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Use of alloy 59 for the transport of highly corrosive dangerous goods

Margit Weltschev[1, a], Ralph Baessler[2,b]

[1,2]BAM-Federal Institute for Materials Research and Testing, D-12200 Berlin, Germany

[a]Margit.Weltschev@BAM.de, [b]Ralph.Baessler@BAM.de

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Abstract

Alloy 59 (NiCr23Mo16Al) with a lot of chromium, molybdenum and nickel possesses excellent resistance not only to reducing but also oxidizing chemicals.

Both the Nickel alloy 59 and the superaustenitic steel alloy 31 have already been used as shell materials for tank vehicles or tank containers. Use of these alloys allows the transport of a significantly wider variety of chemicals and, especially, waste mixtures than the use of common austenitic steels. Another advantage is the extension of test interval for transport tanks.

In Germany the “BAM-List – Requirements for Tanks for the Transport of Dangerous Goods” is the basis for substance-related prototype approvals for tank containers designed for the carriage of dangerous goods issued by the Federal Institute for Materials Research and Testing (BAM). Compatibility evaluations of selected metallic material groups as well as polymeric gasket and lining materials under the influence of approximately 7000 dangerous goods and water-polluting substances are published in the BAM-List. Alloy 59 belongs to the group of metallic materials in the BAM-List.

Due to the large number of dangerous goods in the BAM-List BAM, IKS Dresden and ThyssenKrupp VDM performed a comprehensive corrosion test programme with welded specimens of the nickel alloy 59 and the superaustenitic steels alloy 926 and alloy 31 in the period 2002 - 2010. In particular alloy 59 and alloy 31 were exposed to a large number of corrosive substances such as various mixtures of both nitric acid/sulphuric acid and nitric acid/phosphoric acid at 55 °C. Other corrosive test substances were different organic and inorganic halogenides, peroxyacetic acid and molten substances. In the case of molten chemicals such as monochloroacetic acid the test temperature was increased to more than 100 °C. The test results presented in this paper are already included in the 10th edition of the BAM-List and, therefore, available to the customer.

Introduction

Compatibility evaluations of conventional metallic materials (i.e. carbon , austenitic CrNi-, CrNi-Mo-steels and aluminium) for tank containers and transport tanks are available in the "BAM-List – Requirements for Tanks for the Transport of Dangerous Goods" [1]. Such information about corrosion resistance is applicable for tank trucks and rail cars too.

Unless otherwise specified, the compatibility evaluations apply for average operating temperatures up to 50 °C. They do not only contain the evaluation of corrosion caused by the dangerous good on the material but also potential dangerous effects of the material on the medium to be transported.

According to the international dangerous goods regulations ADR/RID for road and rail transport in Europe and the IMDG-Code for international maritime carriage a compulsory internal inspection of the tank is required after a certain period. The test interval is generally five years for tank containers and six years for road tank vehicles. For rail tank cars test intervals of four and eight years are required by the dangerous goods regulations. For the time of the test intervals the corrosion resistance of the tank material must be provided considering the following criteria.

Material/substance combinations for test intervals of 5, 6 and 8 years are considered suitable if

- wall thickness reduction due to uniform corrosion does not exceed 0.1 mm/year and

Material/substance combinations for test intervals of 2½, 3 and 4 years are considered suitable if

- wall thickness reduction due to uniform corrosion does not exceed 0.5 mm/year

Localized corrosion effects in the form of pitting corrosion, stress corrosion cracking and crevice corrosion have to be excluded.

Corrosive substances, which require materials with a higher corrosion resistance than listed in the BAM-List, are halogen containing media and oxidizing or reducing acids. The corrosion risk while carrying these substances needs to be considered to be very high due to often performed change of transport medium, because after the cleaning process some moisture remains inside the tank. Furthermore costs rise due to additional internal inspections of tanks. One possible way to solve this problem is coating or lining the tanks by a polymeric material. An alternative is the application of high-alloyed steels and nickel alloys for transport tanks.

The nickel alloy 59 (NiCr23Mo16Al, 2.4605) as well as the "super austenite" alloy 31 (X1NiCrMoCu32-28-7, 1.4562) are a good alternative to coated or lined tanks for transport of corrosive chemicals and waste due to its good resistance against pitting and crevice corrosion. Due to the higher strength of the material the tank wall thicknesses can be reduced considering the requirements of the international regulations for transport of dangerous goods. This allows a reduction of the tank weight. Therefore these materials were chosen to be added to the BAM-List.

Experimental setup

Test substances The exposure was carried out according to DIN 50905/4. The test results of one material determined the following corrosion tests either with the lower or higher-alloyed material. The tests were performed in representatives of the following highly corrosive substance groups:

1. Inorganic halogenides (ferric chloride),
2. Halogenic carbonic acids (2-chloropropionic acid),
3. Chlorates and chlorites (barium chlorate, sodium chlorite and sodium hypochlorite),
4. Hydrogen sulphates (potassium hydrogen sulphate)
5. Inorganic acids (perchloric acid, hydrochloric acid)
6. Mixed acids (mixture of nitric and sulphuric acid)

Setup Each set of test specimens was fixed in a sealed 3 l glass receptacle by non-extruding PTFE-threads completely dipped into the solution, in the intermediate phase and in the vapour phase in a temperature controlled box at 55 ± 1 °C (see Fig. 1). The distance between the upper edge of the completely inserted specimen and the surface of the liquid was supposed to be at least 10 mm.

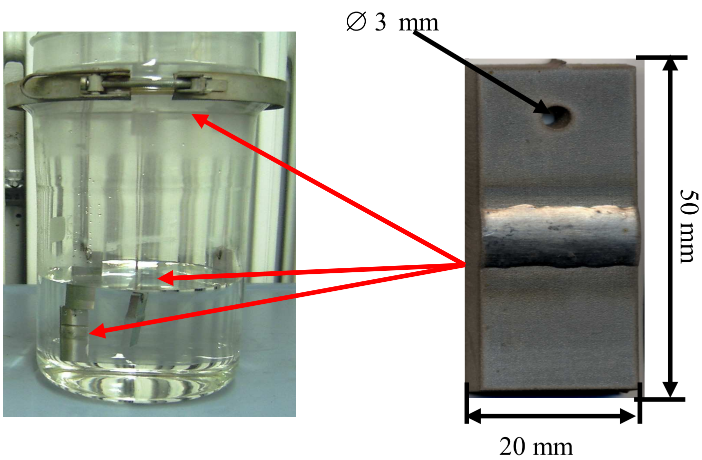

Figure 1: Specimen and exposure location

Preparation Specimens, water jet cut and equipped with a hole, having dimensions of 50 mm x 20 mm x 5 mm with centered located, 20 mm long weld made of FM 59) were deburred by grinding paper, cleaned by brushes under flowing water, degreased by ultrasound and acetone, flushed with water / distilled water / ethanol and dried with warm air.
Mass loss was determined by weighing before and after exposure. After removal from the medium specimens were flushed with water, brushed, flushed with water and acetone and dried with warm air. Specimens were evaluated by optical microscopy. Especially signs of localized corrosion were of interest. After one week the specimens were examined for the first time, following that after two and four weeks. Maximum values were used for the characterization of the corrosion resistance.
It was distinguished between pitting and shallow pit corrosion in order to use the right criteria for suitability evaluation.

Results

Ferric chloride Alloy 59 can be considered resistant in the whole concentration range. Even in the saturated solution the corrosion rate is below 0.005 mm/year.
The steel alloy 31 corrodes in the saturated ferric chloride solutions 55 °C and is resistant in 25 % and in lower concentrated ferric chloride solutions with a corrosion rate < 0.01 mm/year (Figure 2).
The very high corrosion rates occurring during activation can be explained by the high content of oxidizing components in the solution.

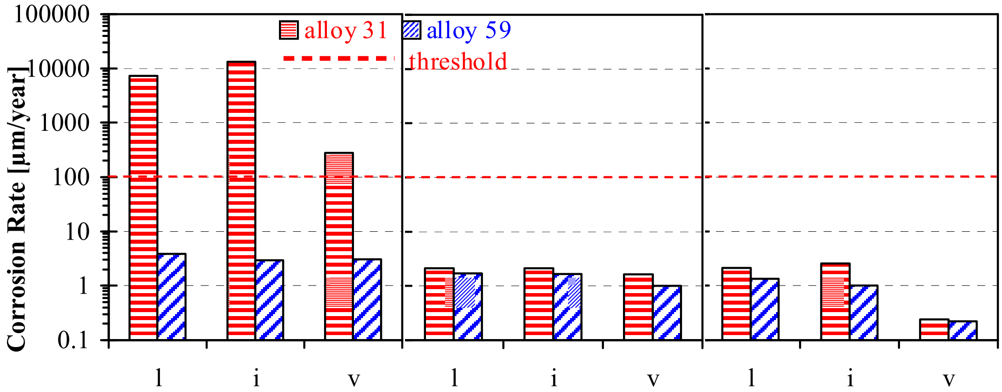

Figure 2: Corrosion rates of alloy 59 and alloy 31 in saturated (left), 5 % (centre) and 0.1 % (right) ferric chloride solutions at 55 °C (liquid (l), intermediate (i) and vapour (v) phases)

2-Chloropropionic acid Alloy 59 is resistant in this representative of halogen carbonic acids up to a acid concentration of 90°% (with 4 – 6 % 2.2-Dichloropropionic acid) du to its corrosion rate of < 0.05 mm/year. However alloy 31 corrodes with 0.5 mm/year in the vapour phase (Fig. 3).

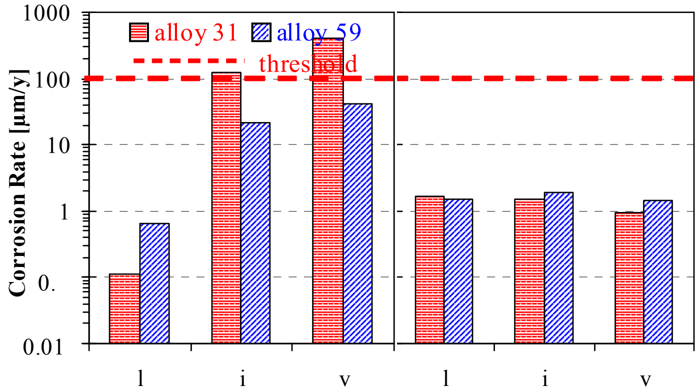

Figure 3: Corrosion rates of alloy 59 and alloy 31 in 90 % (left) and 5 % (right) in 2-chloropropionic acid at 55 °C (l…liquid, i…intermediate, v…vapour phase)

Barium chlorate For alloy 59 corrosion rates < 0.001 mm/year were determined in different barium chlorate solutions at 55 °C. Values for alloy 31 were below 0.002 mm/year (Fig. 4).

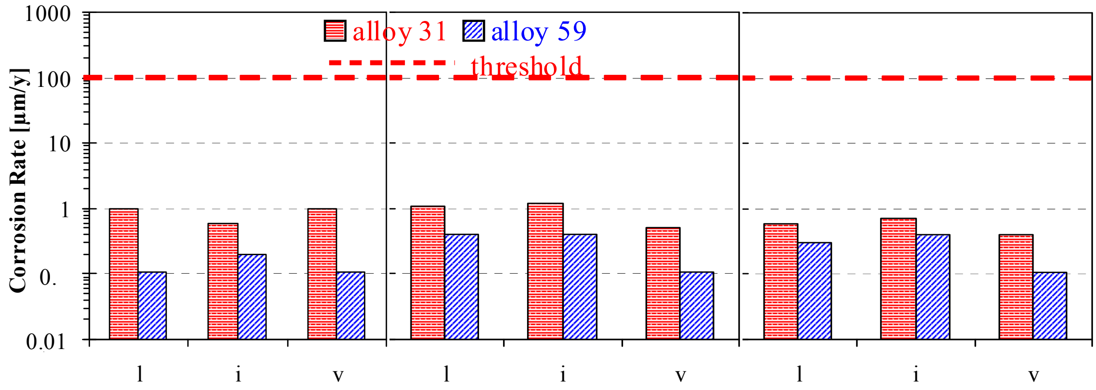

Figure 4: Corrosion rates of alloy 59 and alloy 31 in saturated (left), 5 % (centre) and 0.1 % (right) aqueous barium chlorate solution at 55 °C (l…liquid, i…intermediate, v…vapour phase)

Sodium chlorite and sodium hypochlorite The nickel alloy and the super austenite alloy 31 show a very good corrosion resistance within the whole concentration range of sodium chlorite, having corrosion rates below 0.01 mm/year at 55 °C (Fig. 5)**.** Both alloys can be rated completely corrosion resistant in saturated and 0.1 % sodium hypochlorite solution too.

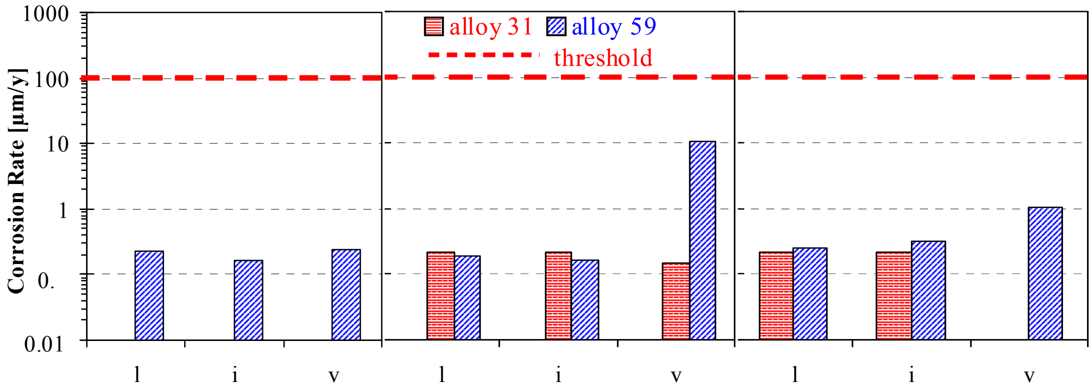

Figure 5: Corrosion rates of alloy 59 and alloy 31 in saturated (left), 5 % (centre) and 0.1 % (right) aqueous sodium chlorite solution at 55 °C; (l…liquid, i…intermediate, v…vapour phase)

Potassium hydrogen sulphate The diagram of measured corrosion rates shows values far below the threshold. It can be concluded that both alloy 59 and alloy 31 are resistant (Fig. 6).

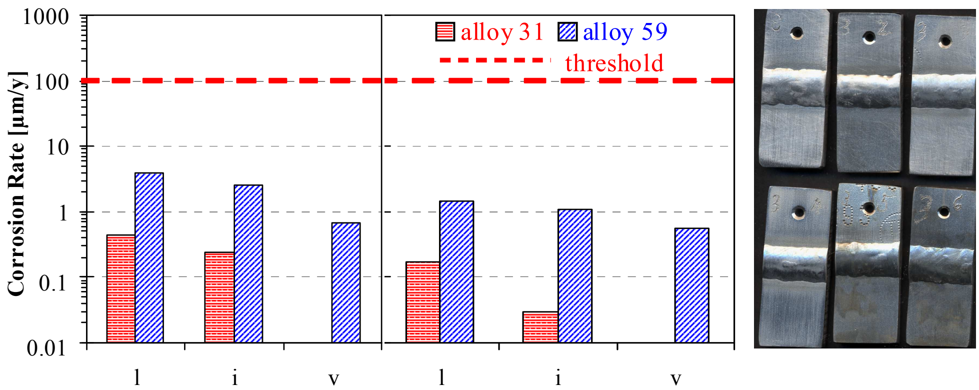

Figure 6: Corrosion rates of alloy 59 and alloy 31 in saturated (left) and 0.1 % (right) aqueous potassium hydrogen sulphate solution at 55 °C; test specimens made of alloy 59 after exposure to saturated solution (l…liquid, i…intermediate, v…vapour phase)

Perchloric acid Alloy 59 is resistant in the whole concentration range of perchloric acid. Alloy 31 is resistant in 0.1 % solution only, otherwise a classic uniform corrosion can be observed, leaving the over-alloyed weld intact (Fig. 7).

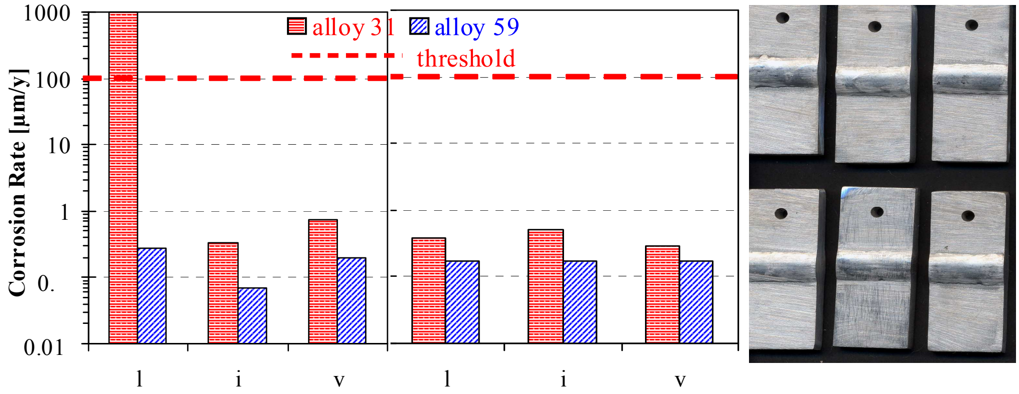

Figure 7: Corrosion rates of alloy 59 and alloy 31 in concentrated (left) and 0.1 % (right) perchloric acid at 55 °C (l…liquid, i…intermediate, v…vapour phase), specimens made of alloy 59 after exposure in concentrated perchloric acid at 55 °C

Hydrochloric acid There are only few materials suitable for this reducing behaving acid. Alloy 31 can only be applied to chemical processes where small amounts of hydrochloric acid are involved. The application of the nickel alloy 59 is limited to a temperature up to 40 °C (Fig. 8).

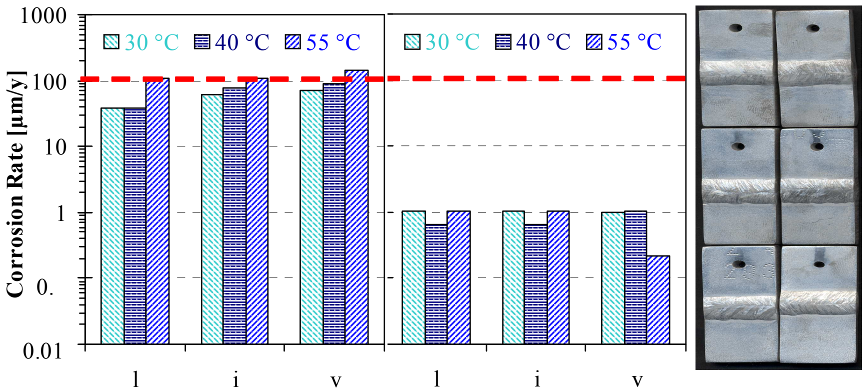

Figure 8: Corrosion rates of alloy 59 in concentrated and 0.1 % hydrochloric acid at different temperatures (l…liquid, i…intermediate, v…vapour phase), specimens made of alloy 59 after exposure in concentrated hydrochloric acid at 40 °C

Mixtures of nitric and sulphuric acid Alloy 59 shows clearly better corrosion resistance in the mixtures of nitric and sulphuric mixtures at 55 °C. A maximum corrosion rate of 0.024 mm/a was determined in a mixed acid of 66 % concentrated nitric acid and 34 % of 96 % sulphuric acid after an exposure time of two weeks. Lower corrosion rates in the liquid phase were measured if the content of the nitric acid is reduced to 33 %. The nickel-based alloy corrodes with increasing content of nitric acid in the vapour phase too, even though the corrosion rates are less than 0.1 mm/a (see Fig. 9).

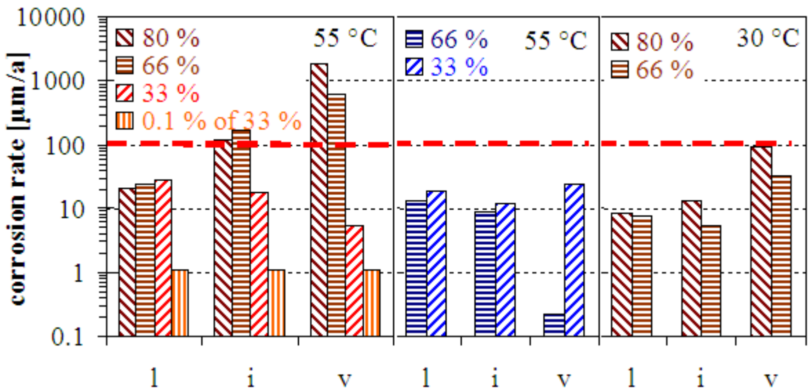

Figure 9: Corrosion rates (left: alloy 31), 55 °C, centre: alloy 59, 55 °C, right: alloy 31, 30 °C after 4 weeks exposure in different HNO_3/H_2SO_4-mixtures (always Vol. %-value of content of 67 % HNO_3, rest is 96 % H_2SO_4)

Summary

As expected due to the different alloying components, especially chromium, nickel and molybdenum, differences of the corrosion behaviour of alloy 59 in comparison with alloy 31 were observed in the various substances. Alloy 59 is more corrosion resistant than alloy 31. However both materials face localized corrosion in substances containing halogenides, which often can be prevented in limiting the transport temperature (i.e. use of insulated tanks).
Concluding, it can be stated, that both alloy 59 and alloy 31 are a good alternatives to the lining of tanks in order to carry corrosive dangerous goods. Intensive publication [2 – 7] of results achieved so far has led to production of new tank trucks and containers made of these alloys. The evaluation of the tested material/medium combination is incorporated in the 10th issue of the BAM-List.

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