

Brazing filler metals for low metal ion leaching in ultra-pure water applications

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Abstract

In applications such as brazed heat exchangers for fuel cells and related hydrogen processing systems, or process chillers for semiconductor manufacturing, understanding the corrosion resistance of the brazed components is crucial for material selection and design. Although corrosion behavior of brazed joints in drinking water has been studied previously, the corrosion behavior in ultra-pure water cannot necessarily be extrapolated. Ultra-pure water is typically defined with a conductivity of 0.055 $\mu\text{S}/\text{cm}$. The metal ion leaching of AISI 316L components brazed with different filler metals, Cu-foil (99,9% Cu), BNi-5, BNi-12, BrazeLet® Ni613, BrazeLet F86 and a Ni-Cr-P-Si-B foil, was investigated and compared to suggest the best choice for minimizing the amount of metal ion leaching. B, Cr, Cu, Fe, Mn, Mo, Ni and P concentrations in water were measured by ICP every two weeks over a total test period of 12 weeks. The effect of water temperature was investigated by comparative testing at room temperature and 80 °C. The components brazed with BrazeLet F86 and BrazeLet Ni613 showed the lowest metal ion leaching, while the Ni-Cr-P-Si-B foil and the Cu-foil showed the worst results in this evaluation with considerable metal ion leaching.

Introduction

In the case of brazed components, such as brazed plate heat exchangers, the leaching of metal ions comes from the interaction of both the base material and the brazing filler metal with the media that passes through it. Increased focus and attention on the amount of metal ion leaching has been seen, in particular for drinking water applications. This was the background for the investigation of metal ion leaching behavior of different brazing filler metals to drinking water that was presented at IBSC2021 [1]. Following this presentation, a number of questions have come up as to how metal ion leaching behavior could differ for applications using higher purity water such as deionized (DI) water or ultra-pure water (UPW). With the basis for a test method already established, and internal capabilities to produce the required UPW, it was decided to undertake a new investigation, as extrapolation of the test results from drinking water is not necessarily possible. Higher purity waters are generally more corrosive to metals compared to drinking water as the tendency for passivation of the metallic surfaces by protective oxide or scale formation is decreased. As higher purity water has limited or no buffering capabilities, small amounts of contaminants (e.g. ions or dissolved gases) can have large effects on the pH.

UPW refers to water that has been purified to very stringent specifications, which normally includes removal of all

contaminant types (organic, inorganic and dissolved gases). Resistivity (or the inverse – conductivity) is often used as a measure of the purity of the water. The theoretical upper limit of resistivity of water is 18.18 $\text{M}\Omega\cdot\text{cm}$ at 25 °C, which equals a conductivity of 0.055 $\mu\text{S}/\text{cm}$. Depending on the application in question, different specifications can be in place to dictate the exact requirements on the water.

Purified water is used for an increasing number of applications that are relevant for brazed components, such as lasers, medical equipment, laboratory instrumentation, pharmaceutical production, food processing and semiconductor manufacturing [2]. In many of these applications, accurate temperature control of the purified water is necessary, achieved by the use of brazed plate heat exchangers. There are also a number of applications where purified water is used for cooling applications, in particular for electrical applications to prevent short circuits. Examples include cooling of induction furnaces, high-power rectifiers for DC-smelters and converters [3]. Further to the applications using purified water, applications involving heating or cooling of hydrogen gas for example for fuel cells also share some similarities. The processing of hydrogen can lead to pure water condensate forming inside the heat exchangers, where corrosion and associated metal ion leaching can affect fuel cell operation.

As the semiconductor and electronics applications are the most well-established, there are clear standards and guidelines existing that puts requirement on the water quality for these systems. For example, the ASTM D5127 standard provides recommendations for water quality related to electronics and semiconductor-industry manufacturing and defines seven classifications of water with varying stringency [4]. Specifically for the semiconductor industry the guide SEMI F63 provides requirements for ultra-pure water used in semiconductor processing [5].

Concerning the operating conditions of brazed plate heat exchangers, the most relevant temperature range for semiconductor and electronic applications is 10 – 45 °C, with most of the applications focused in the lower end of this temperature range. For some of the emerging hydrogen applications, higher temperatures are typical (e.g. 90 °C). Typical applications for brazed plate heat exchangers experience water conductivities in the range 1 – 5 $\mu\text{S}/\text{cm}$, although the most stringent applications can require even lower conductivities < 1 $\mu\text{S}/\text{cm}$.

Austenitic stainless steel is commonly used for brazed plate heat exchangers, as it shows good thermal properties, corrosion resistance and strength. For the brazing filler metals, both Cu- and Ni-based brazing filler metals are well-established in the industry, and Fe-based brazing filler metals

are also gaining ground for heat exchanger applications. In the previous investigation in drinking water, Fe-based brazing filler metals were found to result in lower amounts of metal ion leaching compared to the standard Ni-based brazing filler metals [1]. This was consistent with the work of other authors, on Fe-based development compositions [6]. Whether the same trends translate to high purity water applications, is unclear.

No previous investigations on metal ion leaching behaviour or corrosion properties of brazed joints in high purity water have been identified, in contrast to the work performed for drinking water applications where several researchers have made great contributions to the field [6][7][8][9]. To further strengthen brazing filler material selection for high purity water applications, Höganäs' Fe-base brazing filler metal BrazeLet F86 was evaluated together with various Ni-base brazing filler metals and Cu-foil as reference materials.

Experimental

AISI 316L heat exchanger plates with 0.3 mm thickness and typical fishbone pattern were provided by a manufacturer of brazed plate heat exchangers, formed by simultaneous pressing with Cu-foil. Sections of 70 x 25 mm were cut out from the provided plates. The composition of the plates as reported on the material certificate is given in Table 1.

Table 1: Chemical analysis of AISI 316L plates

Fe	Cr	Ni	Mo	Mn	Si	N	C	P
Bal.	16.6	10.1	2.1	1.03	0.32	0.05	0.01	0.03

The brazing filler metals evaluated are listed in Table 2. For the two reference samples (Cu and Ni-Cr-P-Si-B), brazing filler metal was applied as foil of approximately 30 µm thickness. For the remaining samples, brazing filler metal was in the form of a water based brazing paste, applied by manual spraying, and the plates were dried in a hot air furnace prior to assembly. Eight plates were stacked in alternating direction to form each sample. Weight control of each sample was performed during each preparation step. As paste was applied by manual spraying on small plate samples, there is some variation in the applied amount of brazing filler metal. The total amount of brazing filler metal for each sample varied in the range of 3.50 g – 4.68 g, except for Cu-foil which was 7.14 and 7.17 g for the two samples. The total base material plate weight for each sample varied in the range of 43.71 g – 51.09

g, with the resulting weight ratio of applied brazing filler metal to base material varying in the range of 0.07 – 0.15.

The samples were brazed in a Nabertherm VHT 40/16 Mo vacuum furnace. The ramp rate was 9 °C/min from 20 °C up to 450 °C, followed by a 30 minute hold to ensure complete removal of any polymer in the brazing paste binder. Heating was continued with the same ramp rate to the recommended brazing temperature for each brazing filler metal as specified in Table 2, where the components were held for 30 minutes followed by natural cooling in vacuum (except for the Cu-brazed sample which was held for 60 minutes). The measured vacuum level at the brazing temperature was approximately 10⁻⁵ mbar for all samples, except the Cu-brazed sample which was brazed at approximately 10 mbar partial pressure (Ar). The appearance of the brazed sample geometry is shown in Figure 1 (picture from previous investigation).

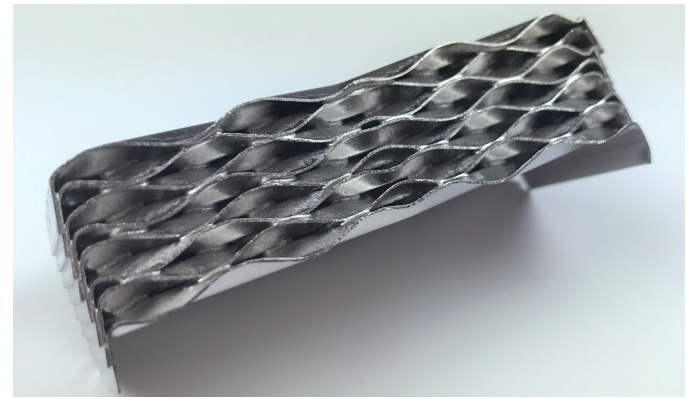


Figure 1: Brazed test sample used for immersion tests.

Each brazed sample and a reference base material sample (subjected to the same brazing cycle as BrazeLet Ni613), were placed into separate borosilicate glass containers and filled completely with UPW. The volume of water added was typically 240 – 250 mL and varied slightly with specimen and container dimensions and tolerances. In addition, one reference container was filled with UPW to evaluate the significance of leaching from the borosilicate glass. The containers were sealed with a plastic cover and stored either at room temperature or in a heating cabinet at 80 °C. Every second week, containers were weighed and refilled to the weight at start of the test to compensate for any minor evaporated amount, the components were removed and water was sent for analysis. To start a new test cycle, the components were immersed in new UPW and the same procedure detailed above was repeated throughout 12 weeks.

Table 2: Brazing filler materials evaluated. Nominal composition in wt%, except for Cu-foil showing actual analysis by ICP.

Material	EN ISO 17672	AWS A5.8	Ni	Cr	B	Si	Fe	P	Cu	Nb	Brazing temperature
BrazeLet BNi5	Ni650	BNi-5	Bal.	19	-	10.2	-	-	-	-	1150 °C / 2102 °F
BrazeLet BNi12	Ni720	BNi-12	Bal.	25	-	-	-	10.0	-	-	1050 °C / 1922 °F
BrazeLet Ni613	Ni740	BNi-15	Bal.	29.5	-	4.0	-	6.0	-	-	1090 °C / 1994 °F
BrazeLet F86	-	-	20	29	-	6.5	Bal.	6.0	-	0.5	1150 °C / 2102 °F
Ni-Cr-P-Si-B foil	-	-	Bal.	25	0.5	1.5	-	6.0	-	-	1100 °C / 2012 °F
Cu foil	-	-	0.005	-	-	-	0.007	-	Bal.	-	1120 °C / 2048 °F

At each test cycle, water was sampled and prepared for analysis on a Spectro ICP-OES ARCOS II. 0.25 mL HNO₃ and 1 mL Sc solution (200 mg/L) were added to each water sample until a total volume of 50 mL. The prepared water samples were analyzed for B, Cr, Cu, Fe, Mn, Mo, Ni and P ions with the following limits of quantification: B < 2 µg/L; Cr < 5 µg/L; Cu < 1 µg/L; Fe < 2 µg/L; Mn < 1 µg/L; Mo < 1 µg/L; Ni < 1 µg/L; P < 1 µg/L. Below these concentrations, the values are given as non-detectable (<LOQ).

When calculating the final results, if both sample and the pure base material were below LOQ, then values were given as <LOQ, if the sample gave a value but pure base material below LOQ, then the value of the pure base material was assumed 0 and if the value measured in pure base material is higher than or equal to the sample, the value was given as 0.

As an additional (indirect) measure of metal ion leaching, conductivity measurements were performed with a PC 2700 benchtop meter (Oakton Instruments, Vernon Hills, IL). Prior to the measurements, the equipment was calibrated with calibration solutions with a conductivity of 1.3 µS/cm, 10 µS/cm and 1413 µS/cm.

After completion of the immersion tests, the components were prepared by standard metallographic methods and investigated using a Zeiss Axio Imager.M2m Light Optical Microscope, a Leica 205M Stereo Microscope and a Hitachi SU6600 Field Emission Scanning Electron Microscope.

Results and Discussions

The values for leaching of B, Cr, Cu, Fe, Mn, Mo, Ni and P of each immersion test were obtained from ICP-analysis. The results were normalized by the amount of brazing filler metal applied on each specimen. The final adjusted results are given in concentration of each metal ion in water (µg/L) per 10 g of brazing filler metal for each sample, at each 2-week interval both at room temperature and 80 °C. The total measured metal ion leaching is shown in Table 3, with the total leaching of each metal ion specified individually for clarity. The measured B-leaching is omitted from the table, as very high B-leaching was observed for all the samples tested at 80 °C. The total B-leaching at 80 °C varied in the range 508 – 22564 µg/L for the different samples. B-leaching was only observed in the cases where a metallic sample was submerged in the UPW, as the reference with only UPW did not result in any significant B-leaching. No B-leaching was observed at room temperature for any of the samples.

The metal ions that were found to leach most significantly into the UPW were Cu, Fe, Mn and Ni. As can be seen from Table 3, the brazing filler metals that experienced the lowest amounts of metal ion leaching were BrazeLet F86 and BrazeLet Ni613. BNi-5 and BNi-12 resulted in moderate metal ion leaching and in some cases corrosion attacks visible to the naked eye in the brazed joint fillets. By far the most extensive metal ion leaching was observed for the two reference samples with Cu foil and the Ni-Cr-P-Si-B foil.

Table 3: Total metal ion leaching of Cr, Cu, Fe, Mn, Mo, Ni and P (µg/L) per 10 g of filler metal after the test period of 12 weeks at room temperature and 80 °C, with total leaching for each individual metal ion provided.

Material	RT	80 °C
Cu foil	11134 Cr: < LOQ Cu: 2746 Fe: < LOQ Mn: 1980 Mo: < LOQ Ni: 6408 P: < LOQ	4158 Cr: < LOQ Cu: 1721 Fe: 90 Mn: 584 Mo: < LOQ Ni: 1737 P: 26
BrazeLet BNi5	654 Cr: < LOQ Cu: < LOQ Fe: 106 Mn: 9 Mo: < LOQ Ni: 539 P: < LOQ	2366 Cr: < LOQ Cu: 224 Fe: 88 Mn: 2 Mo: < LOQ Ni: 1988 P: 62
BrazeLet BNi12	691 Cr: < LOQ Cu: < LOQ Fe: 22 Mn: 125 Mo: < LOQ Ni: 530 P: 14	303 Cr: < LOQ Cu: < LOQ Fe: 52 Mn: 7 Mo: < LOQ Ni: 205 P: 39
BrazeLet Ni613	85 Cr: < LOQ Cu: < LOQ Fe: 17 Mn: 5 Mo: < LOQ Ni: 63 P: < LOQ	322 Cr: < LOQ Cu: < LOQ Fe: 125 Mn: 5 Mo: < LOQ Ni: 55 P: 137
BrazeLet F86	96 Cr: < LOQ Cu: < LOQ Fe: 94 Mn: 2 Mo: < LOQ Ni: < LOQ P: < LOQ	193 Cr: < LOQ Cu: 10 Fe: 77 Mn: 3 Mo: 8 Ni: < LOQ P: 95
Ni-Cr-P-Si-B foil	24792 Cr: 376 Cu: < LOQ Fe: 684 Mn: 479 Mo: 3 Ni: 22689 P: 561	3310 Cr: 9 Cu: < LOQ Fe: 1068 Mn: 68 Mo: < LOQ Ni: 1872 P: 293

To better visualize the development of metal ion leaching over the test duration, the measurements from each sampling interval for Cu, Fe, Mn and Ni are shown in Figure 2 - Figure 5. For Cu-leaching, this is as expected primarily observed from the sample brazed with Cu foil, with higher Cu-leaching at room temperature than at 80 °C. For Fe-leaching the highest values were seen for the Ni-Cr-P-Si-B foil, with lower scattered values also for the other samples. Significant Mn-leaching was observed for the Cu foil sample, but also from the Ni-Cr-P-Si-B foil and BNi-12, with higher leaching at room temperature. For Ni-leaching, very high values were measured for the Ni-Cr-P-Si-B foil, followed by Cu foil. Moderate Ni-leaching was measured for BNi-5 and BNi-12.

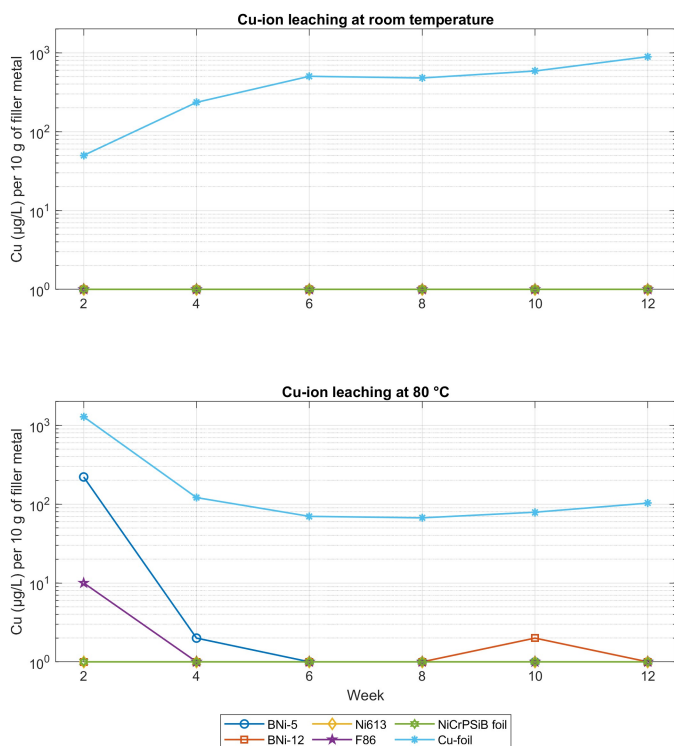


Figure 2: Measured Cu-ion leaching each sampling interval for the evaluated brazing filler metals at room temperature and 80 °C.

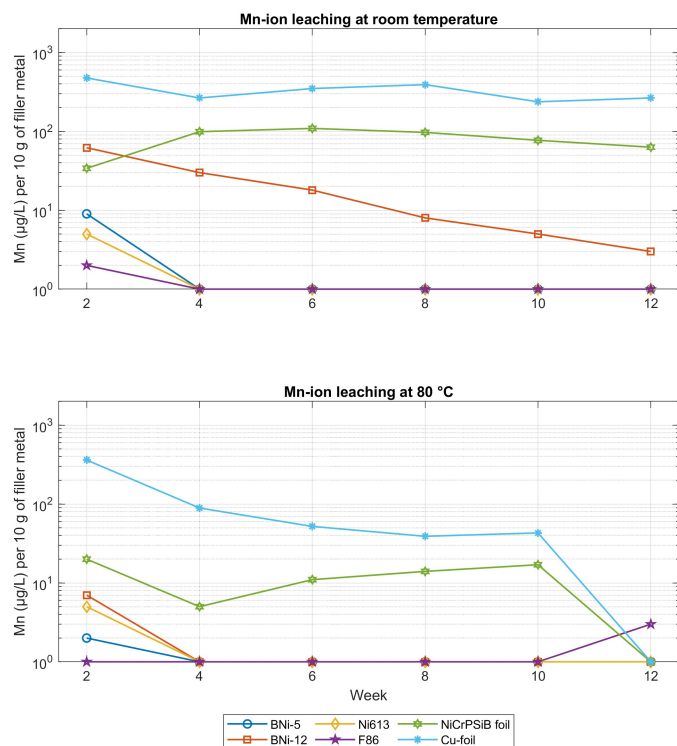


Figure 4: Measured Mn-ion leaching each sampling interval for the evaluated brazing filler metals at room temperature and 80 °C.

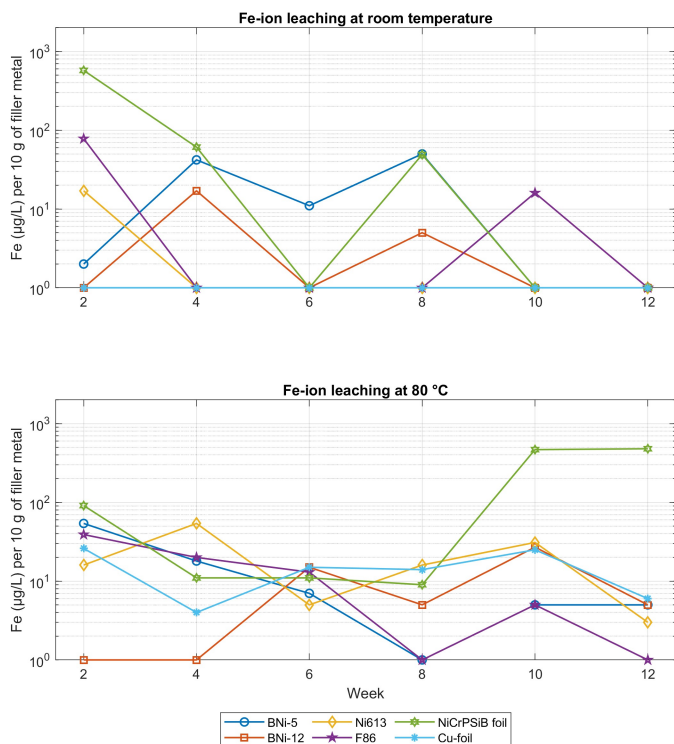


Figure 3: Measured Fe-ion leaching each sampling interval for the evaluated brazing filler metals at room temperature and 80 °C.

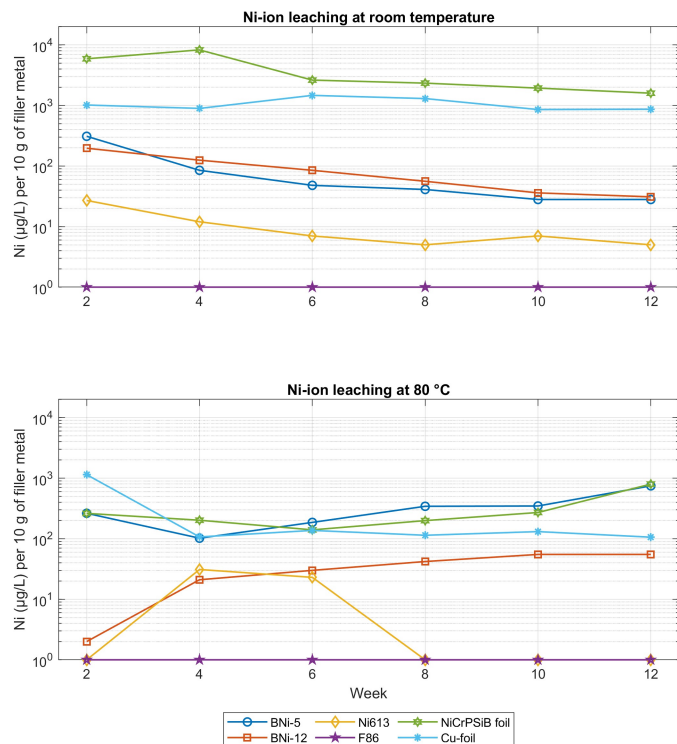


Figure 5: Measured Ni-ion leaching each sampling interval for the evaluated brazing filler metals at room temperature and 80 °C. Note the difference in scale on y-axis compared to the other figures necessary due to very high Ni-ion leaching measured for some samples.

Another way to evaluate the metal ion leaching behavior is by measuring the test water conductivity, which can be seen as an indirect measurement that metal ion leaching has taken place. The measured test water conductivity includes the data for the pure water in the same container, as well as the base material reference samples subjected to a vacuum brazing cycle without any filler metal present. It can be seen from Figure 6 and Figure 7 that the effect on water conductivity is initially high and stabilizes at lower levels depending on the filler metal.

Conductivity measurements taken of the test water prior to immersion of the samples and testing showed an average conductivity of $0.61 \mu\text{S/cm}$ where the results varied in the range $0.34 - 0.99 \mu\text{S/cm}$ for the different test intervals. The conductivity measurements of the reference test water (only water in a borosilicate glass container), showed no significant differences with average conductivity $0.96 \mu\text{S/cm}$ and $0.54 \mu\text{S/cm}$ respectively at room temperature and 80°C . Much more clear differences were observed for the reference samples with the base material plates immersed in UPW, where the conductivity for the room temperature sample averaged at $1.24 \mu\text{S/cm}$ with values in the range $0.75 - 2.56 \mu\text{S/cm}$ and the 80°C sample averaged at $2.00 \mu\text{S/cm}$ with values in the range $0.91 - 4.21 \mu\text{S/cm}$. As concluded from the metal ion leaching measurements, most of the observed increase in conductivity at 80°C is likely to be caused by leaching from the borosilicate glass.

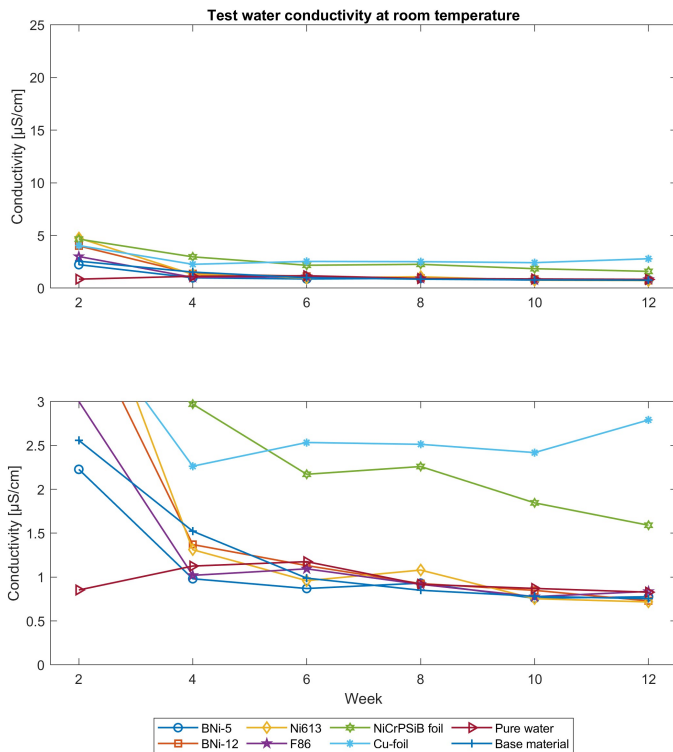


Figure 6: Measured test water conductivity for each brazing filler metal over 12 weeks at room temperature. The lower plot shows the same data with higher magnification of the y-axis.

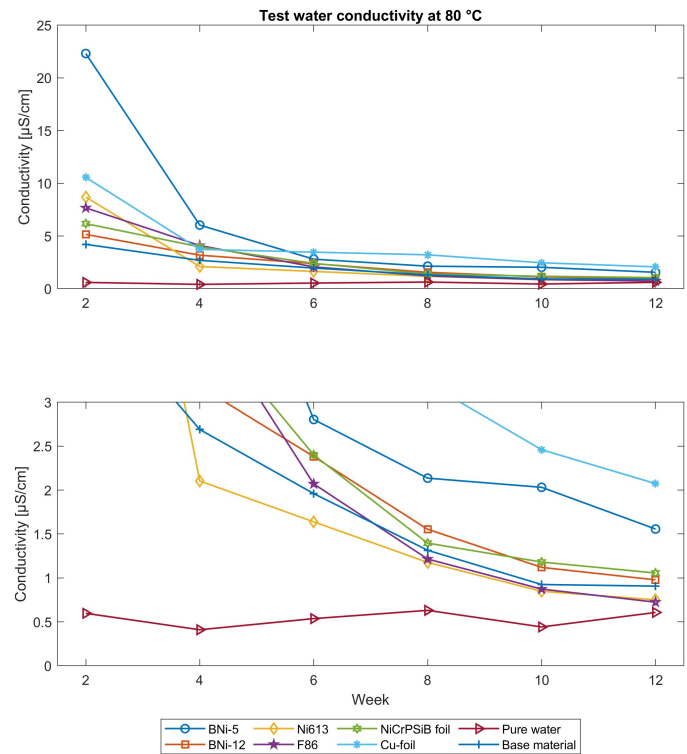


Figure 7: Measured test water conductivity for each brazing filler metal over 12 weeks at 80°C . The lower plot shows the same data with higher magnification of the y-axis.

Base material

The appearance of the base material reference samples (which were exposed to a brazing cycle prior to the immersion tests) are shown in Figure 8. For the sample exposed at room temperature, no notable changes to the surface appearance can be seen that could indicate corrosion. For the sample exposed to 80°C , there is a change in appearance with a straw-colored surface, which suggests that some oxidation has taken place.

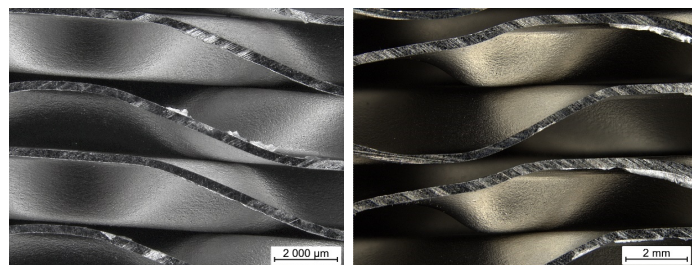


Figure 8: Base material reference samples after testing. Left: room temperature; Right: 80°C .

Cu foil

The specimens brazed with Cu foil show high and relatively stable Cu-leaching during the test. For the sample tested at room temperature, there was a slight increasing trend in Cu-leaching over the test duration, while for the sample tested at 80°C , the highest Cu-leaching is seen in the first sampling interval followed by a stabilization at a level slightly below what was seen for the room temperature sample. Looking to the leaching results, it is found that very little measurable Fe-leaching has occurred, which suggests that the base material is

not extensively corroded. Consistent with previous investigations in drinking water, Ni- and Mn-leaching is also high and follows closely the same trends as Cu-leaching. Both Ni and Mn have considerable solid solubility in Cu, and these elements could therefore be expected to be present in the brazed joints and leach out as the brazing filler metal is corroding. However, as leaching of Ni and Mn is basically equally high or higher than the Cu-leaching, the solid solubility in Cu does not alone explain the high measured leaching values. Further study is required to better understand these observed effects. The metal ion leaching is coming from both the brazed joint fillets, but also from the other surfaces of the sample as all internal surfaces are covered with a thin Cu layer after brazing which is typical for brazing with Cu foil.

From the visual appearance, it is difficult to judge any color differences. This is opposed to the metal ion leaching test performed in drinking water, where a clear green layer was observed on the surface of the 80 °C sample due to formation of a protective Cu-carbonate scale [1]. In UPW the protective Cu-carbonate cannot form, and this color change is therefore also not expected. Metallographic investigations do support the differences between the test temperatures, as more of the Cu layer is remaining outside of the brazed joints in the sample tested at 80 °C which showed the lowest amount of metal ion leaching.

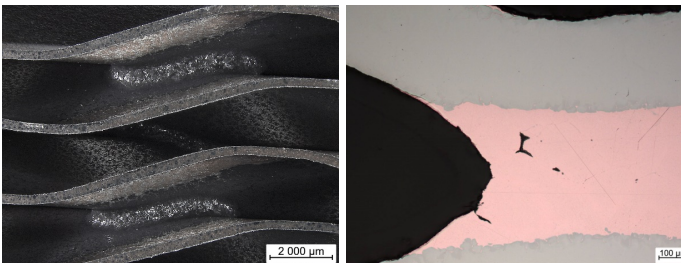


Figure 9: Cu foil sample - room temperature

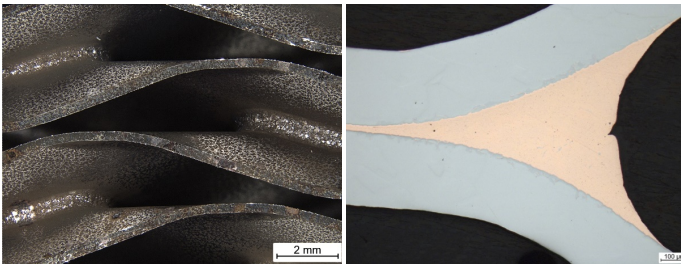


Figure 10: Cu foil sample - 80 °C

BNi-5

The specimens brazed with BNi-5 showed the highest metal ion leaching of the Ni-base alloys (except for the Ni-Cr-P-Si-B foil). Looking to the results, it is clear that the metal ion leaching is dominated by Ni-leaching. The Ni-leaching shows a slowly decreasing trend at room temperature, while at 80 °C the trend is stable or even slightly increasing. The observation of higher metal ion leaching at 80 °C is consistent with the previous investigations in drinking water. At room temperature the total measured metal ion leaching over the test duration is 654 µg/L compared to 2366 µg/L at 80 °C.

The brazed joint microstructure is normal for BNi-5 and consists of a mixture of Ni-Cr-Si-(Fe) solid solution primary phase as well as a Cr-rich silicide ($\text{Cr}_3\text{Ni}_5\text{Si}_2$) and a Ni-silicide ($\text{Ni}_{31}\text{Si}_{12}$). Although former trials have been performed in drinking water, it is considered likely that the same corrosion mechanisms can explain the increased corrosion rates at higher temperature. Fukai et al. studied the corrosion behavior of BNi-5 at 25 °C and 80 °C [7]. They found that at higher temperatures, the potential difference between the AISI 316L base material and the Cr-poor eutectic structure, led to increased corrosion rates.

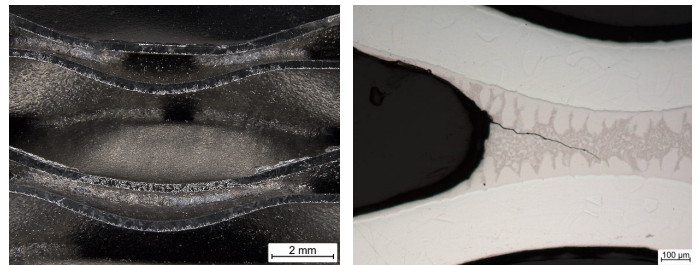


Figure 11: BNi-5 sample - room temperature.

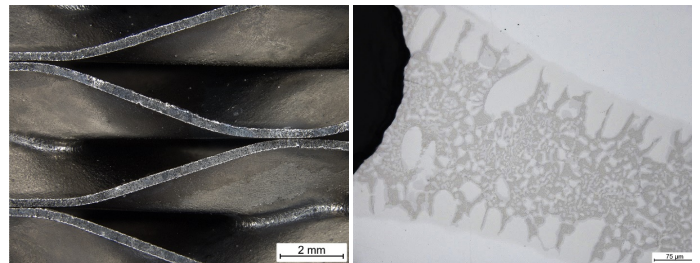


Figure 12: BNi-5 sample - 80 °C.

BNi-12

The specimens brazed with BNi-12 showed moderate amounts of metal ion leaching. The highest metal ion leaching was measured at room temperature with 691 µg/L total over the test duration, compared to 303 µg/L for the 80 °C sample. The metal ion leaching is dominated by Ni-leaching, constituting around 80% of the measured leaching, where the remainder is Fe, Mn and P. At room temperature, a slowly decreasing trend in Ni-leaching is seen over the test duration, opposite to at 80 °C where a slightly increasing trend is seen.

The brazed joint microstructure is normal for BNi-5 and consists of a mixture of Ni-Cr-(Fe) solid solution primary phase as well as the phosphides $(\text{Cr},\text{Ni})_2\text{P}$ and $(\text{Cr},\text{Ni})_3\text{P}$ as part of the eutectic structures. Corrosion is found to occur preferentially in the eutectic structure, with visible corrosion attacks and associated cracking of the $(\text{Cr},\text{Ni})_x\text{P}$ phases.

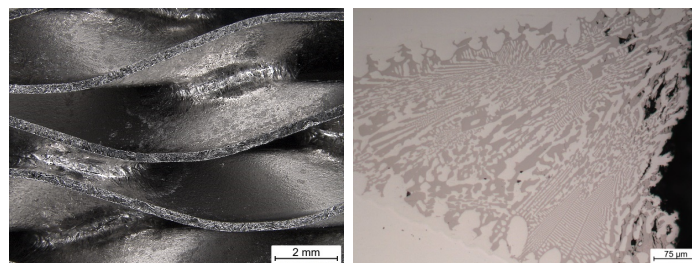


Figure 13: BNi-12 sample - room temperature.

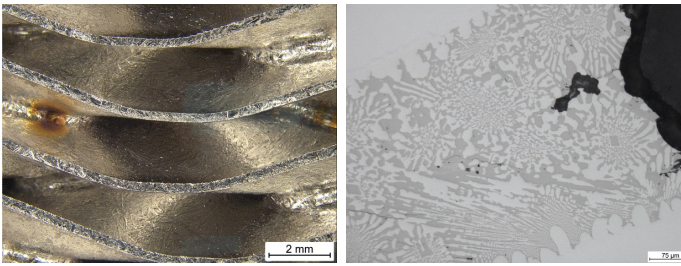


Figure 14: BNi-12 sample - 80 °C.

BrazeLet Ni613

The specimens brazed with BrazeLet Ni613 showed the lowest metal ion leaching of the Ni-base brazing filler metals evaluated with 85 µg/L and 322 µg/L total measured leaching over the test duration respectively at room temperature and 80 °C. The measured metal ion leaching is primarily found as Fe-leaching, with some Ni-leaching as well. For the 80 °C sample, notable P-leaching is also measured which indicates corrosion of the $(\text{Cr,Ni})_x\text{P}$ phases in the eutectic structure. Some corrosion attacks in the eutectic structures can be observed in the metallographic investigation, which supports this observation. Both Ni- and Fe-leaching is found to be relatively stable with no indication of passivation for either of the test temperatures over the test duration.

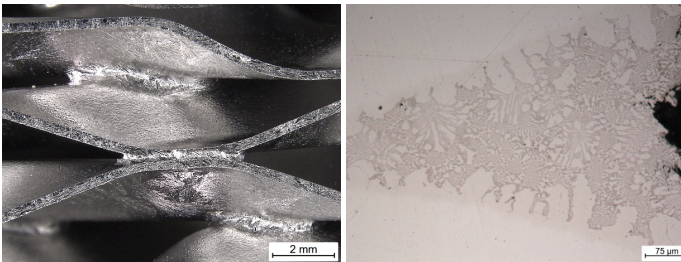


Figure 15: BrazeLet Ni613 sample - room temperature.

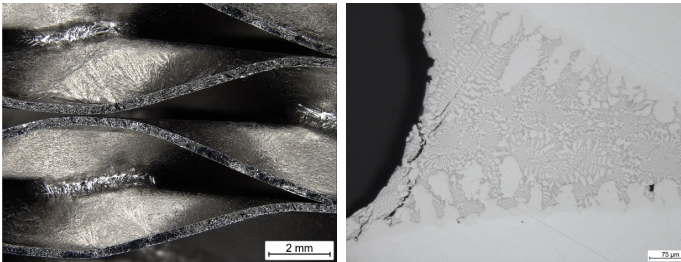


Figure 16: BrazeLet Ni613 sample - 80 °C.

BrazeLet F86

The specimens brazed with BrazeLet F86 showed the lowest metal ion leaching of all the brazing filler metals evaluated with 99 µg/L and 193 µg/L total measured leaching over the test duration respectively at room temperature and 80 °C. The measured leaching is basically only Fe-leaching for the room temperature sample, while the 80 °C sample showed leaching of both Fe and P. For both test conditions, the metallographic investigations show some corrosion attacks in the eutectic structure, which could suggest that the $(\text{Cr,Fe,Ni})_x\text{P}$ phases are preferentially attacked.

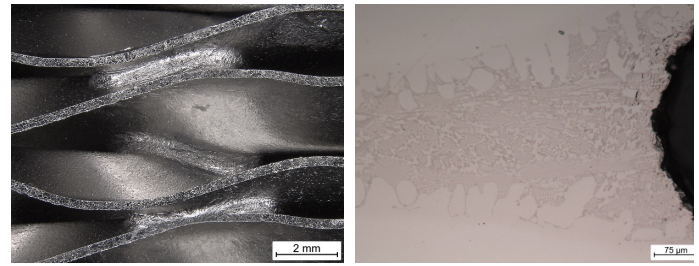


Figure 17: BrazeLet F86 sample - room temperature

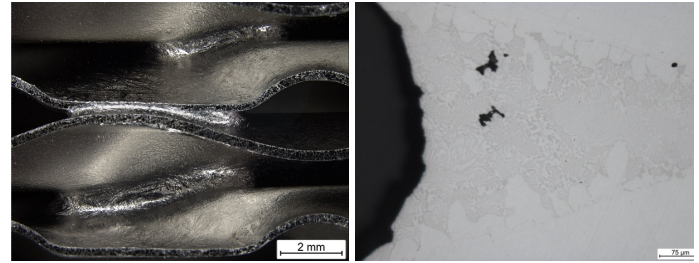


Figure 18: BrazeLet F86 sample - 80 °C

Ni-Cr-P-Si-B foil

The specimens brazed with Ni-Cr-P-Si-B foil showed the highest metal ion leaching of all the brazing filler metals evaluated in this investigation. In particular, the metal ion leaching at room temperature was extremely high with a total measured leaching over the test duration of 24792 µg/L. This can be compared with 3310 µg/L at 80 °C. The metal ion leaching was dominated by Ni-leaching which constituted above 90% of the measured leaching for the room temperature sample. Notable leaching of Fe, Mn and P was also measured for both test temperatures. Corrosion occurs by preferential attack of the eutectic structure, and large discolored corrosion spots are visible in the brazed joint fillets. In some areas, corrosion has developed into localized corrosion pits.

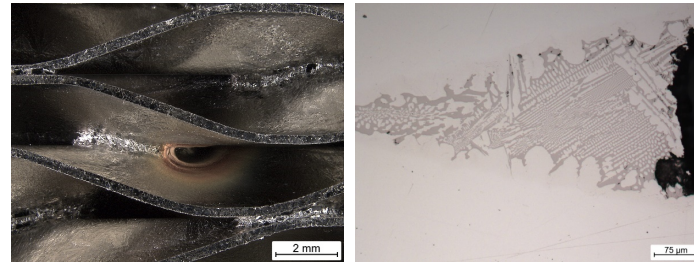


Figure 19: Ni-Cr-P-Si-B foil sample - room temperature

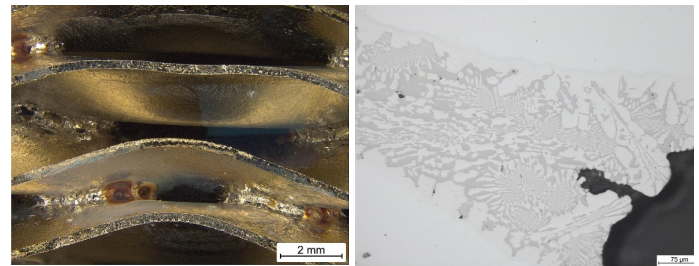


Figure 20: Ni-Cr-P-Si-B foil sample - 80 °C

As shown more clearly in Figure 21, corrosion of the Ni-Cr-P-Si-B foil occurs by preferential attack of certain phases in the eutectic structure. Corrosion of the $(\text{Cr,Ni})_x\text{P}$ phases is observed, while the Ni-Cr-(Fe) solid solution remains.

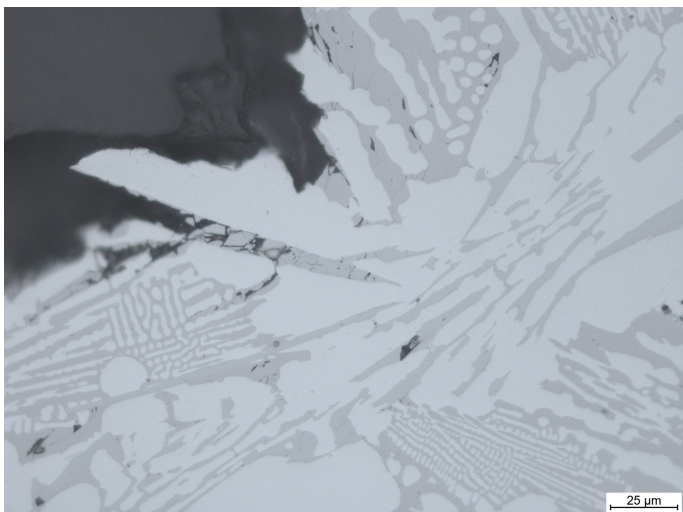


Figure 21: Ni-Cr-P-Si-B sample – 80 °C at higher magnification to better show the corrosion attacks.

Effect of water temperature

In contrast to previous investigations on metal ion leaching to drinking water, where higher temperatures generally favored faster passivation and reduction of metal ion leaching (except for BNi-5), the trends in UPW are not as consistent. For the brazing filler metals with moderate to very high measured metal ion leaching (BNi-12, Ni-Cr-P-Si-B foil and Cu foil), significantly lower metal ion leaching values were seen at 80 °C compared to room temperature. In UPW, higher corrosion rates are expected at higher temperature compared to room temperature, so the observations in this work are most likely attributed to some degree of passivation in the presence of dissolved oxygen or other gases in the water which could not be avoided completely with the current test setup.

For the brazing filler metals with low metal ion leaching (BrazeLet Ni613 and BrazeLet F86), similar or slightly higher metal ion leaching values were observed at 80 °C compared to room temperature.

Consistent with the results in drinking water, BNi-5 also showed considerably higher metal ion leaching at 80 °C compared to at room temperature in UPW.

Effect of brazing filler metal amount

Compared to our previous investigation on metal ion leaching to drinking water, improved consistency of the applied amount of brazing filler metal was achieved in the current investigation. The amount of brazing filler metal applied (weight after brazing) varied between 3.50 and 4.68 g for all samples except the Cu-brazed samples which had significantly more filler metal at 7.14 and 7.17 g respectively for the two samples. The applied amount of brazing filler metal for all samples is seen as close to reality for brazed plate heat exchangers as the amount of filler metal applied for Ni- and Fe-base brazing filler metal is generally lower in order to avoid issues with fillet defects and limit unwanted microstructures. The Cu-brazed samples are prepared from plates that are stamped together with Cu-foil, which means that the applied amount represents what is used in running production.

As discussed in our previous work, a larger amount of brazing filler metal applied can be found to increase the likelihood of corrosion primarily in two different ways. First, the larger amount of brazing filler metal applied will generally increase the size of the brazing fillets which increase the tendency of surface voids and defects caused by solidification shrinkage. These voids can act as initiation sites for corrosion. Second, the larger brazing fillets can also have a different microstructure, with an increased tendency for intermetallic phases. This can increase the tendency for preferential corrosion of certain phases in the microstructure [1].

Summary and comparison with previous investigations

Looking to the metal ion leaching results, there are clear and significant differences between the various brazing filler metals evaluated in this work. It is found that both the iron-based brazing filler metal BrazeLet F86 and the nickel-based BrazeLet Ni613 show clearly lower amounts of total metal ion leaching compared to the other samples. The worst results were observed for the Ni-Cr-P-Si-B foil and the Cu foil. The exact reasons as to why the Ni-Cr-P-Si-B foil resulted in very high leaching values are not clear and require further investigation. The composition (Ni – 25Cr – 6.0P – 1.5Si – 0.5B) is not vastly different compared to some of the alloys performing much better. When comparing the results with our previous investigation, the trends are not always the same, and some brazing filler metals which are suitable for drinking water applications have been found not to be suitable for UPW. This emphasizes the importance of performing tests in the actual environment that the brazed components will be exposed to.

The largest uncertainty is related to the presence of dissolved oxygen (and potentially other gases). Prior to the tests it was discussed how to limit the possibilities for interactions with the atmosphere, and several measures were put in place. This included filling the containers as full as possible and limiting the amount of time the test water was exposed to the atmosphere at each sampling interval. However, the tendency for passivation at higher temperatures and visible oxidation at 80 °C of the base material indicate that there has been dissolved oxygen available in the test water.

Conclusions

- The primary identified UPW applications relevant for brazing includes heat exchangers for semiconductor manufacturing and hydrogen applications. In the semiconductor industry water is used for washing and rinsing during manufacture in addition to a number of other processes. For hydrogen applications, heating or cooling of the hydrogen gas can cause UPW condensate to form inside the heat exchangers. For semiconductor applications the operating temperature of a heat exchanger is normally in the lower end of the temperature range 10 – 45 °C, whilst for hydrogen fuel cell applications higher operating temperatures are typical. In the systems where brazed plate heat exchangers are used, the water conductivities are typically 1 - 5 μS/cm, although some applications have more stringent requirements < 1 μS/cm.

- Conductivity measurements were performed in order to evaluate whether it could provide a simpler and cheaper method for evaluating metal ion leaching compared to ICP-OES. At room temperature, the same trends could be seen, but with limited resolution and understanding of the underlying mechanisms. At 80 °C the considerable B leaching from the borosilicate glass in the presence of metallic samples makes it difficult to rely on the conductivity measurements.
- BrazeLet F86 showed the lowest metal ion leaching of the tested brazing filler metals in this investigation. Still, some corrosion was observed in the metallographic investigation.
- BrazeLet Ni613 also showed very good results with low metal ion leaching. Some corrosion was observed in the metallographic investigation.
- BNi-12 showed moderate metal ion leaching at room temperature, with a tendency for lower metal ion leaching at 80 °C. Visible corrosion attacks of the brazed joints could be observed on the sample after testing.
- BNi-5 showed moderate metal ion leaching at room temperature, which increased considerably at 80 °C. The same trend was also observed in the previous trials in drinking water, which suggests that the same mechanism applies with micro-galvanic corrosion related to the Ni₃₁Si₁₂ phase.
- Cu foil showed very high metal ion leaching, while the worst results were surprisingly seen for the Ni-Cr-P-Si-B foil. Both these brazing filler metals showed considerable corrosion attacks in the brazed joints that could be seen directly during visual investigation of the samples after testing.

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