

CORROSION SIMULATION TESTS ON STAINLESS FOR AUTOMOTIVE APPLICATIONS

B.Michel¹, S.Saedlou¹, J.M.Herbelin² and P.O.Santacreu¹

¹ArcelorMittal Global R&D, ²ArcelorMittal Stainless Europe, Isbergues France

Abstract

Stainless steel is largely used in the automotive market, essentially for exhaust system. In that field of application, designs are more and more complex and the guarantee durations continuously increase. Thus laboratory tests were developed in order to simulate automotive environments and estimate their impact on stainless steel durability. Corrosion mechanisms greatly depend on the temperature and so the exhaust system could be divided in two parts which are: the hot part near the manifold ($400 < T(^{\circ}\text{C}) < 900$) and the cold part near the muffler ($20 < T(^{\circ}\text{C}) < 400$). For the hot part, the main corrosion mechanism is oxidation, also called dry corrosion. Laboratory test used for that high temperature application is the cyclic oxidation. The behaviour of each grade is evaluated through mass variation measurement on specimens exposed to a specific thermal cycle during x-hours. In the cold part, near the muffler, exhaust gas could condensate on the internal surface of the exhaust system to form complex acids. Consequently corrosion mechanism is more complex and is a combination of wet and dry corrosion. On that idea, a "dip & dry" apparatus was developed in order to simulate that kind of corrosion on stainless steel grades, by cyclic dipping in an artificial condensate, drying and oxidized specimens in oven. After test, grades are compared through maximum corrosion depth measures. In addition, the external cold part of the exhaust system is visible and so, guarantee could also include cosmetic requirements. An experiment test based on climatic standard test with periodic heat treatment at 300°C was developed to mimic the external corrosion of exhaust system. Thus treated specimens are evaluated thanks to a cosmetic observation based on comparison with reference samples. All these corrosion simulation tests permit to develop a complete ferritic stainless steel offer dedicated to the exhaust market.

Corrosion in the hot part of the exhaust system

Dry hot corrosion

Context

Closed to the manifold, thermal cycles and high temperature lead to very severe dry corrosion mechanism what could be detrimental for exhaust durability. In cyclic oxidation, not only classical chemical aspect of oxidation needs to be studied. Of course, a mechanical aspect has also to be taken into account because of thermal expansion difference between the metal and the oxide layer formed at high temperature. At high temperature, an oxide scale is formed on the steel surface, with a thickness following a parabolic law vs time. However, during cooling of the system, stresses are generated at the metal/oxide interface what could lead to oxide spallation. As this mechanism is repeated at every thermal cycle, it could cause important metal consumption [1-2].

Experiments

The principle of the test, described on Fig.1, permits to realize thermal cycles in accelerated conditions (Fig.2). The maximum test temperature depends on exhaust gas temperature measured on customer bench but with the improvement of engine performance, this temperature continuously increases up to 1000°C in extreme cases. Consequently the tests are carried out up to this temperature.

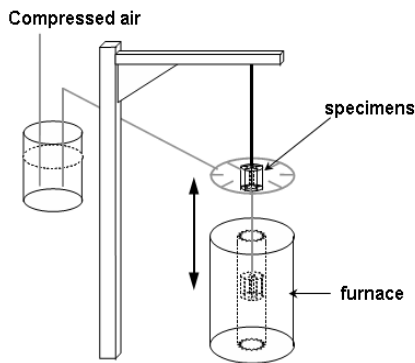


Figure 1: Schematic view of the cyclic oxidation test

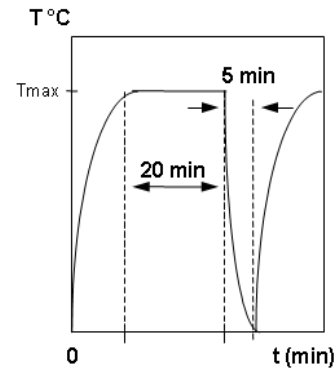


Figure 2: Thermal cycle used for exhaust application

Then samples are characterized by weight variation measurement versus time. The major observation highlighted on these results is the better behaviour of ferritic grades compared to austenitic (Fig.3). This is mainly due to the high thermal expansion of the austenitic compared to the ferritic one, what leads to higher stress concentration at the metal/oxide interface during cooling and then, higher oxide spallation rate.

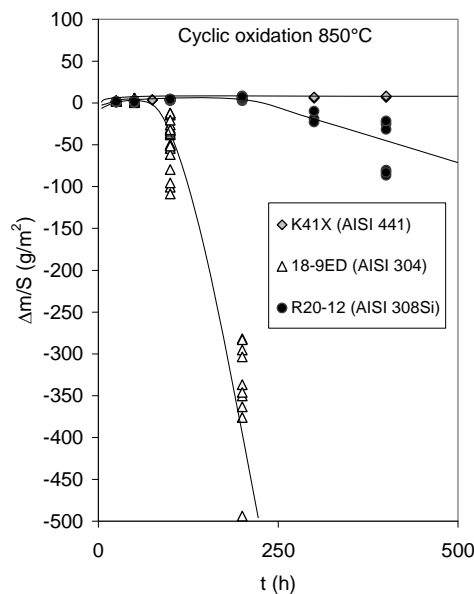


Figure 3: Weight loss measurement vs time on several grades with Tmax=850°C

DeNOx system effect : urea injection

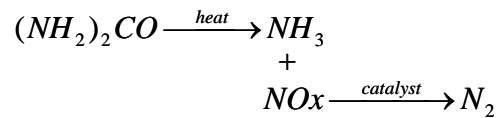
Context

Due to the necessity to reduce NOx emission established by Euro 5 standard (2009), new equipments were developed for diesel vehicles (truck as well as car). The most promising

Postadress	Besöksadress	Telefon	Telefax	Postgiro
Box 1721 111 87 Stockholm	Kungsträdgårdsgatan 10	08-679 17 40	08-611 20 89	3 40 30-7

technology is called Selective Catalytic Reduction (SCR) and takes advantage of the reduction feature of ammonia (NH₃) on NO_x.

As NH₃ couldn't be used for safety reasons (toxicity, flammability of ammonia) because the reactions take place inside the exhaust system, urea solution was selected to initiate the reaction. This molecule, by its decomposition at high temperature releases NH₃ species [3], what permits reduction of NO_x as described on the following scheme:



Scheme of the catalyst reduction of NO_x in SCR system from urea solution to nitrogen

Thus, urea solution is injected in the exhaust system by means of a spraying nozzle. As a result, some urea can enter in contact with internal shell of exhaust system at high temperature and then could cause damages on stainless steel.

Experiments

To get a better understanding of involved mechanisms and afterward to improve material selection, a laboratory test was developed at Isbergues Research center. The simulated test consists in spraying urea solution on cyclic heated stainless steel. After test, cross section analysis were performed on the specimens in order to determine the kind of attack observed and the metal depth which is affected. Depending on temperature and time conditions, we evidenced a carbonitriding mechanism as shown on the 304 grade thanks to cross section analysis with SEM (Fig. 4, 5 and 6). That means urea decomposition on the surface of stainless steel at high temperature could leads to diffusion of interstitial species such as C and N in the metal.

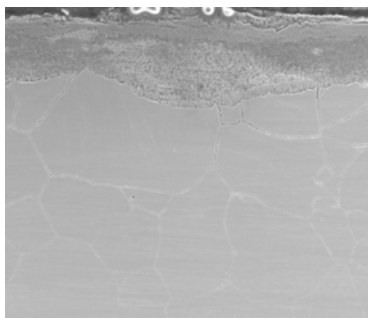


Figure 4: SEM observation of a 304 grade after 150h test 600°C

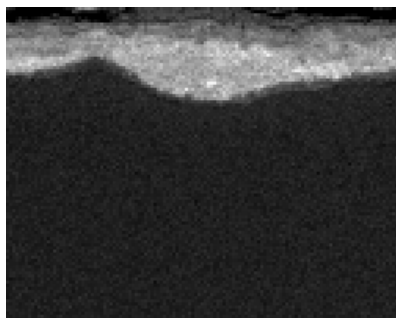


Figure 5: X Cartography of nitrogen

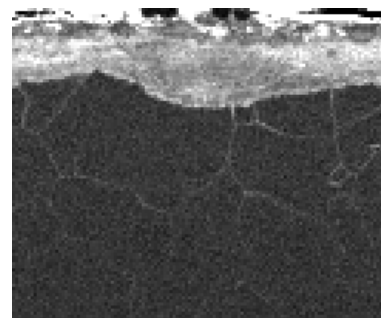


Figure 6: X Cartography of carbon

Corrosion in the cold part of the exhaust system

Internal corrosion

Context

In the cold part of the exhaust system, combustion gases such as SO_x, NO_x... combined with air humidity provoke condensation of an aqueous acid solution on the internal side of the shell (mix of sulfuric acid, nitric acid...). Consequently, this condensate could cause severe corrosion damages, mostly in the muffler where the evacuation of this acid solution is not facilitated. In

particular, the most critical zones are the confined areas between shell and baffles, where crevice corrosion could develop and in extreme case, lead to perforation of the muffler.

Experiments

The test used at Isbergues Research Center to simulate the “internal corrosion” mechanism of the exhaust system is the so called dip dry test which has been especially developed for that application. It permits to simulate exhaust system environment by successive operations described as follows:

- Cyclic immersions and emersions into properly selected solution to simulate exposure to condensate (inner parts) in order to reproduce wet corrosion mechanisms.
- Step in oven simulating high velocity runs and reproducing high-temperature corrosion and oxidation mechanisms.

Different kind of cycles could be performed in order to simulate an urban or a highway type running. However, urban type cycles are the most aggressive due to an important number of dip/dry steps compared to highway type cycles. In these conditions and in order to simulate the most critical areas of the muffler, an artificial crevice is fixed on the lower part of the specimen. After test, the artificial crevice is removed and the maximum corrosion depth in the confined area is measured. On Fig. 7 below are presented the results obtained on stainless steel grades usually used for exhaust applications. These results allow to compare grades and thus to improve grade selection, depending on guarantee requirements.

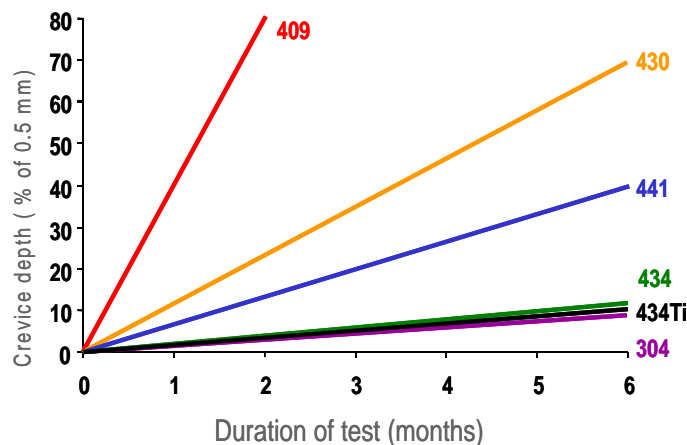


Figure 7: Maximum corrosion depth under artificial crevice after Urban cycle type on dip dry test at 300°C synthetic condensate pH4

Cosmetic corrosion

Context

Depending on the customer, some cosmetic demands could be requested for visible parts of the exhaust system. Effect of deicing road salts combined with oxidation coming from gases temperature cause pitting corrosion of external parts of the exhaust system. Thus, products generated by these corrosion mechanisms could affect the general aspect through coloration of the steel and red rust appearance.

Experiments

This specific corrosion mechanism so called “cosmetic corrosion” is simulated through a cyclic corrosion in climatic chamber. The cycle is based on a classical automotive climatic test which simulates the external environment and use of a car (Fig. 8). After test, samples are visually

Postadress	Besöksadress	Telefon	Telefax	Postgiro
Box 1721 111 87 Stockholm	Kungsträdgårdsgatan 10	08-679 17 40	08-611 20 89	3 40 30-7

evaluated by means of a reference chart which evaluates visual deterioration due to both oxidation (coloration) and pitting corrosion.

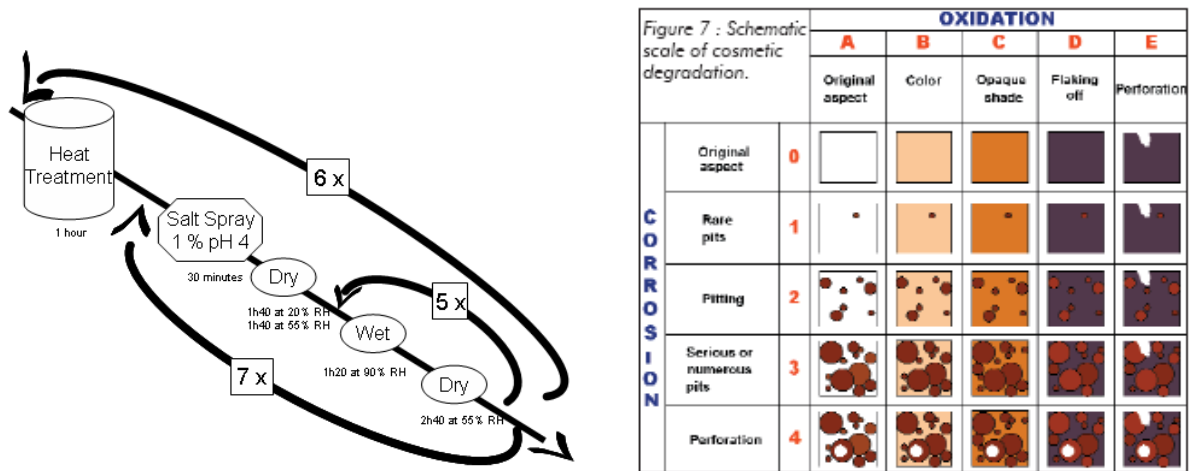


Figure 8: Cosmetic corrosion test and reference chart principle [4].

Based on their field of experience and their cosmetic requirements, customers are thus able to selected appropriated grades for their applications.

Concluding remarks

All procedures presented do not intent to establish an absolute ranking of stainless steel grade performance but they turn out to be efficient methods to characterize more precisely corrosion and oxidation damages undergone by exhaust system materials.

Besides, more exhaust line continues to evolve technically, in particular with the arrival of particulate filter for diesel, the down-sizing in engine and SCR depollution system, more new ferritic solutions are preferred.

Thus ArcelorMittal Stainless approach led to the definition of a complete ferritic offer specially dedicated for both hot and cold parts of the exhaust line able to fit in the same time the durability requirements and the increasing demand of guarantee.

References

- [1] Antoni, L., Herbelin, J.-M., (1999), in EFC Working Party Report on Cyclic Oxydation of High temperature Materials : Mechanisms, Testing Methods, Characterisation and Lifetime Estimation M.Schütze, W.J. Quadackers Eds, Publication N°27 in European Federation of Corrosion Series, Institute of Materials p.187
- [2] Cyclic oxidation behaviour of stainless steels – appliation to the automotive exhaust lines, L.Antoni and B.Baroux, La Revue de métallurgie-CIT Février 2002, pp.178-188
- [3] F. Birkhold et al. “Analysis of the injection of urea-water-solution for automotive SCR DeNOx-systems: Modeling of Two-Phase Flow and Spray/Wall-Interaction”, SAE Technical Paper Series 2006-01-0643, April 2006.
- [4] D.Guillou et al. “Cosmetic analysis of an exhaust system”, Ingénieurs de l’automobile, Juin-Juillet, 2002.