Influence of Selective Catalytic Reduction (SCR) system on stainless steel durability

Influência do sistema de redução catalítica seletiva na durabilidade de aços inoxidáveis

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Abstract

Stainless steel is largely used in the car exhaust market and will be applied now for truck and off-road vehicles. In that field of application, designs are more and more complex with the integration of a catalytic converter and particle filter, consequence of more and more severe diesel depollution regulations. In particular, due to the necessity of reducing NOx emission established by Euro 5 standard (2009), Euro 6 (2014) and American Tier 4 (2014), new equipment were developed for diesel vehicles (truck as well as car). The most promising technology is called Selective Catalytic Reduction (SCR) and takes advantage of the reduction feature of ammonia (NH_3) on NOx. As NH_3 cannot be stored directly within the vehicle for safety reasons (toxicity & flammability of ammonia) urea in water solution was selected to initiate the reaction by means of a spraying nozzle. To get a better understanding of the involved hot corrosion mechanisms and afterward to improve material selection, a dedicated laboratory test was developed at Isbergues Research Center. The simulated test consists of spraying urea solution on cyclic heated stainless steel in a range from 200°C to 600°C. We evidenced a nitriding mechanism due to the urea decomposition on the surface of stainless steel at high temperature, and also the very different behaviours between austenitic and ferritic grades. The last one, in particular K41X (1.4509-441) and K33X (1.4513-molybdenum stabilized ferritic) grades show the best performance in particular when compared to the standard 304 austenitic grade. The paper will review the test set-up, the result obtained and will discuss the stainless steel grade selection for the SCR application.

Keywords: Stainless steel, molybdenum and pitting corrosion.

Resumo

O aço inoxidável é amplamente utilizado no sistema de exaustão de carros de passeio e será aplicado, agora, em caminhões e veículos off-road. Nesse campo de aplicação, os projetos são cada vez mais complexos com a integração de catalisador e filtro de partículas, como consequência dos cada vez mais severos regulamentos sobre despoluição de veículos diesel. Notadamente, devido à necessidade de redução das emissões de óxidos de nitrogênio (NOx), estabelecida pelas normas Euro 5 (2009), Euro 6 (2014) e American Tier 4 (2014), novos equipamentos foram desenvolvidos para veículos a diesel (caminhões, bem como viaturas). A tecnologia mais promissora é chamada de Redução Catalítica Seletiva (do inglês SCR), que aproveita o recurso *de redução por amônia (NH_3) em NOx. Como NH_3 não poderia ser diretamente armazenada no interior do veículo, por razões de segurança (toxicidade e inflamabilidade da amônia), a solução aquosa de uréia foi escolhida para iniciar a reação por meio de um bico de pulverização. Para se obter uma melhor compreensão dos mecanismos de corrosão a quente envolvidos e, depois, para se melhorar a seleção de materiais, um teste de laboratório foi desenvolvido no Centro de Pesquisa de Isbergues. O teste simulado consiste em pulverizar uma solução de uréia no aço inoxidável aquecido ciclicamente na faixa de 200°C a 600°C. Evidenciou-se um mecanismo de nitretação, devido à decomposição da uréia sobre a superfície de aço inoxidável à temperatura elevada e, também, foram observados comportamentos bastante diferentes entre as famílias austenítica e ferrítica. A última família, em particular os tipos K41X (1.4509-441) e K33X (1.4513 molibdênio-ferrítico estabilizado), mostra o melhor desempenho, em especial em relação ao padrão da classe 304 austenítica. O artigo faz uma revisão do teste de set-up, apresenta os resultados obtidos e discute a escolha do tipo de aço inoxidável para a aplicação em SCR.*

Palavras-chave: *Aço inoxidável, molibidênio, corrosão por pite.*

1. Introduction

Since 1995, tolerance in terms of pollutants emission (CO, HC, PM, NOx) for heavy duty vehicles has become increasingly drastic. With the arrival of the new standard Euro 5 (NOx<2.0g/kWh) and even moreso with Euro VI (0.5g/kWh) and Tier 2 Bin 5 (US regulation, 0.4g/kWh), opmitization of the engine is no longer sufficient (Rajasekar, 2010) and most of the diesel heavy duty vehicles must be equipped with the NOx emission reduction system to meet with these requirements. In this context, two major tehnologies were particularly developed: Lean NOx Trap (LNT) and Selective Catalyst Reduction (SCR) system (Johnson, 2008).

SCR technology is currently the most studied for heavy duty and off road application as it is effective and applicable to the exhaust system in short terms.

This system takes advantage of the ammonia property of NOx reduction in the presence of high temperature and is accelerated by a catalystic presence. As ammonia itself could not be used in vehicle because of safety reasons, urea was chosen as the ammonium producer due to its specificity to decompose in ammonia when temperature exceeds 150°C (Koebel. Et al, 2002) (See reactions schematic Figure 1). Urea could be stored under two states: either liquid at 32% in water solution, or solid. Both storage media work use the same mechanism but the solid state requires pre-heating from 180 to 200°C in water vapour presence (Forzatti, P. et al., 2010).

Thus, above 400°C (Koebel M., et al.,2000), a high ratio of ammonia and other decomposition products of urea at high temperature comes into contact with stainless steel internal shells of the exhaust system. This contact could induce severe damages on material durability by corrosion and oxidation under ammoniac components.

While the mechanisms and the influence of urea decomposition products on catalyst (vanadium of zeolite based) have been largely studied during last decade (Johnson, 2008), the influence of these products, in addition to cyclic heat treatment, on the corrosion of the stainless steel tube wall at the injection point upstream of the catalyst shows only little interest in literature. The first conclusion of the few studies is that a lot of work remains before urea corrosion on stainless at high temperatures (Forzatti, P. et al, 2010) is completely understood. To estimate the risk of damage acceleration, we were interested in investigating the durability of a stainless steel tube around the injection point in this specific environ-

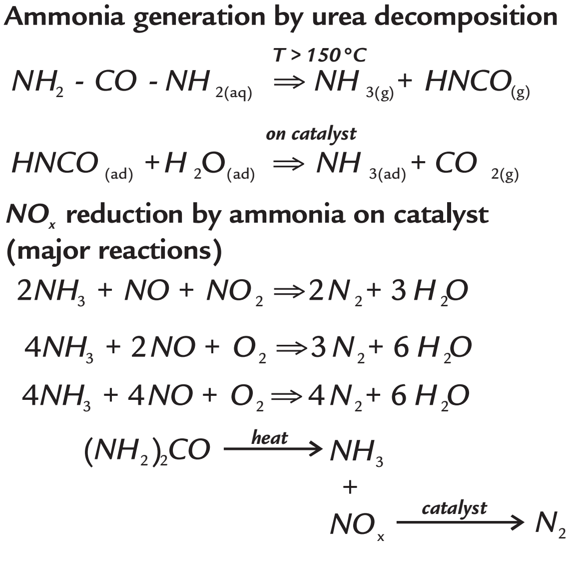


Figure 1
Schematic of ammonia generation from urea thermolysis

ment that forms from cyclic heat treatment, urea decomposition products and pressure of exhaust gas. To help exhaust manufacturers to choose the appropriate grade for future exhaust lines equipped with the SCR system, we carried out laboratory tests, simulating urea spraying on a stainless steel specimen in exhaust line conditions.

2. Materials & Methods

The materials studied were standard automotive grades from the ArcelorMittal Stainless Europe offer. The chemical composition is presented in Table 1.

The simulation bench consists of laboratory handmade rigs dedicated to SCR technology studies and adapted to allow in the same time 1) injection of commercial AdBlue® and 2) cyclic heat treatment in the range of temperature and frequency of the application (between 400 and 700°C for Tmax – cycle duration between 2min and 2h (Kjäll, 2007). The samples could undergo different thermal cycles which could reach up to 700°C and then represent different engine load.

After the test, the samples are cut and the cross-section observed. We proceeded to 1 measurement every 1mm on 10 mm width area in the center of the sprayed zone and evaluated the mean value of the total degradation by addition of the distinguished contributions (Figure 2). Indeed two contributions were observed and called intragranular and intergranular precipitation (see results for analysis of the nature of every contribution).

Nota Bene: As we protected the surface of the sample for technical reasons, the oxide growth is limited and its thickness negligible.

Table 1
Chemical composition of materials.

Grade	Ti	Nb	C	N	Cr	Ni	Mo
K09X **1.4512 - 409**	0.19	-	0.010	0.010	11.30	-	-
K41X **1.4509 - 441**	Ti+Nb=0.65		0.020	0.015	17.80	-	
K36X **1.4526 - 436**	-	0.40	0.015	0.015	17.50	-	1.25
K33X **1.4513 - 433**	0.35	-	0.015	0.015	17.30	-	0.90
18-9ED **1.4301 - 304**	-	-	0.040	0.055	18.20	8.10	-
18-9L **1.4307 - 304L**	-	-	0.025	0.065	18.20	8.05	-

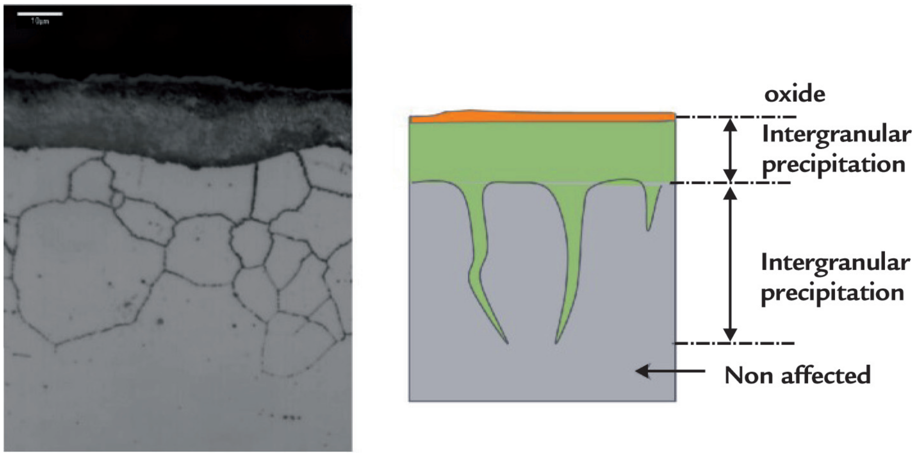


Figure 2
Picture and schematic of the different contributions observed and measured on a sample cross section after laboratory simulation test.

3. Results & Discussion

Temperature activited mechanisms

The first step was to verify that the deterioration mechanisms were temperature activated. Whereas the urea decomposition products present different ratios of ammonia as a function of temperature, it was important to confirm in which scale temperature had an influence on the mechanisms and at which temperature the degradation could be detected at laboratory test duration scale.

To stay close to field conditions, the temperatures tested were above 250°C to ensure a complete urea decomposition and did not exceed 700°C which appears as a very maximum temperature which could be measured on the tube wall upstream the catalyst.

We decided to test 2 representative grades, one austenitic (1.4301) and one ferritic (1.4509) as is presented in the Figure 3.

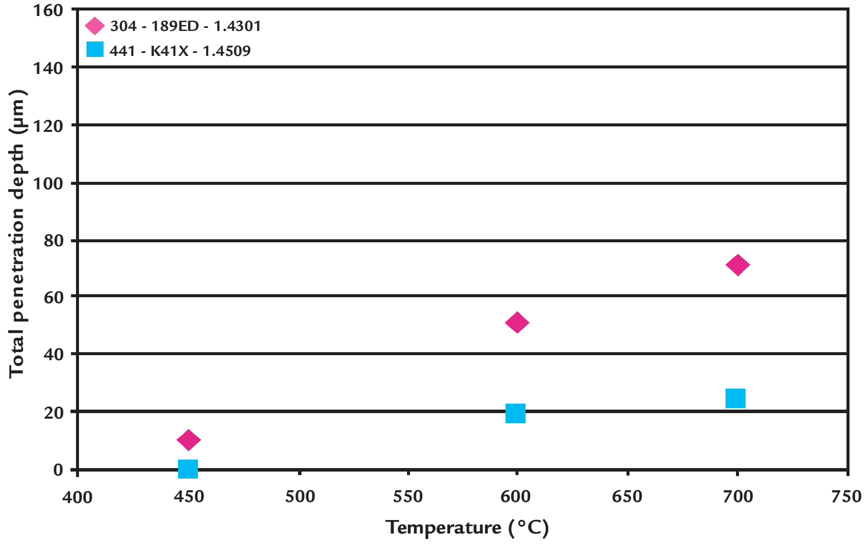


Figure 3
Temperature influence on the stainless steel degradation (150h test).

Mechanisms investigations

After 150h test duration, samples were cross cut and investigated. Two representative samples are presented after SEM investigation (secondary electrons and concentration profiles of involved elements Figure 4).

These observations clearly identify a nitriding phenomenon of the surface on both characterized grades and moreover probably a carbonitriding mechanism on the 189ED (1.4301) austenitic grade. This diffusion mechanism was already highlighted by (Kjäll. J, 2007). A more detailed analysis of this grade permits to exhibit chromium nitrides particles in area [3] (Figure 5).

TEM investigations permitted to identify the nature of particles generated. We evidenced CrN precipitation in the upper layer close to the oxide layer and Cr2N disseminated through the substrate preferentially at the grain boundaries (Simmons, J.W, 1996) in the zone [3] layer (Figure 5). This precipitation, due to nitrogen enrichment from external environment, can lead to a decrease of corrosion resistance due to chromium depletion close to the grain boundaries at the temperature range of the application (Wang, J. et al., 2008).

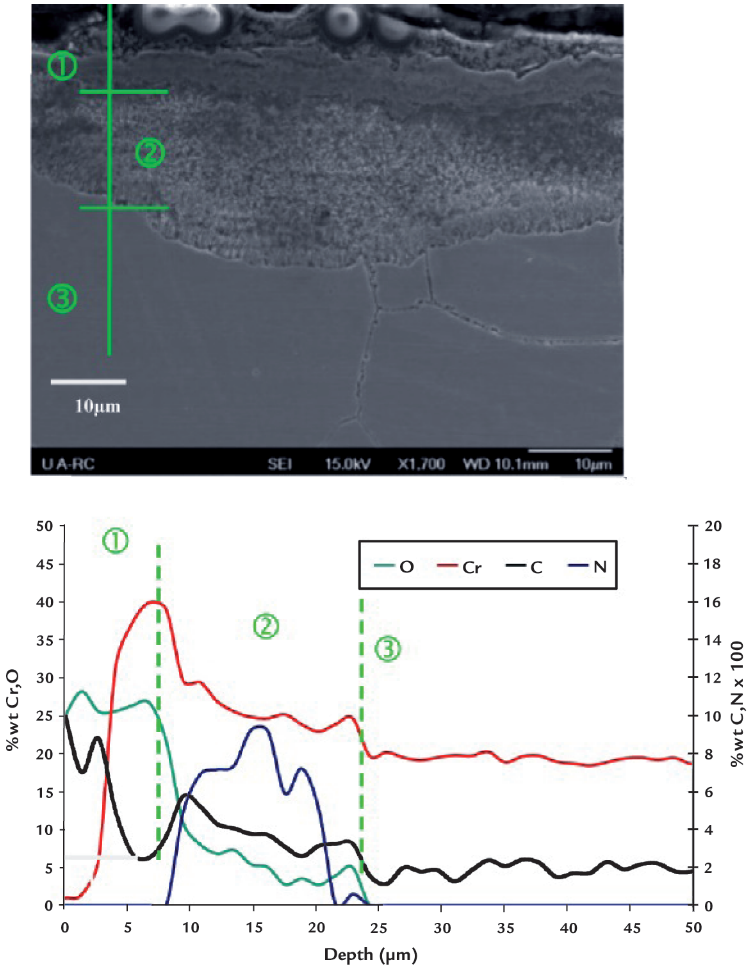
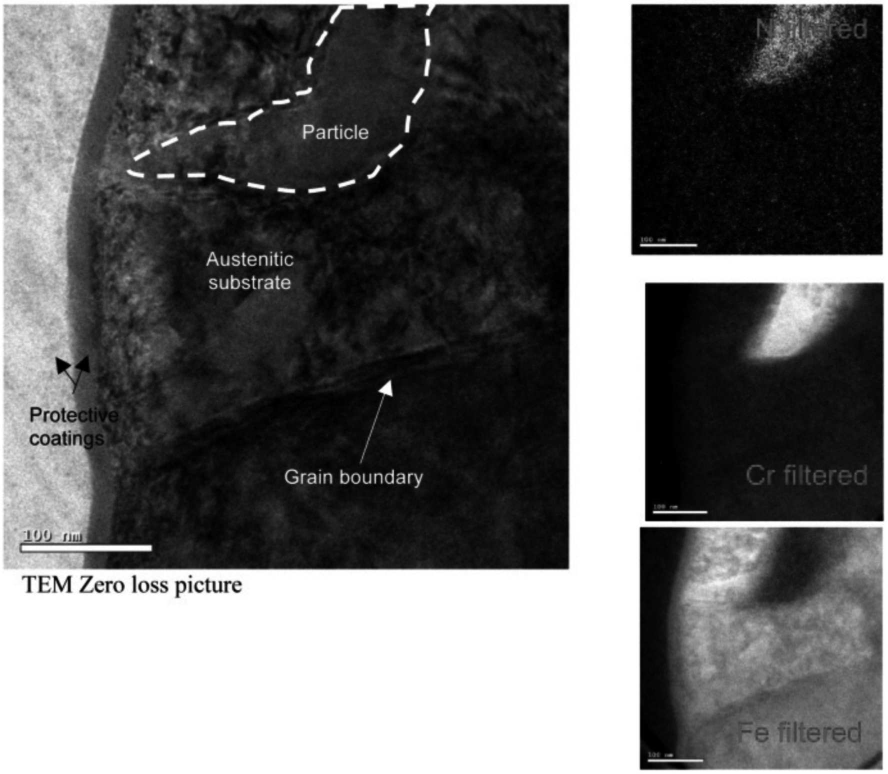


Figure 4
Concentration profiles of
O, Cr, C and N observed on 189ED.
(1): Fe and Cr oxide layer.
(2): carbonitriding layer.
(3): substrate material with intergranular precipitation (not detected here).



TEM Zero loss picture

Figure 5
TEM investigation of chromium nitride particles

Grade ranking

Moreover understanding of the mechanisms, the grade selection is critical for exhaust manufacturers and must be motivated by technical performance arguments. To this aim, we carried out trials with several grades largely used in the exhaust field (see Figure 6). The Cr content above 16% appears as a minimal condition to ensure good urea/ammoniac hot corrosion performance.

If the molybdenium content present undoubtedly advantage against internal corrosion by condensate inwide the muffler, it does not exhibit a positive role in hot corrosion by urea. However as the role of stabilized elements in excess, which could catch nitrogen and carbon diffused from the outside, present the best performance, K33X presents a good material selection by combining high resistance to hot corrosion by urea and high internal corrosion resistance insured by the molybdenium content.

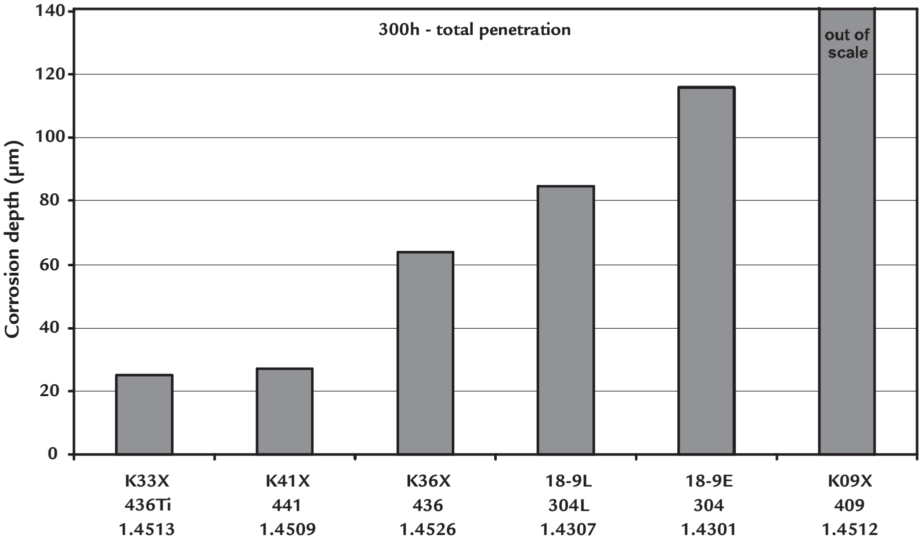


Figure 6
Total penetration of nitriding corrosion attack on laboratory simulation bench after 300h test.

Correlation with field test

Correlation with the field tests was possible thanks to some of our customers, in particular due to a field validation test of the system with austenitic 304 (1.4301) material selection. Courtesy by Tenneco, a SRC system could be examinaned after 2500h of field tests. Their investigations highlighted the presence of 4 different areas (Figure 7): 1)oxide, 2)oxide + nitrided particles + pollutant, 3) nitrided layer and 4) base metal. These observations are equivalent to what we showed with this grade during our accelerated simulation tests in 2008 (Figure 8). The thickness of oxide layer is thinner on laboratory sample due to the presence of isolation material on surface of the sample to ensure contact between liquid urea and hot material.

This correlation confirms necessity of accelerated simulations in the laboratory and the relevance of the test developed.

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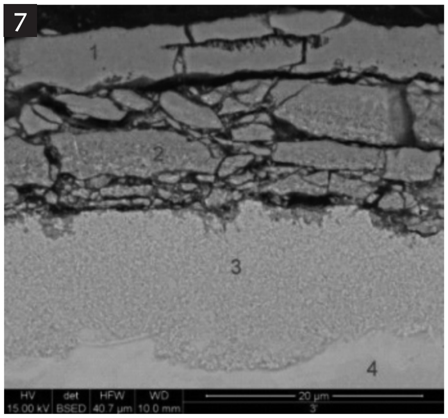

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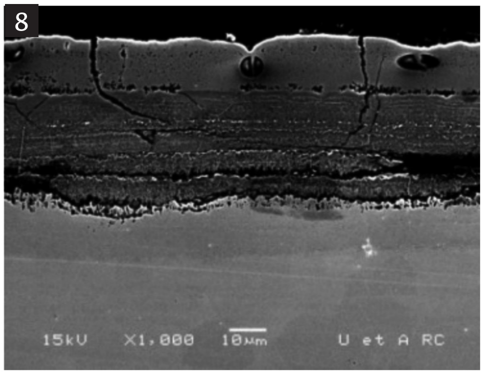

Figure 7
Off-road part in 304
after 2500h, courtesy of Tenneco.

Figure 8
304 after 150h, AMSE-Isbergues
simulation test.

4. Conclusions

The laboratory simulations evidence the consequence of injection of liquid urea in water solution within the exhaust line undergoing cyclic heat treatments on several stainless steels usually used for exhaust line manufacturing. By its decomposition on the stainless steel surface, urea releases nitrogen and carbon species, which are interstitial elements susceptible to diffuse through the steel matrix. Unfortunately, this type of physicochemical reaction, if uncontrolled, as is the case in exhaust gas environment, may have a detrimental effect on the stainless steel durability. Indeed, in this background, the complex nitriding mechanisms combining oxidation and corrosion of the material by diffusion and precipitation generates brittle layers and precipitation at grain boundaries. The affected zones could generate several major damages as:

- Hot corrosion + oxidation on the surface:
  – Decreased material durability (accelerated if chloride or exhaust gas condensate are present).
- Nitriding mechanism:
  – Local chromium depletion and then intergranular corrosion risk.
  – Brittleness in nitrided area.
    - Scaling of the oxide layer in surface and then poisoning of the catalyst.
    - Perforations due to erosion.

In addition to the understanding of the mechanism for which complementary experiments need to be carry out (in particular on lab casts to demonstrate the influence of stabilizing elements, Mo, and level of Cr content), the laboratory simulations exhibited another practical interest which is to be helpful to rank material durability performance quicker than in field tests while staying close to real conditions.

Among all tested grades, K33X (436Ti) and K41X (441) present the best behavior against urea decomposition products at high temperature. However the K33X (436Ti) constitutes the best material selection to combine good durability in presence of SCR system and high corrosion resistance to internal pollutants, thanks to low depassivation pH (<2) and Mo content which increase pitting potential and slow corrosion propagation.

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Paper submitted to INOX 2010- 10th Brazilian Stainless Steel Conference, September 20-22, Rio de Janeiro, Brazil. Revised accepted December, 11, 2012.