New Lean Alloy Alternatives for 300 Series Stainless Steels – a Corrosion Perspective

Gümpel P. and Leu F.
Hochschule Konstanz, University of Applied Sciences, Konstanz, Germany

Burkert A. and Lehmann J.
BAM Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

Abstract
Rising Prices of nickel and molybdenum in the past few years have led to unprecedented interest in substitution of leaner-content alloys for standard 300-series austenitic stainless steels in a lot of applications. Due to the high prices of different alloying elements and to periodic large fluctuations that cause similar large fluctuations in the costs of using 300-series stainless steels; a lot of new materials entered the markets in Europe and also in the rest of the world. A big disadvantage consists in the fact that there are a lot of corrosion results, however, a direct comparison of the corrosion resistance of these new materials does not exist up to now or only incompletely. In this project comparative investigations were carried out and always one or several representatives of a material group were incorporated. These material groups are: Lean Duplex Stainless Steels, Manganese Alloyed Austenitic and Duplex Stainless Steels and Ferritic Stainless Steels. These materials were investigated in a lot of different test procedures and in different conditions focused on the application in civil engineering and common use. Beside the electrochemical investigations all materials were exposed in different surface states in the atmosphere, once in coastal nearness and once in a city centre area. Other exposition tests with material coupons where done in the atmosphere of indoor swimming pools and at the case of food processing machines were corrosion processes are caused by the cleaning procedure. First results are reported.

Keywords*: Austenitic stainless steels, ferritic stainless steels, duplex stainless steels, manganese alloyed stainless steels, pitting corrosion, stress corrosion cracking, passive layer, surface condition*

1 Introduction

Today Stainless steels are more and more used as engineering materials in all kinds of industry, in architecture and building constructions and in our daily life. These steel types are sustainable materials with a high aesthetic attraction and good mechanical properties [1]. The most common ones are austenitic and ferritic stainless steels whereby the rate of austenitic steels with higher nickel contents is still very high [2]. Due to the high prices of nickel and to periodic large fluctuations of the nickel prices the prices of 300-series stainless steels changed and a lot of new materials entered the markets in Europe and also in the rest of the world.Within the last years a trend to an increased use of high strength duplex stainless steels could be observed. In a first step mainly the classic duplex stainless steel 22-05 (X2CrNiMo22-5-2, 1.4462) was utilized. In the last few years new duplex stainless steels have been developed and established on the markets. The main reasons for this development were the more and more increasing costs of alloying elements, especially the elements nickel and molybdenum [2]. Due to this the low cost steel type 23-04 (X2CrNiN23-4, 1.4362) was developed and investigated in a lot of different test procedures and in different conditions focused on the application in civil engineering [2]. In the year 2009 this material got an accreditation for fastening elements in the German Standard Z-30.3-6 [3]. Meanwhile more duplex stainless steels with reduced nickel and/or molybdenum content were developed and brought to the market, for example 22-02 (X2CrNiN22-02, 1.4062) and 21-01 (X2CrMnNiN21-5-1, 1.4162). The most important property constitutes the corrosion resistance of these materials. In other areas of stainless steel supply, for example in automotive industry, food supply industry etc. other steel types with lower alloy contents like ferritic stainless steels, Manganese Alloyed Austenitic and Duplex Stainless Steels and also stainless steels with a lower chromium content were used more and more.

Besides the alloy composition the quality of the surface condition plays an important role on the corrosion resistance of the different alloys. All in all it is important to compare the corrosion resistance of different materials under different corrosion load with a defined surface condition. These data's should help the stainless steel suppliers to make a technical and economical optimized materials selection for the different applications. In the present work a comparative testing of the standard austenitic stainless 300 steels with some lean alloyed stainless with different surface conditions was carried out and an overview of the primary results of these investigations are presented in this paper.

2 Investigations

2.1 *Materials*

A comparative test with different materials concerning their corrosion behaviour has been done. The materials composition is presented in Table 1 and Figure 1, which provides a short overview over the amount of important and expensive alloying elements. All specimen were taken from cold rolled and solution annealed plates in the thickness range of 1 to 2 mm. The investigations have been done in different special worked surface conditions. The surface preparation has been done by different methods, like grinding, polishing, welding and shot-peening. The designation of the specimen is as subsequent:

W: as supplied, pickled and passivated
TS: dry grinded
GP: shot peened
EP: electro polished
S: welded with welding filler material

2.2 *Sample Preparation and Investigations*

The edges of the samples were grinded (220 and 500 grit), cleaned with acetone in an ultrasonic bath, washed with ethanol, dried and stored under defined conditions until the test started. For the electrochemical investigation an electrolyte with the following composition was used: 3 g Cl-/l; pH 4.5. The test procedure was the Potentiostatic Polarization Method at different temperatures with a scan rate dE/dt = 0.2 mV/s. The anodic polarization ended

Table 1: Chemical Composition of the tested stainless steel grades

Nr.	Material			Alloy content in %						
				Carbon	Chromium	Manganese	Sulfur	Nickel	Molybdenum	Nitrogen
1	**1.4301**	X5CrNi18-10	304	0,033	18,30	1,27	0,0038	7,94	0,196	0,048
2	**1.4404**	X2CrNiMo17-12-2	316L	0,016	16,88	0,84	0,0092	10,04	1,960	0,025
3	**1.4003**	X2Cr11	3Cr12	0,027	11,43	1,08	0,0030	0,44	0,021	0,018
4	**1.4162**	X2CrMnNiN22-5-2	21-01	0,027	21,43	4,83	0,0026	1,55	0,287	0,176
5	**1.4062**	X2CrNiN22-2	22-02	0,024	22,90	1,28	0,0037	2,38	0,231	0,165
6	**1.4362**	X2CrNiN23-4	23-04	0,024	23,09	1,41	0,0035	4,64	0,413	0,096
7	**1.4509**	X2CrTiNb18	441	0,019	17,96	0,43	0,0046	0,16	0,032	0,018
8	**1.4521**	X2CrMoTi18-2	444	0,022	17,58	0,29	0,0052	0,14	2,000	0,021
9	**1.4376**	X8CrMnNi19-6-3	H400	0,038	17,89	6,37	0,0038	4,15	0,167	0,148

after reaching a current density of 100 µA/cm². Afterwards a polarisation with the same scan rate in the cathodic direction has been done. As a result of these measurements the critical pitting potential Ekrit0,01 at a current density of 10 µA/cm² and also the repassivation potential ERep0,01 at the same current density of 10 µA/cm² was determined.

For testing the atmospheric corrosion test coupons of all materials were exposed in Helgoland, a German island in the North Sea and in the city of Berlin. The details of this exposure test are presented together with the results of the first exposition period.

3 Results

At a temperature of 20 °C the critical pitting potential of the lean duplex stainless steels is clearly higher than of the austenitic steels 304 and 316 (Figure 2). Every measurement was done 3 times and the average value is demonstrated together with the minimum and maximum value in Figure 2. The lowest resistance against pitting corrosion was observed with the 12% Chromium steel and the Chromium-Manganese steel 1.4376.

The highest pitting potential was always measured in the electro polished condition, whereas the differences between the different materials are stabilizing at the same level for each steel of course with some differences depending on the quality of the surface (Figure 3 - 5). A surprising result is the relationship between the steel types 304 and 316 in this test: in all investigated surface conditions the molybdenum free steel 304 shows a better critical pitting temperature than the steel type 316 with 2 % molybdenum, the reasons for this will be discussed later.

The results show a good reproducibility in all investigated surface conditions, there is no remarkable difference between the single results. Figure 5 gives a summary of the average pitting potentials of all investigated steels in all surface conditions. In the condition as supplied there is some uncertainty about the history of surface preparation

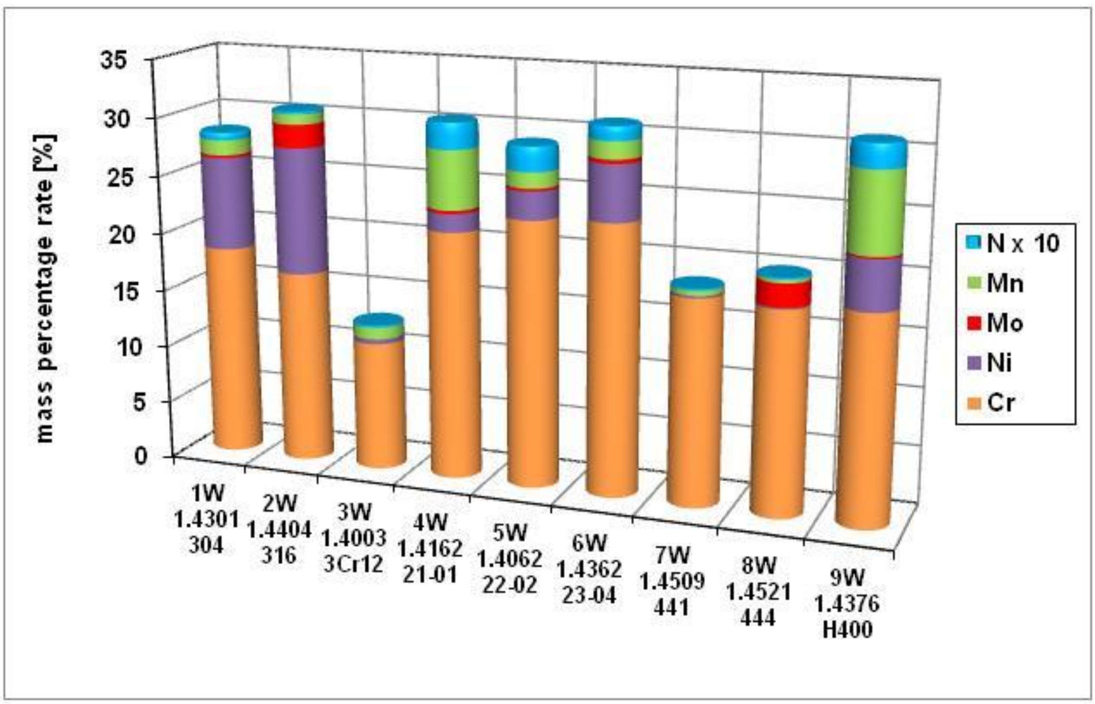

Figure 1: Alloying components Cr, Ni, Mn, Mo in various stainless steels

by the steel supplier. Therefore with some materials after grinding, the electrochemical measurement of the critical pitting potential gives higher and with other materials lower pitting resistance as in the as supplied condition (Figure 3 - 5). The critical pitting potential of the shot-peened specimen mostly degreases in comparison to the as supplied and also to the grinded condition (Figure 5). In the welded condition the pitting potential decreases mostly, especially one of the lean duplex stainless steels, the type 22-02 (X2CrNiN22-2, 1.4062) gets a drop in their pitting potentials, measured at 20°C (Figure 5), this may depend on the welding conditions of the material und will not be a general effect.

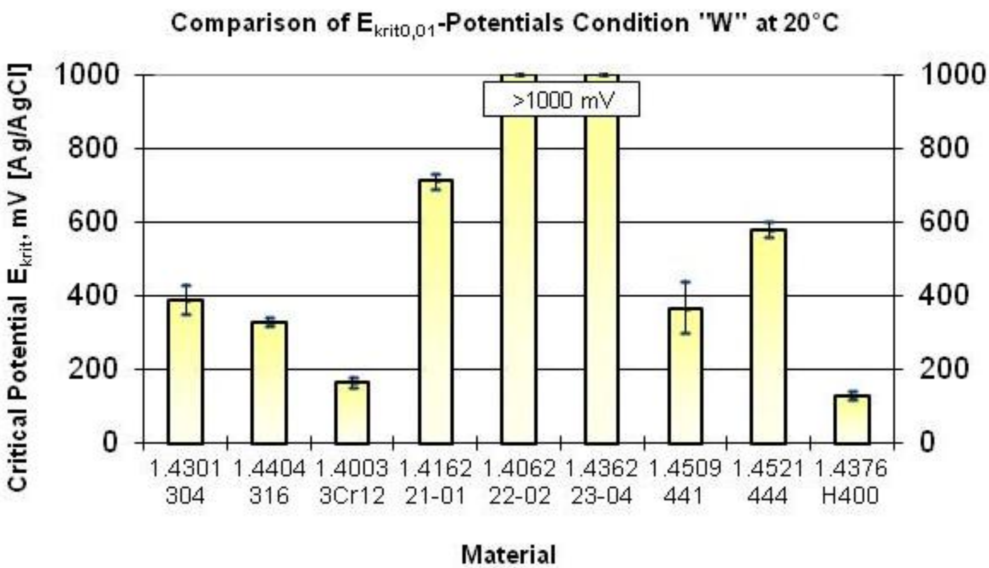

Figure 2: Critical pitting potentials in the 'as supplied condition' at a testing temperature of 20 °C

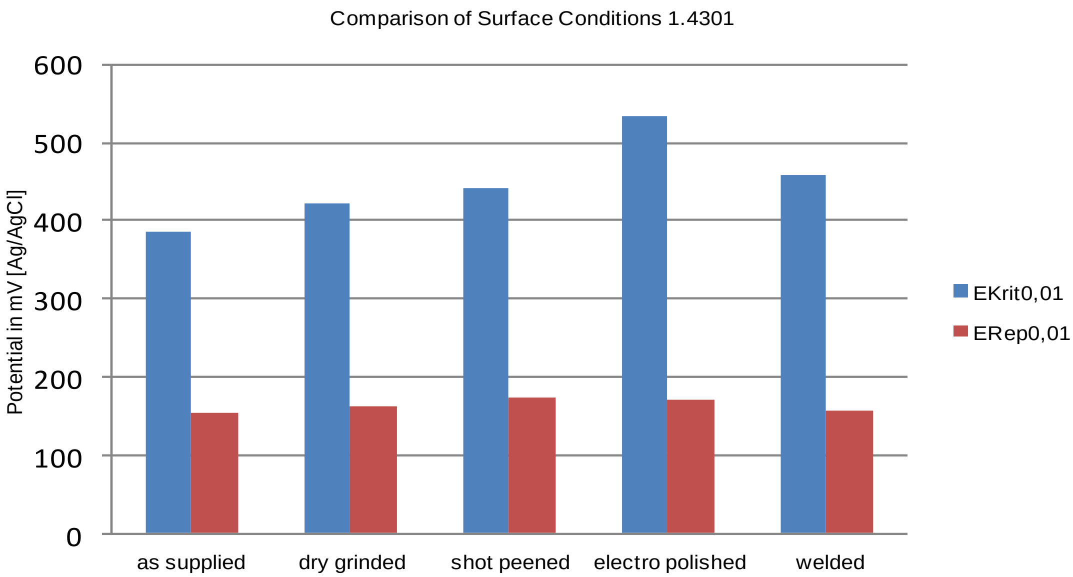

Figure 3: Influence of the surface condition on the critical pitting potential and the repassivation potential of the steel 304 (X5CrNi18-10, 1.4301)

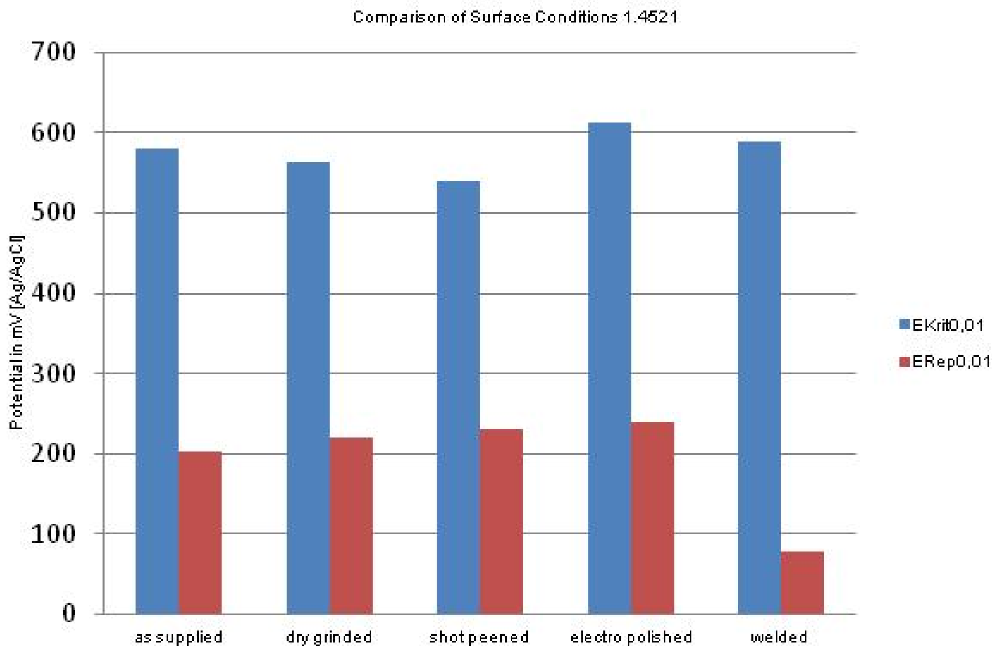

Figure 4: Influence of the surface condition on the critical pitting and the repassivation potential of the steel 444 (X2CrMoTi18-2, 1.4521)

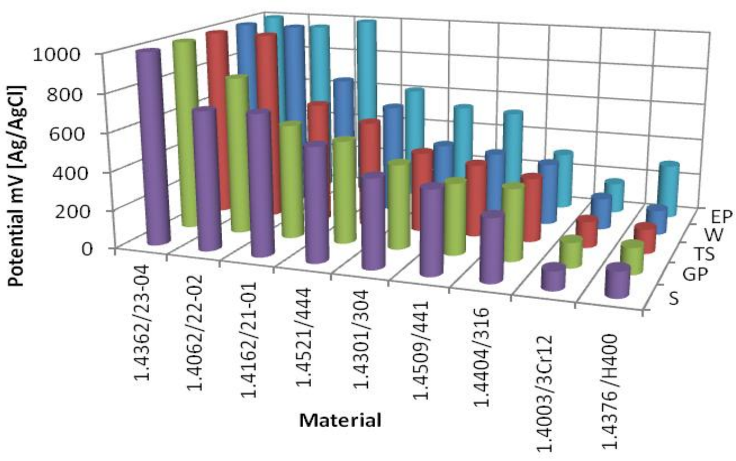

Figure 5: Influence of the surface condition on the critical pitting potentials at a testing temperature of 20 °C (Average values of 3 measurements); ranking

Especially the corrosion resistance of the lean duplex stainless steels 21-01 (X2CrMnNiN21-5-1, *1.4162*) and 22-02 (X2CrNiN22-02, 1.4062) is susceptible to the quality of the surface condition. Comparing the critical pitting potentials of all steels at 20 °C, the duplex stainless steels offer a better pitting resistance than the common austenitic steels 304 and 316. At these testing conditions the best results shows the steel 23-04 (X2CrNiN23-4, 1.4362) (Figure 5). Comparing the critical pitting potentials with the Pitting Resistance Equivalent (PRE) of all steels (Figure 6) there is a clear relationship: with higher PRE-values the pitting resistance rises. Two materials do not follow this general trend; these are the steels type 316 and H400. The reasons for this behaviour will be discussed later. At higher testing temperatures the critical pitting potentials changes to lower values, but the decrease depends on the alloy composition of the materials. Figure 7 shows the relationship between the critical pitting potential of the tested materials and the testing temperature. It is clearly to perceive that the benefit of the duplex stainless steels drops out with higher exposure temperatures. A ranking of the materials shows, that the benefit of the lean duplex steels gets smaller. However, the steel type 23-04 (X2CrNiN23-4, 1.4362) has still a higher pitting resistance in the investigated range than the standard austenitic steels 304 and 316 (Figure 8).

Using the present testing procedure the repassivation potential seems to be more sensitive to the contents of expensive alloying elements like nickel and/or molybdenum which are reduced in the lean alloyed stainless steels (Figures 9 and 10). It must be considered that the repassivation behavior is dependent on the potential where the polarization in the cathodic direction starts (Figure 11), and these potentials are different for the investigated materials and they are high for the lean duplex steels (Figure 7). However, in these tests the ranking of all investigated materials based on the repassivation potential gives the best values to the steel type 23-04 (X2CrNiN23-4, 1.4362) and the molybdenum containing standard austenitic steel 316L. Especially the lean duplex steel grades 22-02 (X2CrNiN22-02, 1.4062) and 21-01 (X2CrMnNiN21-5-1, *1.4162*) show lower repassivation potentials in this test method, even at a temperature of 30 °C and there is a significant drop of these values with higher testing temperatures.

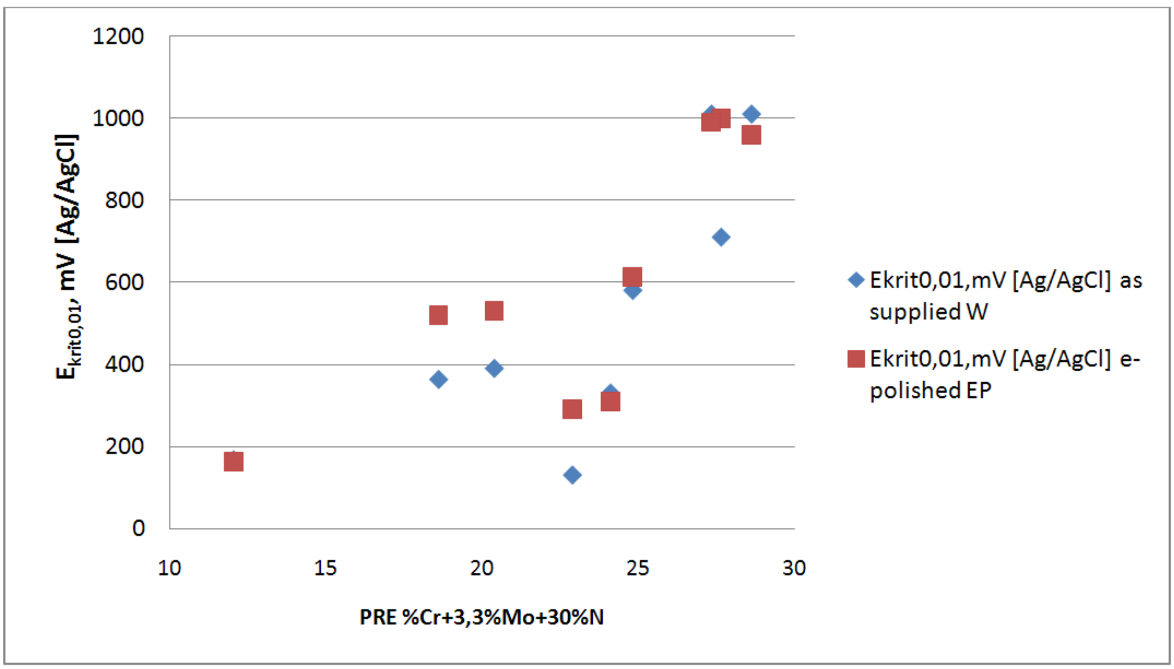

Figure 6: PRE-value versus pitting potentials of all investigated steels at 20 °C

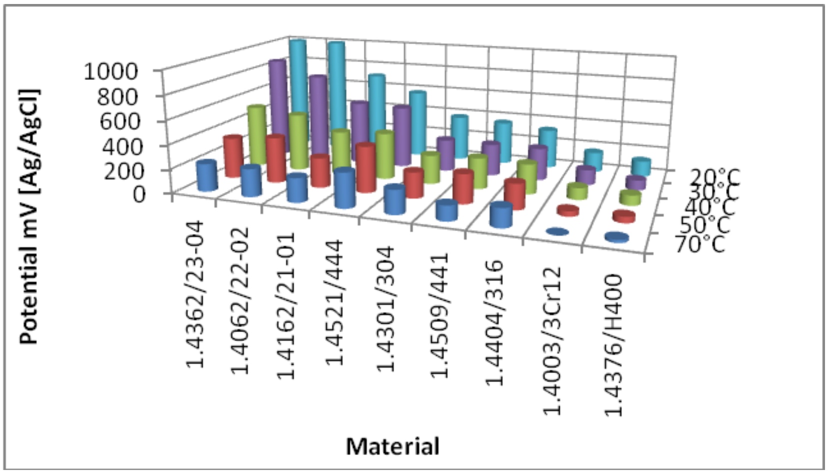

Figure 7: Influence of the testing temperature on the pitting potentials of all investigated steels (Average values of all investigated surface conditions), ranking of the materials

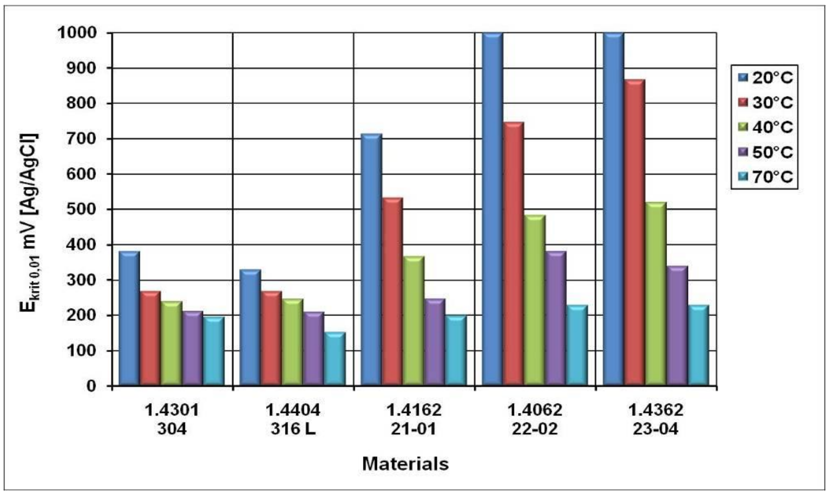

Figure 8: Influence of the testing temperature on the pitting potentials of standard austenitic and lean duplex stainless steels (Average values of 3 measurements)

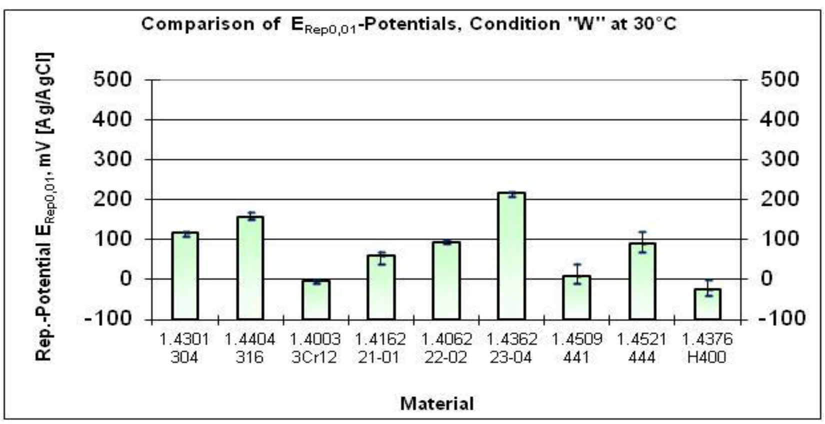

Figure 9: Critical repassivation potentials in the 'as supplied condition' at a testing temperature of 30 °C

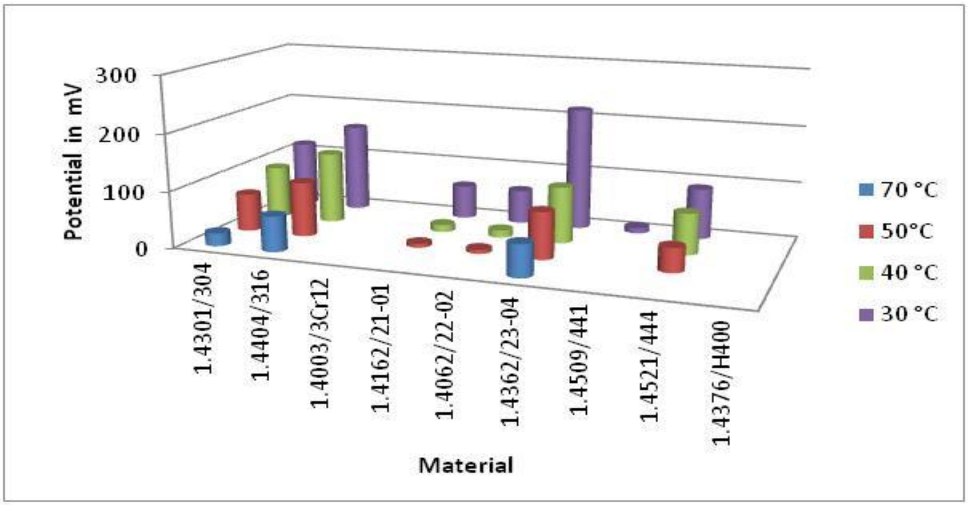

Figure 10: Critical repassivation potentials in the 'as supplied condition' at different testing temperatures (only values above 0)

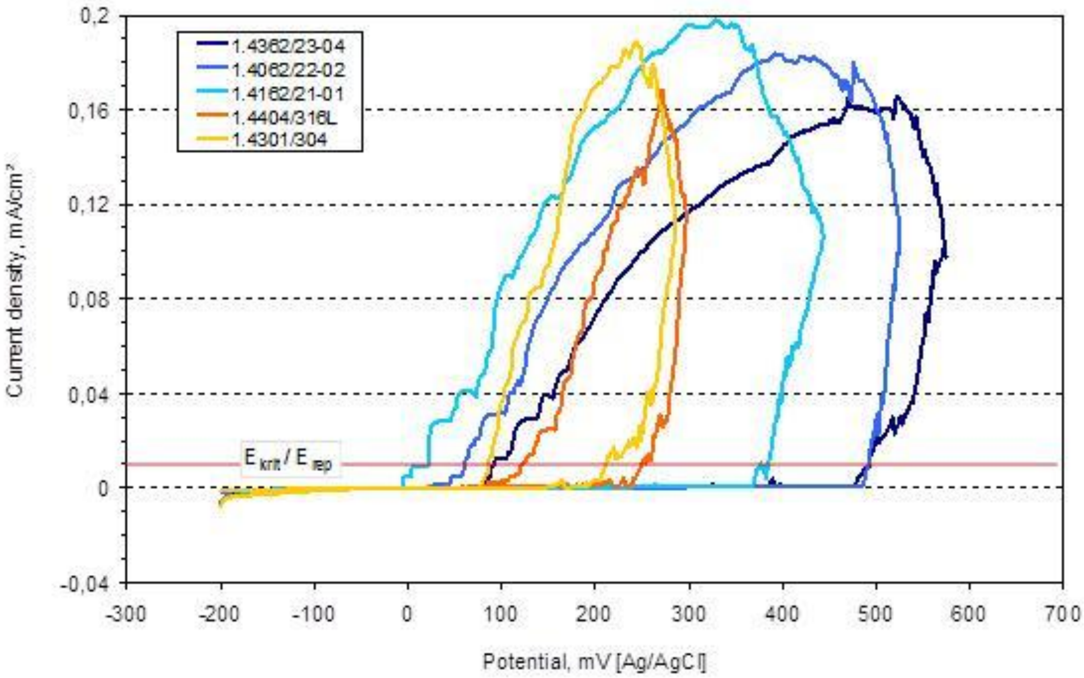

Figure 11: Current density – potential – curve in the "as supplied condition" (W) at a testing temperature of 40 °C

The corrosion resistance in atmosphere was tested at the island of Helgoland (Figure 12) and in an urban atmosphere in the city of Berlin. The same materials were tested. The first results after nine months exposition in this atmosphere show that some of the lean alloyed stainless steels and especially the type 23-04 (X2CrNiN23-4, 1.4362) offers a very good resistance to any changes in the appearance of the surface when they are exposed to a costal atmosphere (Figure 13).

Figure 12: Rack with coupons on Helgoland

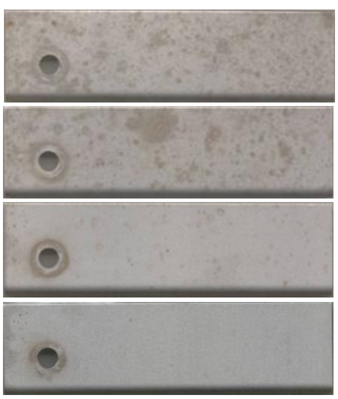

Figure 13: Examples for the surface appearance after 9 months exposition time at the atmosphere on the island of Helgoland, surface condition "as supplied" W

For evaluating the corrosion attack at the surface an image analyzing method according to DIN EN ISO 10289:2001 was used. The results are presented in the Figures 14 and 15. It can be shown that there are some differences in the corrosion resistance depending on the alloy composition and also very sensitive to the surface condition. The best resistance is offered by the Lean Duplex Stainless steels 21-1 (X2CrMnNiN21-5-1, *1.4162*), 23-04 (X2CrNiN23-4, 1.4362) and the molybdenum alloyed Ferritic Stainless Steel 444 (X2CrMoTi18-2, 1.4521).

The resistance of these steels in the atmosphere of an urban area, tested in the city of Berlin is presented in Figure 16. With the exception of the 12% Chromium Steel 3Cr12 (X2Cr11, 1.4003) all materials showed no corrosion effects on the surface and no influence of the different surface conditions could be observed (Figure 16). In could be clearly shown, that in this urban atmosphere some of the lower alloyed stainless steels offer the same and sometimes a little better resistance than the austenitic standard grades 304 and 316.

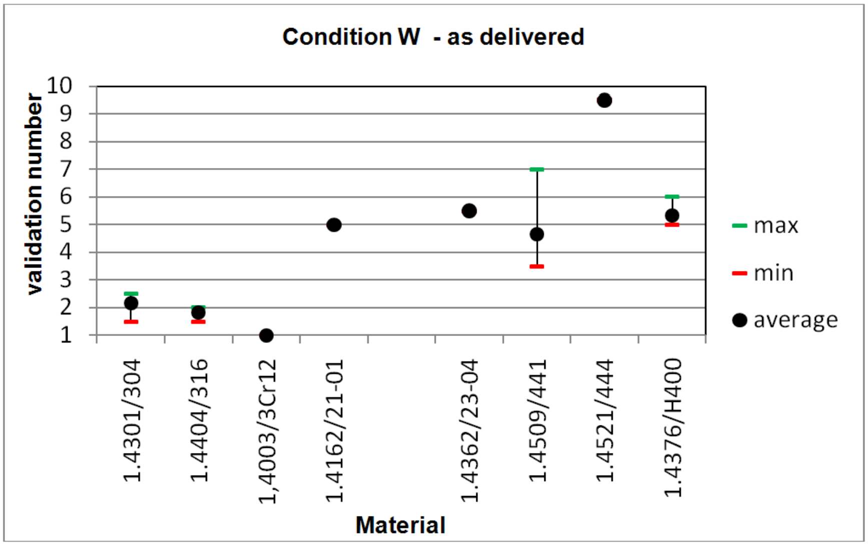

Figure 14a: Evaluation of the surface appearance at the investigated materials after a 9 months exposition period in the open atmosphere at the island of Helgoland (0 is worse, 10 is very good) in the `as delivered´ condition

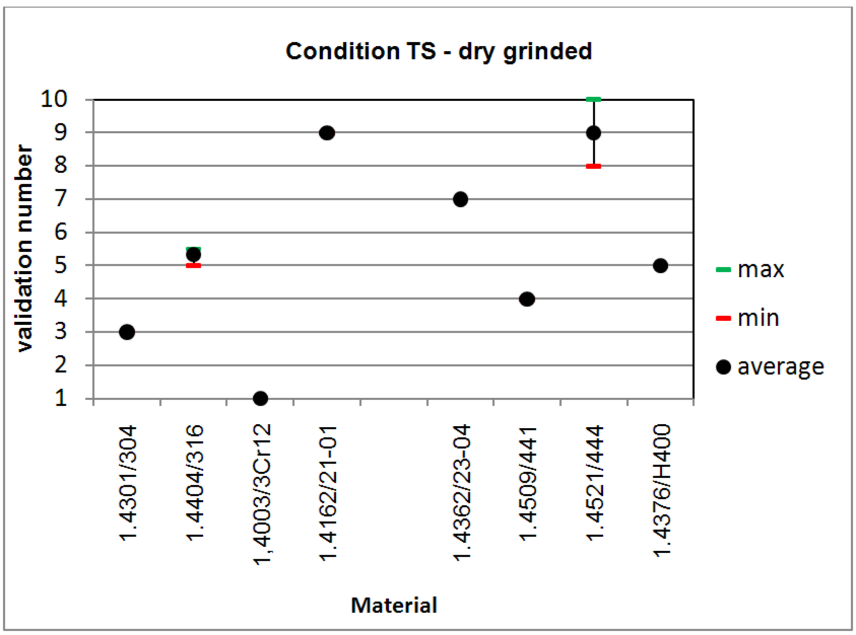

Figure 14b: Evaluation of the surface appearance at the investigated materials after a 9 months exposition period in the open atmosphere at the island of Helgoland (0 is worse, 10 is very good) in the `dry grinded´ condition

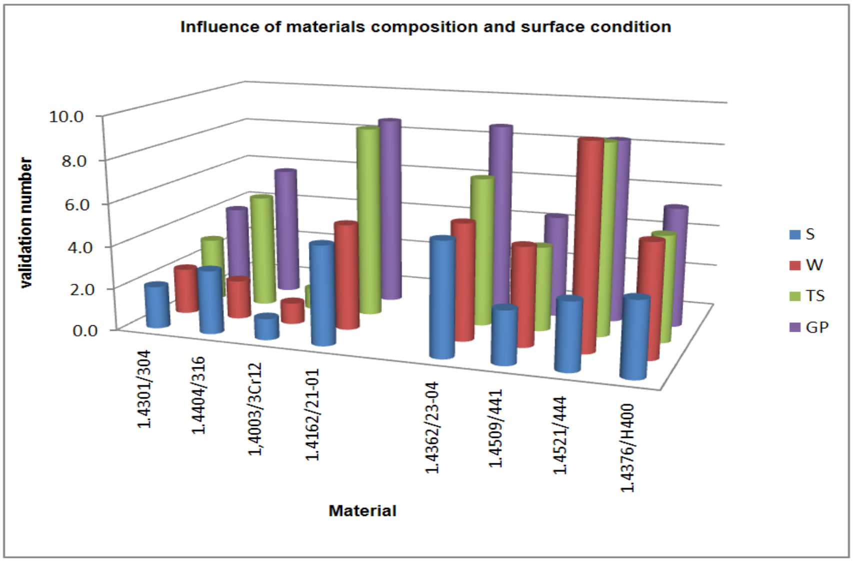

Figure 15: Influence of materials composition and surface condition of the surface appearance at the investigated materials after a 9 months exposition period in the atmosphere at the island of Helgoland (0 is worse, 10 is very good)

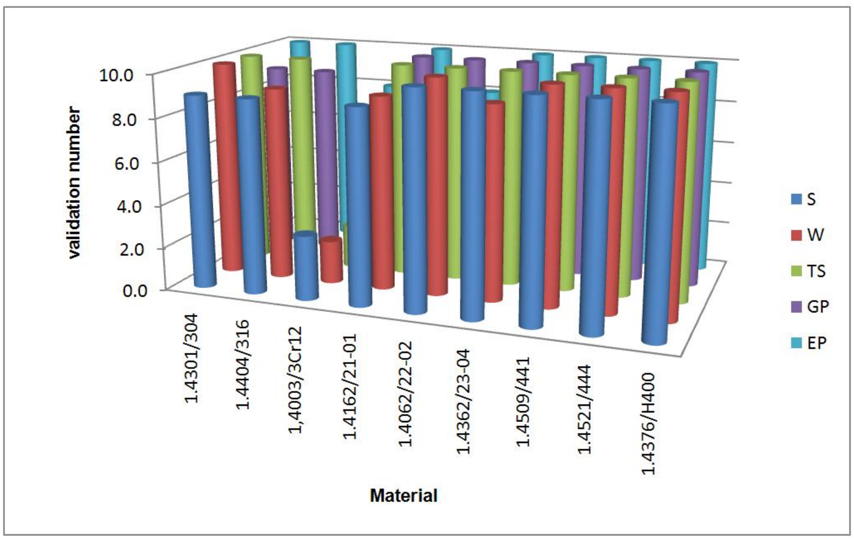

Figure 16: Influence of materials composition and surface condition of the surface appearance at the investigated materials after a 9 months exposition period in the atmosphere at the city of Berlin (0 is worse, 10 is very good)

For comparing the stress corrosion cracking behavior of the different steels a test with salt drops at bended specimen was done, the procedure for this test is described in DIN EN ISO 7539-3. The test results show the time to cracking for all materials. As expected the standard austenitic stainless steels are very susceptible to stress corrosion cracking and first cracks were observed after an exposure time of 600 h with the steel 304 and 1200 h with the steel 316. The manganese containing low nickel austenitic stainless steel H400 seems to be more susceptible to stress corrosion cracking, with this material cracking started after short exposure time below 300 h (Figure 17).

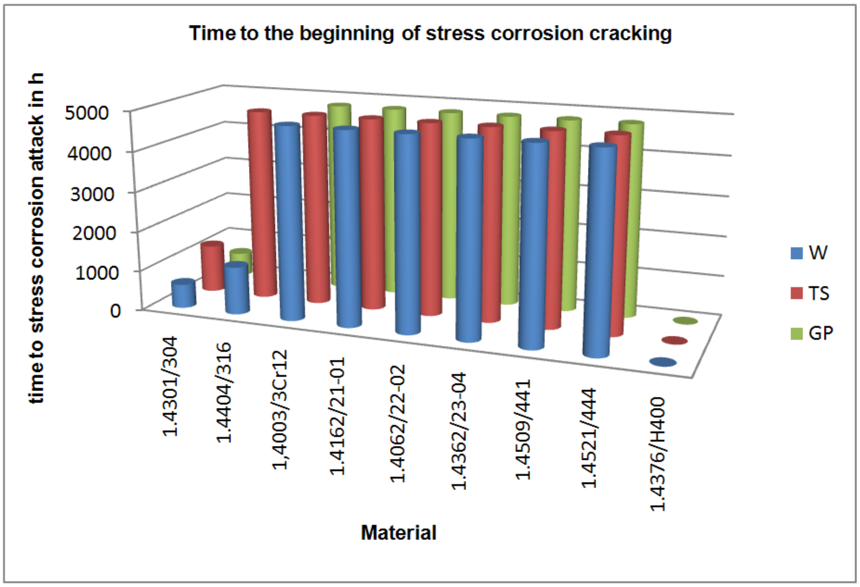

Figure 17: Time to the beginning of stress corrosion cracking under $MgCl_2$-load at a temperature of 30°C

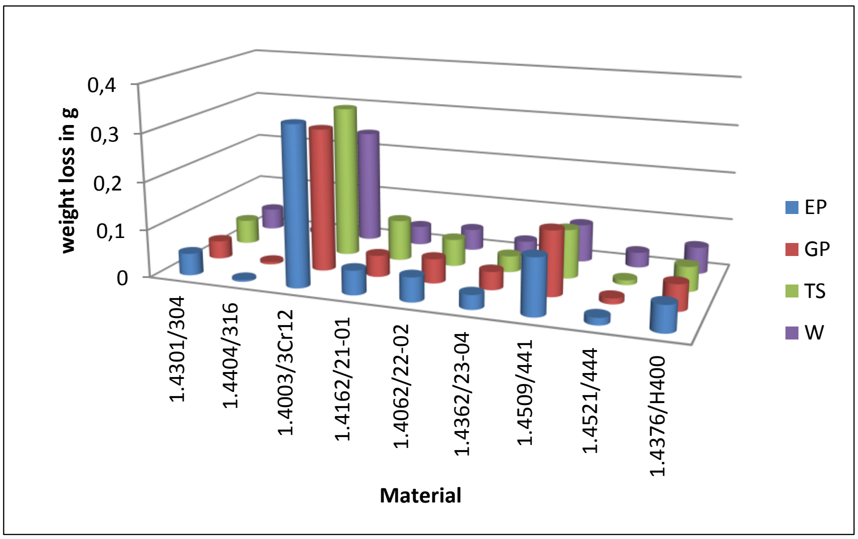

Figure 18: Weight loss of different stainless steels in an acetic, chloride containing atmosphere

The behavior of the different materials in a polluted atmosphere was simulated in a so called Kesternich test, this is a common name for sulfur dioxide testing. A modified test method close to DIN 50018 was used. Before starting every test cycle the specimen were sprayed with a salt solution (3% NaCl) and afterwards dried, this method was done for settling small crystals of NaCl at the surface. Afterwards the specimen were exposed in a humid atmosphere containing a high concentration of active sulfur (2Ltr. SO_2) at 40°C for 8 h and afterwards for another 16 hours held in the test chamber with an open door. The test was done for totally 5 periods. It can be observed, that especially the molybdenum containing stainless steels 316 (X2CrNiMo17-12-2, 1.4404) and 444 (X2CrMoTi18-2, 1.4521) show the highest resistance in this acetic and chloride containing atmosphere (Figure 18). Again the results of the Lean Duplex Stainless Steels are remarkable, their resistance is as good or better than the one of the standard austenitic stainless steel 304 (X5CrNi18-10, 1.4301).

4 Discussion

The electrochemical investigations show an unexpected result concerning the pitting resistance of the molybdenum alloyed austenitic standard steel 316L (X2CrNiMo17-12-2, 1.4404) and the manganese alloyed austenitic stainless steel H400 (X8CrMnNi19-6-3, 1.4376) (Figure 7). Especially the effect that the 304 gives better results in a chloride containing environment than 316L seems to be very surprising. May be the reason for this effect is given by unusual high sulfur content in this material. In a former investigation [4] it could be shown that higher sulfur content leads to a drop in the critical pitting potential (Figure 19). The pit initiation is not only dependent on the amount of the sulphur content in the steel it is also influenced by the shape, size, composition and distribution of the inclusions. In contrast to previous investigations of the steel type 316 the sulfide inclusion in the present material showed higher manganese instead of chromium content, maybe this is the reason for a dilution of the sulfides respectively a breakdown of the passive film.

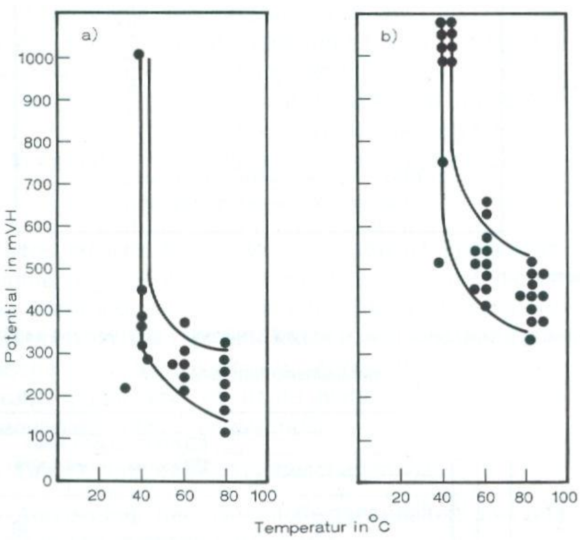

Figure 19: Influence of sulfur content on the critical pitting potential of an austenitic stainless steel X1CrNiMoCu25-20-5, a) sulfur content: 0.010%, b) sulfur content less than 0,003 %, acc. to 4

5 Conclusions

Some of the new lean alloyed stainless steels offer a good option for substituting the high nickel-containing austenitic stainless steels in a lot of applications. Especially the lean duplex stainless steels offer some benefits for the usage in construction elements in civil engineering. Beside their high tensile properties they have a very high corrosion resistance which is remarkable at room temperature. This effect is based on the high chromium content which enables a very good passive layer. In comparison to the common austenitic stainless steels and even to the molybdenum containing grades 316L and 316Ti all investigated lean duplex stainless steels offer a similar or even better pitting potential at room temperature. Under the present test conditions the repassivation behavior of the lean duplex stainless steel seems to be more sensible to the alloy content of these materials and to be very susceptible to the nickel content of these materials. Nevertheless in the applied electrochemical test procedure the lean duplex steel type 23-04 (X2CrNiN23-4, 1.4362) has a better repassivation behavior than the austenitic 316 steel type up to 50°C, with higher temperatures this ranking changes. All in all these steel types can be used for a lot of applications and they are very interesting alternative materials especially when the costs for alloying elements are rising as it could be observed 2 years ago. The application of these materials should also be forced by the need for saving raw elements. Also the ferritic molybdenum containing stainless steel 444 (X2CrMoTi18-2, 1.4521) offers excellent corrosion properties in comparison to the austenitic stainless steels, by using these materials the mechanical behavior of the ferritic steels must be taken into account, specially at lower temperatures.

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