New nickel based brazing alloy suitable for very corrosive environments.

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A new application for plate heat exchangers used in cooling units are subjected to a very aggressive coolant. This means both base material and brazing alloy needs to have very high corrosion resistance to the coolant. As base material high alloyed austenitic stainless steels were identified as available with necessary corrosion resistance. The only braze material on the market with good enough corrosion resistance in these environments was BrazeLet® Ni613. However, when testing this alloy it was early recognized that the melting range of this alloy was not compatible with these base materials. High alloyed austenitic stainless steels may form excessive amounts of inter metallic phases if heat treated incorrectly. Therefore a rapid cooling from above the critical temperature range for the specific base material is necessary. A new alloy with corrosion resistance similar to BrazeLet® Ni613 but with higher melting range was developed and is presented in this paper.

1. Introduction - Problem to be solved

The customer developed a new plate heat exchanger for cooling units using very aggressive coolant. This meant that both base material and brazing alloy needed to have very good corrosion resistance. High alloyed austenitic stainless steel was early identified as base material with required properties. High alloyed austenitic stainless steel may form inter metallic phases during cooling and need therefore a special heat treatment to avoid the formation of these phases. The brazing alloys used needs therefore to be solid above this temperature, called $T_{critical}$.

When looking for brazing alloys, it was clear that the existing alloys with good corrosion resistance, BNi5 and BrazeLet® Ni613 (here after Ni613) did not meet the requirements. The corrosion resistance of BNi5 in chloric solution was inferior to Ni613 and was therefore dismissed at an early stage. The corrosion resistance of Ni613 was satisfactory however the melting range was too low, 985°C-1060°C which is below $T_{critical}$. Secondly, it was desired to have a brazing alloy as close to the chemistry of the base material as possible in order to minimize element migration between the two. It was also desired to keep Si, B and P low as they consume Cr. When all these items were listed it was clear a new brazing alloy needed to be developed.

2. "From idea to product"

2.1 Alloy development – stage 1

In total 34 different compositions were investigated during the development work. The first test was to increase the melting range of Ni613. The obvious action was to reduce Si and P in Ni613. The modified Ni613 had the composition Ni-29Cr-3P-2Si, hence the P+Si was reduced from 10% to 5%. Surprisingly this had no effect on the melting range – Fig 1.

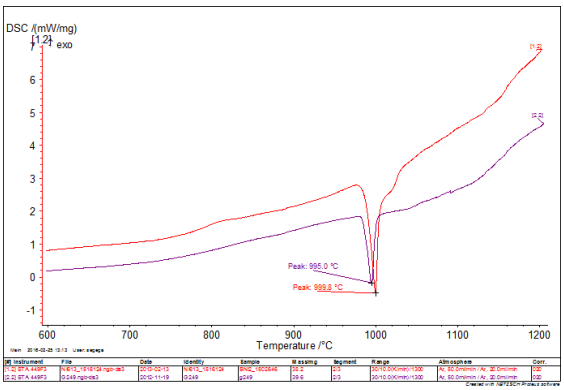


Fig 1. DSC curve for Ni-29Cr-3P-2Si with reference Ni613

Secondly compositions were done where Si, P, Mo, Mn and Fe was varied. At the earliest stage powders were mixed and melted into small tablets. The tablets were then placed on a steel substrate and heated. This gave an indication of the melting temperature. From this it was clear that it was best to keep Si high and P low. At this point atomized test melts were produced. Wetting tests and Simultaneous Thermal Analysis (STA) in Ar was made on the atomized powders. STA combines both Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA).

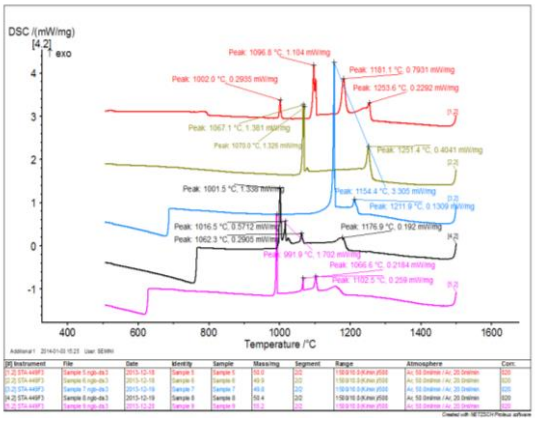


Fig 2. DSC curves

At the end it was decided that the brazing alloy should have as similar composition to the base material as possible. It was also clear that P needed to be removed from the alloy. As soon as P was present the melting temperature dropped. Furthermore the Mo content in the brazing alloy was increased to levels that would diminish migration between the base metals and brazing alloy hence affecting the corrosion resistance. Cr was kept at 29% to ensure good corrosion resistance. This ended up with an alloy with the composition Ni-29Cr-8Mo-xFe-ySi. This composition had a solidus temperature around 1150°C.

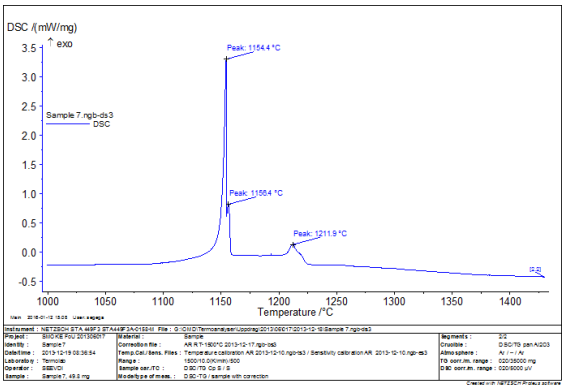


Fig 3. DSC curve for Ni-29Cr-8Mo-xFe-ySi

Alloy development – stage 2

Once the composition was decided further investigations were done on SMO654/254 and 304L base material. All Ni-29Cr-8Mo-xFe-ySi samples were brazed at 1250°C and all Ni613 samples were brazed at 1100°C. T-samples and spreading tests showed less flow and wetting compared to e.g. Ni613. However, the gap filling and the formation of joints were satisfactory as long as capillary flow over long distances was not necessary, i.e. placing the filler where needed. The spreading ratio is calculated as $S=A_m/A_i$ where A_m is the area of the melted powder and A_i is the initial area of the powder.

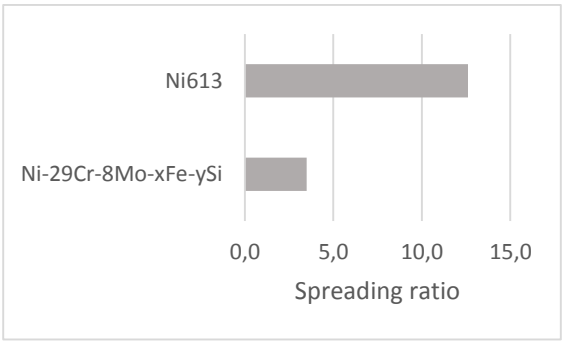


Fig. 2 Spreading ratio on 304L.

The EDX analysis in the SEM showed that the diffusion zone is very limited, only 20µm which means that the goal to minimize element migration was successful.

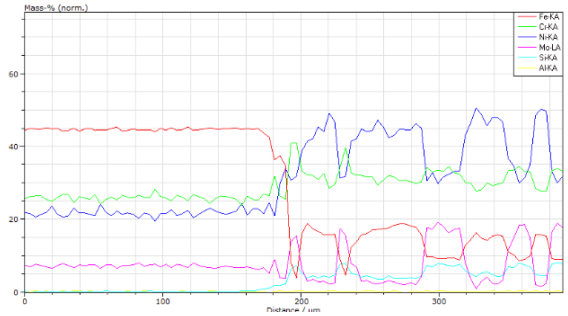


Fig 4. Line scan analysis

Furthermore the strength was measured by single overlap shear strength specimens. As seen, the strength is similar to both BNi5 and Ni613 when brazed on 304L stainless steel. However, when brazed on SMO254 with optimized furnace profile the strength is higher 150MPa, compared to 109MPa when brazed on 304 stainless steel.

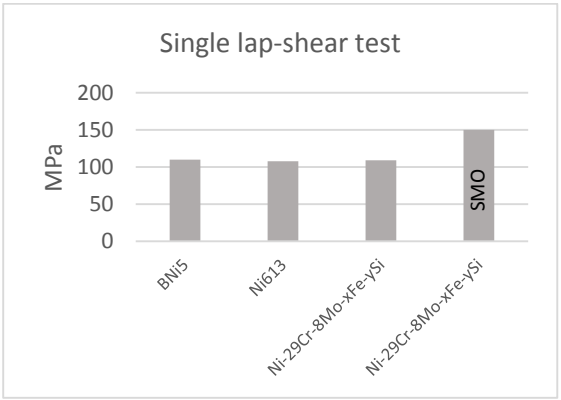


Fig 5. Shear strength

The microstructure consists of hard phases in a soft matrix. The soft, austenitic phase is rich in Fe, Si, Mo and Cr while the more brittle phase is rich in Fe, Ni and Cr. The smaller the joint thickness the less hard phases are fund which of course has a positive effect on the strength of the material

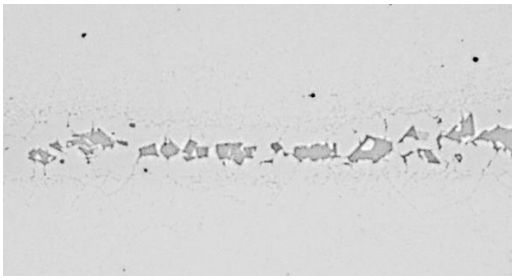


Fig 6. Close up of the joint found in the SMO654 T-sample

Corrosion tests were done in-house in so called “Acid test” where four different corrosion medias were evaluated. Brazed T-samples of 304L base material were placed in beakers containing 10wt% HCl, 10wt% H2SO4, 10wt% HNO3 and 10wt% NaOH.

Table 1 presents the results from the test. The joint brazed with Ni-29Cr-8Mo-xFe-ySi was unaffected in all four media. This means the corrosion resistance in 10wt% HNO_3 and 10wt% NaOH is better for Ni-29Cr-8Mo-xFe-ySi than Ni613. Both Ni-29Cr-8Mo-xFe-ySi and Ni613 is superior to BNi5 in all tested corrosion media.

Tab 1. Corrosion tests

	Ni-29Cr-8Mo-xFe-ySi	Ni613	BNi5
10wt% HCl	+++	+++	--
10wt% H2SO4	+++	+++	--
10wt% HNO3	+++	++	-
10wt% NaOH	+++	-	--

Optimizing the process

Inter metallic phases in high alloyed austenitic base material is formed during cooling which results in a brittle material. The inter metallic phases needs therefore to be minimized. By selecting correct quenching speeds and quenching temperatures, i.e. optimizing the brazing cycle the amount of the inter metallic phases was drastically reduced and the material become less brittle.

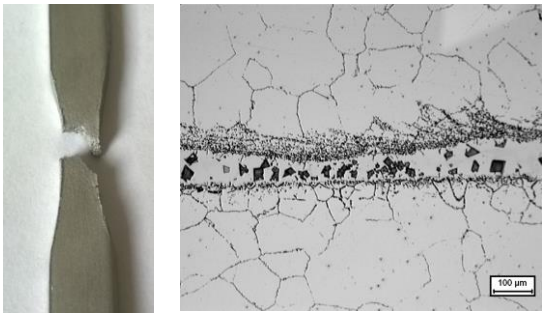


Fig 7. SMO254 brazed with incorrect cycle.

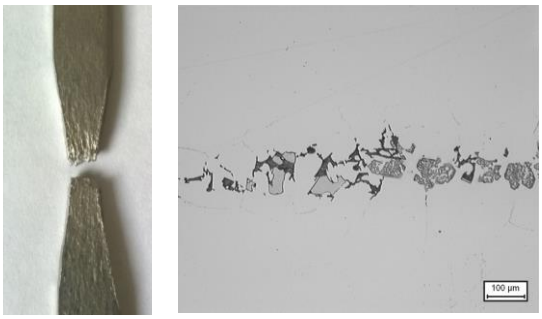


Fig 8. SMO254 brazed with optimized cycle

Conclusions

- ✓ A new material with the composition Ni-29Cr-8Mo-xFe-ySi was developed.
- ✓ The material has a solidus temperature around 1150°C.
- ✓ The material is suitable for use in applications where high alloyed austenitic stainless steels are needed.
- ✓ The strength is equal to BNi5 and Ni613 when brazed together with 304L stainless steel base material
- ✓ The strength is increased by around 37% when brazed together with SMO254 compared to 304L
- ✓ The corrosion resistance is improved compared to BNi5 in HCl, H_2SO_4, HNO_3 and NaOH solutions
- ✓ The corrosion resistance is equal to Ni613 in HCl, H_2SO_4, HNO_3 solutions
- ✓ The material is patent pending