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Effect of NOCOLOK® Flux Dry-off Temperature on Mechanical Properties of Brazed Joint of Automotive Aluminum-Based Heat Exchangers

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Drying temperature of the flux at normal atmosphere has a crucial role in brazing quality in automotive aluminum-based heat exchangers. Over the course of this research, NOCOLOK® flux consists of two phases of $K_2AlF_5.H_2O$ and $KAlF_4$ with melting point around 580 °C was used. A flux slurry was applied on the base metal, and dried at 220, 300 and 380 °C in air. Mechanical assessment revealed that when flux dried at 300 °C, the joint withstands maximum shear stress of 44 MPa with complete bonding. At 220 °C and 380 °C, joint shear stresses are 34 MPa, 30 MPa respectively. 380 °C dry-off temperature under nitrogen gas improved shear strength to 39 MPa. Taking dry-off temperature as 300 °C the amount of defective heat exchangers was reduced from 6% to 2% on a daily basis.

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1 Introduction

Over decades, aluminum alloys have been used to produce auto heat exchangers because of its good thermal conductivity, high corrosion resistance and low density instead of copper and brass [1-3]. Materials used in heat exchangers are generally Al-3xxx substrate with Al-4xxx as external and Al-7xxx as internal claddings when used as tubes. 3xxx series alloys are non-heat-treatable alloys with high mechanical properties and high strength due to the presence of precipitates $Al_6(Mn,Fe)$ in its microstructure and have been used as a base metal in radiators for many years [4]. The external clad, Al-4xxx, is silicon containing aluminum alloy that supplies filler metal at brazing temperature and inner one, Al-7xxx, is used to provide corrosion resistance over service conditions [5-7].

One of the methods used to joint heat exchanger parts is the furnace brazing using NOCOLOK® flux [8]. NOCOLOK® is a mixture of potassium fluoroaluminates. It consists mainly of potassium tetra-fluoroaluminate ($KAlF_4$) and also contains potassium penta-fluoroaluminate (K_2AlF_5). A schematic representation of the whole cycle is depicted in figure 1. It, in general, contains 4 major sequences: (1) Spray the flux on radiators and blowing off the excess flux to have a specified amount of remaining flux in g/m^2 (2) Dry-off section in atmospheric pressure (3) Controlled atmosphere brazing (CAB) section under nitrogen gas (4) Cool down section under atmospheric pressure.

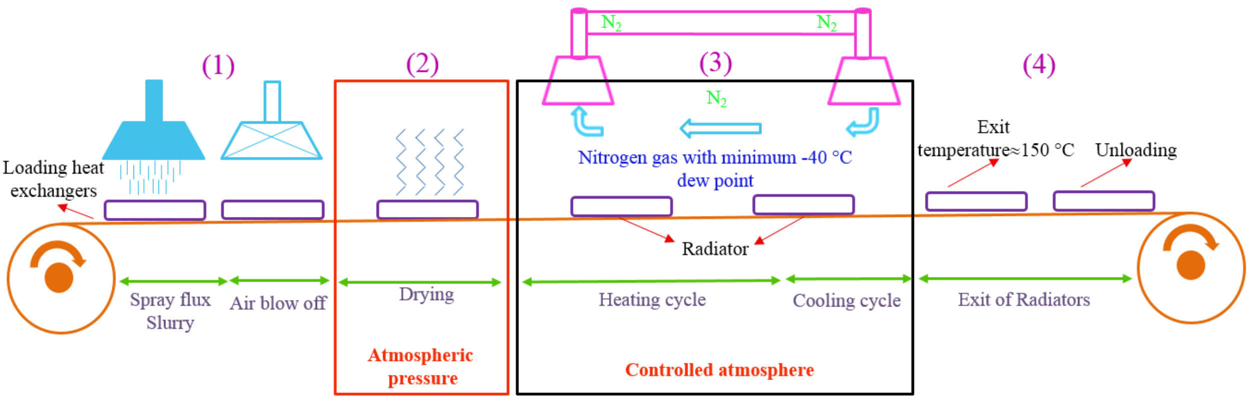

Figure 1: Schematic of the brazing process for aluminum radiators.

Throughout the literature, the concentration of investigations has been made on parameters affecting the braze quality over heating section and kinetics of brazing. Kahl et al. [9] studied just the mechanical properties of the alloy used in the radiator tube at different temperatures. Yun et al. [10] and Kim et al. [11] investigated the effect of thermomechanical treatment on recrystallization and texture of brazed joints. Moreover, different researches have been carried out on the effect of base metal on diffusion characteristics and the braze time on brazed performance for heat exchangers [12-15]. Having done all, there is no evidence of flux dry-off temperature affect on final properties of a brazed joint.

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As shown in figure 1, the entering temperature of the heat exchangers into the furnace with CAB is dictated by drying temperature set point and its maximum temperature, *c.f.* figure 1. It has been usually carried out in an atmospheric pressure that limits the maximum temperature. This temperature can be taken as a matter of concern to get a sound and perfect bonding with sufficient strength at brazed joints. Its variation gives a direct effect in degradation of flux composition leading to increase flux melting temperature and lower the performance of the flux at brazing temperature.

In this research, the effect of the NOCOLOK® flux dry-off temperature will be assessed through characterizations of the flux and scrutiny the effect of dry-off temperature of flux performance and the strength on brazed joints.

2 Materials and experimental procedures

To assess the joint performance, regular aluminum foils with 280 µm thickness used to make tubes, were selected, with three-layers of 4343/3003/7072. The external cladding layer of Al-4343 provides filler metal for joining and an internal layer of Al-7072 providing corrosion resistance of the base metal. Two aluminum sheets are stacked such that the filler metal clads are in contact to each other, as shown in figure 2.

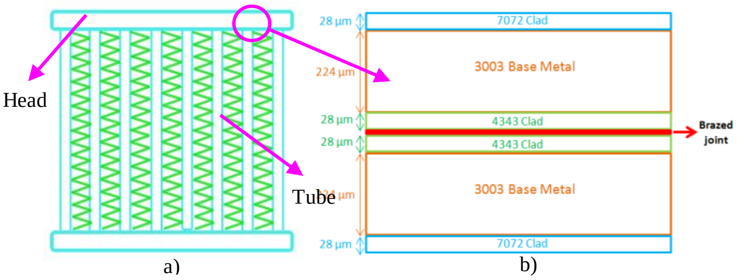

Figure 2: Schematic representation of a) auto radiator, b) tube material stacking to make joint.

Flux with two phases of $KAlF_4$ and $K_2AlF_5.H_2O$ in its composition was used as an oxide removing agent. The brazing of the two aluminum sheets has been carried out in different steps: 1) surface preparation by degreasing and acid pickling, 2) applying flux by 10 g/m^2, 3) drying the whole heat exchanger at different temperatures, 4) brazing in a tube furnace under the nitrogen gas purity of 99.99% and flow 1.5 ml/ min the dew point of nitrogen gas inside the furnace is kept well below -40°C. It should be noticed that the dry-off process is happening in real heat exchanger production lines at different times depending on the mass of the heat exchanger ranging from 5 to 15 minutes to make sure that parts are completely dried off and the moisture is no longer present. This is kept constant at 10 minutes in this research for all dry-off temperatures. Optimal brazing temperature 605±5 °C is applied to create a proper bonding between the radiator components based on 4xxx filler metal properties [16,17]. The brazing cycle, as is identical to industrial scale, is shown in figure 3.

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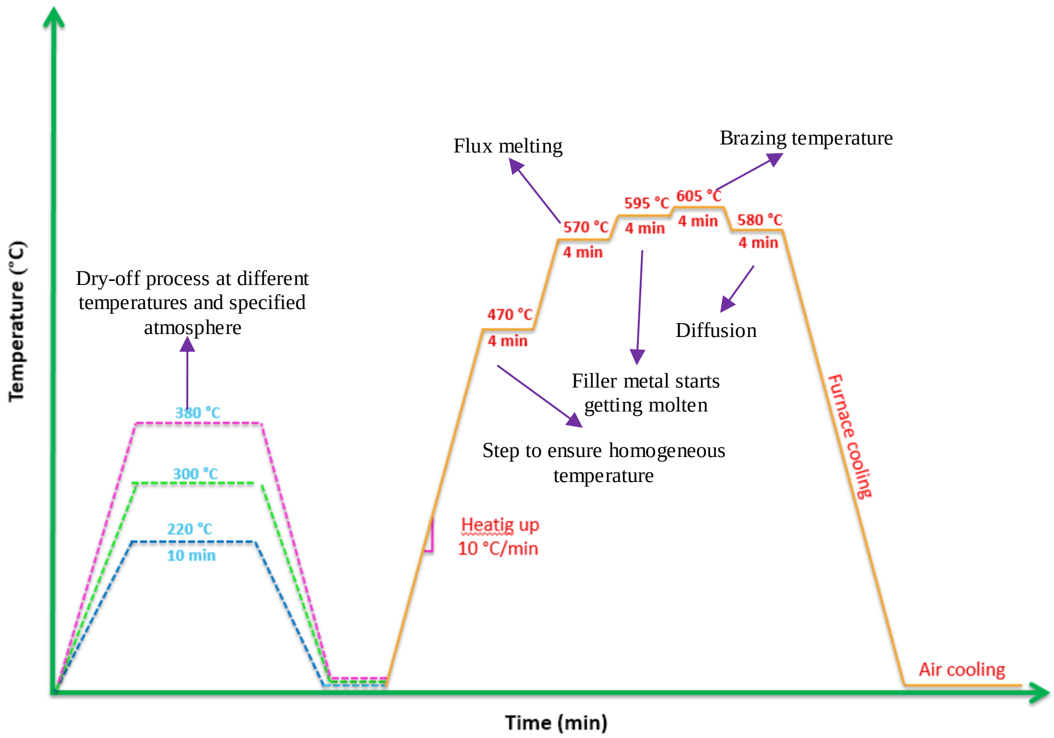

Figure 3: Thermal cycle for brazing.

To have necessary information regarding the NOCOLOK® flux, different analyses were performed. X-ray diffraction (XRD) was performed to identify existing phases in the flux after drying by Bruker D8 Advance with step size (2θ), 0.1 and scanning step time 1s between 10 to 90 degree. Differential scanning calorimetry (DSC) was performed to identify transformation temperatures of the flux in an alumina crucible with heating rate of 10 K/min usingNETZSCHDCS404CPegasus®. Throughout the thermal analysis, the nitrogen gas was injected at a flow rate of 80 ml/min to prevent damage to the components of the device by HF gas generated during the heating process. Particle size analysis (PSA) to determine particle size of flux powder was done by dispersing flux particles in distilled water by ANALYSETTE22-NanoTec-FRITSCH, and the Fourier transform infrared (FTIR) was performed to detect O-H bonding in virgin and dried flux in the range of 3700-3200 cm^{-1} with 0.1 cm^{-1} accuracy by BRUKER TENSOR27.

Optical microscopy and scanning electron microscopy (SEM) were used to study the quality of brazed joints. Two different etchants were used to reveal the microstructure of the base metal and joint area. The base structure was revealed by 0.5ml HF, 6ml H_2O, 6ml HCl and 25ml HNO_3 etchant and the joint structure was revealed by 45ml Methanol, 45ml H_2O, 2ml HCl and 8ml HNO_3 etchant.

The shear strength test is performed according to the AWS C3.2M-C3.2 (2008) standard. In determining the shear strength of the mating plates, as shown in figure 4, two 4343/3003/7072 aluminum sheets with 1 mm overlap are mounted on a fixture and then brazed in the tube furnace.

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The shear test was done at a crosshead velocity of 2 mm/min with SANTAM ST50 universal tensile machine. Average shear strength of the joint is given for five experiments together with uncertainty at 95% confidence level.

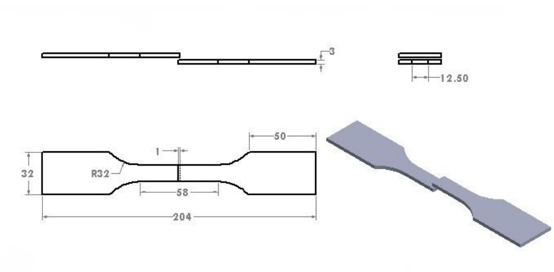

Figure 4: Standard shear test specimen, dimensions are in mm.

1. Results and discussion

In order to analyze the brazing conditions of auto heat exchangers and to identify the main factors affecting the bond strength, the flux properties are specifically obtained, given any factor that causes a change in the chemical composition of the flux directly affects the mechanical properties of the finished product.

X-ray diffraction of the virgin NOCOLOK® powder is shown in figure 5 that the flux is composed of two-phase $KAlF_4$ and $K_2AlF_5.H_2O$. To perform its function at brazing temperature, there must usually be same 20 to 30% of $K_2AlF_5.H_2O$ phase in the flux, according to the KF-AlF_3 phase diagram, (*c.f.* figure 6) to reach a eutectic composition in the mixture. At higher temperature, this phase converts to K_3AlF_6 that is crucial to get eutectic composition at the brazing temperature.

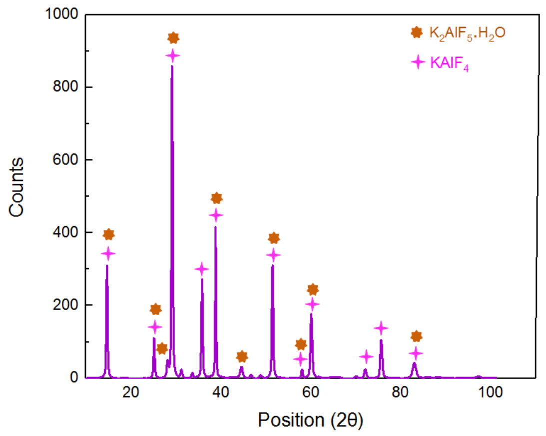

Figure 5: X-Ray diffraction of the NOCOLOK® flux powder.

The eutectic temperature, point E_2, is 558 °C. The precise control of the ratio of the K_3AlF_6 and $KAlF_4$ phases towards the eutectic composition is indispensable.

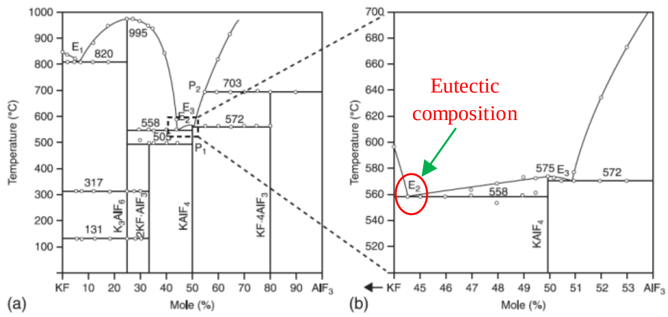

Figure 6: KF-AlF_3 phase diagram [18].

In other words, the actual transformations of the flux drying heating fallow the diagram shown in figure 7. According to this figure, $K_2AlF_5.H_2O$ converts to K_3AlF_6 at brazing temperature and makes a eutectic with $KAlF_4$. Any deviation from this ratio results in moving away from the eutectic composition translating into an increase in the temperature of the melting point [19].

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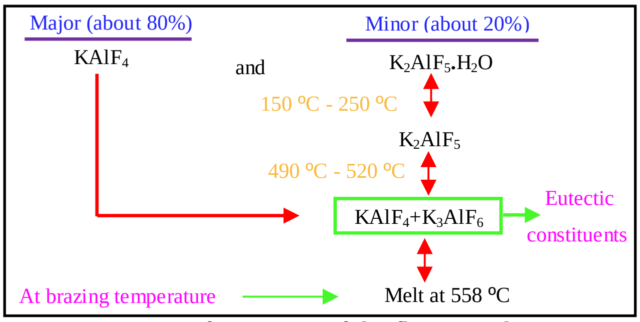


Figure 7: Transformations of the flux upon heating.

Upon heating, the flux undergoes some physico-chemical alterations while the major component $KAlF_4$, is simply heated up without any change in its crystal structure. However, $K_2AlF_5.H_2O$ begins to lose its crystal water at about 200 °C and crystallographic structure change around 500°C. When the temperature is raised to about 550°C, K_2AlF_5 begins to react chemically and produces K_3AlF_6, necessary for a eutectic flux composition together with $KAlF_4$. All these transformations have associated events in DSC pattern in figure 8 as point A, point B and point C respectively. Point D, on the other hand, shows the melting range of the flux is from 560 to 580 °C. The process window for flux performance has a narrow temperature span given the filer metal melting temperature is about 590°C. This proximity between melting range of the flux and filler metal will need a good control over the composition of the flux at elevated temperature.

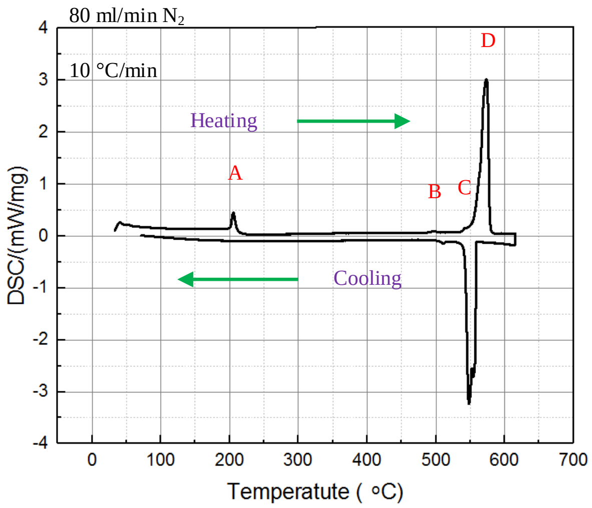


Figure 8: DSC Profile for the flux powder.

To achieve a uniform flux particle distribution in the slurry and the particles remain suspended for long time, figure 9 shows the PSA analysis of the powder with a size distribution within 0.1-10 µm (1µm on average) meaning slurry with uniform suspension can be made. This size distribution is also suggested for suspended slurries elsewhere [19,20]. The other advantage of the fine powder is a full surface coating with high adhesion strength and efficiency for better heat transfer to surface joint. Moreover, when the slurry is prayed and dried, a uniform thin and adherent layer of flux remains on the surface.

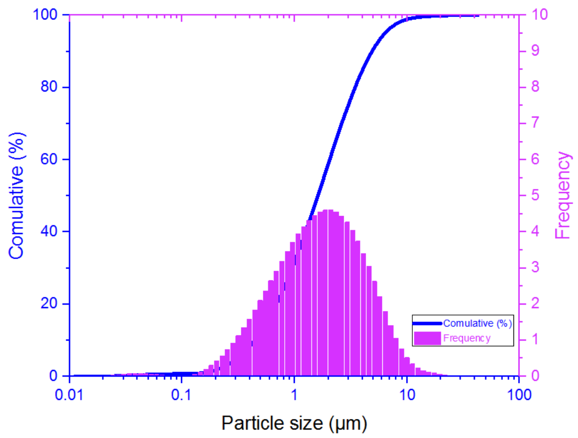
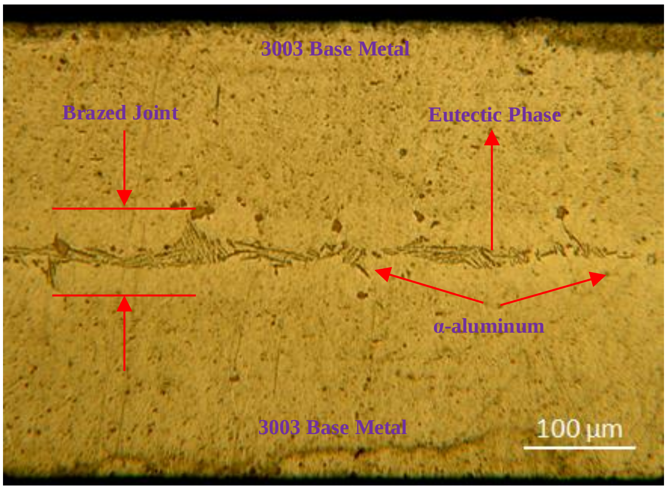
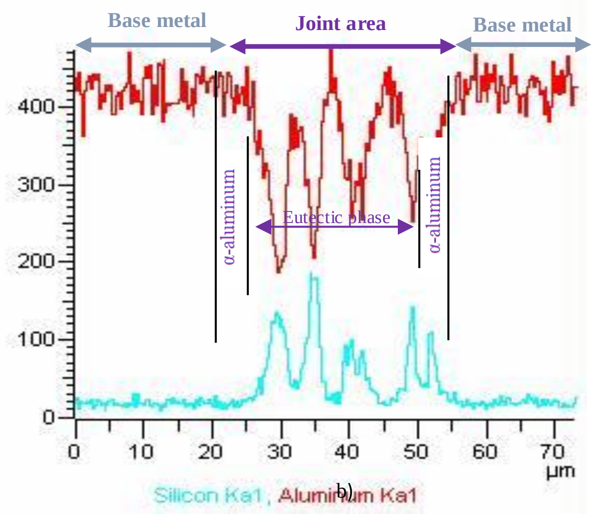


Figure 9: Particle size distribution of the flux powder.

As mentioned in figure 3, the slurry dried at three different temperatures right before getting into the CAB, nominally 220, 300 and 380 °C and then the brazing cycle has been carried out in a nitrogen gas atmosphere. A typical braze joint is shown in figure 10(a) 10consisting, in general, of a eutectic and a solid solution phases with their elemental distribution, figure 10(b). This is the microstructure when flux dried at 300 °C that is a defect free brazing. However, other temperatures show some non-bonded area altogether shown in figure. 11.



a)



b)

Figure 10: a) Optical microstructure of brazed joint, b) EDS spectra of the constituents joint.

As it is clear, 300 °C is the most reliable temperature in which the contact area is free from disconnected area. While, drying at either lower or even higher temperature leave some unbonded region confirming there is an optimum condition for the flux to be properly dried. At high temperature, 380 °C, even when a controlled atmosphere has been applied there are still voids in its structure. One can anticipate the difference in microstructure can translate into the mechanical properties.

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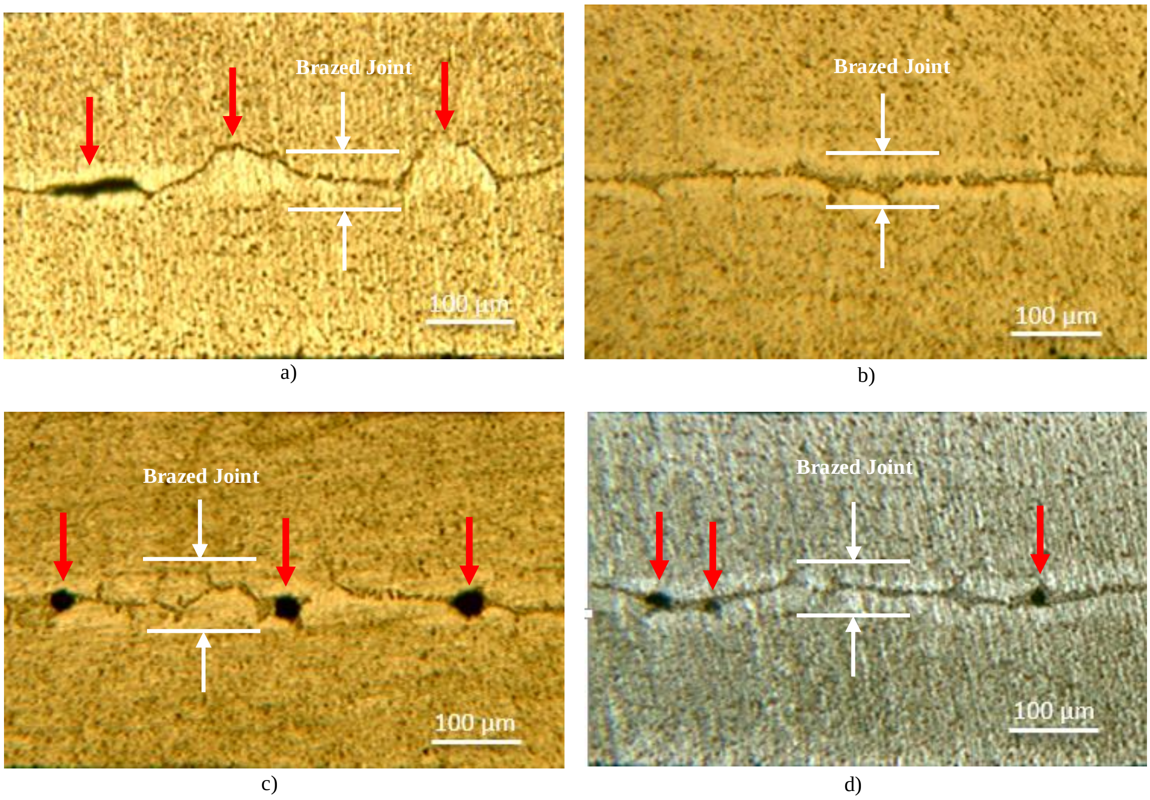

Figure 1: Optical micrographs of brazed joint for flux dried at a) 220 °C, b) 300 °C, c) 380 °C, d) 380 °C -N_2.

Shear stress test results show the highest value of 44 MPa obtained for 300 °C drying temperature, figure 12. When drying occurred in air, the lowest value of shear strength, 30 MPa, obtained at 380 °C and 34 MPa at 220 °C. As expected, the strength of the joint formed when flux dried at 380 °C under nitrogen gas higher that of done in air. This indicates that there are two opposing factors control mating surface condition prior brazing leading up to get a sound joint. On the one hand, water content can change the chemical composition of the flux, $K_2AlF_5.H_2O$ and, on the other hand, high temperature can intensify the oxidation kinetics of the aluminum substrate [21]. Comparing the strength of drying at high temperature with and without controlled atmosphere makes the argument that oxide layer can form extensively such that the flux would not remove it entirely.

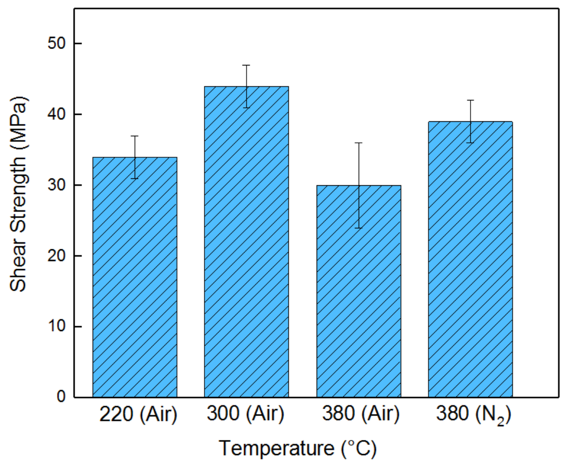

Figure 12: Shear strength of braze joint with different drying conditions.

The X-ray diffraction curves of the flux dried at various temperatures (220, 300 and 380 °C all

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in air and 380 °C under control atmosphere of nitrogen gas (380 °C-N_2)) are expressed in figure 13. The peak height in the virgin powder is higher than the rest of the samples. However, the flux with more drying temperature loses more water resulted in lower peak height.

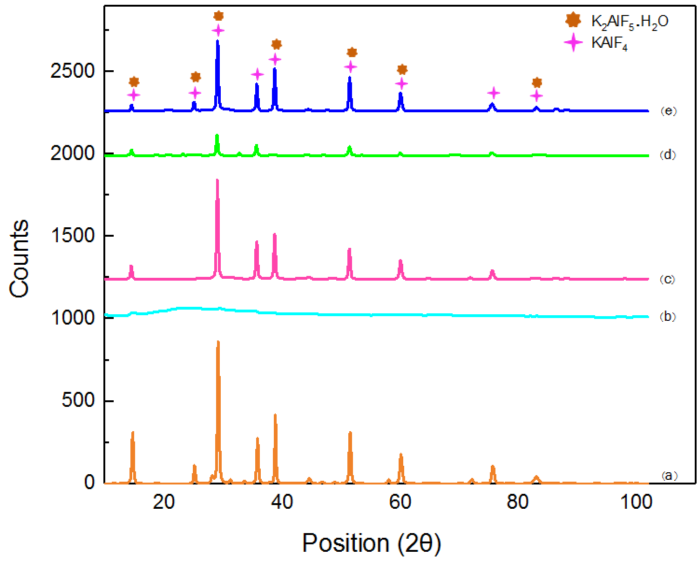

Figure 13: X-Ray diffraction for a) pure sample and dried at, b) 220 ºC, c) 300 ºC, d) 380 ºC, e) 380 ºC- N_2.

In order to justify the difference, a representative peak at 2θ≅29° was chosen as the main peak shown in figure 14. Flux powder dried at 300 °C shows a highest peak compared to the samples dried at other temperatures and at 220 °C has shown the lowest peak height. Peak intensity samples of 380 °C are between 220 °C and 300 °C, so that the sample peak height of 380 °C-N_2 is high compared to 380 °C. The peak height represents the amount of the flux constituents. From this figure, it is clear that the slurry dried at 300 °C gives a peak height relatively the same as that of the virgin powder. The height represents the amount of the two phases, $KAlF_4$ and $K_2AlF_5.H_2O$ that play the very critical role in having a suitable melting point of the flux at brazing temperature.

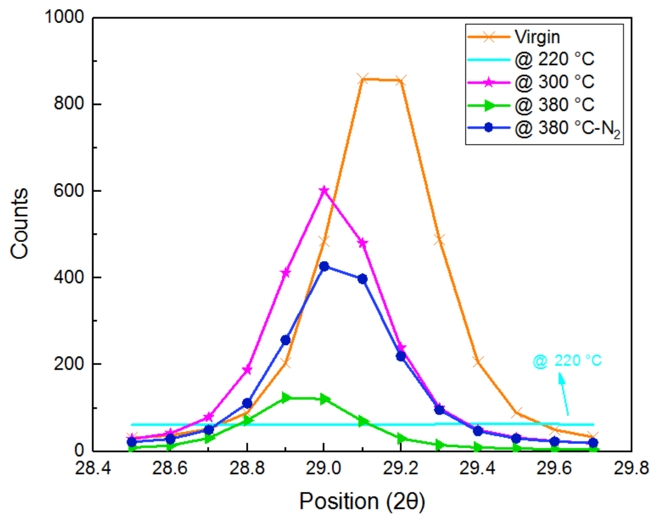

Figure 14: Magnified X-Ray diffraction at different drying temperatures around 2θ≅29°.

In heat exchanger industries, water in inevitably added to the flux to ease spraying over parts, though recently developed cost effective

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dry/electrostatic flux powder eliminates water addition and drying process [21].

In order to get an insight on water content of the dried flux before brazing, FTIR experiments were carried out on the virgin powder as basis and the flux powders mixed with distilled water and dried in a furnace at 220, 300 and 380 °C and 380 °C-N_2 all is gathered in figure 15.

Water bonds (O-H bonds) absorb infrared radiation in the range of 3000-4800 cm^{-1}. This Figure can demonstrate the peak absorption at 3500 cm^{-1} related to the $K_2AlF_5.H_2O$ phase and the moisture content of the powder itself.

The higher the drying temperature of the flux, the less water content remains in the flux. The receiving flux powder carries little amount of water in its structure. This can even confirm the X-ray diffraction on the presence of the $K_2AlF_5.H_2O$ phase in the flux. As shown in figure 15(a), transmittance peak of flux dried at 220 °C is higher compared to other temperatures. This is well associated with lower X-Ray intensity of the flux at 220 °C (*c.f.* figure 14). Given the flux powders have a solubility level of 4.5 g/l in water [21], the O-H peak appeared in the FTIR diagram can be attributed either to $K_2AlF_5.H_2O$ phases or water soluble compounds such as $Al(OH)_3$ or K(OH). However, X-ray diffraction pattern proves, by its peak intensities, that the latter are present in the flux. When temperature rose up to 300 °C, figure 15(a), there is no water soluble compounds in the flux and the water content decreases move toward virgin powder. Therefore, one can conclude that this peak represent only $K_2AlF_5.H_2O$ phase. The high intensity in the x-ray diffraction sample of 300 °C compared to the rest of the samples, (figure 14) is another indication of the presence of $K_2AlF_5.H_2O$ phase. To that sake, the 300 °C drying temperature is anticipated to deliver the best performance of the flux during brazing.

The flux dried at 380 °C does not show any O-H bond meaning the water is completely evaporated, and the $K_2AlF_5.H_2O$ phase is fully dehydrated. However, the use of controlled atmosphere at this temperature keeps a small amount of $K_2AlF_5.H_2O$ phase in the flux and complete evaporation moves toward high temperature, figure 15(b).

Though 380 °C showed no water content in its FTIR experiment, figure 15(b), shear strength is less than other temperatures. This can be either due to the formation of a high oxide layer, or an alteration in chemical composition of the flux and degradation of its functionality. When a controlled atmosphere is applied, oxidation layer would then tend to be reduced and higher shear strength is attainable. In other words, by applying nitrogen gas, according to the FTIR diagram, there is still a certain $K_2AlF_5.H_2O$ phase and the performance of the flux would not exacerbate.

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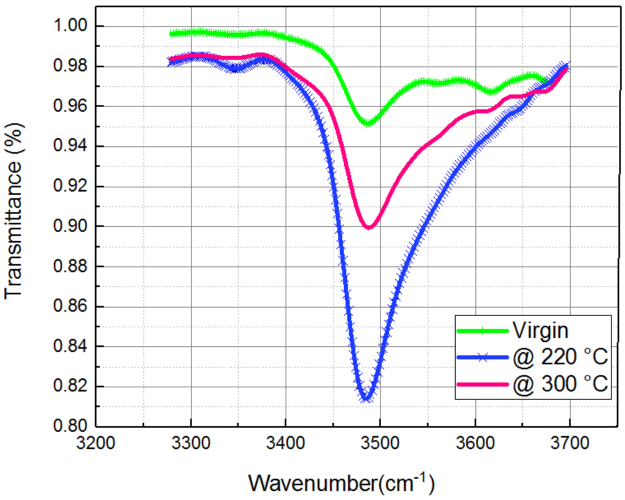
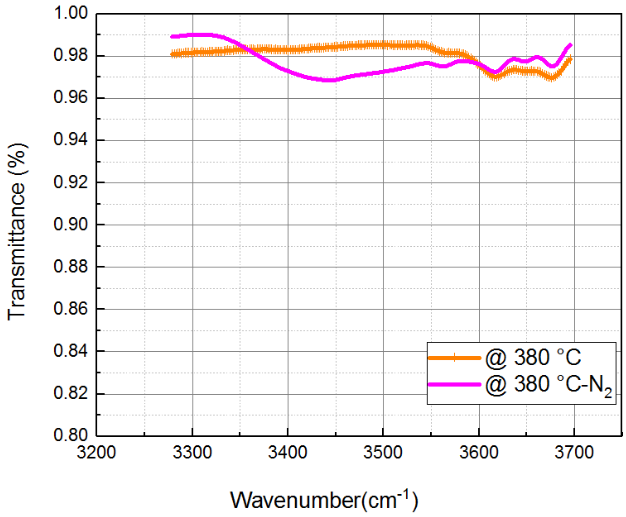


a)



b)

Figure 15: FTIR profile for a) pure state flux and dried at 220 °C, 300 °C, b) flux dried at 380 °C, 380 °C -N_2.

In general, going through the brazing cycle, $KAlF_4$ evaporates on a small scale. If moisture is present, two reactions can take place according to equations 1. This reaction accelerates the evaporation and consumption of $KAlF_4$ and the reaction product is HF. HF gas tends to escape from the system causing the reaction continuously consumes more $KAlF_4$ [19].

$$3KAlF_4 + 3H_2O = Al_2O_3 + K_3AlF_6 + 6HF$$
$$2KAlF_4 + 3H_2O = 2\,KF + Al_2O_3 + 6HF \qquad (1)$$

Any reduction in $KAlF_4$ composition, gives the melting point to be shifted to a higher temperature that leads the flux to be disfunctioned in removing the oxide layer and minimizing re-oxidation effects on the aluminum surfaces.

Having applied flux drying temperature at 300 °C in Radiator-Iran Co .production line, the amount of leakage radiator production is reduced 6% to 2% in a daily basis.

Conclusion

In this study, 3003 aluminum strips with 4343 clad filler material were brazed under the same conditions as Radiator- Iran Co. production line and the effect of drying temperature of the NOCOLOK® flux was studied in the range of 200-380 °C. Out of the results, one can conclude:

- The strength of the joints depends on the drying temperature of the flux slurry. There is an optimum temperature to achieve the proper joint structure, perfect bonding and sufficient strength. In this study, the optimum drying temperature was 300 °C.
- Drying at 220 °C and 380 °C result in low shear strength duo to excess moisture content and oxidation of aluminum sheet surfaces.
- Nitrogen-controlled atmosphere at 380 °C prevents the formation of the oxide layer

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and improves shear strength. This is justified through mechanical properties as well as microstructure of the brazed joints.

- By applying the optimum temperature for drying off the flux slurry in the Radiator-Iran company production line, the rate of failure with leakage based was reduced from 6% to 2% in a daily basis.

Acknowledgment

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