table III: Recommended brazing temperature for the brazing filler metal powders.

Alloy	Recommended brazing range	
	°F	°C
AWS BNi-2	1850 - 2150	1010 - 1175
Nicrobraz [®] 33	1950 - 2150	1066 - 1177
EXP 390	1980 - 2210	1082 - 1210
EXP 391	1980 - 2084	1082 - 1140

It should be noted that there is no specific temperature for brazing. Each combination of parts assembly and brazing filler metal is unique and will have a brazing “window” bounded by time, temperature, atmosphere and fixturing conditions.

Joint Gap Filling Capability

The joint gap filling characteristics of these brazing filler metals were investigated using 316L stainless steel test pieces with a varying gap shown in Figure 3. The samples were brazed at a temperature of 2000°F (1093°C). The filling characteristics for each alloy were measured and the results are presented in Table IV.

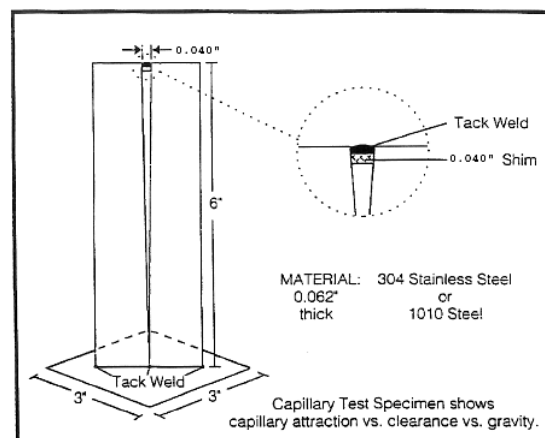


Figure 3: Variable clearance test fixture with vertical orientation. The setup is constructed so there is zero clearance at the base of the v-joint. (Adapted from R. L. Peaslee [4])

Table IV: Maximum gap filling performance of brazing filler metals tested.

Filler Metal	Maximum Gap Clearance (inch)	Maximum Gap Clearance (mm)
EXP 390	0.024	0.61
EXP 391	0.016	0.41
Nicrobraz [®] 33	0.017	0.43
AWS BNi-2	0.022	0.56

Both of the experimental braze filler metals demonstrate good gap filling characteristics which are comparable with or better than the established alloys. The EXP 390 alloy provides the best vertical gap filling capability.

Wettability on 316L Stainless Steel Base Metal

Spreading ratios may be used as an indication of wettability [5]. A spreading test was performed by applying 0.2 g of filler metal near the center of a 1.5"x 1.5" 316L stainless steel coupon and heating in a vacuum furnace to 2000° F (1093°C) for 15 minutes at 10⁻⁴ to 10⁻⁵ torr. The test samples are shown in Figure 4 and comparison data is presented in Table V.

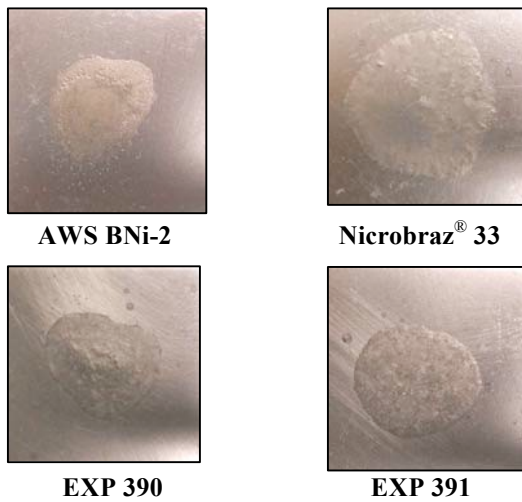


Figure 4: Wetting Tests for Nicrobraz[®] 33, AWS BNi-2, EXP 390 and EXP 391

Table V: Wetting Test Results

Filler Metal	Spreading Area
AWS BNi-2	0.42 in ²
Nicrobraz [®] 33	0.88 in ²
EXP 390	0.48 in ²
EXP 391	0.55 in ²

The test demonstrates the wetting behavior of the filler metals on stainless steel under given furnace atmosphere conditions and provides a basis for comparison. Compared with the boron containing AWS BNi-2 (Nicrobraz[®] LM) the experimental alloys reveal improved fluidity under these brazing conditions. However, neither of the experimental alloys wets out as well as the Nicrobraz[®] 33 material.

Filler Metal Aggression

Filler metal aggression tests were carried out on 316L stainless steel where dilution depth was used to provide an indication of base metal erosion potential. The test coupon design is presented below (Figure 5).

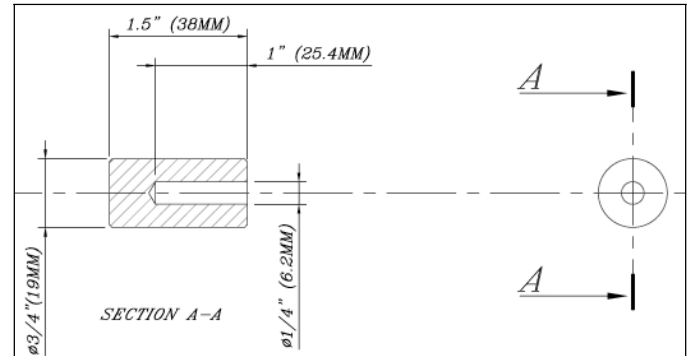


Figure 5: General arrangement of the aggression test coupon.

Adapted from [6].

The aggression tests were conducted at 2000° F (1093° C) for 60 minutes in a vacuum furnace at 10⁻⁴ - 10⁻⁵ torr. After brazing the samples were sectioned and the dilution depth measured optically, the results are presented in Table VI.

Table VI: Dilution depth over an extended period at 2000°F (1093°C) for one hour with 316L stainless steel base metal.

Filler Metal	Dilution Zone Depth (inches)	Dilution Zone Depth (mm)
AWS BNi-2	0.0034	0.09
Nicrobraz [®] 33	0.0049	0.13
EXP 390	0.0033	0.08
EXP 391	0.0042	0.11

The results are generally similar. However, it is clear that both of the experimental alloys produced less dilution than Nicrobraz[®] 33 indicating that both the EXP alloys are less erosive, under these brazing conditions, than Nicrobraz[®] 33.

AWS BNi-2 would be expected to exhibit the highest propensity for erosion (aggression) [1]. This was not found under the given test conditions. Although it was not studied, the authors believe that further diffusion of boron into the base metal became limited due to the relatively long time at temperature and saturation of base metal grain boundaries with boron thus changing the diffusion mechanism and rate over time (Figure 6). Diffusion reaction kinetics are believed to be such that with a shorter time at temperature the AWS BNi-2 would have caused relatively more erosion than the other filler metals under the same conditions of time and temperature.

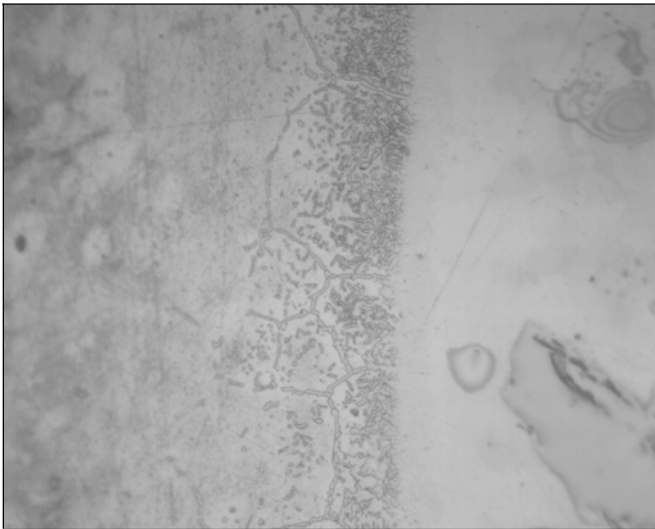


Figure 6: Micrograph showing 316L (left) and BNi-2 (right) interface after filler metal aggression test (original at 500x, etched with marbles reagent).

Joint Tensile Strength

The four brazing filler metals were used to make butt brazed test specimens as per AWS C3.2M/C3.2:2008 [7]. The base metal assembly samples were fixed by tack welding to set a 0.002" joint gap. Brazing of the samples was carried out at 2000°F (1093°C) for 60 minutes in vacuum atmosphere of 10^{-4} torr or lower.

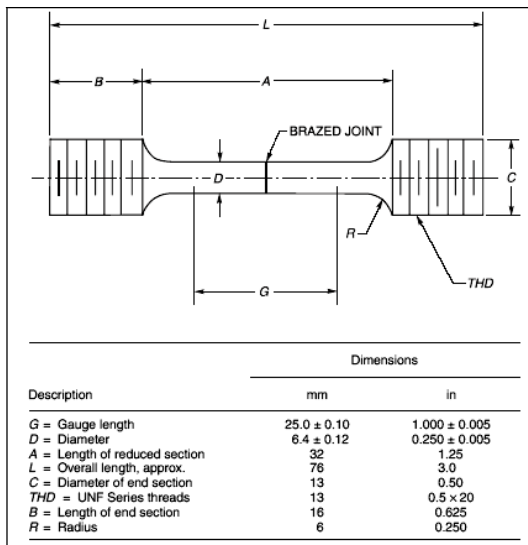


Figure 7: General arrangement of the butt-brazed specimen [6].

The butt joint samples (Figure 7) were subjected to tensile testing in accordance with ASTM E 8-09 and AWS C3.2:2008. Series of butt joint samples were tested at both room temperature and an elevated temperature of 1670°F (910°C) for each of the BFMs. A crosshead speed of 0.2 in / min was used throughout the testing. Figure 8 details the results of the room temperature tests and Figure 9 the elevated temperature tensile tests.

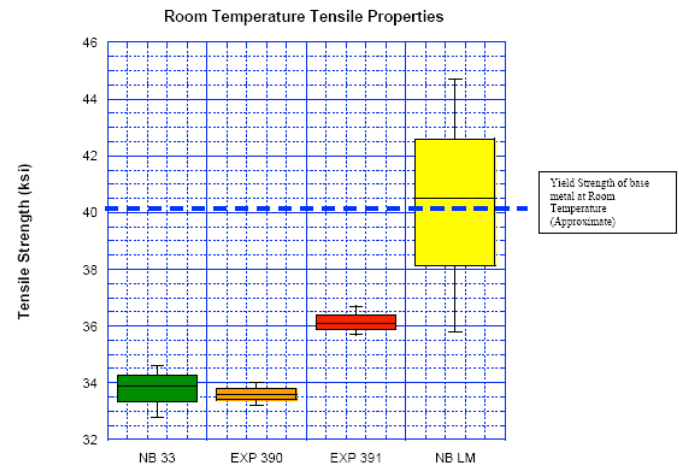


Figure 8: UTS achieved on 316L butt joint test pieces at room temperature for Nicrobraz[®] 33 (NB 33), EXP 390, EXP 391, and AWS BNI-2 (NB LM).

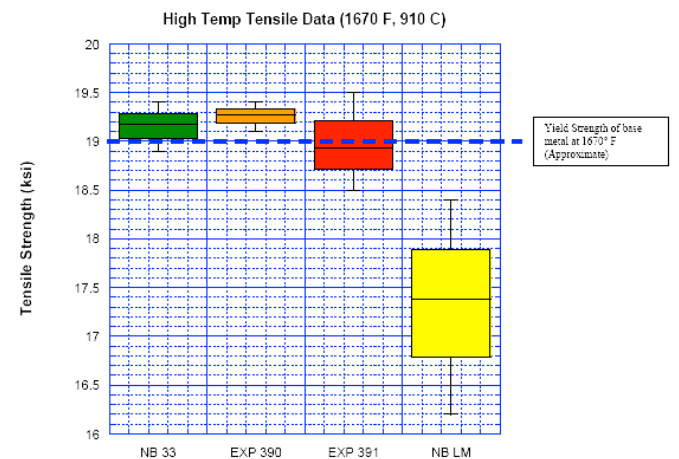


Figure 9: UTS achieved on 316L butt joint test pieces at 910°C for Nicrobraz[®] 33 (NB 33), EXP 390, EXP 391, and AWS BNI-2 (NB LM).

The boron containing AWS BNi-2 (NB LM) gave the highest room temperature UTS result with the two experimental alloys similar or better than the Nicrobraz[®] 33. However, the Ni-Cr-Si-P base BFM's demonstrated higher tensile strengths than the Ni-Cr-B-Si alloy at the higher testing temperature of 910°C. Both of the experimental alloys compared favorably with the Nicrobraz[®] 33 material with the EXP 390 BFM providing very consistent results at both testing temperatures.

Corrosion Resistance

304 Stainless Steel (SS) T-specimens were vacuum brazed at 1093°C for 1 hour prior to corrosion testing in accordance with VDA Standard [8]. A photographic representation of a brazed t-specimen for each BFM is presented in Figures 10a - 10d.



Figure 10a: EXP390 Brazed T-specimen



Figure 10b: EXP391 Brazed T-specimen

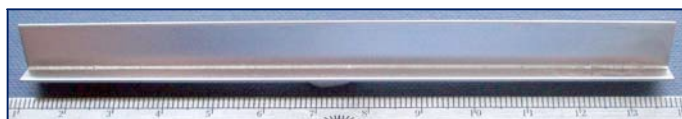


Figure 10c: Microbraz[®] 33 Brazed T-specimen



Figure 10d: AWS BNi-2 Brazed T-specimen

All of the representative filler metals showed very good flow and gap filling capabilities (Figures 10a – 10d) however, strong indication of alloy liquation appear within the filler metal application area for EXP 390 (Figure 10a).

An illustration representing the 7 day test sequence using test condensate K2.1 (Table VII) is shown in Figure 11.

Table VII: VDA Corrosion Test K.2.1 Solution Composition.

Test Condensate Per VDA 230-214	Composition
K2.1 (PH 3.5) Moderate System	4.4% (vol.) Acetic Acid (100%) 4.9% (vol.) Formic Acid (98-100%) ~1.6% (wt.) Sodium Chloride (10 ppm equivalent Chloride)

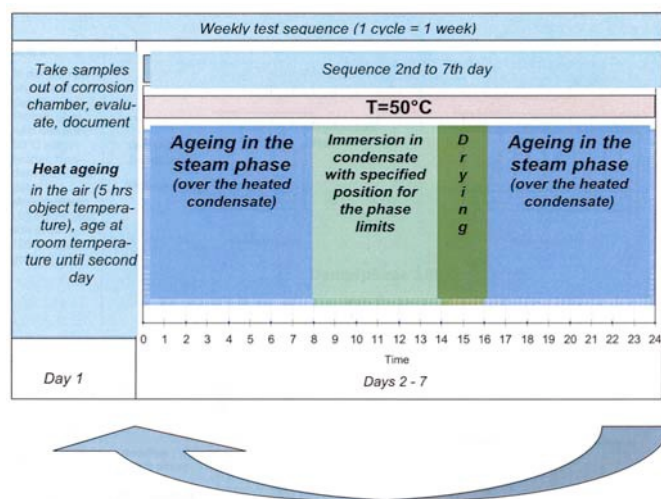


Figure 11: 7 day corrosion test sequence

This VDA test aims to provide information about a test materials tendency to show corrosive reactions when exposed to exhaust gases by using specific test technology [8] and synthetic exhaust gas condensates such as K2.1. It should be

noted that the implementation of the laboratory trials described in the test standard cannot substitute for actual component behaviour under actual field conditions.

The sample surface condition prior to testing is shown in Figure 10a-10d and the resulting T-specimens following corrosion testing are presented in Figure 12a-12d.



Figure 12a: EXP390 Brazed T-specimen after corrosion testing



Figure 12b: EXP391 Brazed T-specimen after corrosion testing



Figure 12c: Microbraz[®] 33 Brazed T-specimen after corrosion testing



Figure 12d: AWS BNi-2 Brazed T-specimen after corrosion testing

Each representative corrosion test T-specimen was subject to cross-sectional examination using an Olympus CH-2 optical light microscope. With the exception of BNi-2, each BFM fillet appeared unaffected following the VDA 7 day corrosion cycle and an example taken from a Microbraz[®]33 T-specimen is presented in Figure 13.

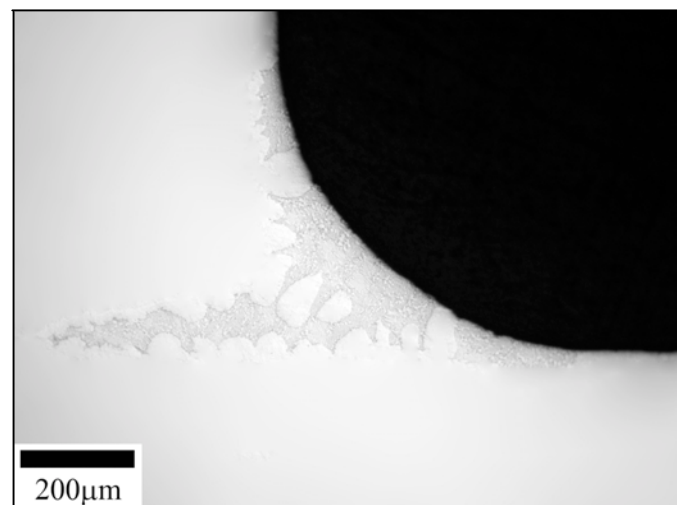


Figure 13: Microbraz[®] 33 Braze fillet appearance after corrosion testing (x100 magnification)

The microstructural appearance of the BNi-2 fillet following the VDA corrosion test is presented in Figure 14.

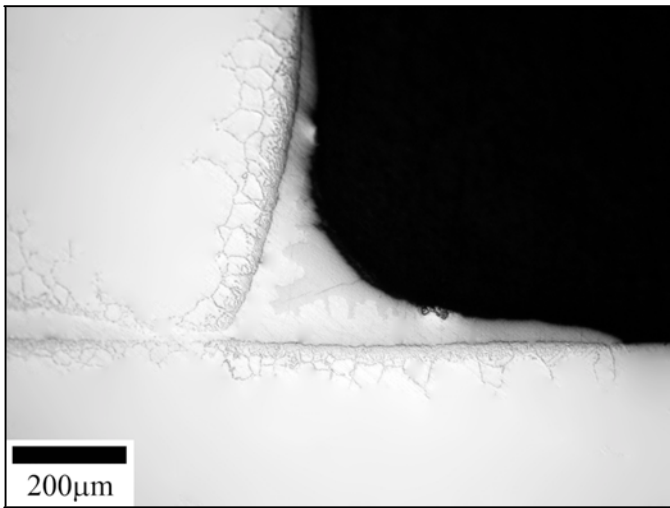


Figure 14: AWS BNi-2 Braze fillet appearance after corrosion testing (x100 magnification)

The BNi-2 post corrosion test microstructure is noticeably different to that observed from the other representative BFMs. In this instance, the BNi-2 braze fillet appears to show signs of chemical degradation. Chromium depletion within the base material due to boron grain boundary diffusion from the BFM may have also diminished the corrosion resistance of the stainless steel substrate material.

Metallographic Examination

Sections for metallographic examination were cut from brazed T-specimen, mounted, polished, and photographed Figures 15 - 18.

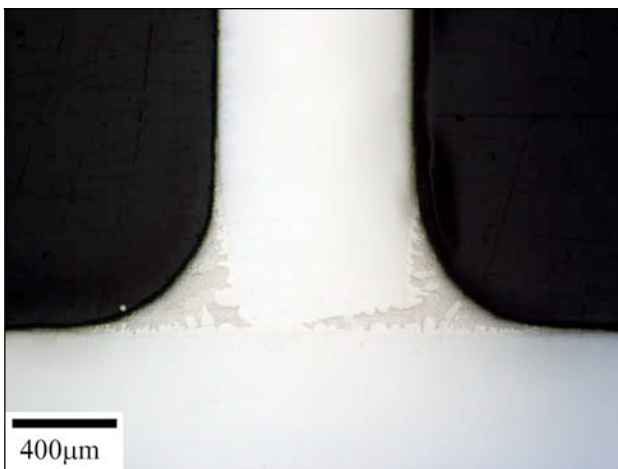


Figure 15: Microstructure from T-specimen cross section Nicobraz[®] 33.

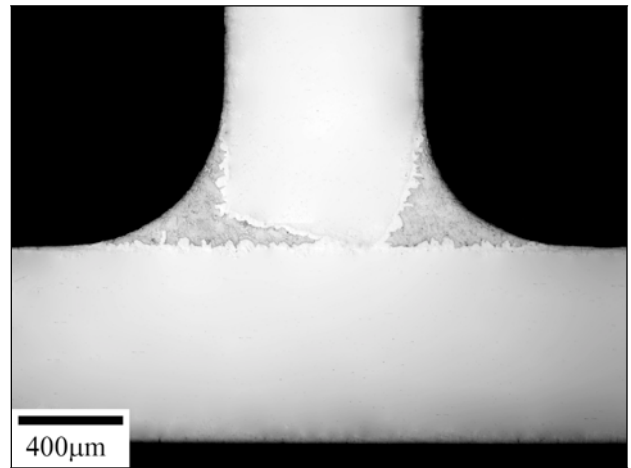


Figure 16: Microstructure from T-specimen cross section EXP 391.

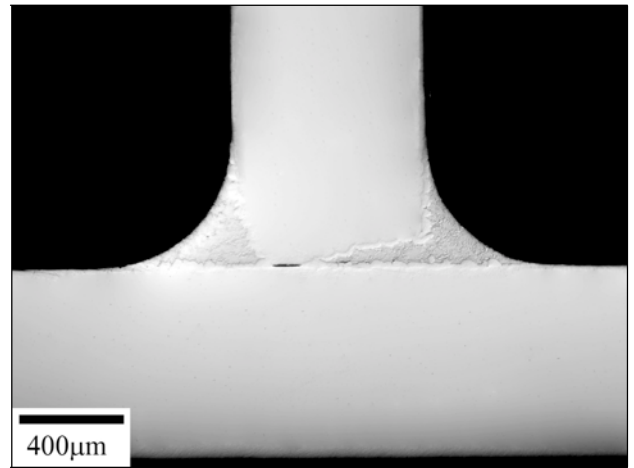


Figure 17: Microstructure from T-specimen cross section EXP 390.

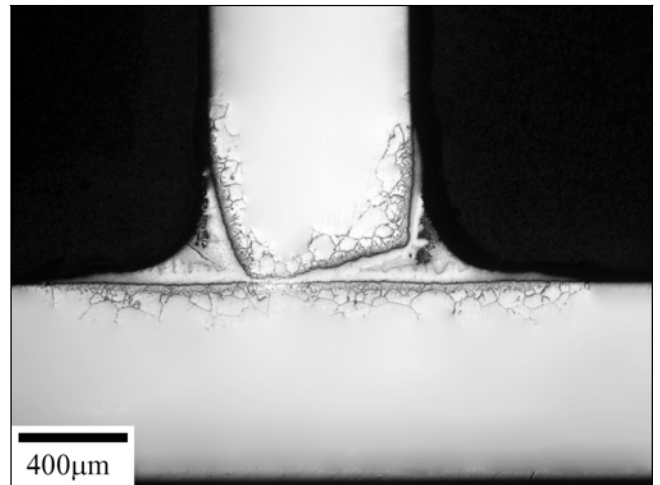


Figure 18: Microstructure from T-Specimen cross section AWS BNi-2.

With the exception of AWS BNi-2 (Figure 18), relatively low levels of T-specimen base metal erosion were witnessed with the other candidate BFMs (Figures 15 – 17). The Nicrobraz[®] 33 (Figure 15) lathe-like structure is known to comprise Cr-Ni-P rich phases within a Cr-Ni rich matrix. Each braze fillet appears to comprise combinations of matrix and precipitation phases which will be determined following further work involving SEM/EDX spot chemical microanalysis.

Discussion

In order to provide the reader with as much information as possible within the scope of this work, a wide variety of tests were performed and the resulting data presented. While no work of this type can be 100% comprehensive, it is the authors desire to encourage designers to incorporate the use of brazing as a joining process into their designs. Understanding the metallurgy, capabilities and limitations associated with brazing should aid in this endeavor.

This evaluation of the addition of solid solution strengthening elements to provide improved joint strength was quite limited in the scope of filler metal alloys tested. Work could have proceeded by testing the mechanical properties of the filler metal alloys in cast form. This avenue was not pursued because, when used to join parts by brazing the filler metal itself, as well as the base metal, are changed during the brazing cycle through diffusion processes. Therefore, testing was conducted on brazements rather than the filler metal alloy itself.

EXP 390 with additions of Mo, W, Co and Cu was expected to demonstrate very high strength braze joints. Although the joint strengths measured were quite good (approaching the yield strength of the base metal) this filler metal exhibits substantial liquation. The difference between solidus and liquidus temperatures is wide for this alloy (compared to the others tested, see Table VIII) and DTA shows multiple phase change or reaction events in this region. Examination of brazed specimens show that the liquid phase separates from the solid phases during heating to the brazing temperature and flows prior to complete melting of entire filler metal alloy. Thus, a joint is formed that is not necessarily composed of the initial filler metal composition. No attempt was made to quantify this phenomenon.

Table VIII: Range of melting behavior by DTA

Filler Metal	Difference Between Liquidus and Solidus (During Heating by DTA)
AWS BNi-2	50° F
Nicrobraz [®] 33	64° F
EXP 390	338° F
EXP 391	77° F

It is anticipated that the liquated portion of EXP 390 approaches a near eutectic (low melting) composition for the Ni-Cr-P-Si-Mo-W-Co-Cu-Fe alloy system. The remaining filler metal is likely depleted (or enriched) of silicon and phosphorus during liquation and its melting point increased further.

EXP 391 exhibits much more normal melting characteristics. The addition of 13% Co and 5% Fe to the Nicrobraz[®] 33 composition improves its room temperature tensile strength under the given brazing conditions.

The solid solution strengthening elements being evaluated in the two EXP alloys are compared to AWS BNi-2. BNi-2 contains boron. In addition to depressing the melting point in nickel alloys, boron is also a potent hardener. Boron is a small atom relative to the transition metals. In addition to forming hard boride phases, it is expected to reside interstitially (similar to C or N) when in solid solution. Elements such as Co, Mo, W and Fe are expected to reside substitutionally in a solid solution. Strengthening effects vary as a function of the difference between solvent and solute atomic radii [9]. Interstitial solute atoms can have very strong hardening/strengthening effects compared to substitutional solute atoms [10]. It is expected that interstitial hardening or strengthening mechanisms are more pronounced than substitutional mechanisms and lead to more brittle modes of failure.

Strong hard-phase forming elements such as boron in nickel alloys with chromium yield filler metals which have pronounced hard centerline phases. These hard phases, if not precluded from forming by allowing for full diffusion of boron, can promote brittle behavior and/or premature failure [11].

Evaluation of wetting characteristics and gap filling capabilities of new filler metals provides evidence of the filler metals ability to be used to join parts. Assembly parts fabricated for mass production may have tolerances which preclude the desirable close fit up beneficial to joining by brazing. Geometry may also limit the points to which filler metal may be applied. These reasons demonstrate why good flow and gap filling abilities are needed for mass production. Good wettability and strong capillary actions at the brazing temperature indicate the best opportunity for forming sound braze joints.

Along with the ability to form a sound braze joint the filler metal must also form a joint which is suitably durable for the service environment and conditions. This includes dynamic loading, temperature and the presence of corrosive media. Therefore, having a base-line performance indicator for tensile and shear strength along with corrosion resistance is important for the design engineer.

Conclusions

- 1.) The melting range of filler metals will be affected by additions of solid solution strengthening elements. Careful control of additions can be made to avoid having too wide of a melting range thus avoiding liquation phenomena.
- 2.) Wide gaps, in excess of 0.010" can be filled by capillary action under good brazing conditions with the filler metals tested.
- 3.) a.) Room temperature tensile strength of butt joints brazed with Ni-Cr-P-Si filler metal can be improved marginally by the addition of cobalt.

b.) At 1670°F filler metals of Ni-Cr-P-Si approach the yield strength of the 316L stainless steel used regardless of solid solution strengthening elements in the range tested.
- 4.) With the exception of AWS BNi-2, the other candidate BFM's appeared unaffected following the 7 day VDA corrosion test cycle.
- 5.) Filler metal aggression tests indicate that when brazing thin sections of base metal with any of the tested filler metals, careful control of brazing cycle will be required to minimize erosion of the thin section by the filler metal.
- 6.) Metallographic examination show low levels of base metal erosion using the non-boron containing BFM's. Further work involving SEM/EDX analysis will help to determine the compositional phase variations of each of the representative BFM's included in this investigation.

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