

Experimental researches concerning the corrosion resistance of stainless steels for automotive exhaust systems

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The special corrosion conditions in the rear section of automotive exhaust systems cause high demands on stainless steels used for these components: ferritic steels with different contents of chromium and molybdenum as well as austenitic steel types. For selecting an appropriate material enabling cost-effective design, the corrosion resistance of different materials has to be rated. The corrosion resistance of different stainless steel grades for automotive exhaust systems has been assayed in a laboratory test on the basis of the standard VDA 230-214-test. Concurrent to the laboratory tests the influence of the active carbon, simulating the soot particles, has been investigated in electrochemically measurements. A new preparation method of the samples has been developed, which eliminates the edge effects and also enables the placement of active carbon on the metallic surface of the samples. The results of the tests show that active carbon has a significant influence on the corrosion attack. This circumstance should be considered in the future test methods for stainless steels used in automotive exhaust systems.

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1. Introduction

Automotive exhaust systems are complex parts with different sections making different demands on the materials. Due to the aspect of corrosion, exhaust lines may be divided into three parts:

- The front part (manifold pipes, catalytic converter), subjected mainly to high temperature oxidation, requires steels with high scaling resistance, an ability to resist oscillating stresses due to vibrations, minimum susceptibility to embrittlement and a low coefficient of thermal expansion.
- The centre section of the exhaust system (centre muffler, connecting pipes) subjected to both: high temperature oxidation with short periods of wet corrosion, requires materials resistant to both high temperatures and wet corrosion.
- The rear part (rear muffler), exposed to lower temperature and subjected mainly to wet corrosion by condensates (internal parts) or by road salt projection (external part), requires materials with high wet corrosion resistance.

Inside the system, the condensation of combustion gases produces sulphurous acid, sulphuric acid and low levels of hydrochloric acid, creating critical conditions with acidic pH-values [1]. These condensates, combined with an accumulation of chloride ions and deposits of electrochemically active soot particles, can yield to a substantial wet corrosive loading on the inner surfaces of the components. Compared to this, the external corrosive loading by rainwater, road dust, slush and de-icing salts are almost negligible.

The high resistance requirements make stainless steels and heat-resistance steels the dominant materials for

automotive exhaust systems. Various stainless and heat-resistant steels are used [2-5] to achieve an optimal combination of properties in each section. They also display good processability and permit thin-walled, weight-saving designs. The availability of various steel grades with different alloy composition is a further advantage.

But even stainless steels do not possess unlimited corrosion resistance and occasionally these limits are exceeded in automotive exhaust systems. Many different test procedures, commonly known as Dip & Dry Tests are carried out to compare the suitability of these materials concerning their application in the wet sections of the automotive exhaust systems. These tests consider the wet-dry-alternation, the impact of chloride ions in an acidic medium as well as the temperature loading inside the system. At the University of Applied Sciences in Konstanz a new laboratory test based on the test method described in the test sheet VDA 230-214 [6] has been carried out. In addition to the new test standard, electrochemically active carbon has been added in order to simulate the impact of soot particles on the corrosion attack. The results of the tests point out that active carbon is decisively intensifying the corrosion attack.

Due to electrochemically measurements as open-circuit-potential measurements of samples with and without active carbon, the influence of active carbon on the corrosion was examined. A new preparation method of the samples has been developed, which eliminates the edge effects and also enables the placement of the active carbon on the metallic surface of the samples so that the results of these measurements reflect just the corrosion attack on the defined surface under the influence of electrolyte and soot particles.

2. Experimental setup

2.1 Laboratory test with active carbon

The new laboratory test based on the test method described in the test sheet VDA 230-214 [6], is illustrated in Fig. 1. The test consists of one temperature loading and a daily cycle which repeats for 42 days and includes a 'half-immersion period', a 'dry period' and a 'humidity period'.

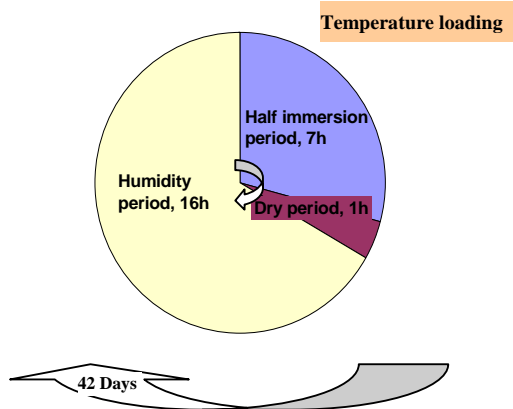


Fig. 1. Schematic view of the new test method with active carbon.

To run the testing, the University of Applied Sciences in Konstanz developed a new test equipment which is compounded of the tank, including the heating facility for the condensate, the test cell with top cover, where the samples are placed, the supply pump, the hot air blower, the three-way valve and the conduit pipes (Fig. 2). All the components are made of high chemically and high temperature resistant plastics.

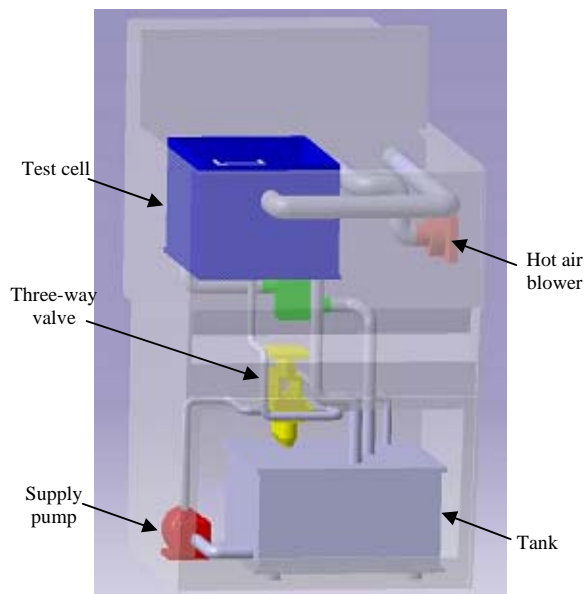


Fig. 2. Test equipment for the laboratory test with active carbon.

During the half immersion and humid period the standard condensate is heated at 50°C and constantly circulated between the tank and the test cell, so that the level of the fluid in the test cell remain constantly despite of the light evaporation of the condensate, what means that also the phase boundary between the wet phase and the vapor phase remain constantly.

The samples are 40 x 70mm stainless steel plates. They are tested in the following states:

- as-received,
- with temperature stress 300°C respectively 400°C,
- with active carbon sticks on their surface and temperature stress 300°C respectively 400°C,
- with Teflon sticks on their surface and temperature stress 400°C (Fig. 3).

In the case of samples with active carbon sticks on the surface there are two extra factors which have an impact on the corrosion attack: the active carbon and the created crevice. To distinguish the influence of these two factors, samples with Teflon sticks on their surface have been also tested. In this case only the created crevice is an extra influencing factor on the corrosion.

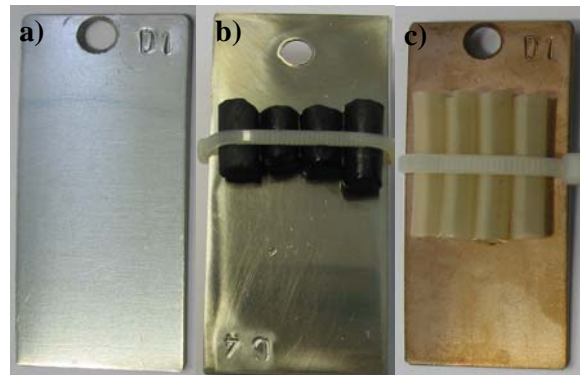


Fig. 3. The samples for the test method with active carbon: a) as received b) with temperature stress and active carbon sticks c) with temperature stress and Teflon sticks.

The tested stainless steels and their alloying composition are listed in Table 1. Austenitic types with and without molybdenum, manganese austenitic types and ferritic types with different contents of chromium and molybdenum are tested.

The condensate consists of an acetate buffer solution with pH-value 4 and 2000 ppm chloride. During the test the condensate is heated up to 50°C. Its pH-value is regularly measured.

2.2. Electrochemically measurements

The open circuit potential is measured for approx. 24 hours at samples with and without active carbon on the surface. After that the potential is switched over for 1 hour to 800 mV(SHE) and then the open circuit potential is measured again.

Table 1. The alloying composition of the materials used for the samples.

Material Nr.	%C	%Mn	%Si	%P	%S	%Cr	%Ni	%Mo	%Nb	%Ti	%V	%Fe
1.4404	0,02	1,26	0,47	0,03	0,001	16,50	11,88	2,00	-	-	-	67,23
1.4301	0,03	1,25	0,45	0,03	0,003	17,88	9,08	-	-	-	-	70,50
1.4376	0,05	7,77	-	-	-	18,93	3,33	-	-	-	-	69,43
1.4526	0,03	0,29	0,32	0,02	0,002	16,86	0,19	1,00	0,60	-	-	80,46
1.4509	0,01	0,42	0,60	0,02	0,002	17,60	-	-	0,45	0,14	-	80,41
1.4512	0,01	0,29	0,46	0,01	-	11,54	-	-	-	0,22	-	87,16

The electrolyte is equal to the condensate from the laboratory test with active carbon: acetate buffer solution with pH-value 4 and 2000 ppm chloride.

To avoid the edge effects during the electrochemically measurements the major part of the surface is covered with a Scotch tape, only a circle with a diameter of 20 mm remains uncovered. In the first step of the preparation a circle with a diameter of 16 mm is covered with Scotch tape and the rest of the surface is pickled. In this way the original metal surface is preserved in this circle. After that the pickled surface is covered with less Scotch tape with a diameter of 20mm including the circle with the original surface, so that the round border of the Scotch tape is bonded on the pickled surface. It might be considered that the weak spot for the corrosion attack is the not pickled surface and not the border of the Scotch tape on the pickled surface.

The samples are dipped in the electrolyte so that only the uncovered circle with the original metal surface comes into contact with the electrolyte. The metal surface is encircled by a rubber ring on the relevant samples. Afterwards the wet active carbon powder is brought on the metal surface (Fig. 4) so that by a careful dipping of the sample into the electrolyte the active carbon powder remains on the surface.



Fig. 4. The sample with and without active carbon.

As a result of these preparation, just the electrochemically processes which take place on the defined surface under the influence of the electrolyte and the soot particles are measured.

3. Results

3.1. Results of the laboratory test with active carbon

The pH-value of the condensate remains constant during the test. This is due the buffer solution and to the fact that only a small part of the condensate gets lost by evaporating compared to the total quantity.

The appearance of the cleaned samples from the ferritic steel 1.4509 (X2CrTiNb18) at the end of the test is illustrated in Fig. 5. It shows that only the sample with temperature stress *and active carbon on the surface* gets pitting corrosion. The same effect can be observed over all material samples, excepted the ferritic steel with low chromium content 1.4512 (X2CrTi12), which shows corrosion attack in all states.

For the evaluation of the corrosion attack the mass loss was determined and the deepest pit was measured with a 3D-Optical Measurement System. The results are graphically represented in Fig. 6. Both charts show the same ranking of the materials. The best results have been achieved by the austenitic steel with molybdenum 1.4404 (X2CrNiMo17-12-2). Between the austenitic steel 1.4301 (X5CrNi18-10) and the ferritic steels 1.4526 (X6CrMoNb17-1) and 1.4509 (X2CrTiNb18) there is no significant differentiation by mass loss or by the deepest pit. The austenitic steel with manganese 1.4376 (X8CrMnNi19-6-3) shows higher mass loss and deeper pits as the above-mentioned materials. The ferritic steel 1.4512 (X2CrTi12) shows both pitting corrosion and general attack. The results show that for the application in the rear part of the automotive exhaust systems this material is overcharged.

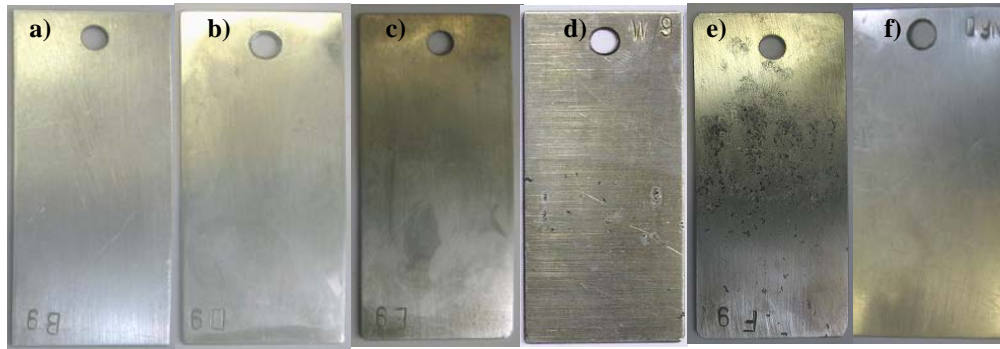


Fig. 5. The samples of the ferritic steel 1.4509 at the end of the test: a) sample as-received; b) sample with temperature stress at 300°C c) sample with temperature stress at 400°C; d) sample with active carbon sticks and temperature stress at 300°C; e) sample with active carbon sticks and temperature stress at 400°C; f) sample with Teflon sticks and temperature stress at 400°C.

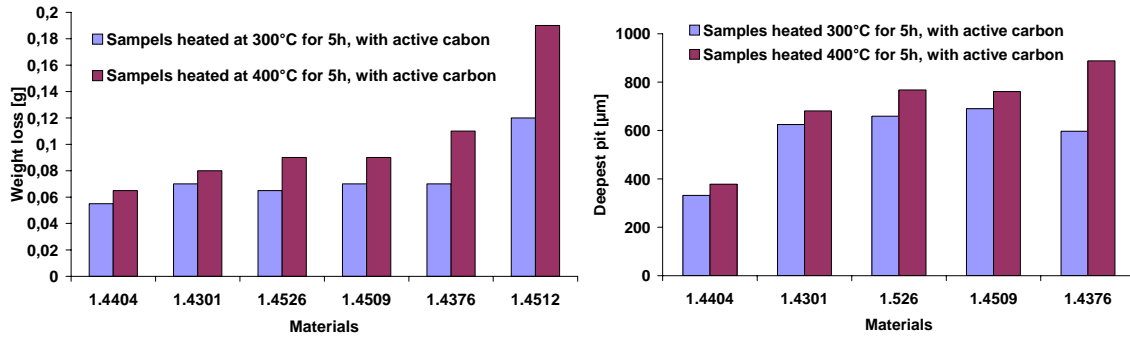


Fig. 6. The mass loss of the samples with active carbon. The deepest pit of the samples with active carbon.

3.2. Results of the electrochemically measurements

The run of the open-circuit potential curve for the different stainless steel grades shows a shift of the open circuit potential to higher values for the samples with active carbon in comparison to the samples without active carbon (Fig. 7), this indicates an increasing susceptibility to pitting corrosion in the chloride containing electrolyte.

During the potentiostatic switch over at 800 mV(SHE) for 1h pitting corrosion occurred. The appearance of the pits on samples with active carbon on their surface are significantly larger compared to the pits on the surface of samples without active carbon (Fig. 8).

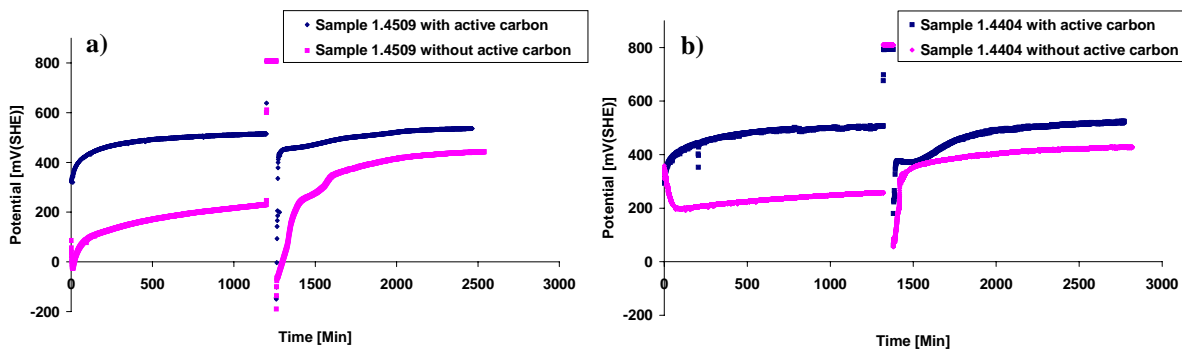


Fig. 7. The run of the open circuit potential curve before and after potentiostatic switch over at 800 mV(SHE) a) for the ferritic steel 1.4509 b) for the austenitic steel with molybdenum 1.4404.

Samples with active carbon



Samples without active carbon



Fig. 8. The appearance of the samples from the potentiostatic measurements, I_h by 800 mV(SHE).

4. Discussion about the influence of the active carbon on the corrosion attack

When pitting corrosion occurs, a corrosion cell is developing with the pit as an anode and the rest of the passive surface as a cathode. At the anode the anodic partial reaction takes place: the dissolution of the metal and the partial cathodic reaction takes place at the cathode: the chemical reduction of the oxygen (Fig. 9).

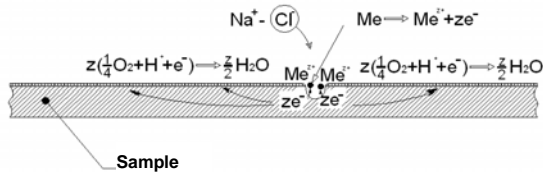


Fig. 9. The mechanism of the pitting corrosion.

The released electrons of the metal atoms in the partial anodic reaction are consumed in the partial cathodic reaction.

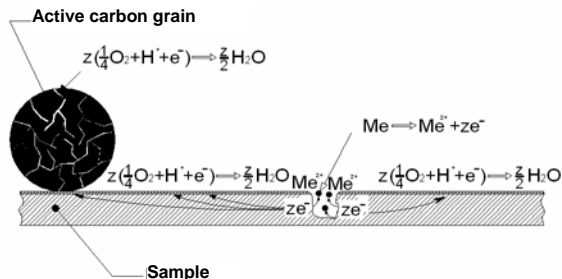


Fig. 10. The mechanism of the pitting corrosion when active carbon is in.

Due to the large specific surface of the active carbon an additional chemical reduction of the oxygen takes place when active carbon is located on the

surface. On account of this the partial anodic reaction (the dissolution of the metal) is stimulated (Fig. 10).

5. Conclusions

The laboratory test with active carbon offers an automatically controlled test with stable test conditions. For the first time the influence of soot particles on the corrosion attack in automotive exhaust systems is considered in a laboratory test. Both laboratory tests and the electrochemically measurements have shown that the active carbon has a significant influence on the corrosion attack. This circumstance should be considered in the future test methods for stainless steels used in the automotive exhaust systems.

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