Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 34
ISSUE 2
June
2009

Pitting corrosion in the wet section of the automotive exhaust systems

C. Hoffmann*, P. Gümpel
HTWG Konstanz University of Applied Scienes,
Brauneggerstraße 55, 78462 Konstanz, Germany
* Corresponding author: E-mail address: choffman@htwg-konstanz.de

Received 17.02.2009; published in revised form 01.06.2009

Materials

ABSTRACT

Purpose: In the rear section of the automotive exhaust systems condensates bearing appreciable chloride ion concentrations and often low pH-values together with particles of electrochemical active soot can lead to pronounced pitting corrosion on the inner surfaces. For selection of an appropriate material that can enable cost-effective construction, the corrosion resistance of different candidate grades has to be rated.
Design/methodology/approach: The different types of occurring corrosion, both general attack and pitting corrosion demands a combination of evaluation methods of the corrosion attack: mass loss measurements and the measure of the average depth of a certain number of pits with an optical 3D-Measuring System MicroCAD were used.
Findings: The two methods for the evaluation of the corrosion attack provide the same ranking of the materials. Both methods are complementary to each other and together they provide a noticeable differentiation between some of the investigated materials.
Research limitations/implications: The average depth of the pits gives no information about the entire rate of the corrosion attack, about the total number of the pits and their depth. In the future, research with the same optical 3D-Measuring System MicroCAD and new software will be carried out. This will form a structured analysis of the entire pits for the quantification of the corrosion.
Practical implications: A higher quantification of the pitting corrosion leads to a better rating of the different stainless steel grades for using them in the wet section of the automotive exhaust systems.
Originality/value: The evaluation of the pitting corrosion by means of the new measurement methods with the optical 3D-Measuring System MicroCAD is more accurate, work fast and is an obligatory complement of the previous methods of evaluation of the pitting corrosion: mass loss and the depth of the deepest pit.
Keywords: Metallic alloys; Pitting corrosion; Evaluation methods for pitting corrosion; Optical 3D-Measuring System MicroCAD

Reference to this paper should be given in the following way:
C. Hoffmann, P. Gümpel, Pitting corrosion in the wet section of the automotive exhaust systems, Journal of Achievements in Materials and Manufacturing Engineering 34/2 (2009) 115-121.

1. Introduction

Automotive exhaust systems are complex constructions with different sections causing different demands on the materials. From the standpoint of corrosion, exhaust lines may be divided into three parts:

- The front part (manifold pipes, catalytic converter), subjected mainly to high temperature oxidation;
- The centre section of the exhaust system (centre muffler, connecting pipes) subjected to both: high temperature oxidation (internal parts) or de-icing salt contamination (external parts);
- The rear part (rear muffler), exposed to lower temperature and subjected mainly to wet corrosion by condensates (internal parts).

The task of our work was to investigate the corrosion inside the rear part of the automotive exhaust systems. Inside the system, condensation of combustion gases produces sulphurous acid, sulphuric acid and low levels of hydrochloric acid, creating critical conditions with acidic pH-values. These condensates, combined with an accumulation of chloride ions and deposits of electrochemically active soot particles, result in a substantial wet corrosive impact on the inner parts of the components.

Various stainless steel grades ferritic, austenitic and manganese containing austenitic steel are used to achieve an optimal combination of properties in the rear section [1-7, 17,18].

The resistance of different steel grades to pitting corrosion can generally be compared on the basis of their alloy composition via their pitting resistance equivalent number, PREN [8-9]. However, this is questionable for the special conditions existing in automotive exhaust systems, with their frequent wet/dry alternation and their short operating times compared with overall life cycles. The 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. For pitting corrosion resistance of a material it is important that the dissolution rate is to be low and the material should possess the ability to repassivate quickly during the idle periods. In this respect, the alloying element nickel also has a favourable effect, although it is not included when calculated the PREN. To compare the suitability of various stainless steels concerning their application in the wet sections of automotive exhaust systems, technological tests are needed which take into consideration the specific features of this corrosion impact [10]. The following factors must be considered:

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

The nature of the corrosion attack is mixed, both, general attack and pitting corrosion occurs. In the laboratory for the evaluation of the general attack usually the mass loss is used. For the evaluation of the pitting corrosion the mass change provides no reasonable information. There are other corrosion measuring values used: the depth of the pits and the pits density [11]. Therefore, the evaluation of the corrosion succeeds by means of mass loss [12-15], visual investigation and the average depth of a certain number of pits. The results of the three methods of evaluation of the corrosion will be compared.

The optical 3D-Measuring System MicroCAD is a device for three-dimensional inspections of surface profiles of small and micro parts with high measuring velocity and high precision. As a measuring method of this contact-less operating micro-optical 3D measuring device the digital fringe projection based on micro mirrors is applied. Thereby the 3D profile of the measured object according to requirements can be measured within milliseconds or seconds and after its calculation it becomes available for further evaluation.

2. Experimental

2.1. Technological test

The technological tests which were carried out consider the specific features of the corrosion loading in the wet section of the automotive exhaust systems.

Those specific features are:

- The wet/dry alternation,
- The impact of a chloride ion-containing acidic medium,
- The presence of electrochemically active carbon.

The samples (Figure 1) are drawn specimens from strips of selected materials (Table 1).

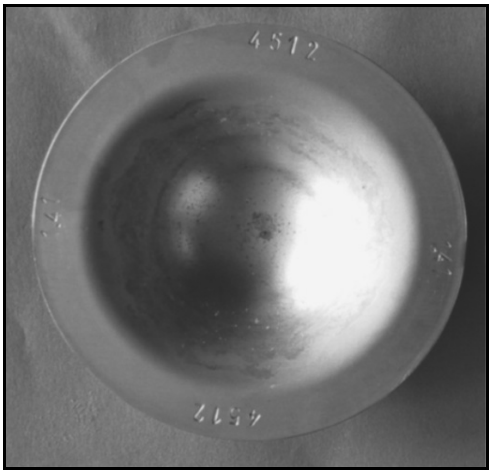


Fig. 1. Specimen

Table 1.
The alloy composition of the specimens

Stainless steel grades	Alloying additions [wt.%]			
	Cr	Ni	Mo	Mn
Cr-Steel 1.4512	11.54	-	-	-
Cr-Steel 1.4509	17.59	-	-	-
CrMo-Steel 1.4526	16.86	-	0.983	-
Cr NiMn-Steel 1.4376	18.93	3.33	-	7.77
CrNi-Steel 1.4301	17.88	9.08	-	-
CrNiMo-Steel 1.4404	16.36	11.88	1.84	-

The specimens were pickled and weighed before the test. They were filled with 10 ml of the corrosive medium with a composition shown in Table 2. The corrosive medium is a buffer solution with an acidic pH value containing sodium chloride and active carbon. The specimens were placed in a climate chamber for 12 hours at 85°C and 50% relative humidity, and then for another 12 hours at 23°C and 50% relative humidity. They underwent several cycles of being filled with corrosive medium and drying. During the first 12 hours an accelerated drying of a part of the electrolyte has taken place. On the surface where the electrolyte could evaporate, the crystallization of sodium chloride was observed. In the next 12 hours, due to the air humidity the crystallized salt also provided a corrosive medium. After 24 hours the electrolyte was replenished. After each 12 cycles, the specimens were cleaned, visual examined for corrosive attack and weighed.

The tests were done up to 48 cycles. At the end of the 48th cycle the specimens were cleaned, weighed and examined for corrosive attack by usage of a stereomicroscope. During the inspection with the stereomicroscope the areas with the deepest and biggest pits were assessed. In these areas the pits were analysed and measured with the optical 3D-Measuring System MicroCAD.

Table 2.
The composition of the electrolyte with pH 4

Electrolyte with pH 4	
Chemicals	Amount
Acetate buffer solution	1 l
Sodium chloride	3.3g
Active carbon	1g

3. Optical 3D-measurement

The optical 3D-Measuring System MicroCAD is designed to inspect the microstructure of surfaces (Figure 2).

The combination of a high resolution CCD camera and the digital stripe projection technique based on micro mirrors is used to determine the most significant characteristics of the inspected part in a fast and easy process.

Light stripe projection is a light-section technique where the object to be measured is lit with an array of equidistant stripes. In contrast to the conventional light-section technique, the projected stripe patterns have a $\cos^2$-shaped intensity distribution and can be understood and evaluated as interferograms. Hence, in addition to stripe position their grey values contribute to height information as well, resulting in a very high resolution regarding the acquisition of surface geometries.

Stripe patterns are projected all over a defined area and observed with a camera (Figure 3). High information is encoded in the deformation of the stripes. By the projection of digital stripe patterns it is possible to analyze larger height differences in the surface geometry. Through the projection of sinus like stripes, height information is encoded not only in the position but in the grey levels as well. Therefore the measuring principle achieves a much higher sensitivity than point or line triangulation.

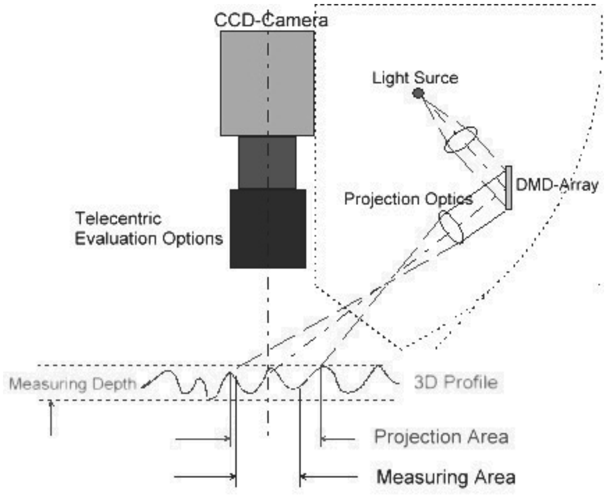


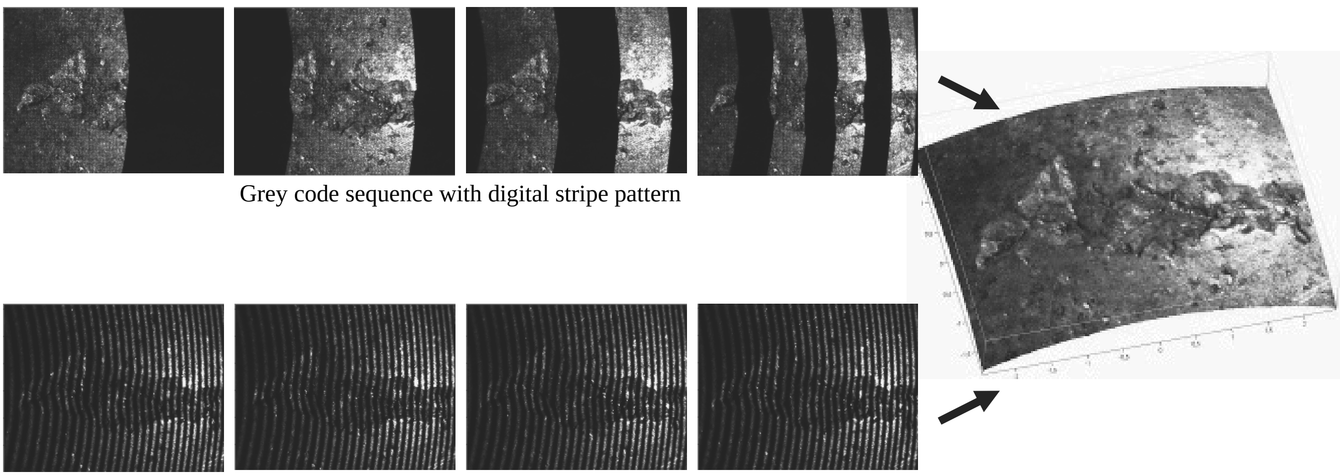
Fig. 2.View of the optical 3D-Measuring System MicroCAD [16]

The measuring device is able to measure the 3D profile of metallic as well as non-metallic materials.

There are also more zoom areas available. The zoom area of our system and its features are listed in Table 3.

Table 3.
System parameter MicroCAD

Zoom Areas [mm]	13 x 10
Measuring points	1600 x 1200
Measuring field Z [mm]	1 - 3
Height resolution [μm]	1
Lateral resolution [μm]	2.5 - 8
Data acquisition [s]	2
Measuring method	Digital fringe projection
Light source	Cold light source 150 W



Grey code sequence with digital stripe pattern

Phase shift sequence with sinus like intensities

Fig. 3. Data acquisition by stripe projection [16]

3.1. The measurement of the average depth of the pits

The measuring area is 13 x 10 mm and for each sample the profile of three or four areas with deep pits were recorded and evaluated.

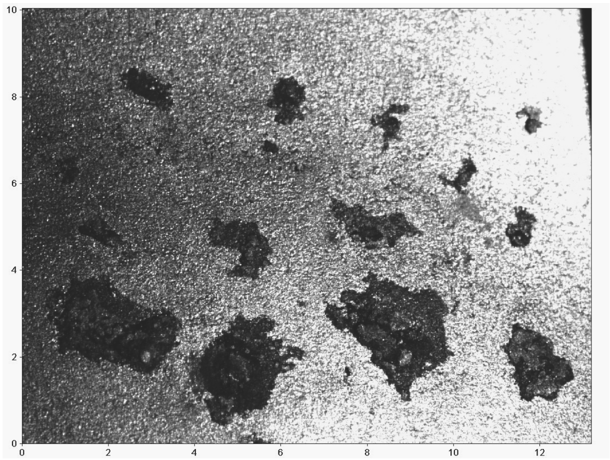


Fig. 4. Live image of a measuring area

Figure 4 shows the real image of one area. The measuring position is always visible with the live image of the camera. The software evaluates the information and compiles a colour-coded 3D image (Figure 5). The colour-coded 3D image would be aligned and the waviness of the samples eliminate with a polynomial filter (Figure 6).

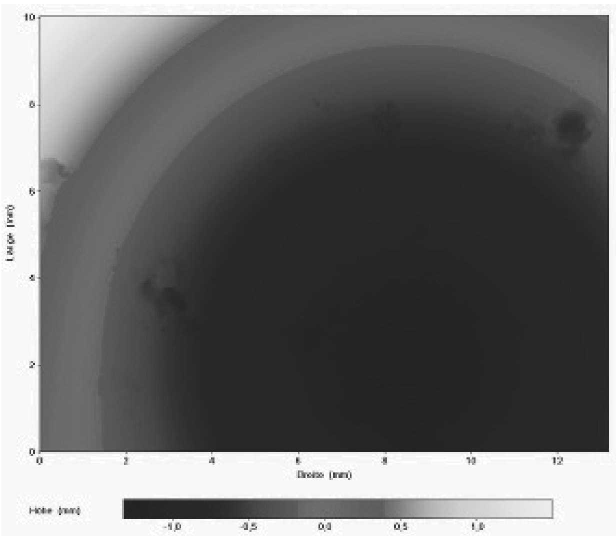


Fig. 5. Colour-coded 3D image

On the basis of the colours, the deepest pits are accurately visible and the cutting line can be drawn through these pits. This cutting line would intersect one or more pits.

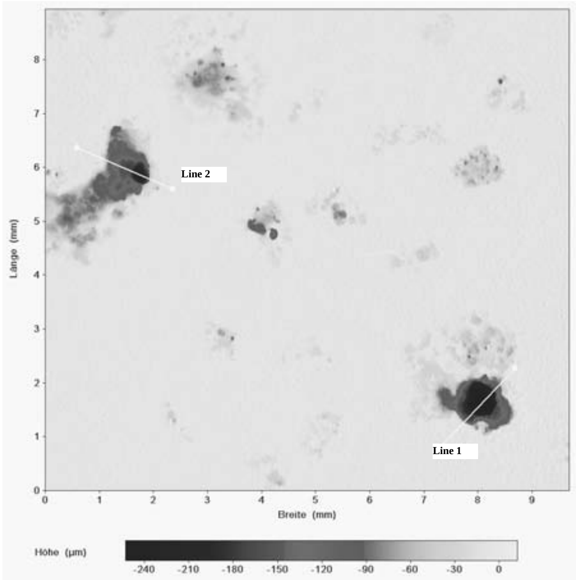


Fig. 6. Filtered and colour-coded 3D image

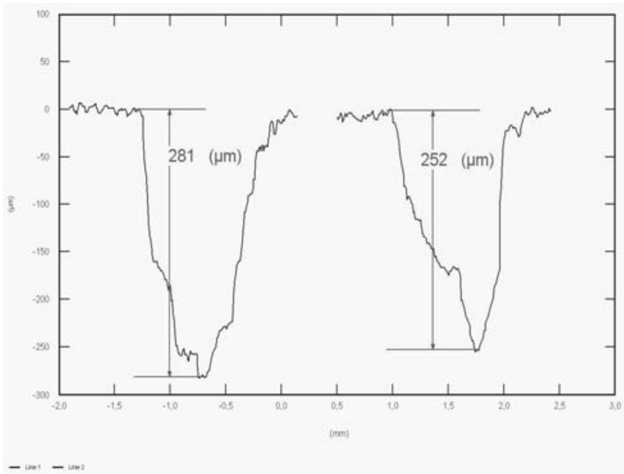


Fig. 7. Cross section

The system generates the cross section along the cutting line and calculates the depth of the pits (Figure 7).

From each sample the depth of 12 pits were measured. The two extremes values, the pits with the highest and lowest depth were ignored and from the other 10 pits the average depth was calculated.

The 3D profile of the measuring object is acquired and calculated within a few seconds and is subsequently available for further analysis.

4. Results and discussions

The corrosion attack is mixed as both general attack and pitting corrosion, occurs.

During the test the pH-value of the electrolyte was regularly controlled. During every cycle the pH-value of the electrolyte was increasing from 4 to 6. Under the temperature conditions in this test a substantial evaporation takes place, not only water in the electrolyte evaporates but also the acetic acid. The electrolyte is not being buffered during the test.

In the Figures 8 and 9 the results of the two methods are shown: measurements of the mass loss and the measurements of the depth of the pits for the evaluation of the corrosion attack.

In the Table 4 the results from the mass loss measurements are listed. Figure 8 shows the run of the mass loss curves. The mass loss and the differentiation among the grades increase with the number of cycles. The highest resistance is achieved by grade 1.4404. The grades 1.4526, 1.4301, 1.4376 and 1.4509 display no significant differences in mass loss. The grade 1.4512 with the lowest chromium content shows the highest mass loss. A relatively good agreement is observed between the mass loss rates and the alloy content of the materials. But based on the pitting attack mechanism the results of the mass loss measurements should always be treated with care.

Table 4.
The mass loss of the materials after 48 cycles

Materials	1.4404	1.4526	1.4301	1.4509	1.4376	1.4512
Mass loss [g]	0.016	0.041	0.051	0.06	0.07	0.124

Table 5 and Figure 9 show the results from the measurements of the depth of the pits.

The grade 1.4512 shows predominantly general attack and few pitting, most of the pits are not very deep. The intense accumulation of the corrosion products on the metal surface leads to crevices. Inside these crevices pitting corrosion takes place and the pits grow very fast. At the end of the test both of the samples are perforated. The corrosion attack concentrates in the few pits which grow fast. The average depth of the pits doesn't illustrate the real dimension of the corrosion attack in this case. The grade 1.4404 shows the least average depth but does not differ much from the next material in the mass loss measurements. The grade 1.4376 shows the highest average depth and differs more from the other grades.

Table 5.
The average depth of the pits

Materials	1.4404	1.4526	1.4301	1.4509	1.4376	1.4512
Average depth [µm]	145.6	175.3	192.0	192.6	235.4	170.4

Both mass loss and the average depth of the pits are marked. As shown in Table 6 the mass loss marks are given from value 1 for mass losses between 0 and 0.04 g up to the value 4 for mass losses between 0.12 g and 0.16 g. Similarly the average depth marks of the pits are given from value 1 for pits less than 50 µm up to value 5 for pits between 200 µm and 250 µm.

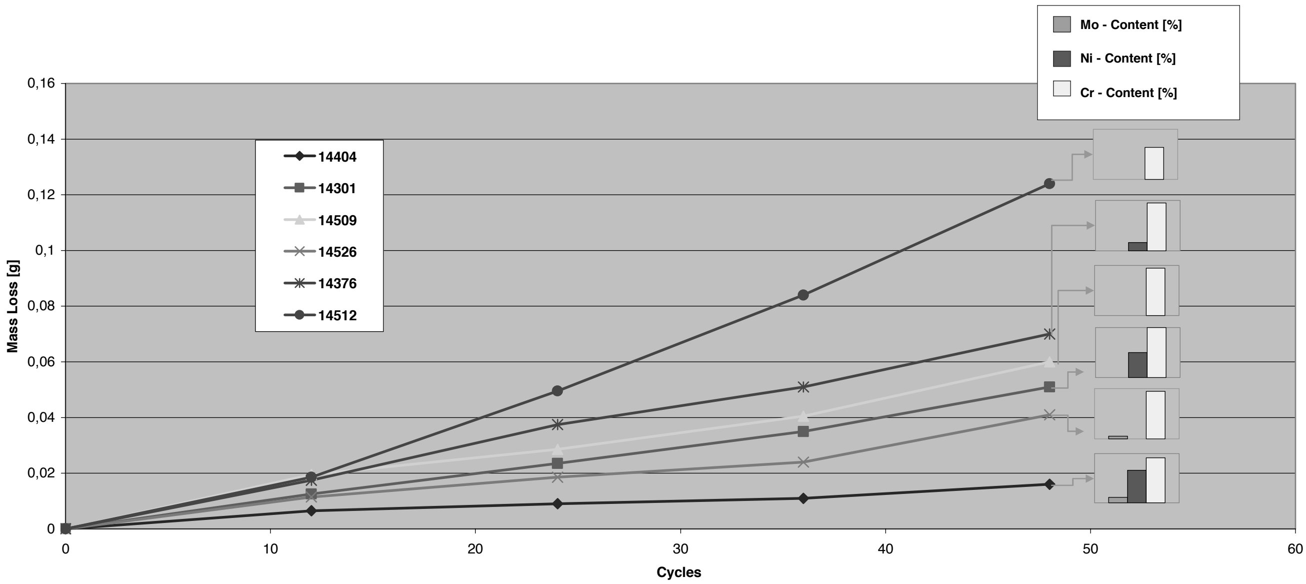


Fig. 8. Run of the mass loss curve and the relationship between mass loss and Mo-, Ni-, Cr-contents [10-13]

Table 6.
The marking of the mass loss and the average depth of the pits

Mass loss [g]	0 – 0.04	0.04 – 0.08	0.08 – 0.12	0.12 – 0.16	
Marks mass loss	1	2	3	4	
Average depth [µm]	0 - 50	50 - 100	100- 150	150 - 200	200 - 250
Marks average depth	1	2	3	4	5

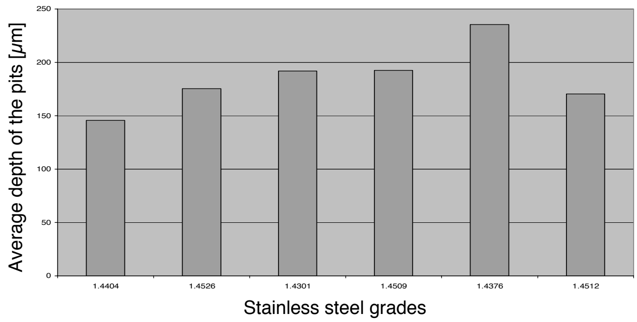


Fig. 9. The average depth of 10 pits

The marks from both methods of evaluation for the stainless steel grades are summarized in Table 7.

Figure 10 shows the ranking of the materials by means of the summarized marks.

Table 7.
Summarized marks for the tested materials from the two evaluation methods of the corrosion

Stainless steels	1.4404	1.4526	1.4301	1.4509	1.4376	1.4512
Marks mass loss	1	2	2	2	2	4
Marks average depth	3	4	4	4	5	4
Summarized marks	4	6	6	6	7	8

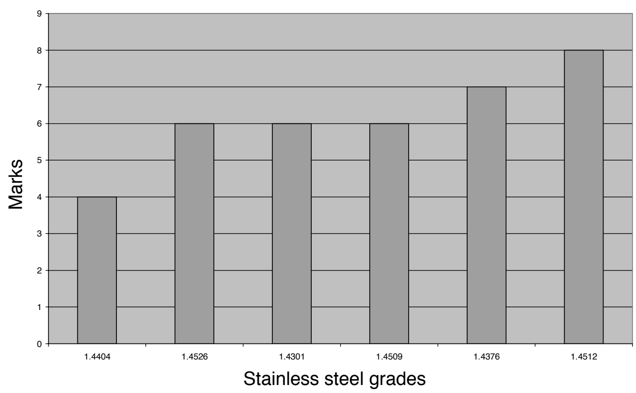


Fig. 10. Ranking of the materials by means of the attributed marks

The best result is achieved by grade 1.4404, which confirms the positive influence of the alloying element molybdenum on the resistance to the onset of corrosion and the positive influence of the alloying element nickel on the repassivation during the idle periods.

The highest mass loss of the grade 1.4512 points to a predominant general attack. But even if most of the pits are not deep there is the danger that some of these pits will grow very fast and become very deep under the deposited corrosion products.

The grade 1.4376 differs from the other grades through its deepest pits and it ranks right below the material places grade 1.4512.

Between the other stainless steel grades 1.4526, 1.4301 and 1.4509 there is no significant differentiation in mass loss and in the average depth of the pits.

5. Conclusions

For the corrosion conditions in the rear muffler the stainless steel grade 1.4512 is overtaxed. In the technological tests which were carried out the stainless steel grade 1.4404 shows the best corrosion resistance.

The combination of the two methods of evaluation of the corrosion, the measurement of the mass loss and the measurement of the average depth of the pits set apart the stainless steel grades 1.4404, 1.4376 and 1.4512 from the other stainless steel grades. Between the other grades 1.4526, 1.4301, 1.4509 there is no significant differentiation.

The technological tests with alternating wet/dry phases are most suited to reflect the particular corrosion conditions in automotive exhaust systems.

For the future tests we propose the following aspects to consider:

- definition of an electrolyte with a proper buffer solution for the test conditions,
- a simplifying of the samples to get a faster evaluation of the depth of the pits,
- an additional temperature stress of the samples, for example regular storage of the samples in an oven at a defined temperature.

With an elaborate method of measuring all pits and their depth and the calculation of the part of the corroded surface related to the whole surface of the samples will lead to a better evaluation of the corrosion attack and a pronounced differentiation between the different stainless steel grades.

References

[1] H. Weltens, P. Garcia, H. Neumaier, New lightweight design in automotive exhaust systems, Company publication, Gillet GmbH (in German).

[2] Stainless Steels in automotive exhaust systems, Company literature, Thyssen Krupp Nirosta (in German).

[3] P.-J. Cunat, Stainless Steel – Stainless Steel Properties for Structural Automotive Applications, Proceedings of the “Metal Bulletin International Automotive Materials” Conference, Cologne, 2000.

[4] J. Kemppainen, Stainless Steel – A New “Light Metal” for the Automotive Industry, Proceedings of the Euro Inox Presentation “Stainless Steel in Structural Automotive Industry Applications – Properties and Case Studies”, Paris Motor Show Mondial de l’Automobil, Paris, 2000.

[5] J. Lagier, P. Rombeaux, J. Ragot, P. Vaugeois, Ferritic Stainless Steels in Exhaust Systems, Proceedings of the “Innovation Stainless Steel” Conference, Florence, 1993.

[6] H. Weltens, P. Garcia, H.-D. Walther, Internal and external corrosion of exhaust systems for passenger vehicles – Test procedures, laboratory and field results, Proceedings of the DVM Berlin, 1998.
[7] Y. Inoue, M. Kikuchi, Present and Future Trends of Stainless Steel for Automotive Exhaust System, Nippon Steel Technical Report No. 88, 2003.
[8] P. Gümpel, Stainless Steels, Third Edition, Expert, 2001 (in German).
[9] H. Gräfen, D. Kuron, Pitting corrosion of stainless steels. Materials and Corrosion 47 (1996) 16-26 (in German).
[10] P. Gümpel, D. Schiller, N. Arlt, D. Bouchholz, Simulation of the corrosion behaviours of stainless steels in automotive exhaust systems, ATZ Worldwide 106/4 (2004).
[11] E. Heitz, R. Henkhaus, A. Rahmel, Corrosionsciences in experiment, Second Edition, VCH, 1990 (in German).
[12] P. Gümpel, C. Hoffmann, N. Arlt, Factors determining corrosion resistance of stainless steels in automotive exhaust systems, Proceedings of the European Corrosion Congress EUROCORR 2007, Freiburg, 2007 (CD-ROM).
[13] P. Gümpel, C. Hoffmann, Corrosion behaviour of different stainless steels in automotive exhaust systems, Proceedings of the Conference and Expo “Stainless Steel World America 2008”, Houston, 2008.
[14] C. Hoffmann, P. Gümpel, S. Zamfira, B. Braun, Evaluation of the pitting corrosion in automotive exhaust systems, Proceedings of the 19th DAAAM International Symposium "Intelligent Manufacturing & Automation", Trnava, 2008, 0599-0600.
[15] P. Gümpel, C. Hoffmann, N. Arlt, Corrosion resistance of stainless steels to wet condensates in automotive exhaust systems, Proceedings of the 6th European Stainless Steel Conference, Helsinki, 2008, 645-651.
[16] M. Liedmann, B. Wielage, T. Lampke, 3D Quantification of Wear, Proceedings of the International Symposium “Friction, Wear and Wear Protection 2008”, Aachen, 2008.
[17] L.A. Dobrzański, Z. Brytan, M. Actis Grande, M. Rosso, Innovative PM duplex stainless steelsobtained basing on the Schaeffler diagram, Archives of Materials Science and Engineering 30/1 (2008) 49-52.
[18] M. Rosso, Contribution to study and development of PM stainless steels with improved properties, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 178-187.