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Arch. Metall. Mater. **65** (2020), 4, 1469-1476

DOI: 10.24425/amm.2020.133715

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SELECTED CYCLIC CORROSION TESTS IN AUTOMOTIVE INDUSTRY

Corrosion is a main problem for longtime exploration of heat exchangers in automotive industry. Proper selection of accelerated corrosion test for newly developed material is a key aspect for aluminum industry. The selection of material based on corrosion test includes test duration, chemical spray composition, temperature and number of cycles. The paper present comparison of old and newly developed accelerated corrosion tests for testing automotive heat exchanger. The accelerated test results are comprised with heat exchanger taken from market after life cycle.

Keywords: corrosion test, automotive, aluminum, heat exchanger, corrosion products

1. Introduction

Currently, heat exchangers in automotive cooling systems are made of aluminum alloys. This material replaced the commonly used copper alloys which were typical until the 90s. The main reasons for the change was economic, but also ecological, consisting in reducing fuel consumption during car driving [1]. Aluminum due to its density (2.7 g/cm^3) and thermal conductivity of 240 Wm-1K-1 [1] turned out to be a material perfectly meeting the expectations. The condenser consists mainly of pipes, fins, collectors, receiver dryer and mounting elements. Tubes, fins and collectors are the main heat exchange surface (Fig. 1, 2). They are joined together in the soldering process. Soldering operations are most often carried out using multi-layer materials, where the core material is based on 3XXX aluminum alloys, and the layer of clad consists of 4XXX aluminum alloys. An example of such a material is a foil intended for the production of tubes, where brazing layer of clad is made by 4343 alloy and the base material is alloy 3003. An example of operation and a schematic structure of a condenser are shown in Figures 1 and 2.

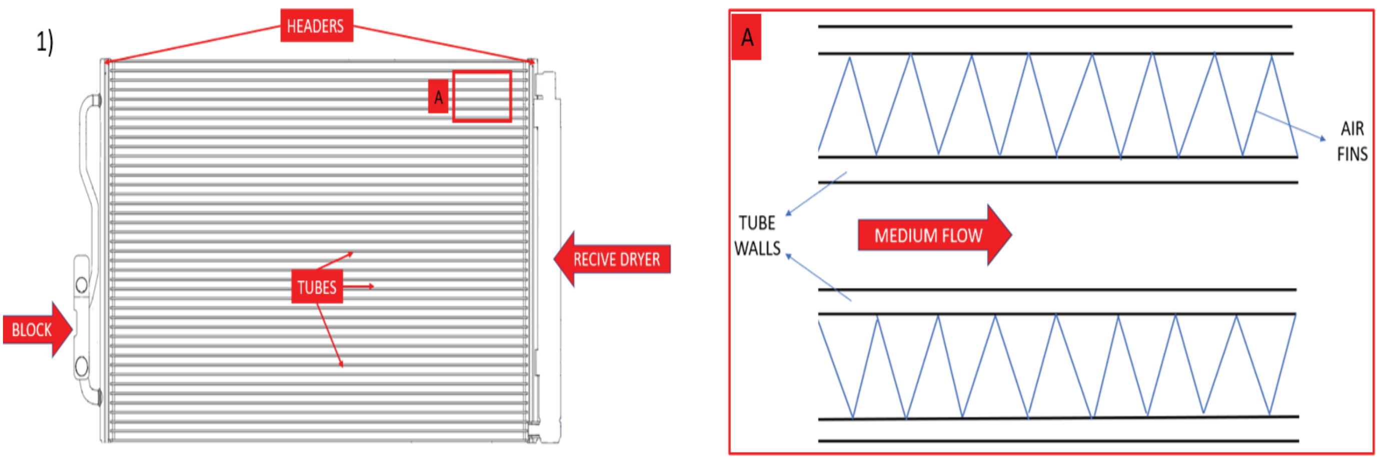

Fig. 1. General view of condenser 1) – Zoom – connection tube-fins, A) – VALEO resources

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Point A. The overheated vapours of the refrigerant enter the condenser, the pressure is high.

Between **point A and B** vapours reach the condensation temperature.

Point B. liquid drops appears, temperature is low This is start of condensation. **Between B and C** there is change of state(condensation). The temperature remains constant. There is less and less vapor and increasing level of liquid.

Point C. End of condensation – last vapors of the refrigerant change into liquid.

Between C and D air circulation around condenser lightly aftercooling the liquid and temperature drops gradually.

Punk D. at the outlet of condenser only liquid remains, liquid has been aftercooled. Pressure remains constant.

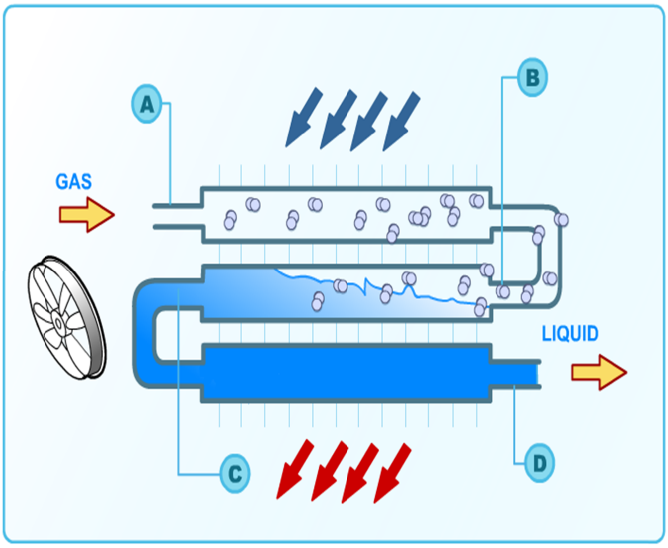


Fig. 2. Scheme of condenser's work –VALEO resources

The materials of which the heat exchanger is made have contact with various chemical substances, i.e. heavy metals, road salt or acid ions. They are also exposed to changing weather conditions, and especially to fluctuations in humidity and ambient temperature. Thanks to many years of research, norms and specifications have been created for reflection the impact of the environment on materials in a much shorter time than it happens in reality.

The oldest and best known tests are ISO 9227 (ASTM B117) or ASTM G85. Due to their universality, they are still a solid base for verification of corrosion resistance. However, the development of materials forces car producers to update and introduce new test methods.

2. Corossion tests – summary

Developing technology and growing quality requirements related to safety and economy are forcing the leading car manufacturers to verify components more efficiently. The Table 1 presented below summarizes the most popular corrosion tests used since the 1970s. The tests are carried out using a continuous salt spray, in the form of salt mist, on samples placed in the chamber. During the corrosion test, constant temperatures is use and its range fluctuate from 35 to 50°C, humidity is assumed to be at 95%. The main difference in tests scheme and time lays in the composition of the solution and its pH.

In the last 10 years, car manufacturers have modified the tests presented in Table 1. Selected tests upgraded in new parameters are presented in Table 2. They are the latest and most common corrosion test specifications currently used on the heat exchanger market.

TABLE 1

Summary of corrosion tests used in the automotive industry since the seventies [6,7]

Test name	Solution	Cycle	Temp.	Humidity	pH	Duration
ISO 9227 NSS	NaCl+ demi water	Continous spraying	35±2°C	>95%	6,5-7,2	2-1000h
ISO 9227 AASS	NaCl + CHCOOH + demi water				3,1-3,3	
ISO 9227 CASS	NaCl + demi water + $CuCl_2$ • H_2O		50±2°C			
ASTM G85 A3	NaCl, MgCl, Na_2SO, CaCl, KCl, $NaHCO_3$, KBr, H_3BO, SrCl, NaF, CHCOOH, NaOH + demi water	30 min – fog phase 90 min – humidity >98%	49±2°C	>98%	2,8-3,0	480-1320 h

TABLE 2

Selected corrosion tests introduced to the market in the last 10 years [2,8,10]

Test name	Solution	Cycle	Temp.	Humidity	pH	Duration
DEFINX	Kärcher solution NaCl + demi water	30 min immersing 12 h climatic cycle	35-45°C	50-95%	6,5-11,0	1008 h
VDA 233-102	NaCl + demi water	24 h fog phase 96h climatic cycle	–15-50°C	Max 95 % Not controlled in minus temp.	6,7-7,2	1008 h
CCCT – MBN10563	NaCl+ demi water +$CuCl_2$ • H_2O	10 min immersing 144 h climatic cycle	30-80°C	50-95%	3,1-3,3	1008 h

2.1. Debonding Fin of Heat Exchangers

The test was introduced by the Valeo group. Determining test requirements, focus was on three aspects that were to be tested in a broader way than before. The first was the overall resistance of the tube material to potential leakage of coolant and the resistance of the tube-collector solder connection. In the second point, special interest was directed to the assessment of soldering quality and corrosion resistance of the tube-fins connection for heat exchange. The last topic on which attention was focused was the validation of the fins corrosion resistance. This has a direct impact on the heat exchange efficiency for which the component is responsible [2]. The DefinX test was Valeo's response to the corrosion of heat exchangers caused by the harmful effects of cleaning agents named debonding fin.

It has been shown that the action of alkaline agents with a pH above 9 (according to the Pourbaix diagram) [9] causes the dissolution of aluminum oxides and leads the material from the inactive state (immunity) to the active state [3]. On exchangers from the field in some cases debonding fins was observed. This damage of fins lead to the loss of cooling system efficiency.

The test is performed in stages. In the first phase, samples – 10×20 cm fragment is cut out from whole exchanger. Then they are immersed in a cleaning agent with a pH above 9. In the next stage the sample is placed in a climatic or corrosion chamber, which has the ability to regulate humidity and temperature according to Fig. 3. The sample is sprayed with a mixture of water and salt. Test duration is 6 weeks.

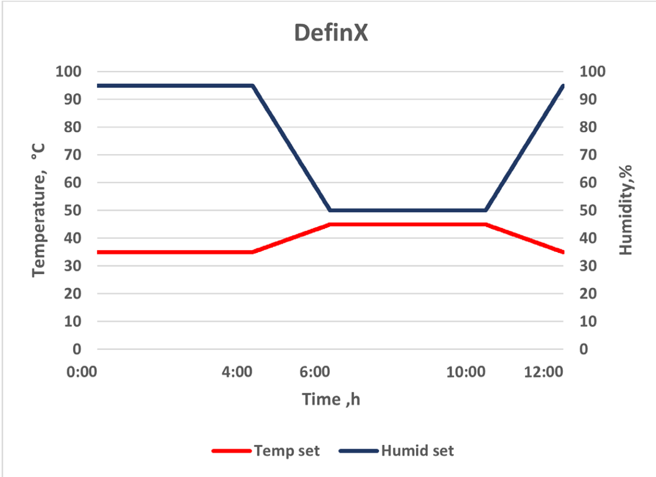


Fig. 3. DeFinX test cycle [2]

2.2. CCCT – MBN10563

Corrosion test was developed in 2018 and implemented by various manufacturers e.g. Mercedes-Benz company in order to verify the corrosion resistance of automotive heat exchangers in a shorter time than before. It is a combination of corrosion and climate tests in the range of positive temperatures. Humidity is changed in within the given values. Moreover, additional flexibility was introduced in the form of a "immersion" cycle of samples, which is an alternative to the typical spraying in a corrosion chamber [10]. The solution itself is not new and is based on the ISO 9227 – CASS standard, which has been used since the 1970s. As a result of using the above-mentioned solution, a corrosion catalyst in the form of Cu ions appears in the test, which largely promotes the local corrosion on the surface of the materials tested. It is directly related with interaction of copper ions with alumina surface . The cycle diagram is presented on the Figure 4. Test duration is 6 weeks.

2.3. VDA 233-102

The test was developed by a group of experts with the support of Voestalipne company [10] in order to materials validation such as steel, steel coated with zinc and aluminum alloys. The describe test is reflected in natural atmospheric tests (DIN 55665). It is based on variable temperature and humidity cycles. Taking

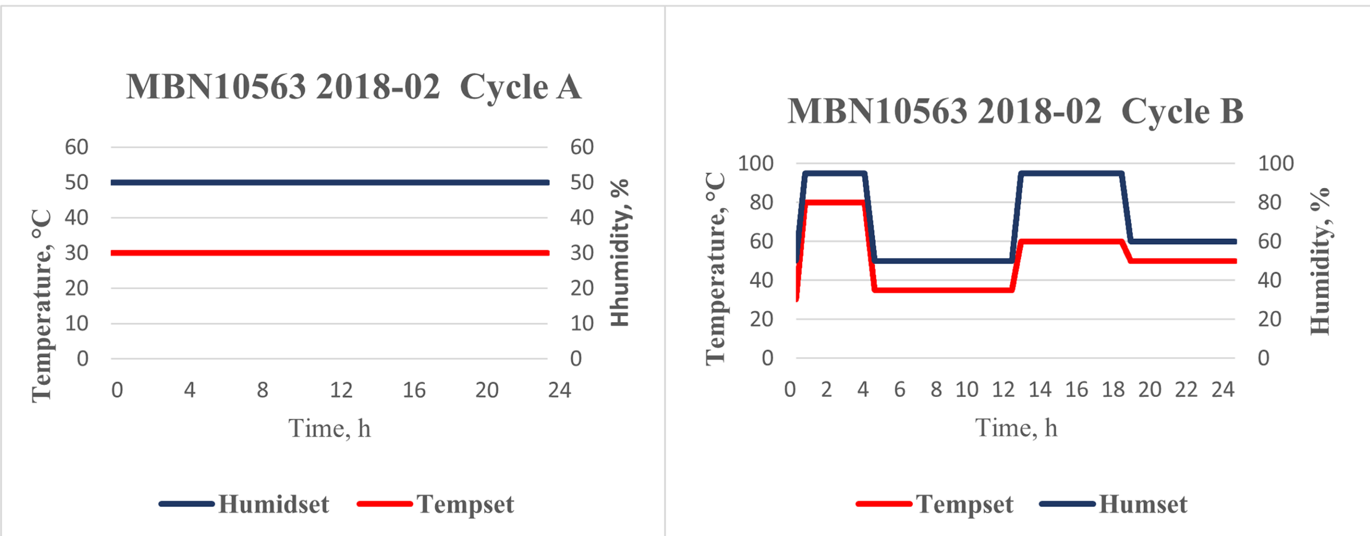


Fig. 4. MBN10563 test cycles [2]

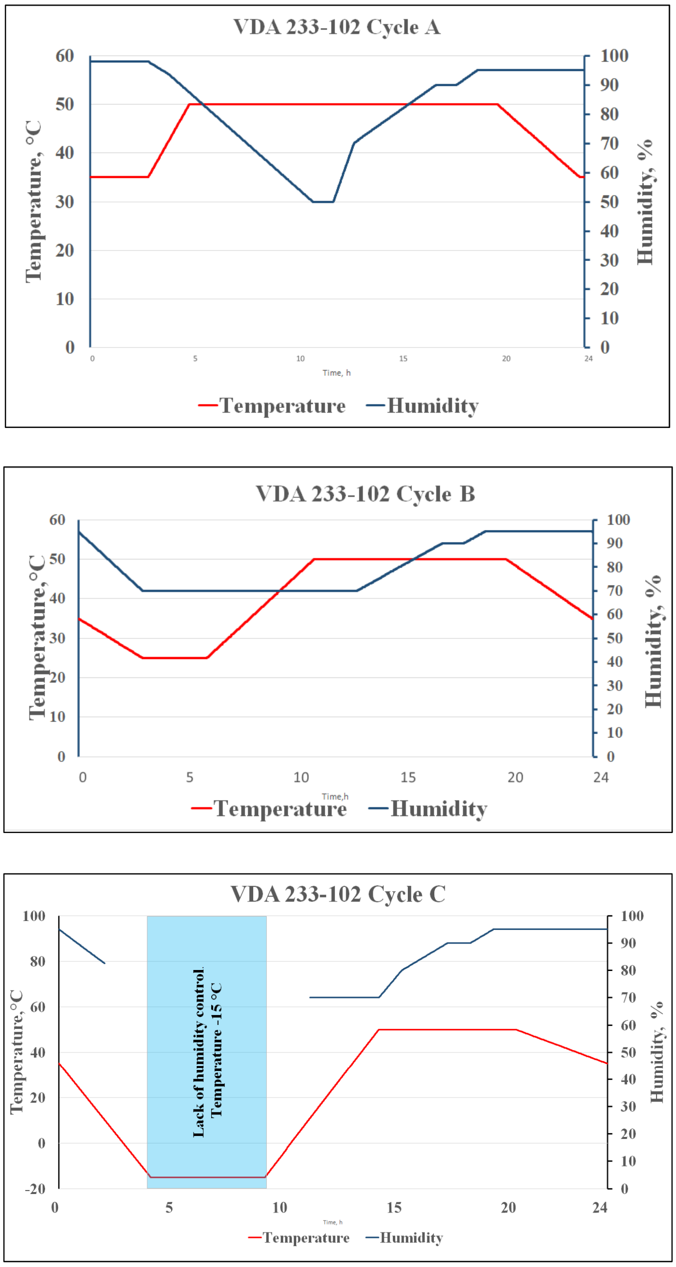


Fig. 5. VDA 233-102 test cycles [9]

into consideration a temperature range it such be noted that the test includes temperatures below zero as well. Test consists of 3 sub-cycles (A, B, C) with different courses. It was presented on Figure 5 below. The test scheme is specified as a combination of B-A-C-A-B-B-A cycles. Cycles A and B are about change of temperature in the range of 35-50°C and humidity on the level of 50-98%. The difference between A, B and C cycle is related to the introduction of temperature range to –15°C in the C cycle. Such attitude is not often found in corrosion tests.

3. Experimental

3.1. Sampling

CCCT, ASTM, VDA 233-102, DefinX tests were carried out in the experimental part. The tests omitted the ISO 9227 test due to the specifics of the

test and its sporadic use, in the basic form, for testing aluminum heat exchangers. The above tests were carried out on condensers manufactured in a serial process using CAB soldering [4]. The condensers are made of 3XXX series aluminum alloy with aluminum 4XXX series as a soldering medium. The chemical composition of the alloys is given in Table 3.

TABLE 3

Example of chemical composition (wt.%) of aluminum alloys [6]

Alloy	Si	Fe	Cu	Mn	Zn	Al.
AA3003	0,08	0,16	0,19	1,1	0,1	Bal.
AA4343	7,86	0,09	0,11	0,01	0,09	Bal.

The material of the tube was analyzed. It is most exposed to the harmful effects of the environment. The measurements concerned on the type of corrosion formed on the tube and its nature (pitting depth and chemical composition of corrosion products). The microstructure of the tube material (before and after brazing) was presented on Figure 6.

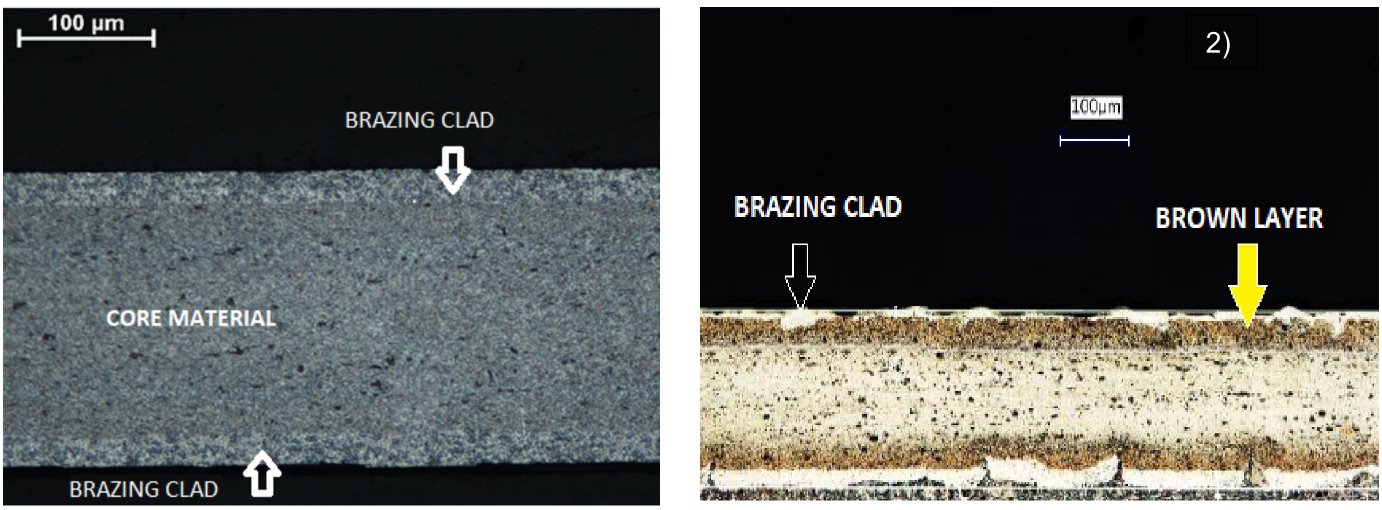


Fig. 6. Foil for tube 1) before brazing, 2) after brazing process

The tube material consists of two layers. The first layer is brazing clad – 4XXX aluminum alloy and the second is material of the tube core – 3XXX aluminum alloy. As a result of the soldering process, the plating layer melts and then weld is forming. It becomes white during etching process (Figure 6). In addition, a diffusion transition layer is created (called brown band), which also provides additional corrosion protection for the tube. Samples 1 cm thick and 2 cm long were taken from the exchangers, as a sections of tubes connected with a fin. Sampling locations are shown in the Figure 7.

The obtained corrosion depth was measured and presented in Figure 8 for individual tests. This results are in the range of 35-46 μm, which is from 20.7% of the tube thickness for the VDA test to 13.5% for the DEFINX test. Corrosion formed on the tested material has a superficial and irregular character for CCCT, VDA, DefiniX tests and for the exchanger taken from

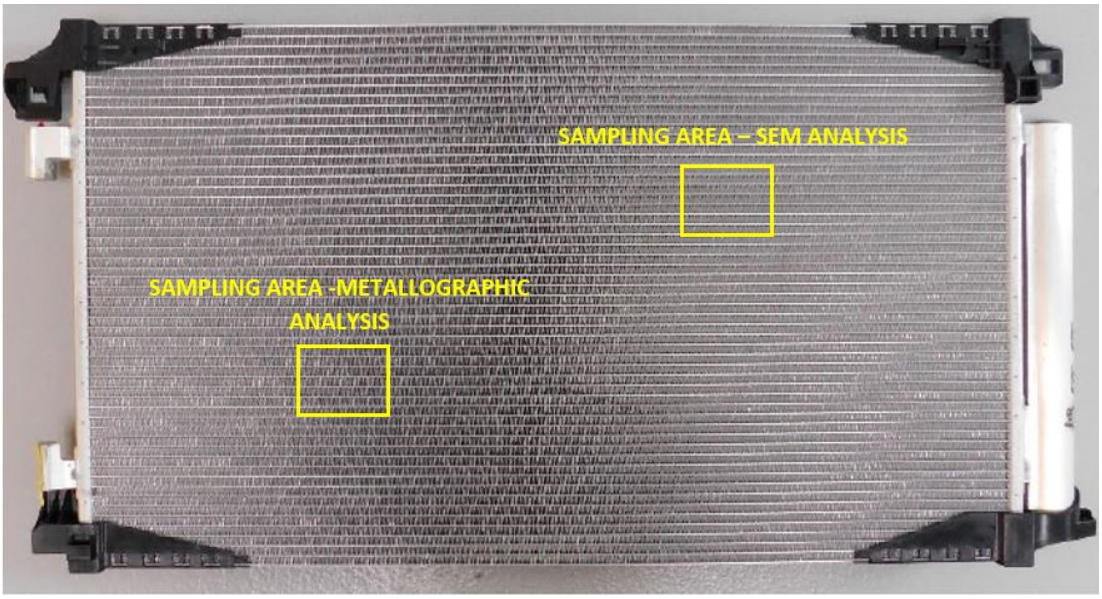


Fig. 7. Example of sampling area marked on condenser's core

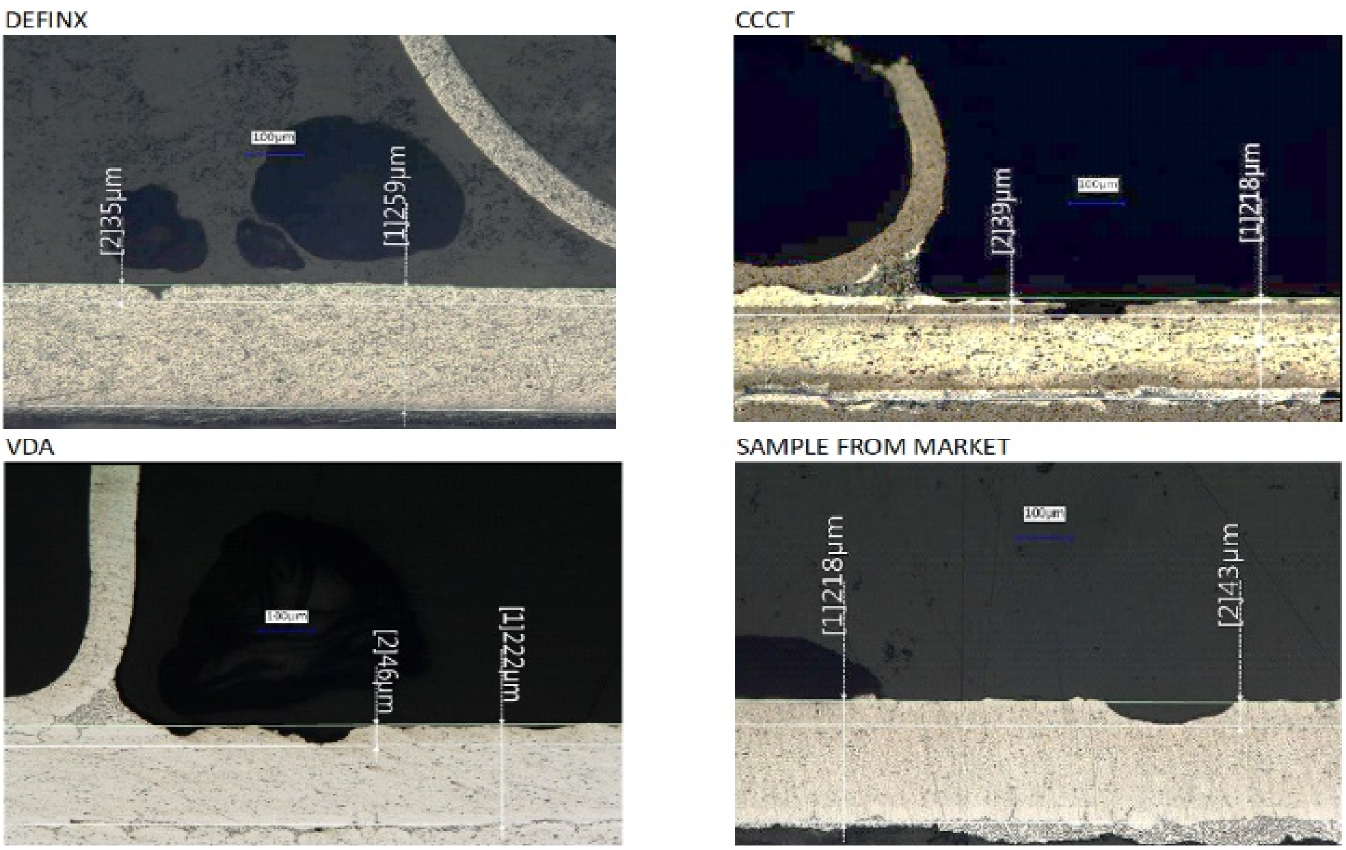


Fig. 8. Measured corrosion on tested sample

the market. The pitting corrosion was observed in Valeo Group test. It was detected within the solder layers.

3.2 SEM analysis

The cut samples were dried at 50 ± 2°C and analyzed under an ASPEX scanning microscope. The analysis showed the appearance of sodium and chlorine ions for all performed tests Their presence has been confirmed on exchangers coming directly from the market as well. The market samples were taken from regularly used car after end of its technical life. The results of SEM analysis (Table 4) shown that the chemical compositions of used solutions were significantly influenced on the tests results

The presented tests shown a significant diversity of chemical composition of corrosion products. Most of the observed elements are components of the used solutions. Overlapping groups of elements is common to all tests. This is clearly visible for Na^+ and Cl^- ions, which confirms the presence of a significant amount of sodium chloride on the surface of the analyzed sample.

TABLE 4

SEM analysis summary for all performed tests

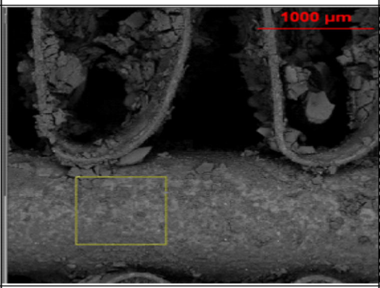
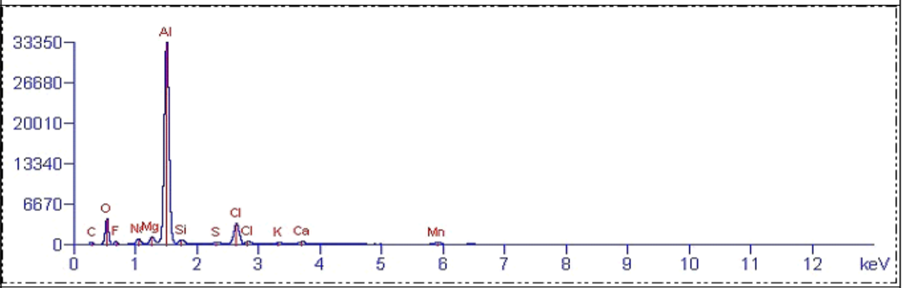
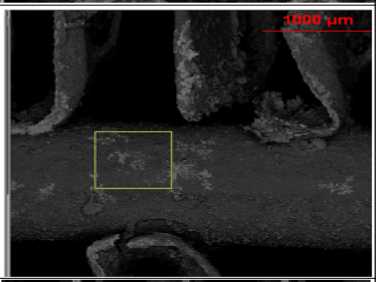
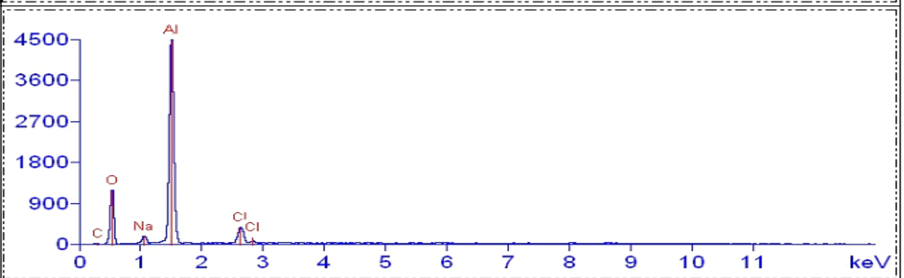
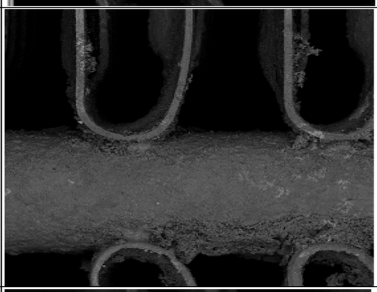
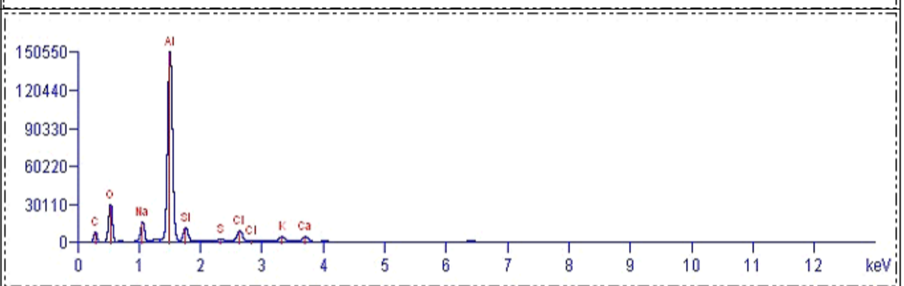
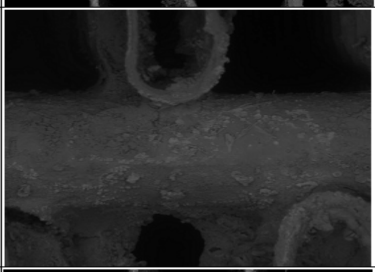
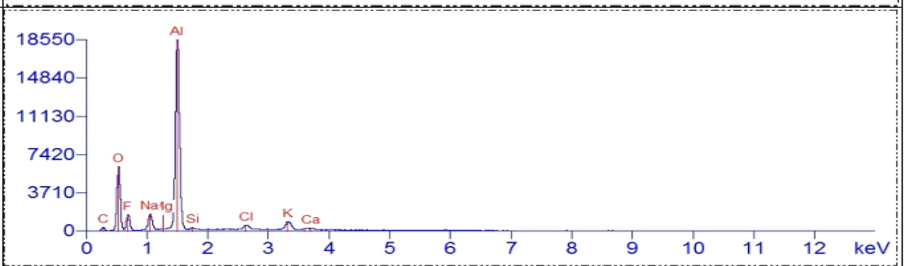
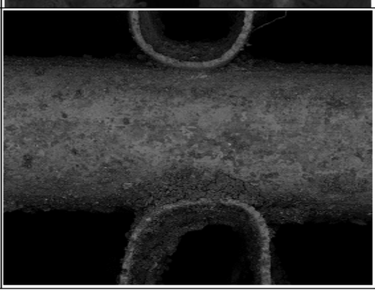
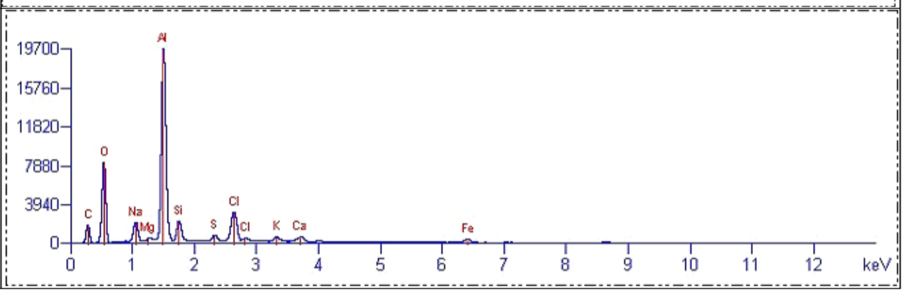
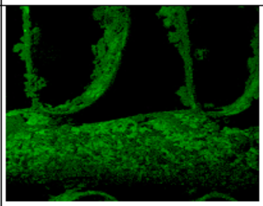
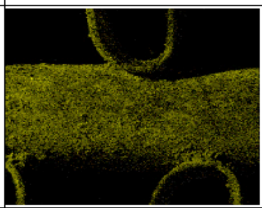
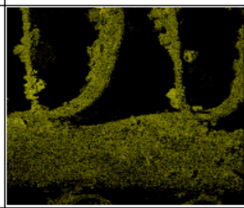
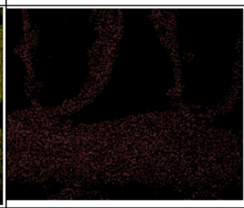
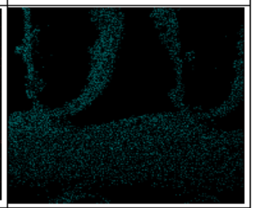
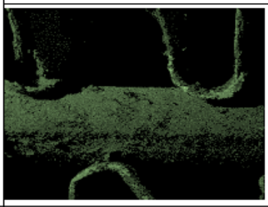
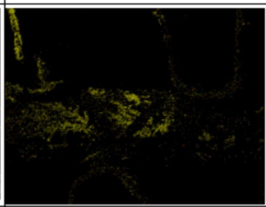
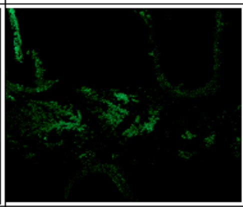
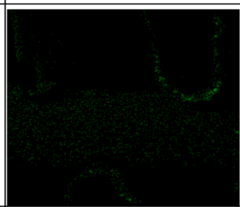
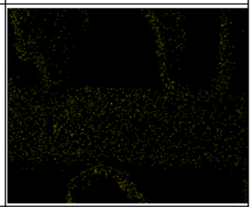
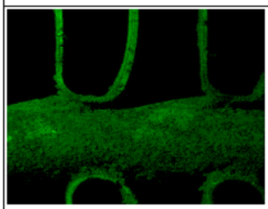
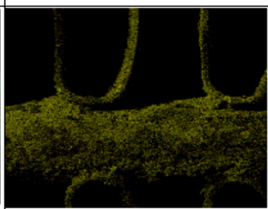
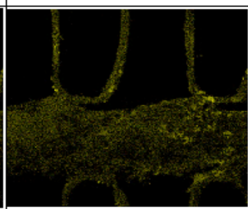
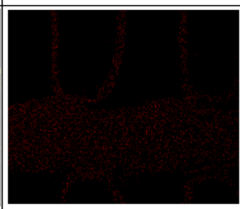
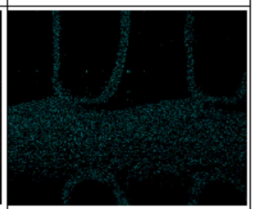
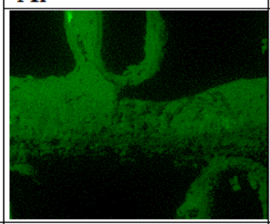
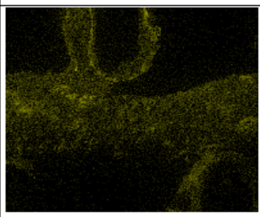
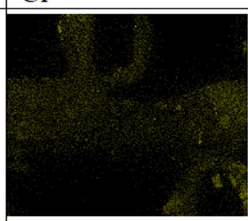
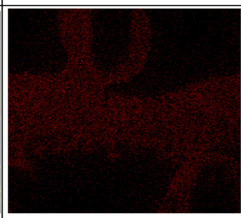
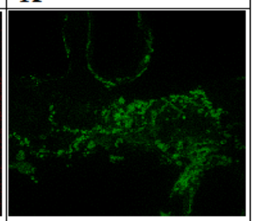
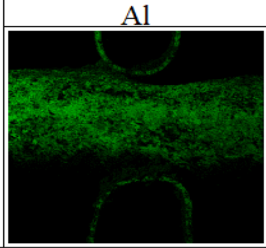
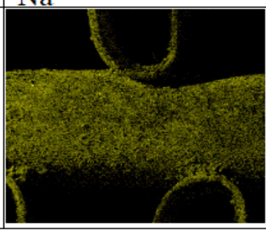
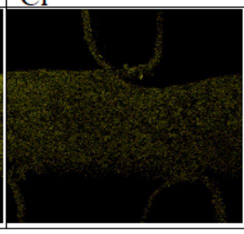
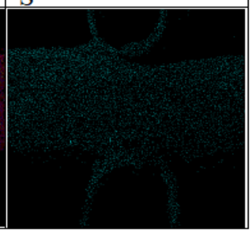
TEST	ANALYSDE PLACES	SPECTRUM
ASTM G85		
CCCT		
DEFINX		
VDA 233-102		
SAMPLE FROM MARKET		

TABLE 5

Elements mapping performed for all tests

	Elements				
	Occurred in all solutions / all tests			Specific for given test	
TEST	Al	Na	Cl	Ca	S
ASTM G85					
CCCT	Al	Na	Cl	K	Cu
					
DEFINX	Al	Na	Cl	Ca	K
					
VDA 233-102	Al	Na	Cl	Ca	K
					
SAMPLE FROM MARKET	Al	Na	Cl	Ca	S
					

In addition, for the ASTM test, the Mn peak in corrosion products is visible and it is not the result of the chemical composition of the solution used, but it is derived from the tube material. Same as for the Fe peak, it is an external contamination or comes from the tube material.

The elements mapping was performed to refine the information. The results are shown in Table 5.

4. Disscusion

Studies have shown that ASTM and DefinX tests present the chemical composition of corrosion products in the way most similar to the spectrum determined for a sample from the market. In the range of elements could be found sodium, chlorine, sulfur, magnesium, calcium and potassium.

All tests performed showed the same nature of corrosion. Only the DefinX test revealed the pitting corrosion by using a special solder layer. Based on the observation of the tube after the soldering process, it was found that the pitting corrosion is the effect of the erosion of the plating itself and it falls within the scope of the solder layer itself formed after the soldering process.

Taking into account the above information, it has been shown how important it is to choose the right test for a given exchanger material. Different information can be get resulting from using the given test.

However, for better understanding this phenomenon, solutions uses in cyclic corrosion tests should be developed with a composition similar to the chemical composition of potential impurities shown on the basis of sample analysis taken directly from the market. Moreover, important aspect that should be modified are the test parameters, i.e. temperature, duration and humidity. All of this activities lead to a better selection of materials for heat exchangers by more accurately predicting the corrosion process during their exploitation.

5. Conclusion

The analysis of performed corrosion tests of automotive heat exchanger leads to following conclusions:

1) The results of corrosion analysis after the tests overlapped with the results obtained for the sample from the market.
2) All performed tests can be used to compare the corrosion resistance of various aluminum alloys used in the production of automotive heat exchangers.
3) Differences in metallographic analysis and SEM analysis may result from the chemical composition of the alloy itself, the heat treatment during brazing process, test parameters. It follows that the study should not only include corrosion products, but also the chemical composition of the alloy within the resulting corrosion.
4) The selection of an appropriate test determines the assessment of the product in terms of requirements specified by OEMs.

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