PRODUCTION OF DUPLEX STAINLESS STEELS IN ARCELORMITTAL INOX BRASIL

PRODUÇÃO DE AÇOS INOXIDÁVEIS DUPLEX NA ARCELORMITTAL INOX BRASIL

FARIA, Ricardo Augusto[(1)], FOURMENTIN, Richard [(2)],
JUNIOR, Oswaldo Celestino Pires[(1)] & CASTRO, Geovane Martins[(1)],
[(1)] ARCELORMITTAL INOX BRASIL
[(2)] ARCELORMITTAL STAINLESS EUROPE

Abstract
Duplex stainless steel consumption is in full development. The nowadays biggest geographic area of stainless consumption is Europe while, the most expected growth is in Asia. These grades represent around 2% of the stainless world consumption. It is foreseen a high growth rates in the next years, which will be more than 6% a year got at the last decade. The Brazilian market has become very important for duplex grades due to the recent development on the oil & gas activities, the exigencies of sugar & alcohol and pulp & paper industries.
The purpose of this paper is to present the three duplex SS grades whose production has been developed in ArcelorMittal Inox Brasil since 2008: dual certificated UNS S31803/32205 (usually known as 2205) and lean duplex UNS S32304 and UNS S32202. Lean duplex designation has a lower cost due to the suppression of Molybdenum and reduction of Nickel content.
Grade 2205 is commonly used in chemical and petrochemical plants, pulp and paper industries in parts that need higher corrosion resistance as well as mechanical strength. Grades 2304 and 2202 present lower corrosion resistance than 2205 but its corrosion behavior allied to its high mechanical strength can be considered as a possible alternative to the grades 316 and 304, respectively, as well as painted carbon steel with weight saving and better mechanical and corrosion properties.
From now on, ArcelorMittal Inox Brasil offers a wide range of manufacturing measures both in hot and cold rolled products of this type of stainless steel family, which is supplied by a reduced number of companies around the world.
Key-words: duplex stainless steels, properties, applications

Resumo
O consumo de aços inoxidáveis duplex está em pleno desenvolvimento. A maior área geográfica atual de consumo de aço inoxidável é a Europa, enquanto para o futuro a maioria do crescimento é esperado ocorrer na Ásia. Esta família de aços inoxidáveis representa em torno de 2% do consumo de aço inoxidável mundial e está previsto que o mercado vai atingir altas taxas de crescimento nos próximos anos, tendo ocorrido mais de 6% ao ano na última década. O mercado brasileiro tornou-se muito importante para aços inoxidáveis duplex devido ao desenvolvimento recente de atividades petróleo e gás, as exigências de açúcar e álcool e indústrias de papel e celulose.
O objetivo deste trabalho é apresentar os três tipos de aços inoxidáveis duplex cuja produção está sendo desenvolvida na Arcelor Mittal Inox Brasil desde 2008: duplo certificado UNS S31803/S32205 e os lean duplex UNS S32304 e UNS S32202. A designação lean duplex deve-se a seu baixo custo, devido à eliminação de molibdênio e redução no teor de Níquel.
O duplex 2205 é comumente usado em indústrias químicas e petroquímicas, indústrias de celulose e papel em partes que necessitam maior resistência à corrosão e resistência mecânica. Os aços 2304 e 2202 apresentam menor grau de resistência à corrosão que o aço 2205, mas seu comportamento à corrosão aliado a sua alta resistência mecânica faz com que eles sejam considerados como alternativas possíveis para substituir os aços 316 e 304, respectivamente, bem como aço carbono pintado com redução de espessura e melhores propriedades de resistência mecânica e corrosão.
De agora em diante, a ArcelorMittal Inox Brasil oferece uma ampla gama de medidas de produção tanto em produtos laminados a quente e a frio deste tipo de aço inoxidável, o qual só pode ser fornecido por um número reduzido de empresas no mundo.
Palavras-chave: *aços inoxidáveis duplex, propriedades, aplicações*

1. Introduction

Stainless steels can be divided into different families of grades primarily designed to withstand corrosion. Among these families, austenitic stainless steels, mainly the 304 / 304L and 316 / 316L, represent 60% of stainless steels used in the world due to their good corrosion resistance and high ductility. However, with nickel content comprised between 8 and 11%, austenitic steels present a high susceptibility to raw material cost fluctuation (FOURMENTIN, 2009; CHARLES, 2008)

A most significant contribution to the fight against corrosion offshore has been made by duplex stainless steels. These grades have often been adopted on offshore structures in preference to carbon or other stainless steels. Duplex grades combine basic toughness and improved corrosion resistance of the more common austenitic grades with the higher strength of ferritic ones. Its chemical composition provides a high corrosion resistance level in chloride media and high mechanical strength and ductility. Other benefits include the ability of some duplex grades to be used at quite low sub-zero temperatures and be able to resist stress corrosion cracking (CHARLES, 2008).

Elevated characteristics of duplex grades make it ideal candidates for applications encountered in the process industry where a high corrosion resistance is considered as a key parameter (e.g. gas and chemical industry, pulp and paper industry or desalination plant (ALVAREZ-ARMAS, 2008; LILJAS, 2008). Furthermore, with a yield strength twice as high as that of austenitic steels, Duplex grades allow a significant weight saving, especially in pressure vessels or storage tanks.

Duplex grades production is currently dominated by quarto plates, while industrialization of thinner gauges, thicknesses lower than 6mm, remains technically challenging (CHARLES, 2007). Indeed, production of duplex coils has to overcome two well-known hurdles during their process: a poor hot-workability (IZA-MENDIA, 1997) and a critical pickling operation after annealing (DONIK, 2009). So in 2007, the market in Duplex coils was estimated at 35,000t versus 90,000t quarto plates. The second feature of Duplex market concerns the supremacy of grade 2205 (UNS S32205), around 85% of the total Duplex production due to its well-established technical properties and cost efficiency (SOULIGNAC, 2007). Nevertheless, with 22% Cr, 5% Ni and 3% Mo, 2205 is still exposed to the volatility in raw material cost and is rather meant chosen to replace 4Mo grades. As a result, Lean Duplex grades, such as 2304 and UR2202 have been recently considered as a possible alternative to the grades 316 and 304 (PEULTIER, 2008; PEULTIER, 2008).

2. Chemical composition

Table 1 shows the typical chemical composition of duplex grades produced in ArcelorMittal Inox Brasil. The Pitting Resistance equivalent Number (PREN = Cr+3.3Mo+16N) is an interesting index to easily predict the corrosion resistance of stainless steels.

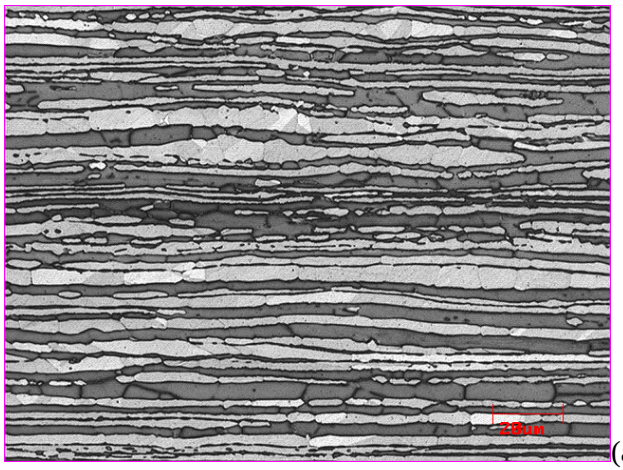
Table 1 – Typical chemical composition of duplex grades (% weight)

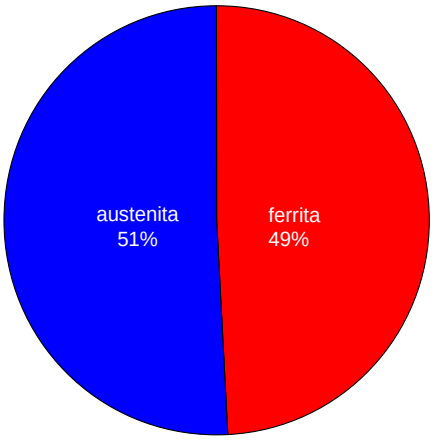
	C	Mn	Si	Cr	Ni	Mo	N	PREN
2202	<0.03	<2.0	<0,50	22.5	2	<0,3	0.20	27
2304					4		0.14	25
2205					5	3.0	0.17	34

While grade 2205 is characterized by 3%Mo addition and hence a PREN of 34, Lean Duplex 2304 and 2202 with no deliberate addition of Mo exhibit a PREN of 25 and 27, respectively. However, their values are higher than austenitic grades due to their higher nitrogen content, 0.14% and 0.20%, respectively. Nitrogen is an important austenite stabilizer and contributes to the improvement of the mechanical strength and corrosion resistance. The reason of the higher nitrogen content in grade 2202 compared to 2304 is due to its lower nickel and the control of ferrite/austenite balance (around 50% / 50%).

3. Microstructure

The chemical composition of duplex steels is designed to give approximately equal amounts of ferrite and austenite in solution-annealed condition. The higher the annealing temperature, the higher the ferrite content. Figure 1 shows a typical microstructure of the grade 2205 with the austenite/ferrite ratio around 50%.

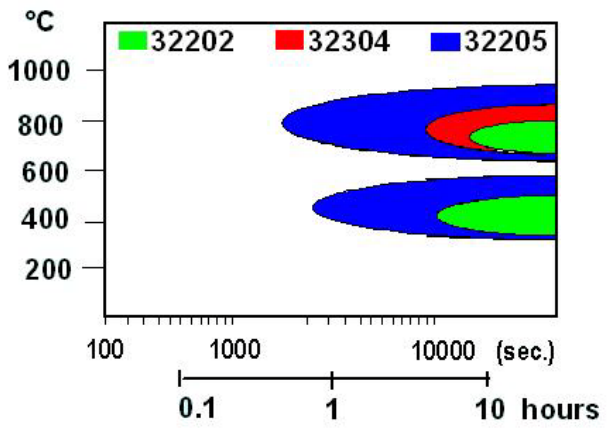

(a)



(b)

Figure 1 – Microstructure of grade 2205: (a) ferrite (dark) and austenite phase; (b) austenite/ferrite ratio

Duplex steels are also well-known to be more prone than austenitic steels to the precipitation of phases causing embrittlement and reduced corrosion resistance. The formation of intermetallic phases such as sigma phase occurs in the temperature range of 600°C-950°C and formation of α' occurs in the range 350°C-525°C (475°C embrittlement).Figure 2(a) illustrates the relation between time and temperature that leads to embrittlement due to intermetallic phase formation and to 475°C embrittlement.



(a)

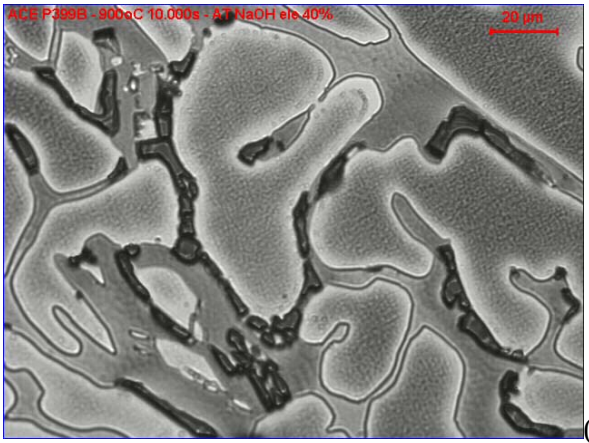

(b)

Figure 2 – Curve TTT of duplex stainless steel (a) and microstructure of grade 2205 with Sigma phase precipitation (in dark).

Grade 2205 is more susceptible to Sigma phase precipitation than other duplex grades because of the Mo presence. This brittleness must be avoided, mainly during welding of plates (thicker materials) though the control of interpass temperature, heat input and filler metal selection.
Exposures at these temperature ranges should therefore be avoided. The risk of embrittlement is low in single pass welding processes and heat-treatment operations. However, certain risks exist, for example in heat treatment of thick sections, especially with slow cooling.

4. Corrosion resistance

Among all the qualities of duplex stainless steels, their corrosion resistance and mechanical strength are the most important. Standard austenitic grades can be susceptible to stress corrosion cracking (SCC) in chloride environment at high temperatures. Duplex grades, due to a continuous ferritic phase, are much less sensitive to this type of corrosion.

Figure 3 shows a comparison of pitting potential of the three stainless families. The corrosion test condition was pH8, 3.5%NaCl, room temperature.

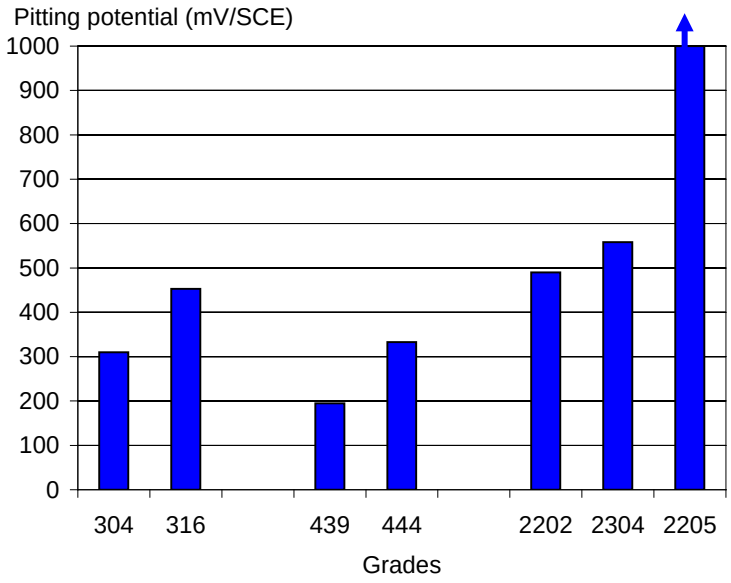


Figure 3 – Corrosion resistance of different stainless steels measured through pitting potential.

Grade 2205, with a value above 1000mV/SCE, confirms a higher corrosion resistance compared to austenitic (304 and 316), ferritic (439 and 444) and, even, lean duplex grades 2202 and 2304. Its real value could not be determined at this corrosion test. This ranking is coherent with the PREN calculated in Table 1.

Duplex grades are resistant to dilute reducing acids and moderate to high concentrations of oxidizing acids. Grade 2205 is resistant to low concentrations of organic acids, but should be used with caution in higher concentrations at elevated temperatures. Welded joint of grade 2205 resists to intergranular corrosion as measured by the 16% sulfuric acid-copper sulfate test (ASTM A 262 Practice E).

5. Mechanical properties

Alloy addition, like chromium, molybdenum and nitrogen, contributes to the increase of mechanical strength and corrosion resistance of duplex grades. The two-phase microstructure allows obtaining intermediate elongation and better yield and ultimate tensile strength than ferritic and austenitic grades.

Figure 4 and 5 shows the tensile and toughness properties of duplex grades compared to austenitic and ferritic stainless steels. This comparison was performed using 5.00mm thick materials.

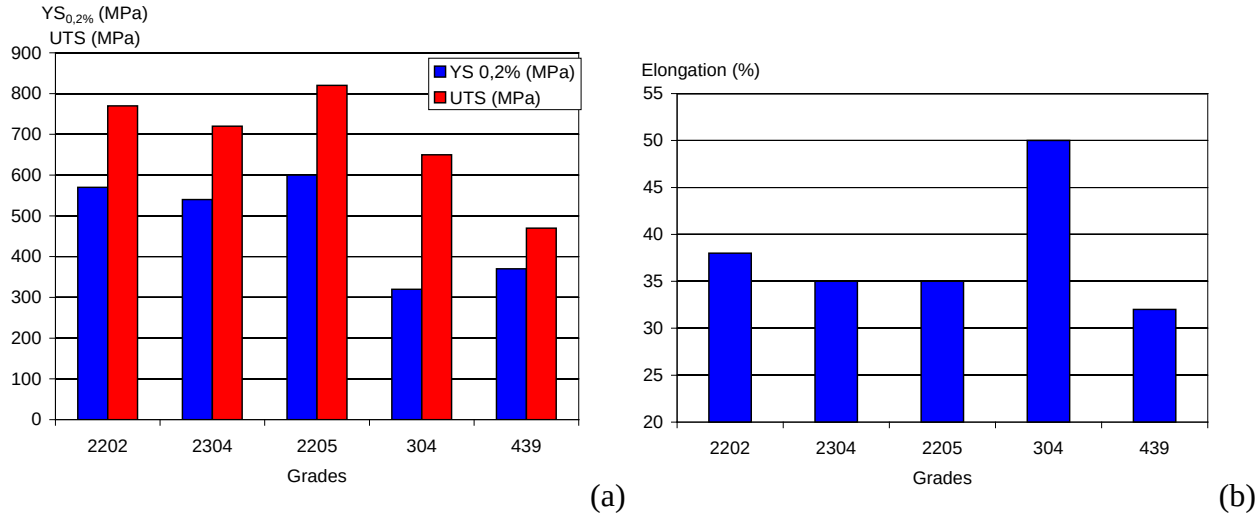


Figure 4 – Tensile properties of stainless steels. (a) Yield and ultimate strength. (b) Elongation.

As a collateral effect, the higher yield strength of duplex grades can result in a springback effect. For that reason, duplex grades need adequate equipments for their mechanically transformation grades. Duplex grades present good ductility as compared to ferritic ones, although their high mechanical strength.

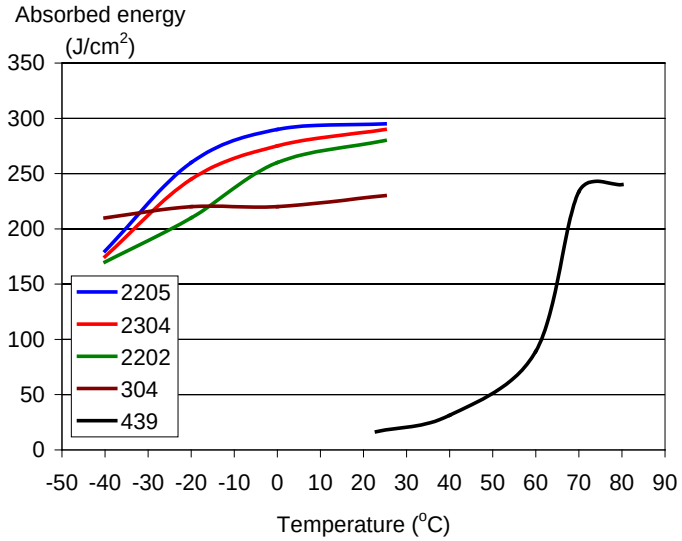


Figure 5 – Toughness properties of stainless steels after Charpy V test. Thickness 5.00mm

Duplex grades have higher toughness at room temperature than ferritic and austenitic grades. An inversion of behavior in toughness between the Lean Duplex 2202 and austenitic 304 is observed around -20°C. Although duplex grades present a drop of absorbed energy with the temperature decrease, which characterize a DBTT (Ductile to Brittle Temperature), its value is lower than ferritic grade 439 and the toughness value (absorbed energy) is very high at low temperatures, which allows using this material down to -50°C. According to ASTM A923, practice B, the minimum impact energy must be equal to 54J at -40°C.

6. Weight-lightening:

Thanks to their strength difference, some applications such as storage tanks have been testing the substitution of the grades 304 and 316 by 2202 and 2304, respectively in order to have substantial weight saving and better corrosion resistance. One example is shown in Figure 6.

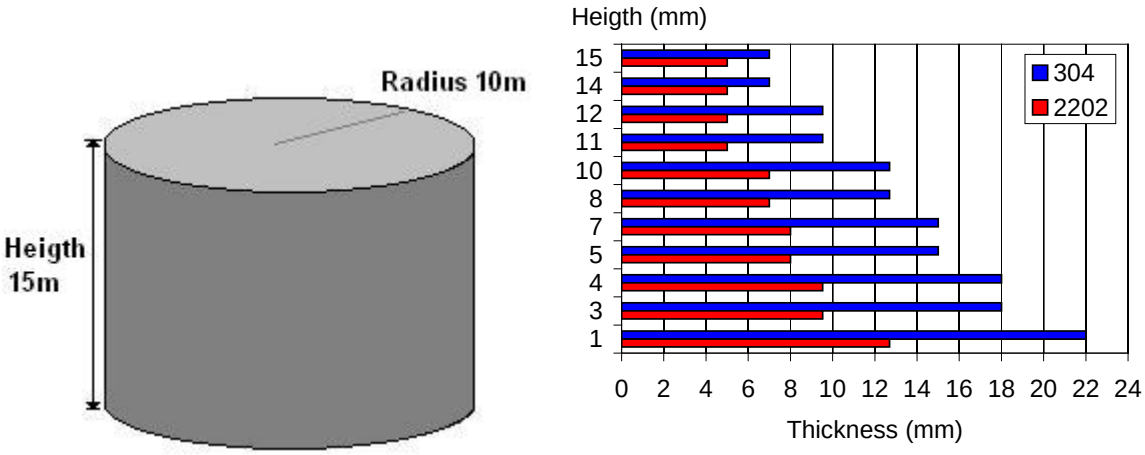


Figure 6 – (a) Dimension of storage tank. (b) Grades 304 and 2202 - Thickness x Height curve.

This weight saving is mainly obtained through a significant thickness reduction of plates used for construction as can be calculated from design standards. Thus, in the case of a silo of 15m height and 20m diameter, the calculated weight saving is around 40% that means 40t. Other gains that must be considered are the use of coils instead of plates as using thinner materials and the lesser quantity of welding consumables (filler metal, shielding gas), safety and weld defects.

7. Weldability

The molten zone and heat affected zone of duplex grades must assure a quite similar corrosion resistance as the parent metal and sufficiently high impact toughness for the application. The heat input control must be done in order to assure the phase balance (ferrite/austenite). Low heat input (high cooling rate) is supposed to produce a predominantly ferritic heat-affected zone with reduced toughness and corrosion resistance, while high heat input (low cooling rate) can take to precipitation of embrittling intermetallic phases. Typical heat inputs for GTAW range from 0.5 to 2.5kJ/mm.

Autogenous welding, as GTAW process, is supposed to increase the ferrite ratio in molten zone and Heat Affected Zone. One way to solve it is through post-welding heat treatment, although the ferrite ratio tends to be more than 50%. The maximum acceptable ferrite ratio is around 70%. The fully

ferritic grains may lower impact ductility at room temperature. Shielding gas for autogenous welding has nitrogen addition around 2 to 3% to Argon. This nitrogen addition helps austenite re-form quickly during cooling so that the weld and heat affected zone are more easily converted back to the optimal austenite ferrite balance.

In case of using filler metals, like GMAW or FCAW processes, the most indicated is AWS E2209, which contains more nickel than the base metal in order to produce a phase balance within the weld that is approximately the same as the base metal. Filler metal producers have been developing special alloys to weld.

8. Applications

The high chromium content of duplex grades can causes embrittlement at temperatures over about 300°C. At low temperatures duplex stainless steels have better toughness than ferritic grades. Duplex grades can readily be used down to at least -50°C. For these reason, duplex grades are supposed to be used at the in-service temperature range -50 to 300°C.

- **Duplex 2205**

In Brazil, customers produce petroleum flow lines with this grade due to the higher H_2S gas content found at deeper water. Chemical plant equipments are made in grade 2205 due to its higher critical pitting temperature and high chloride environment resistance, like pulp batch digester. According to Figure 7, despite of the high initial cost of duplex grade 2205, compared to covered carbon steel, its minimal maintenance cost justifies its application.

Table 1-1 Life Cycle Cost Comparison

	Carbon Steel		Duplex
6500 Cu Ft Batch Digester – Replacement Cost (13.25 ft. diam. x 57 ft. high – 2000 sq. ft. ID)	$300,000	300,000	500,000
Corrosion Allowance – inches (mm)	0.50* (12.7)	0.50* (12.7)	0.25* (6.4)
Overlay	Type 309L	Type 312	none
Maintenance Costs			
Years 1–9	minimal	minimal	minimal
Year 10 Overlay full surface of C.S. digester	300,000	350,000	minimal
Years 11–14	minimal	minimal	minimal
Year 15 Repair 100 sq. ft. of overlaid surface	20,000	minimal	minimal
Year 16 "	20,000	minimal	minimal
Year 17 "	20,000	minimal	minimal
Year 18 Arc gouge off and apply new overlay	350,000	minimal	minimal
Year 20	minimal	minimal	minimal
20 year totals	1,010,000	650,000	500,000

** The 0.50" corrosion allowance provides 10 years' service for the steel digester before weld buildup is required to restore the corrosion allowance. The 0.25" corrosion allowance for the duplex digester provides 25 years' service before weld buildup to restore the corrosion allowance is needed.*

Figure 7 – Batch digester life cycle cost comparison between grade 2205 and C steel (Nickel Institute).

- **Lean Duplex 2304**

Today raw material prices have widened the price gap between the duplex steels and more costly equivalent austenitic grades. Grade 2304 constitutes an excellent cost/performance alternative to austenitic grade 316L. This grade combines good corrosion resistance and high strength, as well as low nickel content and no Mo addition, which results in a low price compared to austenitic grades or 2205. The material high strength enables the use of thinner gauges at several applications such as tanks, pressure vessels, piping, transportation, civil engineering and structures, thus bringing considerable savings in material costs.

The high use potential of this grade is in capital goods, such as storage tanks (food, grains), sugar & alcohol and pulp and paper equipments. Some tests have been carried out in order to use it at the production of petroleum flow lines. Another end use is for abrasion resistance equipments due to its high mechanical properties.

- **Lean Duplex 2202**

Grade 2202 can be used in many construction or transport applications, replacing grade 304 and galvanized carbon steel. Its higher mechanical properties and, at least, same corrosion properties than austenitic grades, make this material able to provide the potential for weight savings and other ones. For instance, to decrease the fuel consumption for transport tanks application. However, the alternative substitution of grade 304 by 2202 strictly depends on the operating conditions (temperature and medium composition) and has to be made carefully.

9. Conclusions

The main conclusions are:

- Duplex stainless steels are a reality, with a participation increase of 6% a year at the stainless market share;
- ArcelorMittal Inox Brasil is now offering a wide range of duplex grades as different products: hot and cold bands as well as plates. Tubes has been developed since last year;
- Lean duplex grades (2304 and 2202) are considered as a possible alternative to austenitic grades (316 and 304). The main expected gains between Lean Duplex and austenitic grades are: better price stability, better or at least an equivalent corrosion resistance, elevated yield strength about twice as high and good toughness properties even at -50°C. All these characteristics might give a considerable weight saving potential for structural constructions.
- Grade 2205 is the most important duplex stainless steel and is developed to be used in high corrosive application, where standard stainless steels have failed.

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Corresponding author: Ricardo Augusto Faria (ricardo.faria@arcelormittal.com.br)