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Simulation des Korrosionsverhaltens von nichtrostenden Stählen in Pkw-Abgasanlagen

Simulation of Corrosion Behaviour of Stainless Steels in Passenger Car Exhaust Systems

Passenger car exhaust systems make high demands on the stainless and heat-resistant steels used for these components. Condensate formation and particles of electrochemical active soot in the colder section of exhaust systems can lead to pronounced wet corrosion on the inner surfaces. To allow a comparison of different steel types in this respect, Konstanz University of Applied Sciences and ThyssenKrupp Nirosta carried out investigations under simulation of these special corrosion conditions.

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1 Introduction

Passenger car exhaust systems are complex constructions, **Figure 1**, with different sections placing different demands on the materials. Various stainless and heat-resistant steel grades are used to achieve an optimal combination of properties in each section [1-4].

The hot front section of the exhaust system (manifold pipes, catalytic converter) requires steels with a high scaling resistance, an ability to resist oscillating stresses due to vibration, optimal elevated-temperature and creep strength, minimum susceptibility to embrittlement and a low coefficient of thermal expansion.

In the centre section of the exhaust system (centre muffler, connecting pipes) resistance to both high temperatures and wet corrosion are needed. Depending on running conditions, either hot conditions prevail (full throttle) or wet corrosion loading dominates (short-distance driving).

In the rear section (rear muffler) wet corrosion becomes the main factor. Inside the system, condensation of combustion gases produces sulphurous acid, sulphuric acid and low levels of hydrochloric acid, creating critical conditions. These condensates, combined with an accumulation of chloride ions, some acidic pH values and deposits of electrochemically active soot particles, can result in substantial wet corrosive loading on the inner surfaces of the components. Compared with this, the external corrosive loads through rainwater, road dust, slush and de-icing salts are almost negligible.

The high resistance requirements make stainless and heat-resistant steels the dominant materials for auto exhaust systems. They also display good processability and permit thin-walled, weight-saving designs. The availability of various steel grades with differing alloy compositions for different requirements is a further advantage, **Table 1**.

Even stainless steels do not possess unlimited corrosion resistance and occasionally these limits are exceeded in auto exhaust systems. Failure examinations have shown that in the rear, high-condensation section the primary cause is internal attack by chloride-induced pitting and crevice corrosion. This takes the form of pits, shallow pits or uneven local attack.

Stainless steels are also subject to pitting and crevice corrosion loads in many other applications. The resistance of different steel grades to this kind of exposure can generally be compared on the basis of their alloy composition via their pitting resistance equivalent number [8], Eq. (1).

However, this is questionable for the special conditions existing in auto exhaust systems, with their frequent wet/dry alternation and their short operating times compared with overall life cycle. Of importance here is not only resistance to the onset of corrosion – as described by the PREN concept – but also low corrosion rates with a view to achieving long system lifetimes. If an attack has already started, the dissolution rate should therefore be low and in particular the material should possess the ability to repassivate quickly during idle periods. In this respect, the alloying element nickel, for example, should also have a favourable effect, although it is not included when calculating the PREN.

To compare the suitability of various stainless steels for use in the wet sections of auto exhaust systems, tests are needed which take into account the specific features of this corrosion loading. The following factors must be considered

- wet/dry alternation
- impact of a chloride ion-containing acidic medium
- presence of electro-chemically active carbon (occurring as soot particles in the systems).

The objective is to draw up a material ranking for loads of this kind. System-specific particularities must be excluded. In this paper, a corrosion test is proposed which should allow a comparison of materials for applications of this kind.

2 Experimental

Specimens deep drawn from strip of selected materials in Table 1 are used for the tests, **Figure 2**. The specimens are filled with 10 ml of a corrosive medium with a composition shown in **Table 2**. The filled specimens are then exposed an oven at a defined temperature or in a climate chamber at a defined temperature and humidity. A specimen undergoes several cycles of being filled with corrosive medium and drying. After completing a pre-set number of cycles, the specimen is cleaned, its mass loss is measured and the visual appearance of the corrosive attack assessed. The exposure conditions and the composition of the corrosive medium are varied to optimize the process. Where it appears necessary, details of the test execution are presented together with the test results.

3 Tests and Test Results

3.1 Tests with Drying at a Defined Temperature and no Humidity Regulation

The electrolyte in the specimens was evaporated in an oven at 85 °C and then replenished. After 12 cycles, the specimen was

2 Experimental

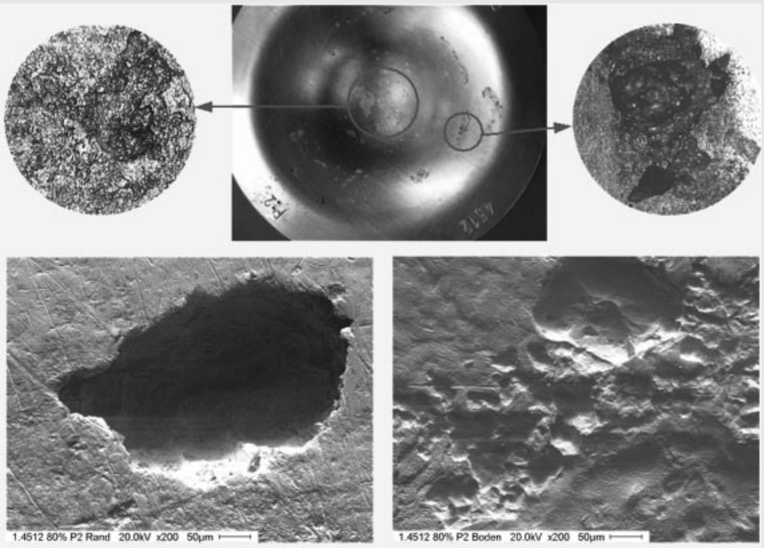

Figure 9: Pattern of attack on material 1.4512 at 80 % humidity
a) Overview and detail under the VIDEO microscope
b) SEM photograph of a corrosion site in the bottom area
c) SEM photograph of a corrosion site in the edge area

cleaned, examined for corrosive attack and weighed. The test process with accelerated drying of the corrosive medium is shown schematically in **Figure 3**.

The results of these tests are summarized in **Figure 4**. They show a virtually linear increase in mass loss with the number of test cycles. The corrosion pattern with pitting and uneven local attack corresponds to that occurring in cases of genuine damage to auto exhaust systems. The intensity of attack diminishes from 1.4512 to 1.4509 to 1.4510. The highest resistance was achieved by grades 1.4526, 1.4376, 1.4301 and 1.4401, which displayed no significant differences in mass loss. This lack of differentiation among the higher-resistance grades is on the one hand inconsistent with our expectations and on the other hand also fails to reflect the results of a similar earlier test carried out elsewhere [5]. Tests of this kind with the boundary parameters described would therefore appear unsuitable to assess the resistance of the materials.

In a variation on this test series, the corrosive medium was kept wet longer to intensify the attack. For this, the specimens with 10 ml electrolyte were placed in a temperature-controlled climate chamber for 6 hours at room temperature (approx. 28 °C). Following this they were placed in an oven for 4 hours at 85 °C as in the previous tests. The process is depicted in **Figure 5**.

The results of this test series, depicted in **Figure 6**, show that mass loss was higher and corrosion attack visibly greater after the first 12 cycles than was the case in the accelerated-drying tests, but that after 48 cycles this difference had become smaller. Overall, the additional wet phase results in a slight increase in corrosive attack, but not in any fundamental change in performance. Here again, it is practically impossible to differentiate between the higher-resistance grades.

3.2 Exposure Tests at Defined Temperature and Humidity

The aim here was to investigate the influence of humidity as a major parameter and also to compare different types of active carbon. After pouring in the corrosive medium, the specimens were placed in a temperature and humidity-controlled climate chamber. Exposure was carried out analogously to the oven tests with accelerated drying at a temperature of 85 °C and various humidity levels, in line with the test procedure outlined in **Figure 7**.

Again, the mass losses were found to increase approximately linearly with test duration. The severity of attack depends to a key extent on the type of active carbon used and the humidity level, **Figure 8**. The highest mass losses occur at the middle relative humidity level of 50 %, but the greatest differentiation between steel grades of different resistance is found at 80 % relative humidity, where clear differences in severity of attack are observed between the grades 1.4512, 1.4301 and 1.4401.

The nature of the corrosion attack on the specimens was mixed. Both classic pitting and more general attack were observed. Examples of the corrosion morphology are shown in **Figure 9**. Based on these attack mechanisms, the results of mass loss measurements should always be treated with caution. In the present case, however, relatively good agreement was observed between the visual appearance of the specimens and the mass loss rates.

3.3 Tests with Alternating Wet/Dry Phases in comparison with Conventional Pitting Potential Measurements

The tests described, involving repeated drying of the corrosive medium in the specimen, simulate important aspects of wet corrosion in car exhaust systems: they produce a similar pattern of attack and show differences in the resistance of different steel grades under conditions of alternating corrosion propagation and repassivation, as they occur in exhaust systems.

In designing tests it is important to recognize that the type of active carbon used and the air humidity in the drying phase have a decisive influence on corrosion attack and these parameters therefore have to be defined. High levels of relative humidity in the region of 80 % are more suited to showing up differences in resistance between different materials.

Conventional methods of measuring pitting and crevice corrosion on stainless steels are not geared to conditions of alternating corrosion propagation and standstill, but instead attempt to measure resistance to the onset of corrosion attack. One widely used method is to measure the critical pitting potential: The higher the potential up to which a material withstands pitting under test conditions in comparison with another, the higher the material's resistance. **Figure 10** shows the results of such measurements by way of example.

Such electrochemical measurements of critical potential levels produce slightly different results than those of the tests which simulate exhaust system conditions. In the tests involving repeated drying of the corrosive medium, for example, the nickel-free ferritic steels 1.4509 and 1.4510 show significantly lower resistance than, say, grade 1.4301, whereas the critical pitting potentials do not show the same level of performance decrease, Figure 10. Such electrochemical measurements are less suitable for comparing the suitability of materials for car exhaust system conditions.

4 Conclusions

Critical pitting potentials and pitting resistance equivalent numbers are less suitable for comparing different stainless steels in terms of their performance in the wet region of car exhaust systems.

More preferable are simulation tests with alternating wet/dry phases which better reflect the particular corrosion conditions in car exhaust systems.

In the specimen tests it must be ensured that the humidity content in the air is constant during exposure and that a standard type of active carbon (grain size, pore volume) is used.

For good differentiation, relatively high humidity levels of around 80 % should be targeted.

Austenitic steels with high nickel content perform better given the same chromium and molybdenum contents

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