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Novel, high chromium containing braze filler metals for heat exchanger applications

A new family of boron-free, high chromium containing braze filler metal compositions were developed. Filler metal properties including metallurgical phases, melting range, flow, corrosion resistance and high temperature oxidation resistance are reported. Additionally, the technical and economical advantages of using these new filler metals in fabricating flat plate type of heat exchangers and metallic catalytic converters are discussed.

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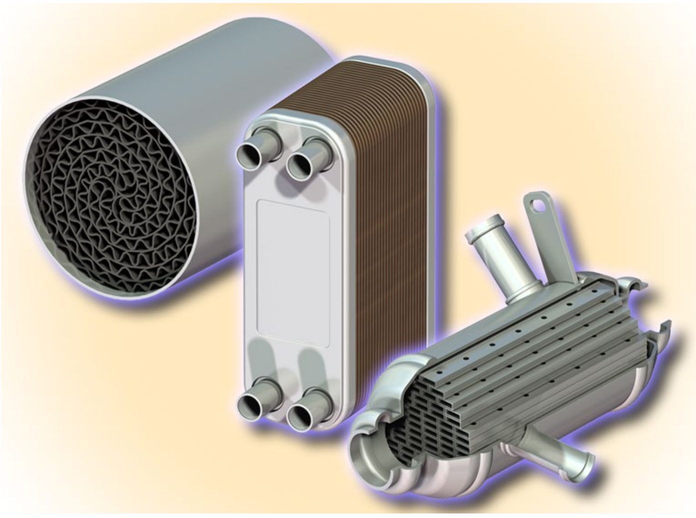
Introduction

Nickel-based braze Filler metals are widely used for brazing high temperature plate type heat exchangers and metallic catalytic converters in automotive applications. The recent emission / gas regulations and the development of efficient EGR coolers by the automotive industry require filler metals with an increased resistance to high temperature oxidation and corrosive atmospheres.

Many of the conventional braze filler metals used for these applications have technical limitations. BNi-2 braze filler metal, for example, contains a relatively high amount of boron as an alloying element [1]. During the brazing process, the boron diffuses into the thin stainless steel sheet metal and subsequently reduces its strength. For this reason, boron-free filler metals are required for brazing many stainless steel heat exchangers. Although another conventional filler metal, BNi-5, does not contain any significant amount of boron, it has a relatively high melting point. This induces grain growth in the stainless base metals during the brazing cycle, which may degrade the strength of the sheet metal after brazing is completed.

Whether boron-free or not, many of the above-mentioned conventional braze filler metals contain a high percentage of nickel. Extreme volatility in the price of nickel has significantly affected the cost and affordability of conventional braze filler metals. This effort was directed towards developing new braze filler metals to overcome some of the technical and commercial limitations of conventional nickel base filler metals.

Three new compositions were developed:
a) Nichrome-based Amdry™ 105;
b) Inconel-based Amdry 108 and
c) High chrome, stainless-based Amdry 805.



All of the compositions contain high amounts of chromium (at least 23 weight percent) and employ controlled amounts of silicon and phosphorus alloying elements to depress the melting points.

The remainder of this paper presents the details of these filler metals and results of laboratory evaluations. Based on the results, it has been determined that these new filler metals could offer technical and commercial advantages in the manufacture of brazed stainless steel heat exchangers and metallic catalytic converters.

New filler metal compositions

Table 1 shows the nominal chemical composition (in weight percent) of Amdry 105, Amdry 108 and Amdry 805. It should be noted that all three filler metals are boron free and contain at least 23 percent of chromium. Carefully controlled amounts of silicon and phosphorus have been utilized as melt depressants in all cases. While Amdry 105 contains no iron in its composition, Amdry 108 contains approximately 15 weight percent iron in its formulation. This partial substitution of iron was made in Amdry 108 to determine if a nominal cost savings could be accomplished without significantly affecting brazeability and high temperature performance. On the other hand, Amdry 805 is a stainless steel-base alloy with a small amount of nickel (15 weight percent) contained in it. This addition of nickel in Amdry 805 was made to optimize the melting point as well as to retain the austenitic phase structure in the alloy. Metallographic examinations of all the filler metals were performed on solid buttons prepared by melting the powder in a ceramic crucible in a vacuum furnace. Cross sections of the melt buttons were prepared by grinding , polishing and etching prior to examination under an optical microscope. The nickel based filler metals were electrolytically etched with a solution of 100 ml ethanol, 10 ml of hydrochloric acid and 5 ml of nitric acid. The stainless steel based alloy, Amdry 805, was electrolytically etched with an aqueous solution of ten percent potassium hydroxide.

Optical micrographs revealed three distinct phases in each of the alloys: a matrix phase, a primary precipitated phase and a eutectic-like structure. These are shown for each of the alloys in Figures 1 through 3.

	Ni	Cr	Fe	Si	P
Amdry 105	Balance	23	0	6.5	4.5
Amdry 108	Balance	23	15	6.5	4.5
Amdry 805	15	29	Balance	6.5	6.5

Table 1. Nominal Chemical Composition (wt %)

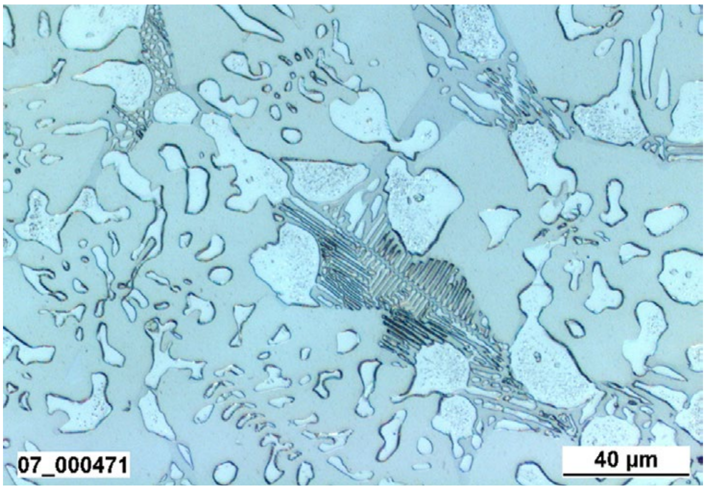


Figure 1. Amdry 105 electrolytically etched with a solution of 100 ml methanol with 10 ml hydrochloric and 5 ml nitric acids

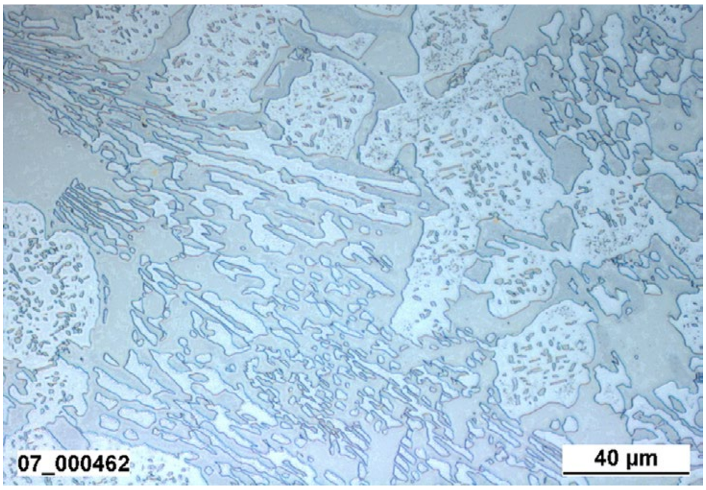


Figure 2. Amdry 108 electrolytically etched with a solution of 100 ml methanol with 10 ml hydrochloric and 5 ml nitric acids

Metallurgical phase analysis was done using a combination of XRD and SEM-EDAX analysis. The XRD scan provided only limited data due to the non-availability of proper standards. Therefore, semi-quantitative elemental analysis was performed on several similar phases in the SEM microstructure as shown in Figures 4 through 6. Identification of phases based on the combined information from XRD and the elemental analysis is shown in Tables 2 through 4.

Amdry 105 contains three major phases — a nickel-chrome-silicon–rich matrix, and two major phases — a nickel-chrome silicide and a chrome- nickel silicide. The eutectic-like phase appears to contain both a Ni-Cr-silicide and a phosphorus-rich Ni-Cr-P-Si phase.

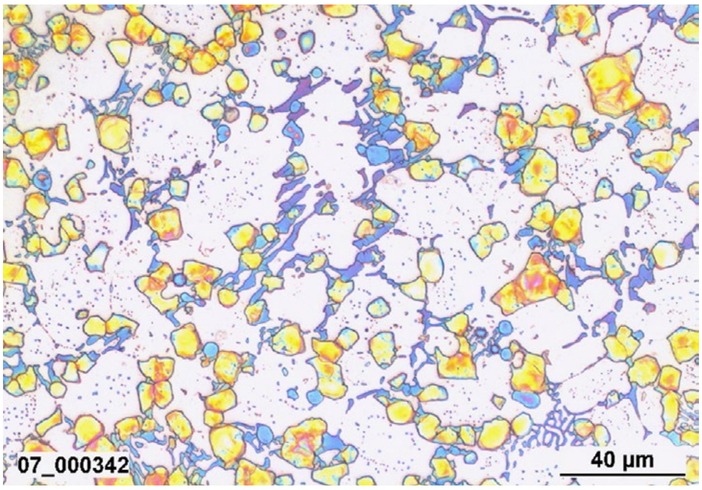


Figure 3. Amdry 805 electrolytically etched with an aqueous solution of 10 % potassium hydroxide

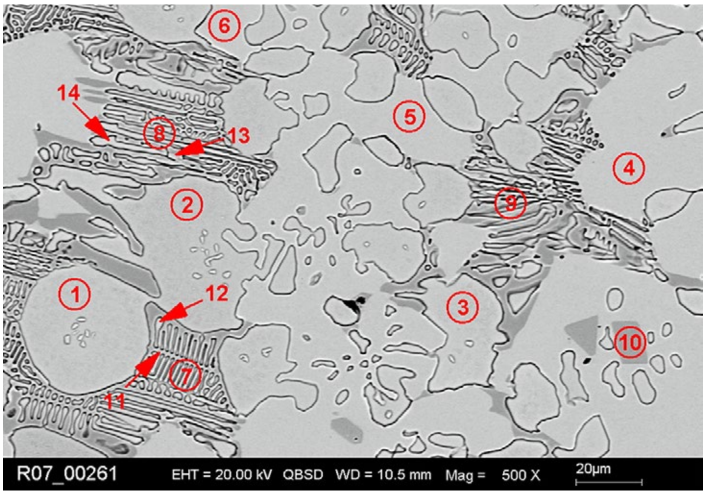


Figure 4. SEM Microscopy of Amdry 105

	Elemental Composition (wt %)				
Phases	**Ni**	**Cr**	**Si**	**P**	**Phase Identity (XRD Analysis)**
Matrix (4, 5, 6)	67	17	11	6	γ-Matrix; a = 11.06 deg A
Major precipitate (1, 2, 3)	67	26	5	0.5	Ni16-Cr6-Si7 phase cubic a = 3.549 deg A
Minor precipitate (10)	38	51	9	1	Cr-Ni-Silicide phase
Eutectic – overall (7, 8, 9)	48	34	2	14	Ni-Cr-Si and Ni-Cr-P-Si phases
Eutectic – comp. 1 (11, 12)	67	27	3.7	0.5	Ni16-Cr6-Si7 cubic phase
Eutectic – comp. 2 (13, 14)	45	33	3.1	18	Ni-Cr-P-Si phase

Table 2. Amdry 105 Phase Analysis

Amdry 108, which contains 15 weight percent iron in the chemical formulation, has a similar microstructure — a nickel-based matrix with significant amounts of Cr and Si, a major phase of NiCrFe silicide and a eutectic structure comprised of a silicide and a CrNiP phase.

Amdry 805 appears somewhat different. It contains a FeCr-rich gamma matrix, a major phase comprised of a FeCrNiP composition and at least two more minor phases which appear to be a combination of a silicide and a phosphorus-rich phase.

From the above, it appears that all phases, including the matrix, contain significant amounts of chromium. The relatively small amounts of phosphorus in all the microstructures appears to be tied up as compounds containing high amounts of chromium.

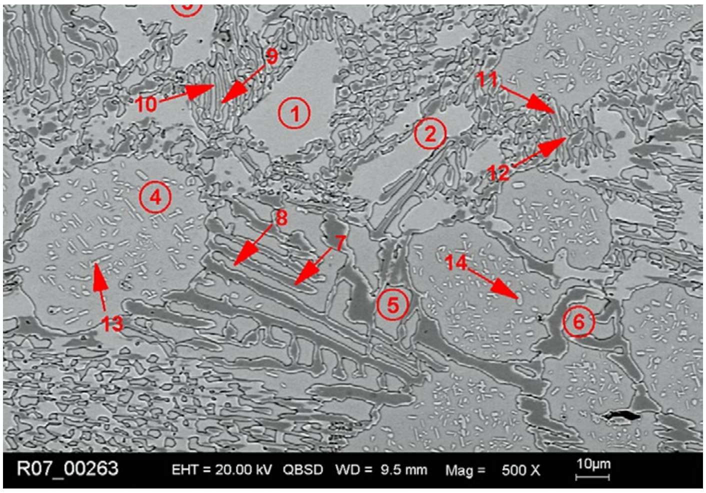


Figure 5. SEM Microscopy of Amdry 108

	Elemental Composition (wt %)					
Phases	Ni	Cr	Fe	Si	P	Phase Identity (XRD Analysis)
Matrix (1, 2, 3)	62	17	3.5	12	5	Cr-Si–rich matrix
Major phase (4, 5, 6)	54	22	18	5	–	Ni-Cr silicide
Eutectic – comp. 1 (7)	54	21	18	4.6	–	Ni-Cr silicide
Eutectic – comp. 2 (8)	26	45	8	2.5	21	Cr-Ni-Fe-P phase

Table 3. Amdry 108 Phase Analysis

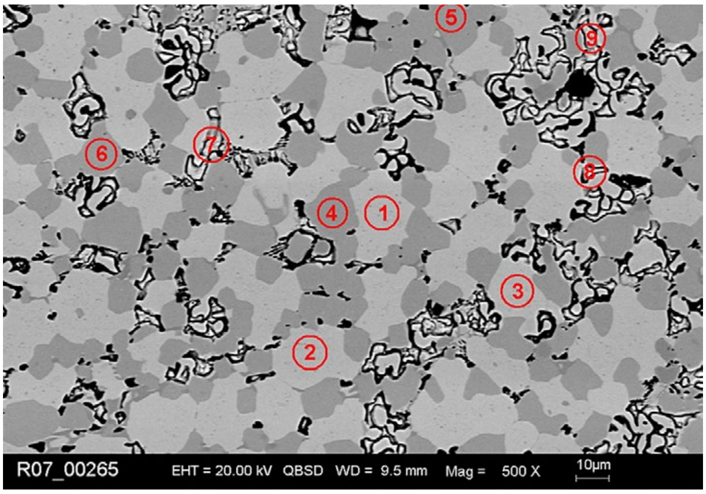


Figure 6. SEM Microscopy of Amdry 805

	Elemental Composition (wt %)					
Phases	Fe	Cr	Ni	Si	P	Phase Identity (XRD Analysis)
Matrix (1, 2, 3)	44	25	18	10	1	Fe-Cr (γ) phase a = 3.56 A
Major phase (4, 5, 6)	30	46	5	1	16	Cr-Fe-P phase (EDAX)
Secondary phases (7, 8, 9)	54	19	18	6	0	Fe-Cr silicide phase a = 6.117 A
Minor phase			— Unknown —			Fe-2Ni-P tetragonal phase

Table 4. Amdry 805 Phase Analysis

Braze performance

The following tests were conducted to evaluate the suitability of these filler metals for brazing applications:

1. Measurement of solidus and liquidus temperatures by DTA (Differential Thermal Analysis).
2. Vacuum furnace brazing of a T-joint and metallography of the joints
3. Corrosion tests in several aqueous solutions
4. High temperature oxidation tests at 815 °C (1500 °F)

Measurement of solidus and liquidus temperatures

These were done in commercial test labs that perform these measurements routinely. A forward heating cycle and a cooling cycle were used. The measured solidus and liquidus temperatures are shown in Table 5.

It should be noted that BNi-2 and BNi-5 alloys are used for comparison purposes. The three new Amdry braze filler metals have melting points that are in the intermediate range between the melting points of BNi-2 and BNi-5. Amdry 105, which does not contain any iron, has the lowest melting point (comparable to BNi-2). As the iron content increases, the melting points also increase. Amdry 805 has the highest melting point; however, this is still lower than the melting point of BNi-5. It should also be noted that the temperature differential between the solidus and liquidus in these alloys is on the order of 20 to 30 degrees Celsius as compared to 30 to 55 degrees Celsius in conventional alloys such as BNi-2 and BNi-5. Such a narrow gap is an indication of the 'flowability' of the alloy at brazing temperatures; thus enabling 'tight' joints with the highest strengths.

Filler Metal	Solidus (°C)	Liquidus (°C)
BNi-2	970	1000
Amdry 105	990	1010
Amdry 108	1025	1055
Amdry 805	1075	1105
BNi-5	1080	1135

Table 5. Measured Solidus and Liquidus Temperatures

Corrosion resistance tests

The resistance of these new alloys to several types of corrosive media was studied. Separate brazed coupons were immersed in a ten percent solution of sulfuric acid, a ten percent solution of hydrochloric acid and a saturated salt solution. The coupons were immersed at room temperature for 150 hours and examined under the microscope for pitting, etching or other possible corrosive damage. They were also examined for stability and strength before and after the immersion test.

High temperature oxidation resistance was measured by exposing melt buttons to a temperature of 815 °C (1500 °F) for 24 hours and measuring for weight gain.

In all cases, the brazed samples of Amdry 105, Amdry 108 and Amdry 805 exhibited excellent stability and minimal degradation.

It is believed that the presence of at least 23 percent chromium and 6 percent silicon in these alloys enhances their oxidation and corrosion resistance.

Vacuum furnace brazed joints

The new filler metals were applied to a stainless steel T-joint with a 0.002 inch gap and vacuum furnace brazed. The joints showed that all the alloys had excellent flow and filled the gaps with clean fillets. A typical microstructure of these braze joints is shown in Figure 7.

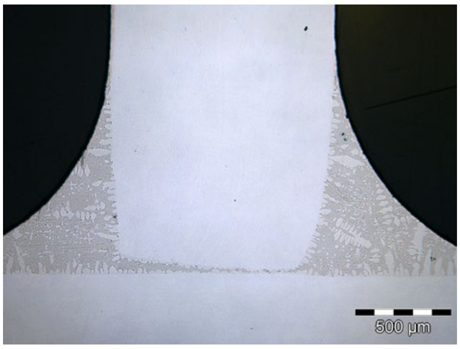


Figure 7. Brazed joint on a T-speciman (Amdry 105)

Similar microstructures were obtained for all the new filler metals. It may be noted that the vacuum brazing atmosphere must be carefully controlled for these alloys. Specifically, these alloys contain high amounts of oxygen-sensitive elements such as chromium and silicon. Also, they do not contain fluxing elements, such as boron, that would inherently tolerate some oxygen partial pressures in the vacuum furnace. For these reasons, we have observed that leak up rates of less than 30 microns per hour and vacuum levels of 1 x 10-4 Torr work best. The furnace cycles may include a soak at approximately 400 °C (760 °F) for about 30 minutes, another soak at 960 °C (1760 °F) for 30 minutes and brazing at recommended temperatures for 15 to 30 minutes.

Recommended brazing temperatures are typically 50 °C (90 °F) above the liquidus. This will ensure excellent melting and flow of the filler metal into the joint gaps.

Similar experiments have demonstrated that the above filler metals braze well on several ferrous base metals, nickel alloy base metals and, in some cases, even copper base metals.

Conclusion

The three new alloys — Amdry 105, Amdry 108 and Amdry 805 — belong to a new family of boron-free, high-chromium containing filler metals that utilize relatively small amounts of silicon and phosphorus as melt depressants. Braze tests show that these alloys have melting points within the range of conventional nickel braze filler metals and are capable of producing excellent braze joints that can withstand the corrosive and oxidation conditions expected in modern high temperature applications like heat exchangers and catalytic converters. Among these alloys, Amdry 105, a nickel-based filler metal, was developed as a benchmark.

Subsequent alloys (Amdry 108 and Amdry 805) were developed to maintain the high performance of Amdry 105, but to reduce the cost of the filler metal. This was accomplished by replacing a portion of nickel with iron. Based on the significantly lower cost of iron compared to nickel, it is estimated that raw material costs for Amdry 108 and Amdry 805 would be approximately 30 percent and 70 percent less when compared to conventional BNi-2 and BNi-5 alloys. Based on the technical performance and cost advantages, it is believed that these new alloys are worthy candidates for brazing heat exchangers and catalytic converters.

Acknowledgements
Dr. Rajiv Damani and Sulzer Innotec (for metallography support and X-ray diffraction analysis)

Notes
- Amdry is a registered trade mark of OC Oerlikon Corporation AG, Pfäffikon
- The composition of Amdry 805 is covered by a pending U.S. Patent Application by OC Oerlikon Corporation AG, Pfäffikon

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Keywords
nickel braze filler metal, iron braze filler metal, heat exchangers, catalytic converters, corrosion resistance, joint strength