Lean duplex UNS S32202 (EN 1.4062): a new stainless steel for drinking water applications

P. Boillot, D. Rückle, V. Baudu and J. Peultier

Arcelor Mittal R&D, Specialty Plate

Industeel, BP19, 71201 Le Creusot - France

I. Abstract

Thanks to their low Ni content, duplex stainless steels are less sensitive to fluctuations in raw material pricing when compared to austenitics. In numerous applications, a very cost effective duplex solution can now be proposed as an alternative to an austenitic material with at least a similar corrosion resistance and better mechanical properties. For instance, 1.4362 (UNS S32304) replaced 1.4404 (316L) material in evaporators for sea water desalination units or in pumps and valves for process and water industries.

This paper presents the new Mo free duplex stainless steel UR 2202 (EN 1.4062 - X2 CrNiN 22-2, UNS S32202) developed to have a cost effective alternative to 1.4306 or 1.4307 (304L), concrete, coated or galvanized carbon steel in construction applications such as potable water systems and the pulp and paper industry. The reduction of Ni is balanced by a nitrogen addition in order to obtain a microstructure containing approximately 50% of ferrite and 50% of austenite.

After a brief discussion of mechanical properties, results of corrosion tests performed on hot rolled plate in conditions representative of drinking and waste water are presented. Then a comparison of investment costs for tanks constructed of 304L or UNS S32202 is provided taking into account French storage tank design rules. The results demonstrate that the new lean duplex stainless steel may be a good candidate to manufacture welded storage tanks and pipes for drinking water.

Keywords: austenitic stainless steel, duplex stainless steel, localized corrosion, potable water, waste water, life cycle cost

II. Introduction

Numerous materials like cement, galvanized steel, ductile or cast iron have been used in potable water distribution systems depending on their availability and ease of installation. Even if these materials have been in operation for decades, they are known to suffer from external corrosion (by soils or environment) and internal corrosion (by water) [1].

Selecting stainless steels may offer several advantages. Due to their extremely low corrosion rates in a wide range of waters, stainless steels appear more hygienic [2-3]. In fact, the leaching rates of stainless steels are in agreement with different drinking water standards as previously shown for 316L in a solution simulating drinking water [4]. Moreover duplex stainless steel grades, as UNS S32205 / EN 1.4462 or UNS S32304 / EN 1.4362, have been incorporated into the NSF/ANSI Standard 61 after successful leaching tests [5]. NSF/ANSI Standard 61 also includes grades 304, 304L, 316 and 316L.

Stainless steels have been used for more than fifteen years for manufacturing, storage and transportation of beer, juice soda and wine. Due to their excellent corrosion resistance, monitoring of water chemistry to mitigate corrosion attack is not necessary.

Within the stainless steel family, very cost effective duplex solutions can now be proposed as an alternative to the austenitic materials with at least similar corrosion resistance and better mechanical properties. This paper presents the new Mo free duplex stainless steel UR 2202 (EN 1.4062 - X2 CrNiN 22-2, UNS S32202) developed to have a cost effective alternative to 1.4306 or 1.4307 (304L), concrete, coated or galvanized carbon steel in construction applications, potable water systems and the pulp and paper industry.

Table 1 compares the typical chemical analysis, Pitting Resisting Equivalent Number (PREN) and main mechanical properties of the stainless steels considered in this study: the new low alloyed duplex grade UNS S32202 / 1.4062 and the austenitic grade 304L / 1.4306.

Low alloyed duplex grade UNS S32202 contains higher Cr (22.5%), higher N (0.20%) and lower Mo amount combined with increased mechanical properties. This grade was developed to match the corrosion resistance of 304 or 304L in most environments and provide twice their mechanical strength [6]. The Ni content was optimized to obtain crevice corrosion resistance and toughness properties without increasing the material's cost. The N content was adjusted to obtain a microstructure of approximately equal amounts of ferrite and austenite after an annealing treatment performed in the range 980 - 1100°C range. This grade is Mo free to provide a more stable microstructure and an additional cost stability. The PREN value is typically used to rank stainless steel grades in relation to their pitting corrosion resistance. This commonly used PREN formula is valid in a ferric chloride solution which is an oxidizing and acidic media. The ranking in potable water, which is a near neutral slightly oxidizing media, could be different.

Table 1: typical chemical analysis (weight%) and mechanical properties of 304L and UNS S32202 (PREN: Pitting Resisting Equivalent Number PREN = Cr%+3.3XMo%+16N%, $YS_{0.2\%}$: Yield Strength at 0.2%, UTS: Ultimate Tensile Stress)

Trademarks	UNS/AISI	EN	C	Cr	Ni	Mo	N	PREN	$YS_{0.2\%}$ (MPa)	UTS (MPa)
CLC18.10L	**304L**	**1.4306**	< 0.030	18.5	10.5	-	-	>18	200	500
UR2202	**S32202**	**1.4062**	< 0.030	22.5	2	-	0.20	>26	450	650

Mechanical and corrosion properties will be presented in more detail along with a cost comparison between UNS S32202 and 304L in a water storage tank application.

III. Mechanical properties

The mechanical properties of UNS S32202 are increased due to its duplex microstructure (~ 50% austenite and 50% ferrite) and its high nitrogen content. Figure 1 shows the Elongation (E), Ultimate Tensile Strength (UTS) and Yield Strength at 0.2% ($YS_{0.2\%}$) of UNS S32202 measured on hot rolled plates as a function of the thickness of the material between 7 and 20 mm [7]. From these results, the minimum value obtained is 450MPa for $YS_{0.2\%}$ which corresponds to about twice the mechanical properties of 304L (200 MPa).

Figure 2 shows the toughness properties of UNS S32202 in the transversal direction relative to the temperature [7]. The new lean duplex achieves about 70J at -40°C. The lower the Ni content, the lower the toughness properties. As a consequence, UNS S32202 has lower toughness properties than 304L (200J at -40°C), but it remains acceptable values.

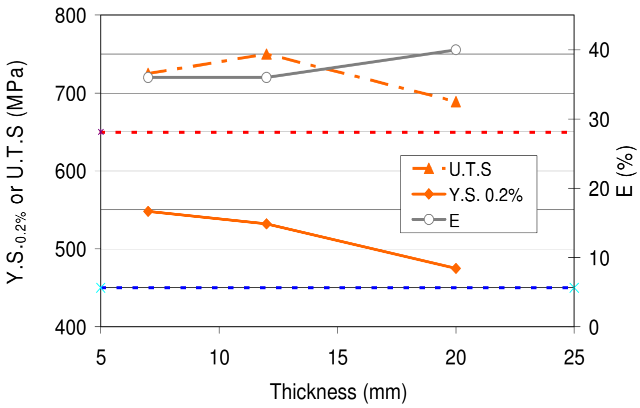


Figure 1: tensile properties (UTS, YS $_{0.2\%}$, E) vs. thickness (mm) of UNS S32202 in the transverse direction

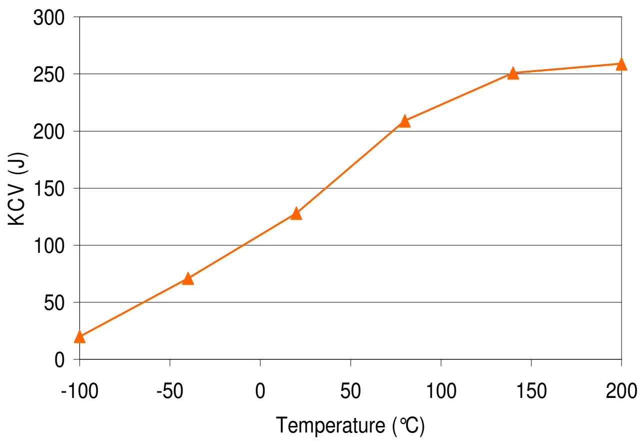


Figure 2: Charpy V curve of UNS S32202 in the transverse direction

IV. Corrosion properties

Two of the main corrosion risks which can occur in potable water applications like pipelines or storage tanks have been studied: pitting and crevice corrosion. These studies were carried out on samples removed from a 7mm thick hot rolled plate. All coupons were mechanically polished with SiC paper to 600 grit finish followed by a cleaning with ethanol. The tests began at least 24h after polishing to allow the passive layer to be able to form naturally in contact with air. All chloride containing solutions were prepared using deionised water and an analytical grade of NaCl. pH adjustments were carried out with HCl or NaOH additions.

1. Pitting corrosion resistance study

IV.1.1. Critical Pitting Temperature (CPT) - Several standard corrosion tests are used for evaluating the pitting corrosion resistance of stainless steels. Among these, the most common are the determination of the Critical Pitting Temperature (CPT):
- by immersing the sample for 24h in a ferric chloride solution (6% $FeCl_3$ + 1% HCl) and visually inspecting for pits deeper than 25µm onto its surface (ASTM G48-03 method E) [8-9].
- By using a potentiostatic technique and a temperature scan. The specimen is exposed to a 1M NaCl (35 500ppm chloride) solution, initially at about 0°C. After the initial temperature stabilization period, the solution is heated at a rate of 1°C/min. About 60s before the start of the temperature scan, the specimen is anodically polarized at 700mV/SCE. The current is monitored during the temperature scan, and the CPT is defined as the temperature at which the current density exceeds 100µA/cm^2 for 60s. Pitting on the specimen is confirmed by a visual examination performed at the end of the test (ASTM G150-99) [10-9].

Figure 3 shows CPT results according to ASTM G150 and G48E standards. Both methods show nearly equivalent CPT values with a higher value for the lean duplex grade in comparison with the austenitic grade: 13.5 and 15°C for UNS S32202 and less than 5°C for 304L. In fact, these two tests can not accurately determine the low CPT of 304L.

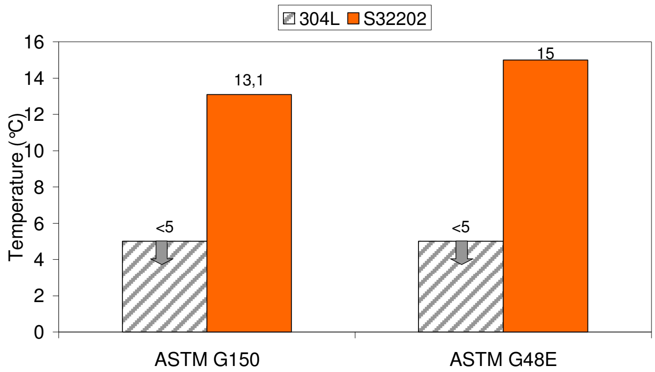


Figure 3: CPT values according to ASTM G150 and ASTM G48E on UNS S32202 and 304L. Vertical arrows indicate that CPT is lower that 5°C.

The ferric chloride solution is acidic (pH 1 - 2) and strongly oxidizing, so it does not represent the aggressiveness of potable water where initiation mechanisms for localized corrosion are very different. In addition, the ASTM G150 test is performed in a chloride containing neutral solution, which is representative of seawater (synthetic seawater). The applied potential of 700mV/SCE is chosen to provide a solution as aggressive as the ferric chloride solution [11]. As a consequence, the results obtained in ASTM G48E and G150 cannot be used for estimating the pitting corrosion resistance in potable water. To assess the pitting corrosion resistance of UNS S32202 and 304L in potable water applications, the study of pitting and open-circuit potentials, in a media representative of potable water application, is more relevant.

IV. 1. 2 Pitting potential - Pitting corrosion resistance was evaluated by measuring the pitting potential (Epit). The electrochemical test consisted of plotting a potentiodynamic curve in order to measure the pitting potential of the sample in several chloride containing media.

A 3-electrode electrochemical cell was used (Saturated Calomel Electrode (SCE), platinum and sample). The surface of the material specimen is pressed against an opening on the electrochemical cell, so that 1cm² of the sample is in contact with the solution. After 1h at the rest potential, polarization curves were plotted at a scan rate of 900mV/h from the rest potential - 50mV/SCE until the current density reaches 500µA/cm². The pitting potential was measured at a current density of 100µA/cm².

While immersion tests (part *IV. 1. 3*) simulates the real operating conditions; the polarization curve plot is not representative of the in-service behavior. Actually, the increase of the sample potential allows the media's aggressiveness to increase until it favours a localized breakdown of the passive layer. The pitting potential value, for which pits are in fact observed, represents the ability of stainless steel to resist pitting corrosion. The higher the pitting potential is, the lower the risk that pitting corrosion will occur.

Figure 4 shows the results obtained in a 250 ppm chloride containing solution at pH 5.5 and 25°C. This concentration was chosen because 250 ppm of chloride is the maximum concentration allowed in drinking water standards [12-13-14]. No pitting potential has been measured for the UNS S32202 coupon whereas pits do initiate around 800mV/SCE on 304L coupon.

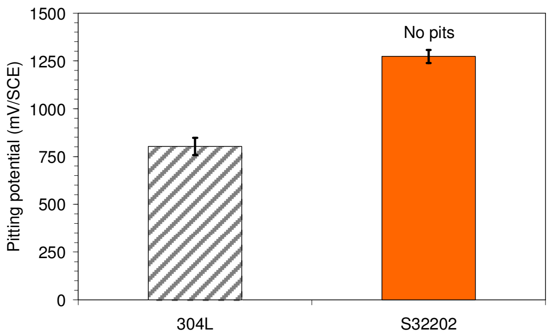


Figure 4: pitting potential in 250ppm chloride containing solution at pH 5.5 and 25°C.

When pH is reduced to 4.5 and the chloride concentration increases up to 1000ppm, the test conditions are more representative of waste water applications and are, of course, more aggressive. Under these conditions, the pitting potential of 304L decreases to 670mV/SCE whereas UNS S32202 is still not prone to pitting (see Figure 5). At 50°C and then 80°C, the pitting potential measured for the duplex grade is slightly higher than that of the 304L samples.

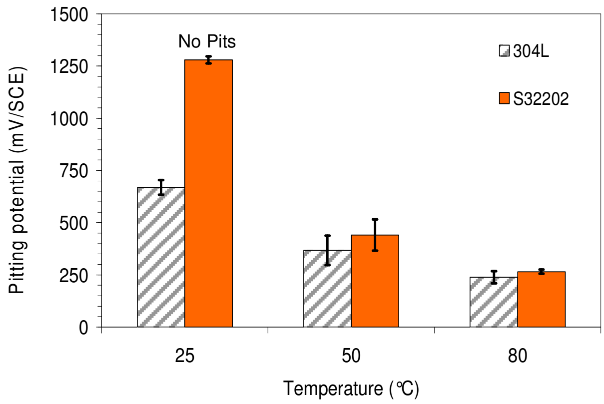


Figure 5: pitting potential in 1 000 ppm chloride containing solution at pH 4.5

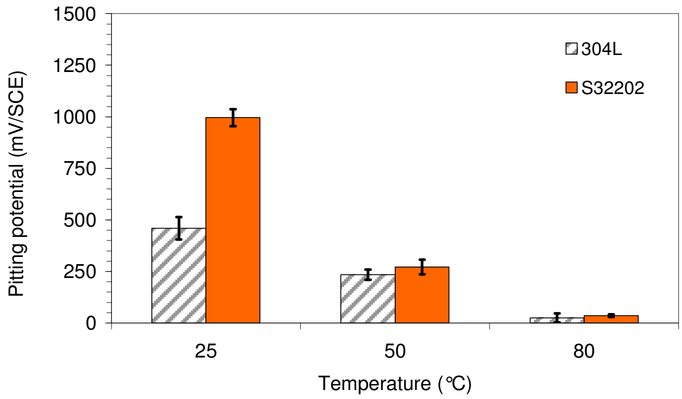


Figure 6: pitting potential in 5 000 ppm chloride containing solution at pH 4.5

In our test program, 5000ppm is the lowest chloride concentration for which pitting corrosion initiates on UNS S32202 at 25°C and pH 4.5. The pitting potential of the lean duplex grade still decreases when compared to lower concentrations but it remains higher than that of the austenitic grade in all concentrations (see Figure 6).

In summary, at ambient temperature, the pitting corrosion resistance of UNS S32202 is much better than that of 304L and when the temperature increases up to 50°C and 80°C, it is at least similar.

IV. 1. 3. Immersion test at the open circuit potential (OCP) - UNS S32202 and 304L specimens were immersed in a stirred 1000ppm chloride containing solution at pH 4.5 and 25°C. The duration of the test was 720 hours and potential was observed as a function of time. The stability and the value of the free potential allow the behaviour of the passive film to be observed. After the completion of immersion test, the 20 - 25 × 50 × thickness (mm) coupons were weighted and examined using an optical microscope.

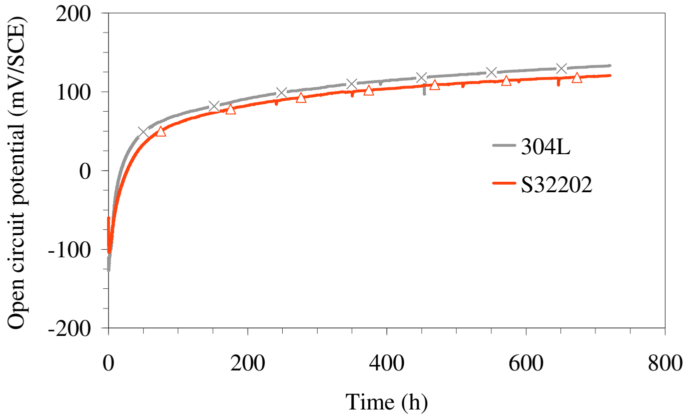
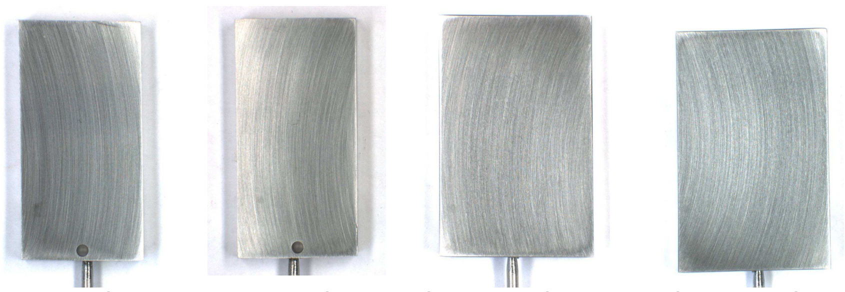


Figure 7: Immersion test in 1 000 ppm chloride ion at 25°C and pH 4.5 : corrosion potential vs. time

The corrosion potentials of the two stainless steels increase quickly during the first 4 days then reach a relatively stable value around 100 – 120 mV/SCE (see Figure 7). A limited number of potential instabilities were observed during the one month immersion showing that the passive layer built in this environment is relatively stable. After one month, no pits were observed and the calculated uniform corrosion rate is lower than 0.5 µm/y (see Figure 8).



a) 304L – Side 1 b) 304L – Side 2 S32202 – Side 1 c) S32202 – Side 2

Figure 8: Pictures of surfaces after 1 month immersion test in 1 000 ppm chloride ion solution at pH 4.5 and 25°C

2. Crevice corrosion resistance study

The crevice corrosion mechanism which occurs where a chloride containing solution stagnates in a shielded area can be divided into two steps: initiation and propagation. In this paper, the crevice corrosion resistance is discussed based on the value of two electrochemical parameters. The first, the depassivation pH (pH_d), is characteristic of the initiation step. The second, the maximum current density in the active domain (i_{max}), is typical of the propagation step [9].

The electrochemical testing consisted of plotting several potentiodynamic curves with pH values decreasing from 3 to 0.5 in order to measure pH_d and i_{max}. pH_d corresponds to the onset of an active peak in the potentiodynamic curve series. The lower the value of the pH_d, the greater the resistance to crevice initiation will be. The ability of a material to resist crevice propagation can be estimated from i_{max} for pH values slightly lower than the pH_d.

For one hour before the beginning of the test and during this test, the solution and the cell are deaerated with nitrogen. After 15 minutes at free potential, a fixed potential of –750mV/SCE was applied for 2 minutes in order to reduce any surface species. Then, the potentiodynamic curve was plotted in the anodic direction at a scanning rate of 600mV/h from –750mV/SCE until the current density reaches 500µA/cm². The test was performed in a 2M NaCl (~70 000ppm chloride) solution, which corresponds to the generally accepted chloride concentration inside a crevice, at 20°C and 50°C and at different pH values. Then, the i_{max} was plotted as a function of pH value and the pH_d was measured at 10µA/cm².

For the both grades tested and both temperatures, pH_d values are very similar, approximately 1.7 (see Figure 9).

On the other hand, for pH values lower than the depassivation pH, the current densities measured at 20°C are lower for 304L (136µA/cm²) than for the duplex grade (483µA/cm²). So 304L is slightly more resistant to crevice propagation than duplex grade at this temperature. This may be due to the higher nickel content of 304L. But at 50°C, UNS S32202 (800µA/cm²) is more resistant than 304L (1158µA/cm²). This means that at this temperature, the higher Cr content of the duplex grade provides at least a similar resistance to propagation compared to the lower Cr - higher Ni content of the austenitic grade. In addition, the maximum current density increases with temperature and this indicates that the uniform corrosion rate increases quickly with temperature (see Figure 10).

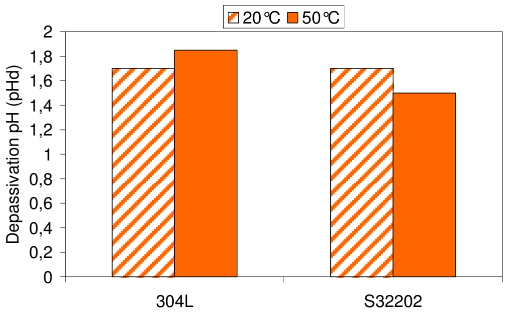


Figure 9: study of crevice initiation with depassivation pH measured at 20 and 50°C in NaCl 2M for I = 10µA/cm²

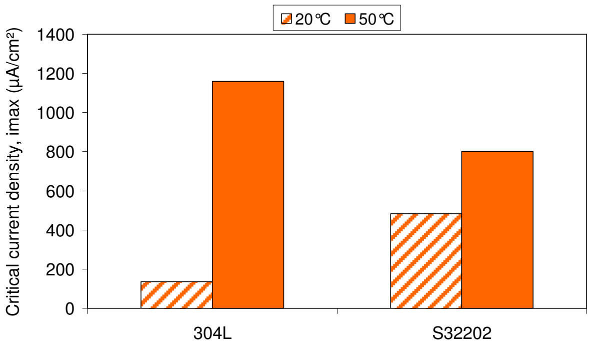


Figure 10: study of crevice propagation with critical current density measured in NaCl 2M at pH 1, 20°C and 50°C

Summarizing, the resistance to crevice corrosion initiation will be equal for both grades while the propagation resistance is potentially a little bit higher for 304L at 20°C and lower at 50°C when compared with UNS S32202. For a high crevice corrosion risk it is recommended that a Mo containing duplex stainless steels like UR2205 / EN.1.4462 be used [9].

3. Water storage tank application

Based on the previous results on the two main corrosion risks in potable water applications, pitting and crevice corrosion, the new lean duplex UNS S32202 appears to be a suitable candidate for 304L in mildly aggressive environments such as potable or drinking water.

Another point to be considered in material selection is the mechanical characteristics. Using high strength grades allows a reduction of the wall thickness for pipes, especially in the case of higher design pressures (10 bars and more), or for storage tanks.

Tank investment costs can be calculated using an Excel® based software named CALRES [15]. Calculations are based on the French CODRES standard for construction of cylindrical and vertical welded storage tanks. CODRES contains the rules for designing and dimensioning a tank's constitutive elements like the shell, roof and bottom [16]…Thus this study is based on a vertical, cylindrical tank with flat bottom and self-supporting roof.

The total investment costs are composed of the following: material costs (plate costs according to their weight with minimum thickness calculated according to the CODRES code), forming costs, welding costs and pickling costs.

As the raw material price has had significant fluctuations over the last few years, three different situations are studied for a 304L and a UNS S32202 storage tank (see Table 2): low, intermediate and high raw material prices.

Price	Low (a)	Intermediate (b)	High (c)
Ni ($/t)	10 000	20 000	40 000
Cr ($/t)	2 000	6 000	8 000
Mo ($/t)	20 000	40 000	80 000

Table 2: Three levels of raw material price used for CALRES calculations with €/$=1.3.

Investment costs for a tank of 1600 m^3 with a diameter of 10 m and a height of about 20m are estimated according to the three previous situations of raw material prices (see Figure 11).

The thickness reduction in the first ring is about 31 % using UNS S32202 instead of 304L based on the CODRES rules. This explains in part their difference in material cost. With the lowest raw material price (a) nearly equivalent to recent situations, the investment cost savings is estimated less than 1% using UNS S32202 instead of 304L. The main cost advantage for using UNS S32202 instead of 304L is thus the reduction in total weight (-8% here) that can lead to a reduction of transportation and installation costs. The investment cost saving goes up to 7 and 18%, respectively for intermediate and high raw material prices which are related to values of the last several years. Pickling costs are a little bit higher for UNS S32202 than 304L because the lean duplex steel has a better uniform corrosion resistance [6].

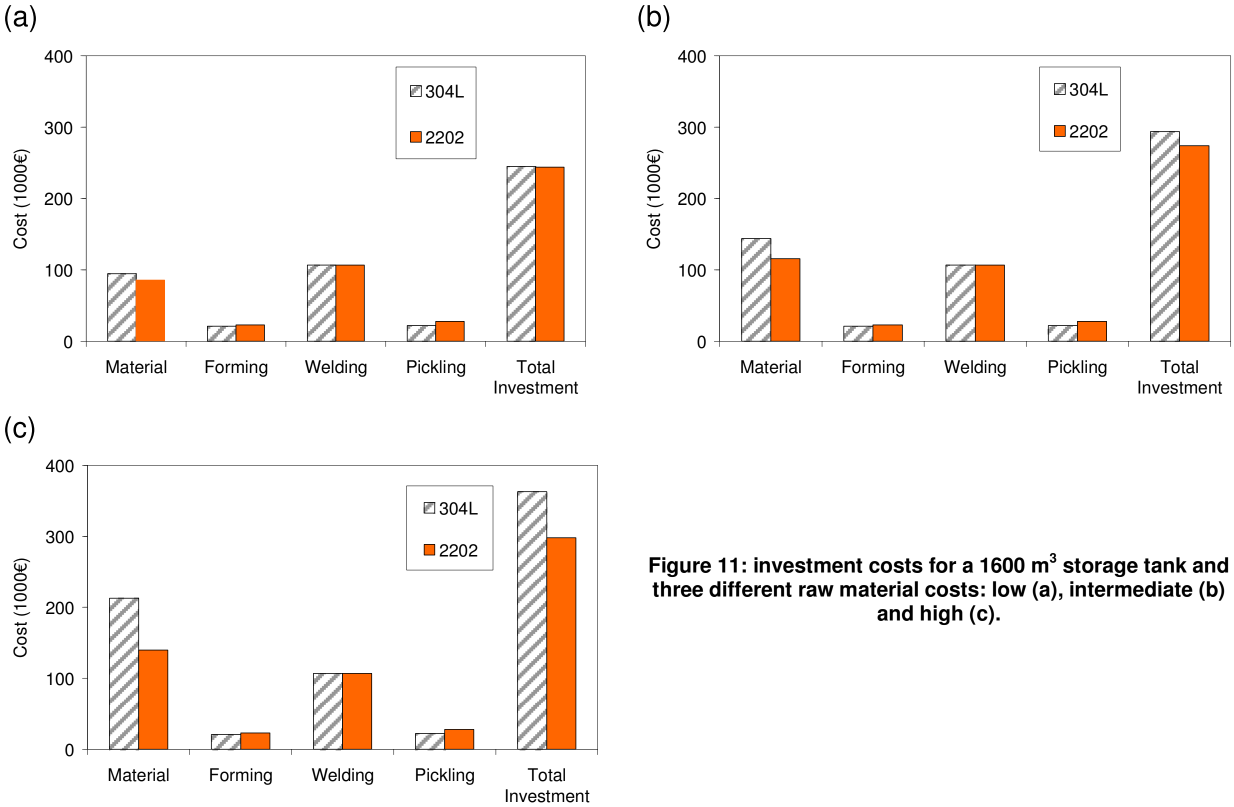


Figure 11: investment costs for a 1600 m^3 storage tank and three different raw material costs: low (a), intermediate (b) and high (c).

UNS S32202 grade can help reduce investment costs for storage tanks or pipes in potable water distribution systems when compared to 304L. Moreover, as stainless steels are not coated (internal and/or external), modifications of water systems are more easily and quickly achieved.

V. Conclusion

By combining lower price, equivalent or better corrosion properties and higher mechanical characteristics, the new lean duplex UNS S32202 is a very promising candidate for potable water storage tank or pipeline applications.

Two of the main risks for stainless steel materials in contact with potable water are pitting and crevice corrosion since it is a near neutral chloride ion containing environment. In media representative of potable or waste water applications, the high Cr content of UNS S32202 contributes to its good pitting corrosion resistance properties. UNS S32202 is significantly better than 304L at room temperature and as good at higher temperatures. The crevice corrosion resistance of UNS S32202 and 304L are similar (initiation step) or slightly different (propagation step) depending on temperature. It is always recommended to avoid crevice corrosion by selecting an adequate geometry in potable water applications or to select a more alloyed duplex grade like UR2205 / EN.1.4462 for the high risk zones [9].

Thanks to the duplex microstructure combined with a 0.2% N addition, the UNS S32202 has mechanical properties that are greater than the austenitic grade 304L (twice the yield strength).

Results of investment cost simulation for a water storage tank show an economical interest to use UNS S32202 instead of 304L.

Duplex stainless steel grades and in particular UNS S32202 with its low Ni and no Mo chemistry are less sensitive to raw material price fluctuations which allows better forward planning of material costs in a long term project.

VI. References

[1] P. Cutler, *Stainless steels and drinking water around the world*, Euro Inox, Brussels, November 19, 2003, www.euro-inox.org/ .

[2] J. Peultier, J. - P. Audouard, I. Chessa, V. Baudu, *Using duplex stainless steels to improve the reliability of water pipes*, CEOCOR 2001, Biarritz, France.

[3] S. Jacques, J. Peultier, V. Baudu, J. - P. Audouard, *Influence of acidity and NaOCl concentration on the corrosion resistance of stainless steels in chlorinated water*, CEOCOR 2006, Mondorf-les-Bains, Luxembourg.

[4] *Assessment of the stainless steels compatibility in food and health applications regarding to their passivation ability*, ECSC Contract Eur n°19986, ISBN 92-894-1578-9, 2001.

[5] ANSI / NSF Standard 61, *Drinking water system components - Health effects*, Appendix C. http://www.nsf.org/business/water_distribution/

[6] J. Peultier, E. Chauveau, S. Jacques and M. Mantel, *A new lean duplex stainless steel with high mechanical and corrosion properties: 1.4062*, 6th European Stainless Steels Conference Science and Market 2008, Helsinki, Finland, June 10-13, 2008.

[7] A. Fanica, A. Day and B. Chareyre, Mechanical *properties and structural stability of a new Mo free duplex steel UNS S32202*, Stainless Steel World 2008, Houston, USA, September 9-11 2008.

[8] ASTM G48-03: *Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution*, 2003.

[9] S. Jacques, J. Peultier, J. - C. Gagnepain and P. Soulignac, *Corrosion resistance of duplex stainless steels in thermal desalination plants*, NACE 2008, New Orleans, USA, March 16-20, 2008.

[10] ASTM G150-99: Standard *Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels*, 1999.

[11] H. Andersen, C. - O. A. Olsson, L. Wegrelius, *Critical pitting temperatures in sodium chloride and ferric chloride solutions – Determined using the Avesta Cell*, Materials Science Forum, 1998, 289-292, p. 925.

[12] *Guidelines for Drinking Water Quality*, World Health Organisation, 1993.

[13] *European Commission directive on the quality of water intended for human consumption (98/83/EC)*, 1998.

[14] *United States Environmental Protection Agency (USEPA) requirements based on the National Primary Drinking Water Regulations as amended under the Safe Drinking Water Act of 1996*.

[15] J. - P. Audouard and C. Dernoncourt, *Life cycle cost evaluation of carbon steels, austenitic and duplex stainless steels for storage tanks*, Proc.6th Duplex Stainless Steel conference 2000, Venezia, Italy, October 17-20, 2000, p485.

[16] *CODRES*, code français de construction des réservoirs cylindriques verticaux en acier, published by S.N.C.T, 39-41 rue Louis Leblanc, 92400 COURBEVOIE, France, 2007.