DUPLEX STAINLESS STEELS, A REVIEW AFTER DSS '07 held in GRADO.

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ABSTRACT

Duplex stainless have always been an exiting area of interest for researchers, stainless steel producers, fabricators and end users. They present simultaneously very diversified technical challenges and very attractive in service properties with on top of that excellent cost/properties ratios particularly in very critical markets including : oil and gas, chemical industry, pulp and paper industry, water systems, desalination plants, pollution control equipments, chemical tankers,.. .
This explains why although they still remain a marginal production in the stainless steel business (less than 1%) dedicated international conferences have been organised since about 25 years (St Louis USA '82).
The purpose of this paper is to present a review of the 100 scientific contributions presented during the latest international duplex stainless steel conference witch took place in Grado, Italy the 18-20 of June 2007..
The conference was a real success with about 300 attendees issued from XX countries including overseas contributions from Asia and USA.
The main topics concerned: structure and mechanical properties, weld ability, corrosion resistance properties and extensive papers dealing with in service properties. The "standard" duplex stainless steels i.e. the 2304, 2205 and the family of 2507 (Cu,W,…) grades were confirmed as very valuable grades with outstanding performances confirmed by more than 20 years successful in service applications. New grades including the so-called lean duplex dedicated to volume oriented markets (possible replacement of 304/316 grades) and some "niche" grades dedicated to very specific markets were presented.
After the scientific excitement of the first the first duplex conference, we discovered at the Grado conference that the duplex grades start to be well established products particularly suitable for corrosion resistance applications but also have a two digit yearly growth thanks' to the production of new grades and production ranges (coils and bars) targeting the replacement of more costly 300' series including 304 but also rusty carbon steel in for ex. structural application.

KEYWORDS

Duplex Stainless Steel, Markets and Applications, Chemistries, Metallurgy, Mechanical Properties, Corrosion Resistance Properties, Weld ability.

1 - INTRODUCTION

The first international duplex conferences (St LOUIS/USA/82 and Den HAGUE/NL/86) were mainly focused on "scientific" aspects since they appeared very attractive for the metallurgical aspects including phase precipitations (structures, kinetics'), corrosion resistance, mechanical properties. The world wide industrial production in that time was almost very marginal and standardization has still to be implemented. The main applications concerned Oil and Gas Industry.
BEAUNE '91/France conference was the first duplex conference with a mix between scientific and number of market applications. The new grades with increased nitrogen additions were presented**.(1)** Duplex grades gained in structure stability, weld ability and corrosion resistance properties! New standards were proposed. The duplex family included the popular 2205 grades with

increased nitrogen additions (0.16/0.18%N instead of 0.12/0.15%N) and optimized Mo contents. PREN values were proposed between 33 and 36 with a most common value 34/35. Sigma free grades were recommended as well as a minimum Mo level of 3%.
Grade 2304 was already developed but for marginal applications. Several super duplex grades were also promoted – SAF 2507, UR 52N+, Zeron 100… - for the most severe applications including off-shore. Those super duplex grades were also redesigned before the BEAUNE'91 conference in order to have a PREN value minimum of 40 and a nitrogen level minimum of 0.25 %.
The grades were mainly produced with EF + VOD or AOD + continuous casting devices i.e. the most efficient stainless steels tools.
First extensive applications were reported as well as new areas of developments. Confidence in duplex grades gained the end-users and the cost savings aspects partially obtained through the high mechanical properties were expected. New codes for duplex grades had to come. The potential growth of the grades was clearly emphasized. All this partially has explained the extremely wide audience of the BEAUNE'91 conference.
York'94, Maestricht'97 and Venice'2000 conferences were also successful conferences with increasing return of information on practical experiences**.(2-3)** Most of the applications still concerned the quarto plates and tubing. The first lean duplexes appeared.
This paper is a review of the scientific and technical contributions presented on the latest International Duplex Stainless Steel Conference held in Grado, Italy the 26/28 of June 2007. With about 300 attendees and 100 contributions, the conference appeared to be an excellent mix of outstanding scientific contributions and technical presentations covering field experiences in many areas of applications.

2 - STAINLESS CRUDE WORLDWIDE PRODUCTION AND CONSUMPTION.

Figures 1 presents the worldwide yearly crude steel production for flat stainless steels Stainless Stainles Steel production is booming since an average growth of 6% is observed since more than 50 years.

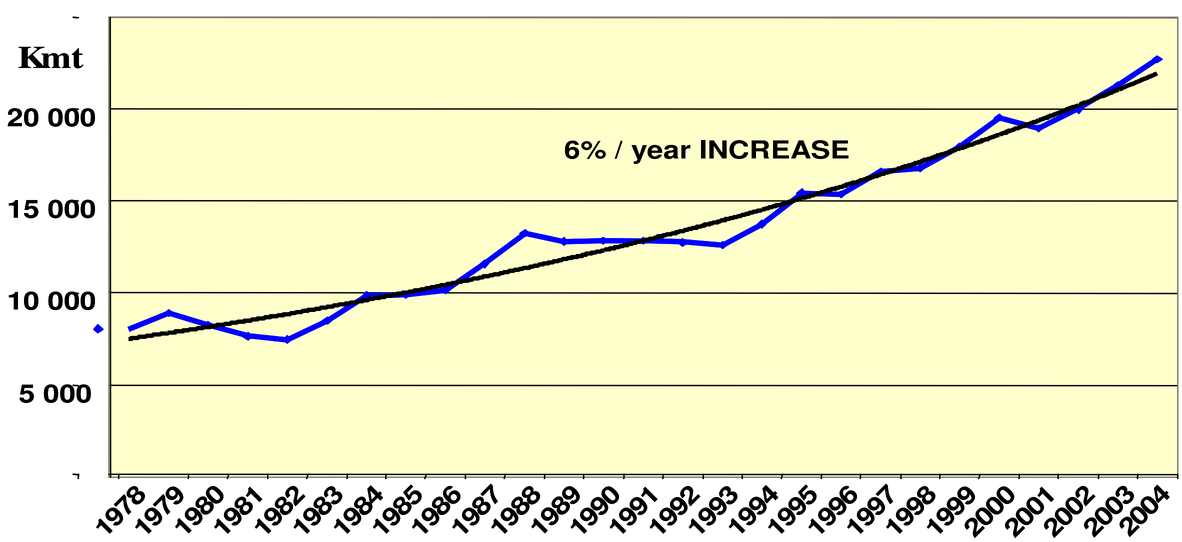


Figure 1 : Flat Stainless Steel Crude worldwide production

Figure 2 shows that stainless steel production is less than 1% of that of carbon steel **(4);** 304 grade being the most widely used. **Figure 3** presents the present and expected flat stainless productions per geographic areas. The nowadays biggest geographic area of stainless consumption is Europe while for the future most of the growth is expected to take place in Asia. Production capacities are booming mainly in China and are expected to come in India. Asia witch has since many years imported part of their needs will be soon able to export stainless steel due to possible overcapacities. The booming demand in Asia particularly in China and a certain lack of regulations made it possible to develop new grades with less alloying elements. China and India are the countries where the new 200 series were developed. More recently China has used more than 1 million of tons of those new grades which do not have specific norms. **(Figures 4 and 5) (5)**

Austenitics remains the most popular grades thanks' to their unique combination of high ductility, high potential of strengthening, weld ability, toughness even at extra-low temperatures and of course corrosion resistance. Ferritics represent about 25% of the total production and due to welding aspects and toughness properties; they are restricted to thinner gauges even if they are often the cost saving grades. Duplex grades cover about 1% of the total production (**Figures 6 and 7), (5).**

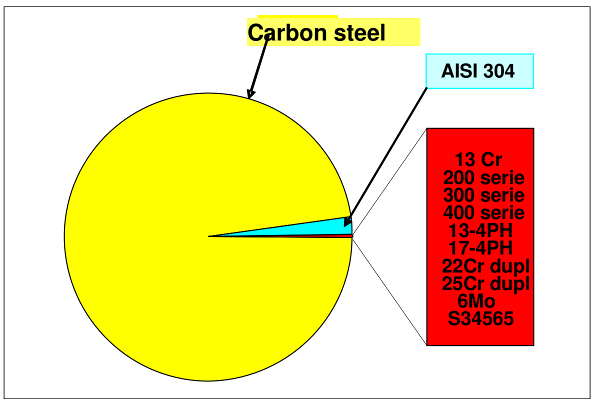


Figure 2: Stainless worldwide production compared to flat carbon steel.

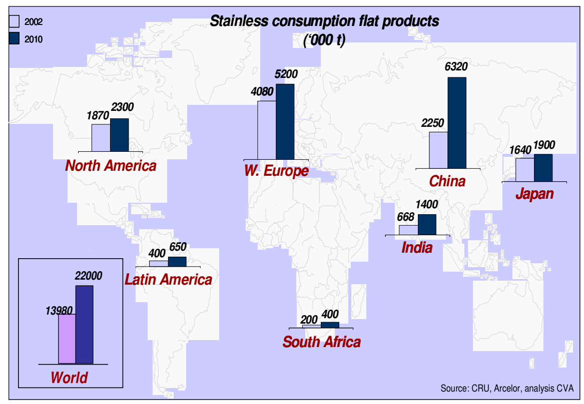
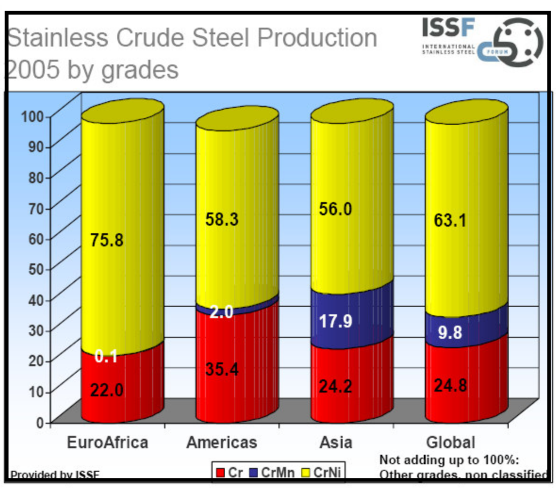
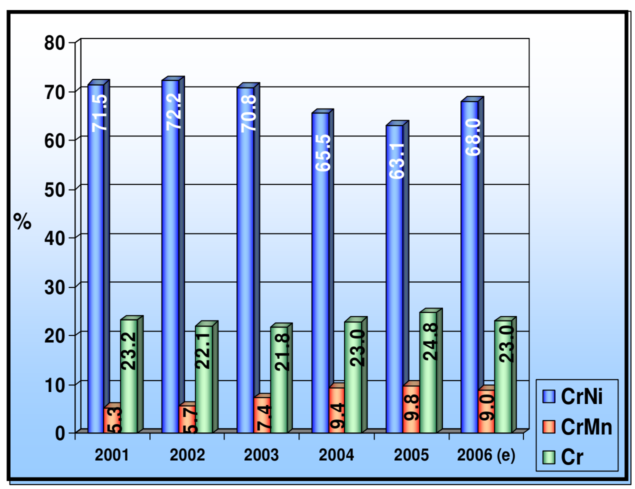
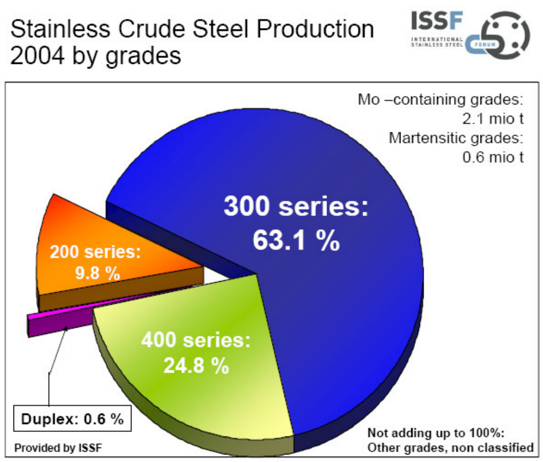


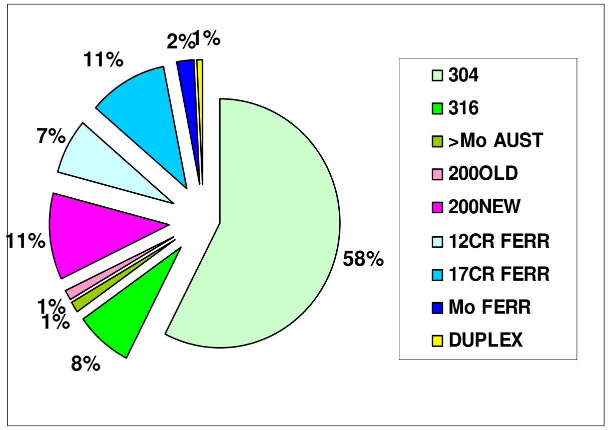
Figure 3: 2002 Stainless Steel worldwide consumption and 2010 expectations.





Figures 4 and 5 : Stainless Steel crude steel production (2001-2006) by grades. (ISSF documents)

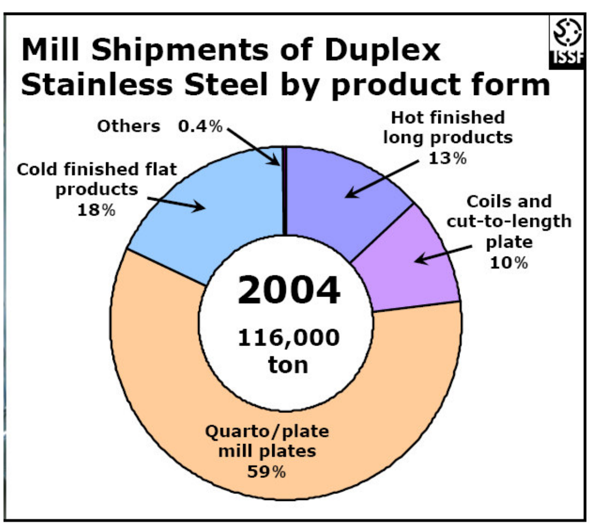


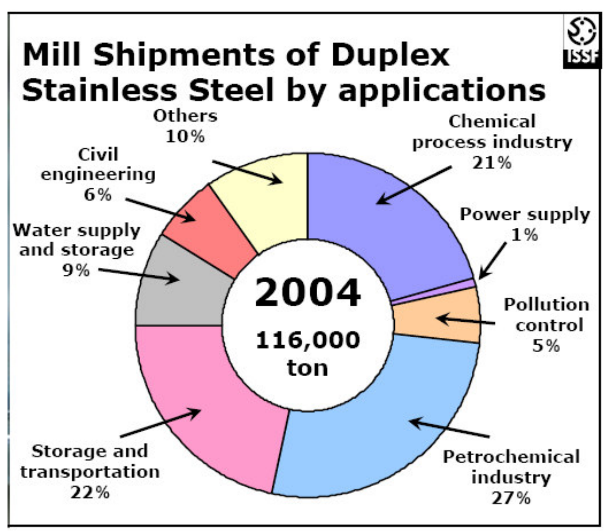


Figures 6 and 7: 2004 stainless worldwide crude production by grades.

3 - DUPLEX STAINLESS STEELS AND MARKET APPLICATIONS.

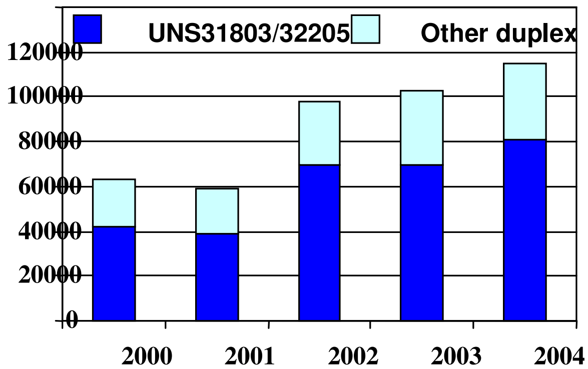
Most of the duplex grades in services are 2205 hot rolled products. In the recent past strong demand and developments concerns cold finished flat products and hot finished long products (rebar). Duplex grades production, worldwide, represent nowadays about 200KT i.e. less than 1% of the total Stainless Steel production although the production has growth of more than 100% in the latest decade. Most of the production concerns the so-called quarto plate's i.e. wide –more than 2M- and thick – more than 6mm- plates. For those productions weight savings are often obtained taking advantage of their high mechanical properties. Most of the applications concerns highly corrosion resistance properties encountered in process industry. (Chemical, petrochemical, off-shore, chemical tankers, pulp and paper industry, pollution control equipments-FGD-, desalination, sea-water applications...). In those applications 2205 grades have always been very competitive compared to 317(LMN) and 904 grades due to their reduced Nickel content and high mechanical properties compared to austenitics which make it possible to reduce thicknesses (quarto plates).



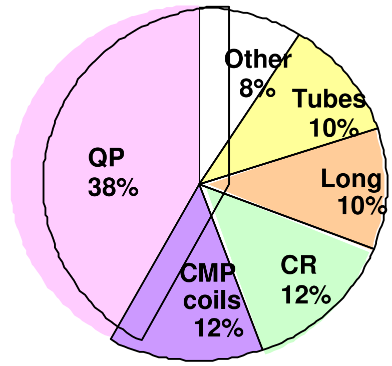


Figures 8 and 9 : 2004 main duplex production and market applications.(ISSF documents)

Duplex Crude Productions (tons)



Crude Productions in 2006 (160000T)



Figures 10 and 11: Duplex -2000/2004 crude productions and 2006 applications (by products) **(6).**

Superduplex grades (2507 Cu,W) represent about 10% of the total duplex productions and are designed to replace 6Mo austenitic grades in the most severe applications. Lean duplexes including the 2304 and 2101 grades contribute to slightly more than 10% of the total duplex production.
The booming applications concerns products recently developed i.e. new grades including lean duplex and new production ranges (coils and bars). The lean duplexes are expected to replace 304/316 in volume markets. If coils production can be achieved with high productivity and quality, duplex uses will grow very fast. Another potential booming market could be duplex for rebar.

4 - STAINLESS FAMILIES and ALLOYING COSTS.

The recent evolutions of raw material costs particularly Ni have a drastic impact on 304 and 316 alloy surcharges. They are nowadays higher than the base material price!! As a result differences of several thousands of euros per ton are observed for the 300 series prices in a few years. Of course ferritic steels are almost not affected by those effects. Replacement of 304 and 316 grades by ferritic grades is nowadays the cost saving solution! This concerns particularly thin gauges applications since ferritics are difficult to weld in thicker sections.

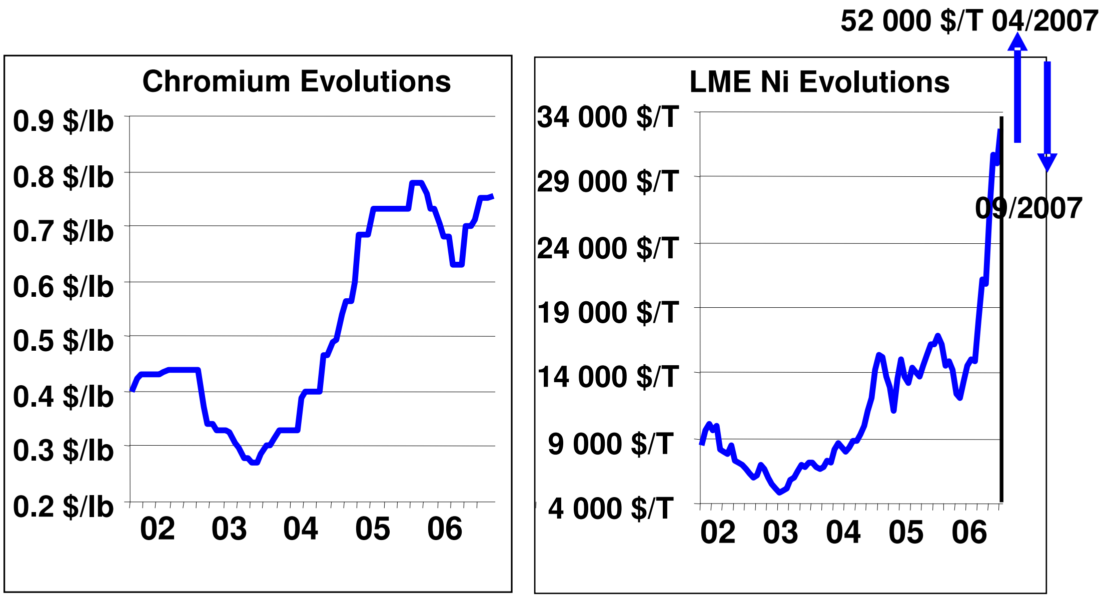


Figure 12 : Cr and Ni volatility this latest years.. (**5**).

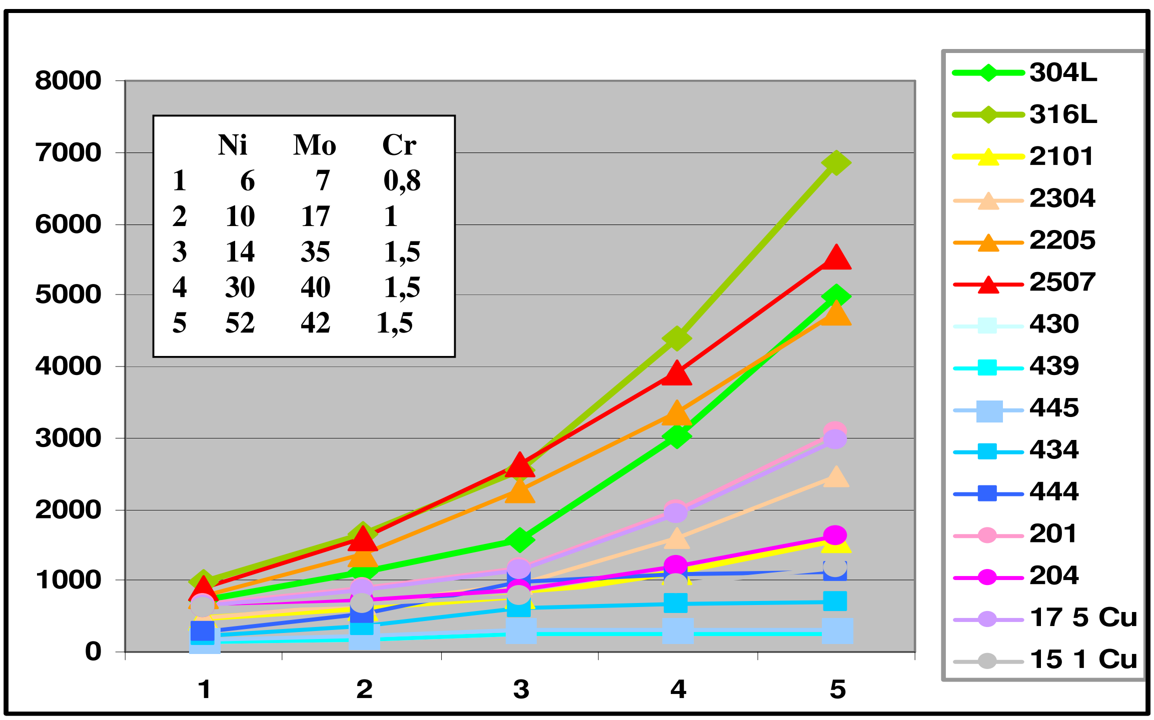


Figure 13: Evolutions of raw material costs (2004/2007). **(5)**

Although Ni price as recently dropped from 50$/T to 33$/T, duplex grades start to be very cost competitive answers for thicker gauges. Replacements of 316 grades by 2205 duplex grades are now to be considered: cheaper grade for much more corrosion resistance properties and high mechanical properties! Same results are observed for 2304 duplex versus 304 and 316!!! And the new lean duplexes 2101 type are even less alloyed in Ni, Mo expensive elements. This provides new powerful driving forces for a further increase duplex uses in new applications! **(Figure 13)**

5 - DUPLEX STAINLESS STEELS GRADES, PAST AND PRESENT.

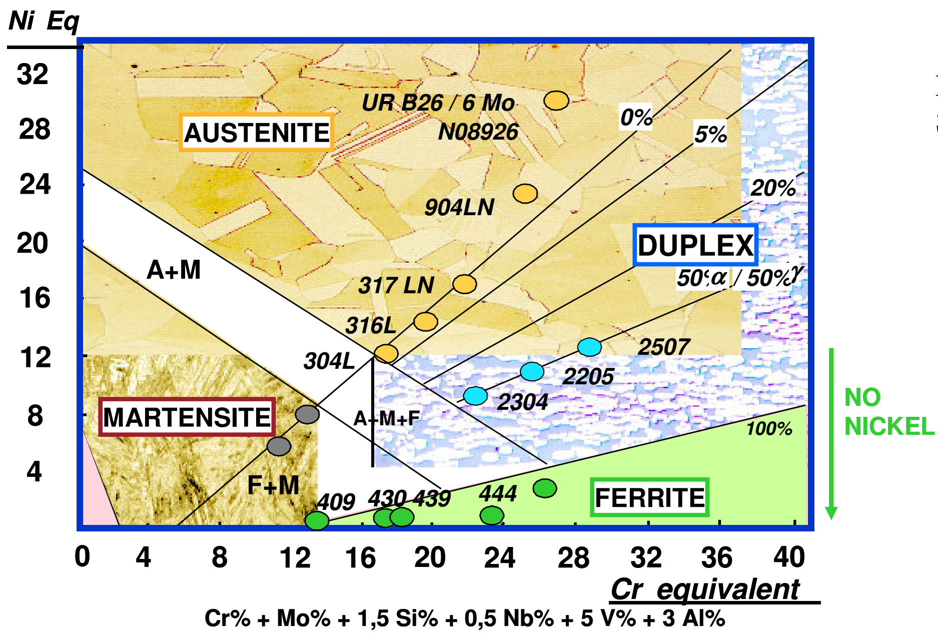


Figure 14 : Schaeffler diagram

Although Schaeffler diagram is mainly used for welded structures, it is very useful to illustrate roughly the areas of stability of the different stainless microstructures. Between the austenitic and the ferritic areas, we obtain a mixed ferrite + austenite microstructure: the duplex area. Most of the duplex industrial grades have a typical 50%ferrite/50%austenite microstructure. The three classical families of duplex grades are plotted in the Schaeffler diagram: the 2304 Mo free grades, the standard duplex type 2205 and the superduplex grades of 2507 type.

As observed it is almost impossible to develop duplex grades having less than 20%Cr without possible formation of martensite. Those grades even having after water quenching an austenite/ferrite microstructure may undergo an austenite/martensite transformation when plastic deformation occurs.

With the extreme volatility of alloying element costs **(Figure 13)** – Ni for example has increased of more than 500% this latest 3 years - but now is going back to a more reasonable level - new grades have been introduced in the market **(table I).** The newly developed grades are on both sides of the standard 2205 grade. A first family of grades concerns the so-called lean duplex ,having lower costly Mo and Ni additions – the phase stability may be achieved thanks' to complementary manganese , another austenitic stabilizing element, additions. The new designed grades have also increased nitrogen content since nitrogen additions – extra low cost element! - are know to improve the austenite stability of the grades and localised corrosion resistance properties**.(Figure 14)** The main targets of those grades is a partial replacement of 316 and even 304 austenitic grades depending upon their properties related to the chemistry of the alloy. Some of those grades have still high Mo contents combined to Ni additions. When using the world "lean" for duplex grades we should restrict our definition to almost Mo free grades and nickel content lower than 3%. Grade 32003 is obviously less expensive in alloying elements than the 2205 grade but more expensive than the 2304!! It should not be considered as a lean duplex.

On the other corner – more alloyed grades – new grades have also been introduced. This concerns alloys having mostly higher corrosion resistance and structure stability than the 2507 type grades.

They are often called hyperduplex grades. The driving forces are higher Cr additions with complementary increased nitrogen additions and possible partial replacement of exclusive Mo additions by mixed Mo+W additions which seems to contribute to stabilise the grade providing less sensitivity to intergranular phase precipitations when heated. This concerns mostly the very high Mo content duplex grades.

TABLE I: Typical chemistry of several stainless steels.

FAMILY	USA	EURONORM	Cr	Mo	Ni	Mn	Cu	N	Others	PRE	PREN	PRENW
300	304L	1.4307	18	0	9	1	0			18	18	18
	316L	1.4401	17	2	11	1	0			24	24	24
	904LN	1.4339	20	4	25	1	1,5	0,1		33	35	35
Standard DUPLEX (1996)	S 32304	1.4362	23	0	4	1		0,13		23	25	25
	S 32205	1.4462	22	3	6	1		0,17		32	35	35
	S 32750	1.4410	25	3,5	7	1		0,27		37	41	41
	S 32760	1.4501	25	3,8	7	1	0,7	0,27	0,7W	38	42	43
	S 32520	1.4507	25	3,5	7	1	1,5	0,25		37	41	41
New DUPLEX (EX)	S 31500		18,5	2,7	5	1		0,1		27	29	29
	S 32101	1.4162	21	0	1,5	5		0,2		21	24	24
	S 32001		20	0,3	1,7	5	0,3	0,15		21	23	23
	S 32003		20	1,7	3,5	2		0,15		26	28	28
	S 31260		27	3	7	1	0,5	0,16	0,3W	37	39	40
	S 39274		25	3	7	1	0,6	0,27	2W	35	39	42
	S 32906	1.4362	29	2	6	1		0,4		36	42	42
	S 32707		27	5	6,5	1		0,4		44	49	49

PRE = %Cr + 3.3%Mo ; PREN(W) = %Cr + 3.3%Mo + 16%N + (3.3(0.5%W)).

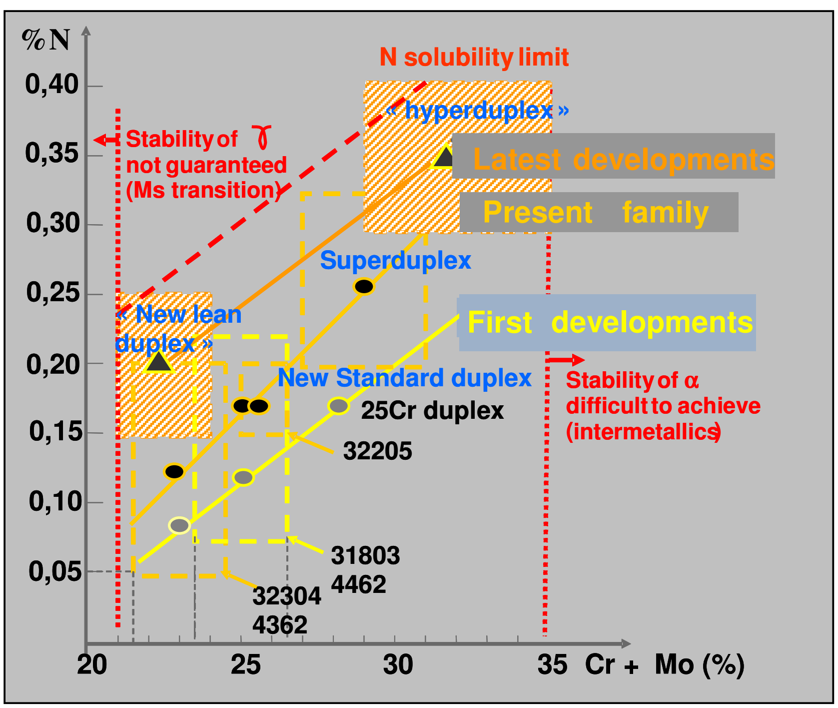


Figure 14: Newly designed duplex grades have increased nitrogen content (**2**).

6 – STRUCTURE STABILITY AND DUPLEX STAINLESS STEELS GRADES.

Typical phase diagrams of duplex grades are presented **Fig.15.** Phase precipitations are clearly related to the Mo, Cr and W additions. Alloying in Cr, Mo, W make the grades more prone to transform the ferritic phase in intermetallic (sigma, chi ..), nitrides, carbides or even at lower temperature in alpha prime microstructures (Spinodal decomposition). With copper additions complementary precipitations of epsilon-Cu in the 600/300°C range may occur.

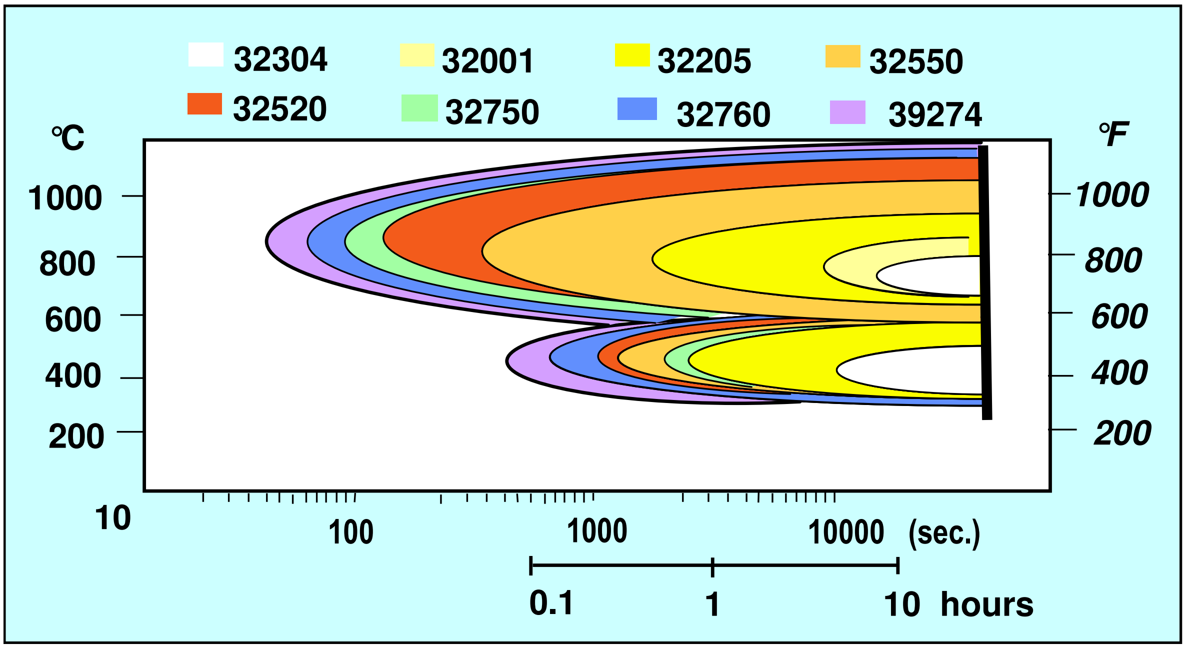


Figure 15: typical isothermal phase diagrams of duplex grades. Increase of Cr, Mo and W increase the kinetic of decomposition of the ferritic phase.

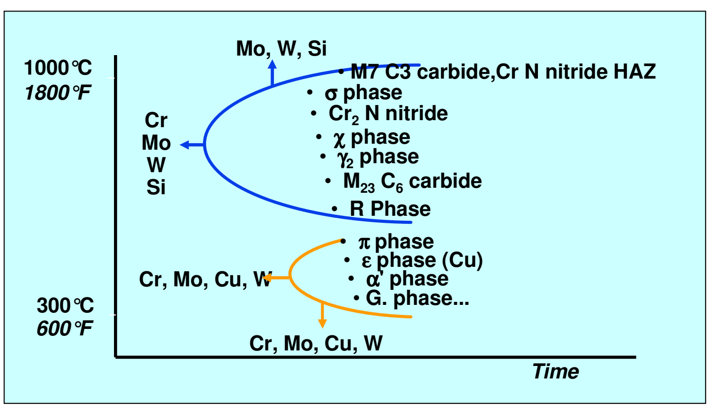


Fig. 16: Typical phase precipitations which may occur in Duplex grades.

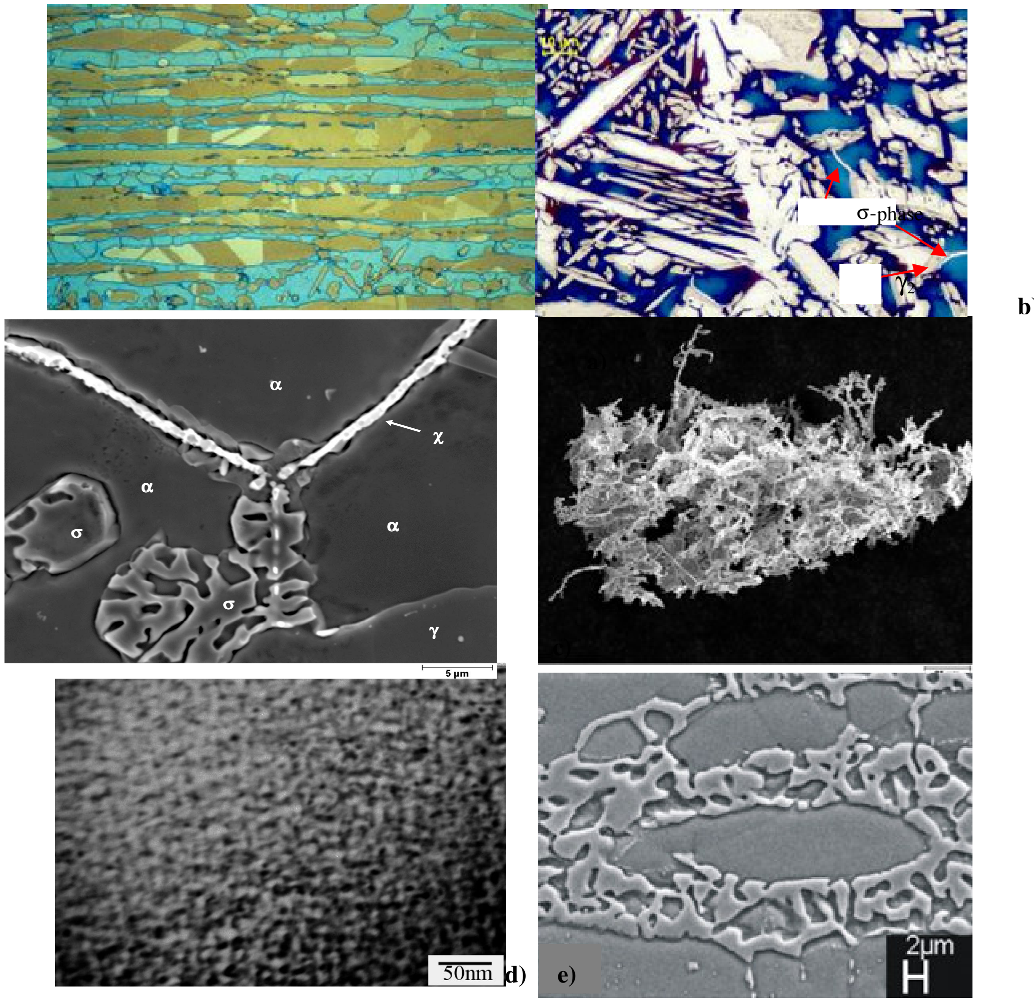


Fig.17 : a) Ferrite (blue) and recristallised austenite **(8)** **b)** 2507 920°C/600sec treatment **(9)**
c) 2205 after an 850°C annealed sample (1H) **d)**2507 100H/475°CTEM high resol**.(11)**
e) Coral kind three-dimensional sigma phase precipitations **(12)**

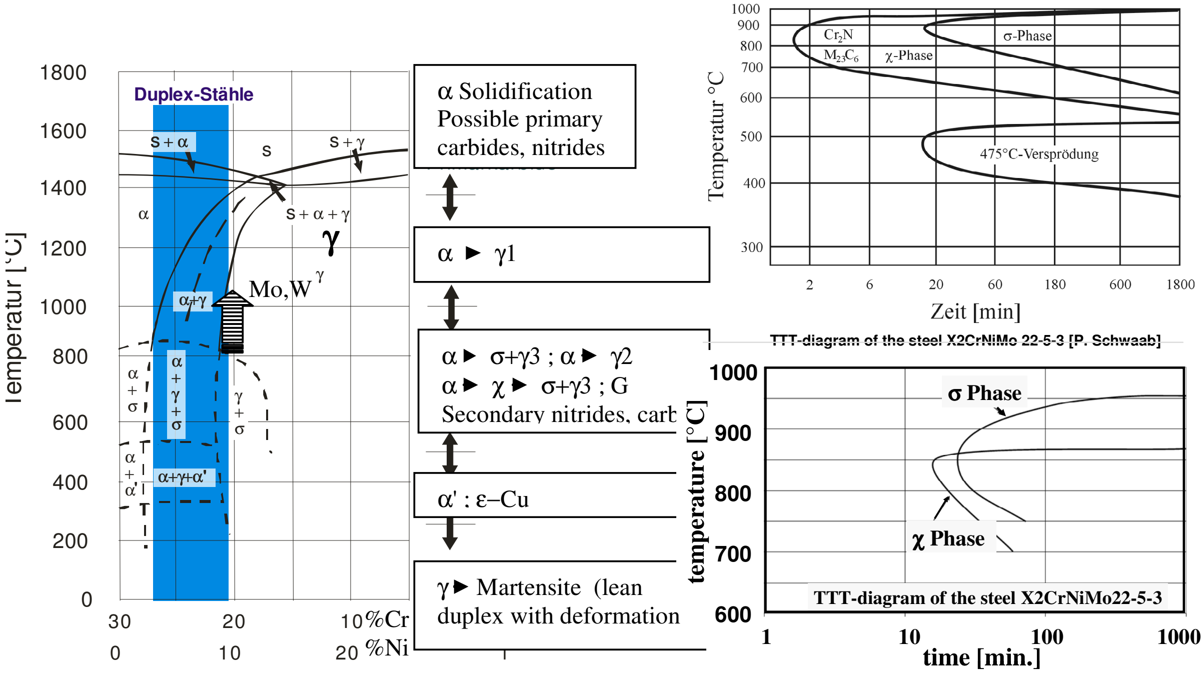


Figure 18: a) Pseudo-phase binary diagram of duplex grades (2205/2507).
b) Old 2205 duplex phase diagram emphasizing the nitrides precipitations.
c) High temperature phase transformations 2205.

Most of the duplex industrial grades solidify in the ferritic mode and undergo a partial transformation of the ferrite in austenite by cooling down. The volume fractions of austenite/ferrite are clearly linked to the composition and temperature. (Thermocalc model is useful for such investigations). As a result the room temperature microstructure and properties are closely linked to the solution annealed temperature i.e. higher solution annealed temperatures produces higher ferrite contents and lower toughness properties **(13).**
Step cooling, for example 700°C, with or without mechanical deformation, can lead to the precipitation of numerous small acicular austenite grains (gamma two), presenting a {111}γ//{110}α Kurdjumov-Sachs relationship. At lower temperatures and even finer structure may be formed ({123}α habit plane with a Nishyama-Wasserman orientation).**(1)**

6.2) High temperature precipitations.

For the most alloying duplex grades it has been confirmed that sigma phase issued from an eutectoid decomposition of austenite is the most common brittle phase observed. Typical chemical compositions are 60Fe30Cr7Mo3Ni. (2205). Sigma phase precipitates with γ2 phase which is an austenitic phase having a lower PREN value than the matrix, typically 36 instead of 42 for a superduplex grade. Chi phase is often observed as an intermediate precipitation before to transforms in sigma phase.
Sigma and Chi phases have a strong embrittlement effect while γ2 lowers the average corrosion resistance properties of the grade.
Model based on Avrami's equation are now available to predict the microstructure after both iso and an isothermal heat treatments of industrial grades. Typical minimum cooling rates of 0.3°C/sec are requested to avoid sigma phase precipitations in a 2205 duplex alloy**. (14)**

W additions are know to stabilise at high temperature the sigma phase. W containing grades request higher temperatures for solution annealing treatments. Some papers underline also the benefit of W additions in order to improve the phase stability of the duplex grade. Clearly after long term isothermal treatment the amount of sigma phase is reduced when comparing a Mo containing grade with a equivalent Mo+W addition where part of the Mo is replaced by W additions. This seems to result from slower diffusion of big W atoms. Precipitation for significant phase transformation seems also to be more intragranular. Nevertheless, when looking to the first steps of intermetallic formation, no clear evidence of W additions seems to be observed i.e. the first precipitations happens for the same holding time. As a result no clear benefits of W additions on structure stability of duplex grades are observed!

On the contrary the simultaneous increase of Cr (29%) ,decrease of Mo(2% instead of 3.5-4%) and increase of nitrogen (0.4%) is a good way to develop superduplex grades with higher structure stability.(X) (SAF 2906). The DP28W grade of Sumitomo has a close philosophy (27Cr, 1Mo, 2W,0.35N) but with mixed W and Mo additions.

Newly developed "hyperduplexes", with PRENW higher than 45, combine very high Cr+Mo+W additions with significant nitrogen additions (..0.4%). One example is the UNS 32707 grade (SAF2707) with 27Cr and 5Mo and the second the UNS 39274 DP3W grade (25Cr, 3.3Mo, 2.1W). For those grades high solution annealing temperatures are needed and they are more to be considered for thinner gauges.(CCC)

Cr_2N and carbides (M_7C_3, $M_{23}C_6$) are also expected to form during high temperature treatments. Clear evidences have been observed. Nevertheless the detrimental effects of sigma/chi phases precipitations in the superduplex grades as well as 2205 grades seems to overdo the nitides/carbides precipitations effects in most of the cases. On the contrary thermal cycles including very high temperatures (1300°C ..),which may increase the volume fraction of ferrite, followed by fast cooling treatments plus possible intermediate reheating – typical HAZ (of multipass) welds – may be subject to significant nitrides precipitations due to excess of nitrogen content in the ferritic grains and lack of time for austenite transformation and nitrogen diffusion**.(1,15)** Carbides precipitations are generally of the second order of importance.

For the less alloying grades i.e. Mo free grades, Sigma/Chi phase precipitations need much more holding time (several 10 hours) and nitrides precipitations, particularly in the newly designed grades with higher nitrogen contents may be the first driving force to reduce corrosion and toughness properties when heated in the 600/850°C range. Brittle behaviour have been reported but holding time much exceed the normal industrial treatments. The Mo-free duplex grades may be considered as very stable microstructure when considering standard heat treatments including solution annealed treatments. Air cooling can even be considered for some applications and very thick products for the solution annealed and water cooled conditions. In those lean duplex (2101) nitrides precipitations have been observed after a holding time of 45min in the 650/750°C range. This explains why toughness properties are reduced end values less than 50J observed in those conditions**. (16)**

6.3) Phase precipitations in the 550/300 /20°C range with ferrite hardening effects.

At lower temperatures diffusion mechanisms are slowing down and as a result precipitations needs more time and finer microstructures are generally founded which makes the optical investigations and phase identifications more difficult.

Since nitride solubility in ferritic grains decrease with temperature, nitrides precipitations generally occurs on the ferrite/ferrite boundaries. Some complex intermetallic phases R, π, G, might also be formed particularly in the Mo containing grades.

The most popular transformation is the Spinodal decomposition of the ferrite in to α' – demixion of the ferrite in poor and high chromium contents on a very small scale. This transformation is known as the 475°C transformation (it occurs mainly between 475 and 280°C). A subsequent hardening and embrittlement of the ferrite is observed. This explains why most of the applications are restricted to

temperatures lower than 250°C. Superduplex grades having 25Cr are very sensitive to this phenomenon. 2205 grades are also sensitive but much less tan the 2304 grade without Mo although their Cr content 22% is less than the 23% of the 2304! The clear effect of Mo in this transformation is not completely understood.W and Cu additions have also specific effects.
Cuε particules may precipitate in the ferrite grains after heat treatment in the 550/300°C temperature range. A hardening effect can be obtained.
The Mo free grades seem to be less prone to low temperature hardening phenomenon. Holding times of about 10H are needed to have α' precipitations!
For the less alloying grades (lean duplexes) large amount of martensitic transformations may occur when plastically deformed **(16).**

7- MICROSTRUCTURE and MECHANICAL PROPERTIES.

Several papers have presented the links between mechanical properties and microstructure. This includes the effect of heat treatments / phase precipitations and mechanical properties**.(10,13,12,16,17,18)** It is confirmed that for the 2205 and 2507 grades a few percentages of sigma phase (1-2%) already reduce drastically the toughness of the grades even if the tensile properties are less affected.
Heat treatments of 5 minutes in the 1035/ 1050°C for the 2205 duplex grade are enough to restore the austenite/ferrite microstructure. Lower heating temperature needs longer holding time.
The influence of those phase transformations on low cycle fatigue tests was also presented. Results included heat treatments in the low temperature range (Spinodal decomposition).
It is concluded that duplex grades, including the 2507 superduplex grade, are, in the solution annealed condition, characterized by high fatigue crack propagation resistance with crack propagation micromechanism that are mainly ductile. Precipitation heat treatments decrease the fatigue crack propagation resistance and increase the fatigue crack growth. The surface morphology is strongly affected. Cleavage is commonly observed in the presence of improper ferrite/austenite microstructure. **(19-21,22,23)** Smaller grain sizes improve the crack propagation properties. TEM investigations are presented and mechanisms discussed. One of the authors has even observed martensitic transformation of the austenite in a 2507 alloy.

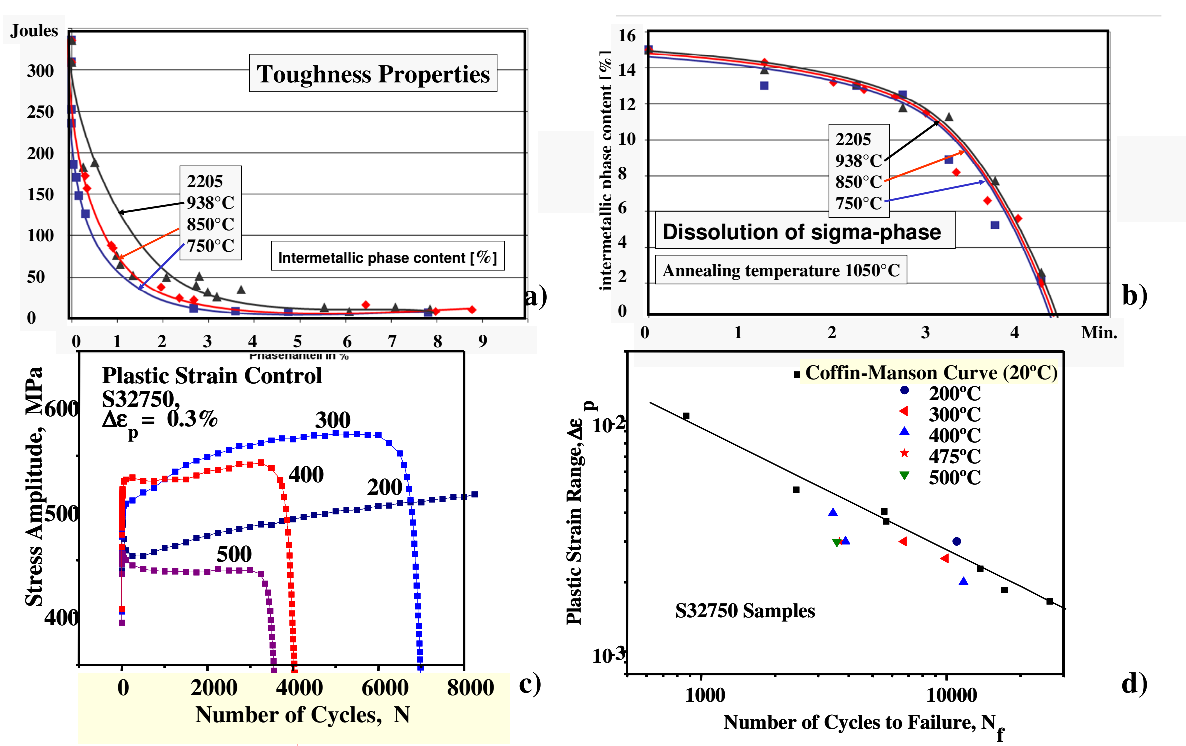
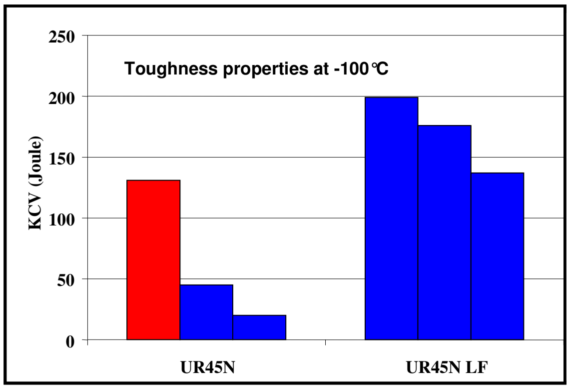


Figure 19 : a) 2205 grade, effects of sigma phase precipitation on toughness properties.
b) 2205 grade, annealing time and sigma phase dissolution.
c),d) 2507 grade, fatigue crack propagation properties.

Some papers have also investigated the stress distribution in the 2304, 2205 and 2507 alloys. Elastoplastic behaviour of both phases, $\alpha-\gamma$, are presented by using X-rays and neutron diffraction methods.(18,22)

For the Mo free duplex grades, including the 2101 grade, nitrides precipitations occurs after 20 minutes in the 600/750°C range. Toughness values lower than 50J were reported in such conditions

One of the most interesting topics discussed in Grado conference was the improvement of low temperature toughness properties of duplex alloys by appropriate chemistry and heat treatment presented by Industeel. As a result very high toughness can be obtained on both base metal and welded joint at -100°C. Furthermore the nightmare of welding parameter of former 22Cr duplex grades completely disappear ; excellent mechanical and corrosion resistant properties of welded structures can be very easily been obtained!



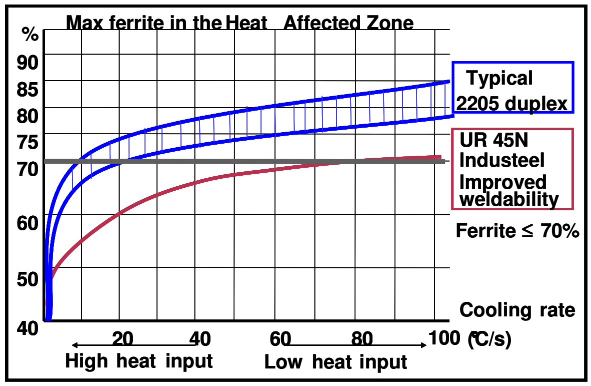


Figure 20 : Improvements of structure stability of 22Cr duplex by appropriate design **(24,25).**

9- APPLICATIONS.

9.1 Oil & Gas.

Several extended papers issued from Oil & Gas companies (Total, Statoil, Shell…) have been presented **(26 to 29).** All of them underline the very satisfactory behaviour of 22 and 25Cr duplexes which have been experienced since more than 25 years in a large set of applications i.e. top side, sub sea piping's, manifolds, umbilicals, wells applications, fire systems, … .

Some failures have been observed. Most of them are related to unintended service conditions including poor design, high local stresses, overloaded conditions, unexpected microstructure defects (sigma phase), local saturated brine solutions (evaporation/condensation phenomenon's associated with high temperature), and some HISC cases.

In order to avoid HISC phenomenon's, the DNV RP F112 document has been prepared as well as possible implementations. Clearly HISC results from a source of atomic Hydrogen (generally cathodic protection by sacrificial electrodes) , high local stresses (overload phenomenon's associated with stress concentration factors like surface irregularities) and possible improper microstructures (sigma phase precipitations, high ferrite contents in HAZ or welds, ..).**(30,31**)

Castings and forged products with big grain sizes seems to be more sensitive to HISC phenomenon.

A new improved test method for qualification of stainless steels exposed to HISC under cathodic protection in seawater is proposed.**(31**). The two key elements to be controlled for a specific level of hydrogen are : the stress concentration factor and the net section stress per yield stress. Oh course

the most effective solution is to decrease the risk of hydrogen pick up and special care will be forwarded to the conditions of cathodic protection (avoid to cathodic conditions).
Some linkages umbilical due to crevice corrosion phenomenon's have also been discussed.**(32)**
Aker Kvaerner paper **(4)** underlines the possible benefits of the uses of lean duplex in structural applications for platforms. Pipe racks, pipe supports, architectural walls, insulation claddings, cable trays could be typical applications where carbon steel is replaced by lean duplexes. Typical cost savings of 20 to 40% are considered when including material costs and welding plus corrosion resistant coatings. Aluminium stairs and ladders are also to be proposed in lean duplex. In most of those applications the existing 316 should be replaced by a lean duplex. Special care should nevertheless be made in material selection taking in to account the in service conditions since among the lean duplexes, a wide range of chemistries are proposed (PREN from 23 to 28).
A paper from Butting **(33)** has provide technical information concerning longitudinally welded pipes products issued from strips) of both 2101 and 2003 grades. Grith welds have also been produced successfully. It is concluded that lean duplexes can meet 13%Cr specifications for welded pipes and that their corrosion resistance are superior to the martensitic grade. Differences in corrosion resistance properties of the duplex grades are observed and closely linked to the chemistry of the grades.

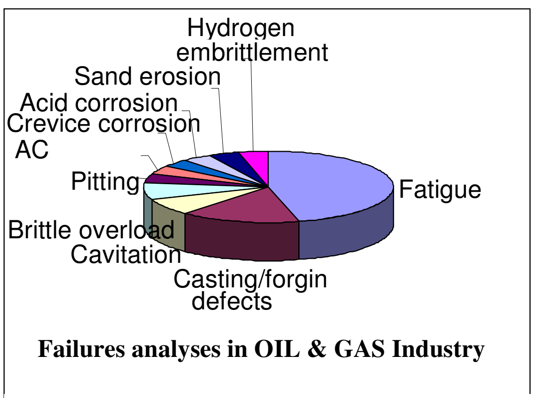


Figure 21 : Origins of failures cases in oil& gas Industry

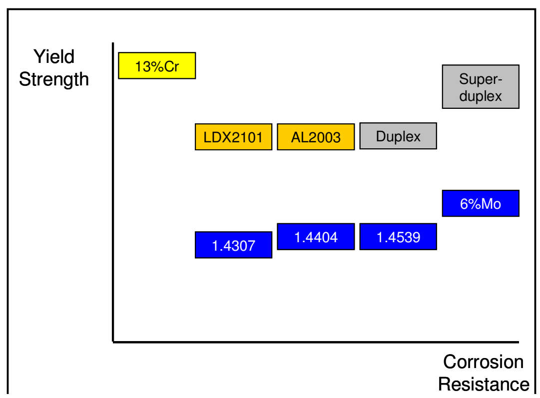
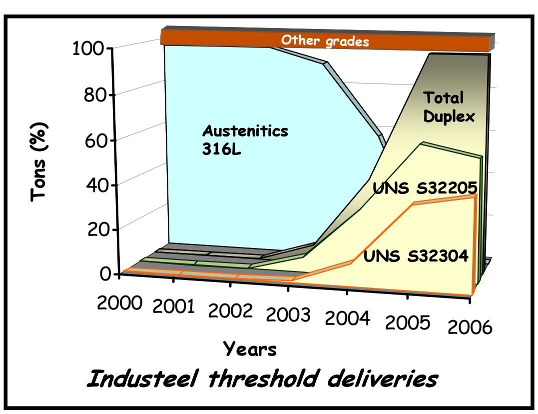


Figure 22 : Austenite-duplex Mechanical /Corrosion resistance properties rankings **(33)**

9.2 Desalination and severe chloride containing environments.
J.Peultier **(34)** from Industeel has presented an overview of the uses of duplex grades in desalination plants. It is concluded that recently some Engineering companies have completely shifted from austenitic to duplex grades. 2205 grade is the cost saver material bringing weight reductions and low maintenance costs due to their excellent corrosion resistance properties. More recently 2304 kind material has been introduced for the les severe conditions.
For the most severe conditions the classical superduplex are to be considered. The newly "hypeduplex" grades seems to offer improved properties**.(35-37)**



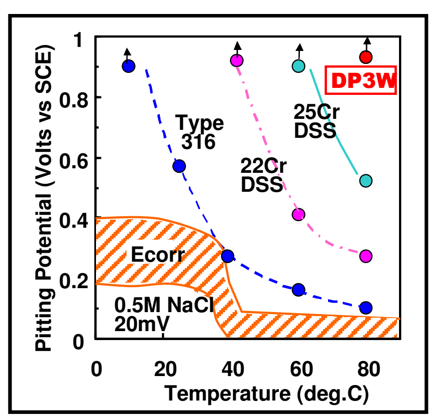
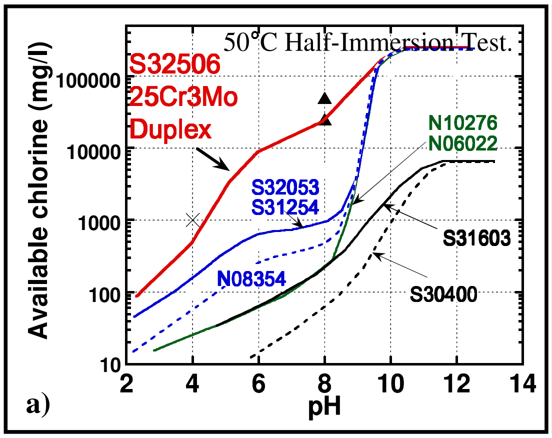


Figure 23: Duplex versus austenitics in desalination plants deliveries **(34)**

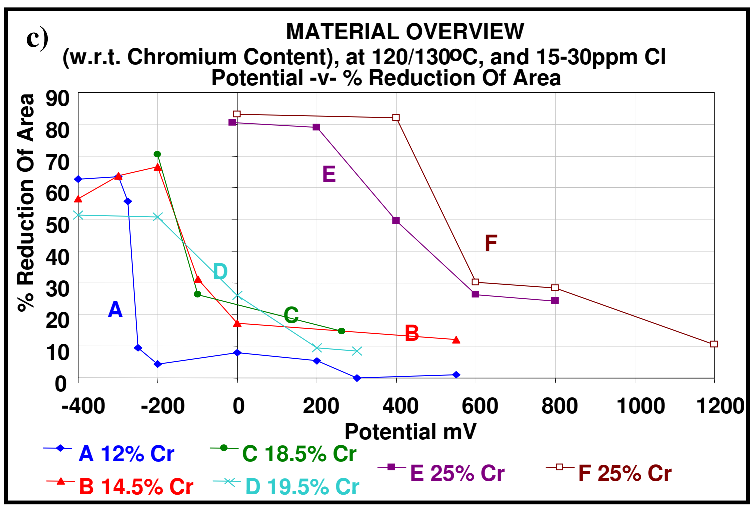
Figure 24: Pitting Corrosion resistance of Duplexes versus temperature.**(35)**

Linkages resulting from both pitting/crevice and stress corrosion phenomenon's have been reported in many industries dealing with hot concentrated saline solutions. One typical case is the corrosion associated to brine solutions/salt deposits resulting from sea water evaporation (sea water in contact with heated tubes…). Wetting/heating cycles and/or drop evaporation tests have been developed. Some experiments have also been conducted in autoclaves.



NORSOK M-001

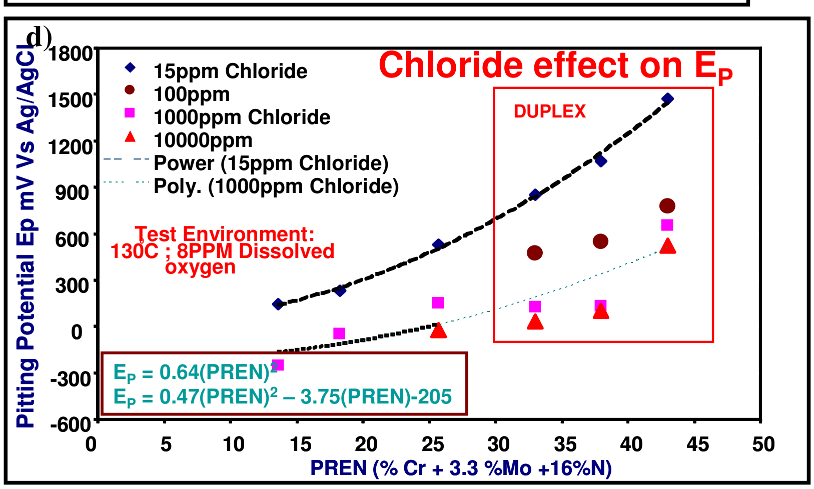
T (°C)	22 Cr DSS			25 Cr SDSS		
	Stress (MPa)	Stress (% $\sigma_{0.2}$)	Result	Stress (MPa)	Stress (% $\sigma_{0.2}$)	Result
110	418	88	Fail	471	88	Fail
110	395	83	Fail	445	83	Fail
105	-	-	-	494	92	Fail
100	335	70	Pass	494	92	Fail
90	452	92	Fail	508	92	Fail
80	-	-	-	507	90	Fail
70	461	90	Pass	518	90	Pass



b)

c)

Figure 25 : Behavior of duplex grades in brine solutions.
b) Influence of pH, salt concentration **(38)**
b) Influence of temperature / applied stress **(39)**
c) Influence of deformation and potential **(40)**
d) Effects of chlorides contents and PREN **(41)**



Obviously damages results from complex interactions between chemistry (higher PREN values preferred even if N effects seems weaker at temperature higher than 65°C), microstructure (avoid phase transformations), temperature (worst when increased!), local potential (avoid too oxiding conditions), level of oxygen, level of stresses SCC start in the micro plastic deformation zones)..,
As a result of extensive tests performed with a modified drop evaporation test that in the case of duplex 22Cr and 25Cr grades subjects to wetting by sea water (offshore platform).. that 70°C is the threshold temperature when local applied stresses are of the magnitude of 90% of the yield stress (at the temperature investigated) . Critical temperature for coating duplex products on offshore applications could than be revised! In most of the cases micro plastic deformations are observed and as a result design considerations and appropriate welding parameters are of key importance.
Of course in closed loops with control of the free oxygen, higher temperatures can be considered with save uses.

9.3 Pollution control equipments / FGD.

Extensive data concerning the behaviour of stainless steels in FGD scrubber conditions have been presented by J Peultier**.(42).** Guide map for material selection charts including chloride and fluorite contents, pH, temperature.. are provided. It is clearly confirmed that 2205 duplex grade behave much better than the 317LN grade and is to be considered in medium severe environments (up to 30000ppm Chlorides at 55°C and pH 6. The more corrosive conditions require superduplex grades preferentially with Cu additions (UNS 32520) or even 6Mo super austenitic grades (80°C applications).
For such applications Ni based filler materials have been successfully used to weld superduplex. J/ Peultier has provide a very extensive list of projects were the stainless steels and in most cases duplex alloys have been selected. Ron Richard's paper **(43)** clearly confirms Industeel R&D results since he report a 20 year success story by using 25Cu superduplex grade in Indiana power station.

55°C F-<50ppm pH	Chloride (ppm)					
	10000	20000	30000	40000	50000	60000
6		UNS 32205 UR45N				
5			UNS S32520 UR52N			
4				UNS S34565 UR B46		UNS S31266 URB66

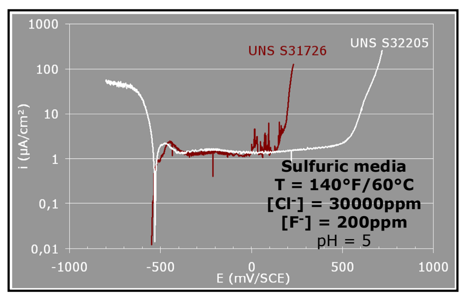
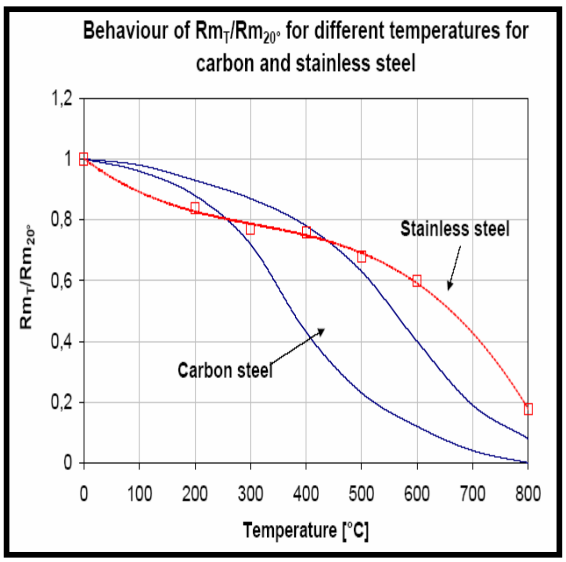


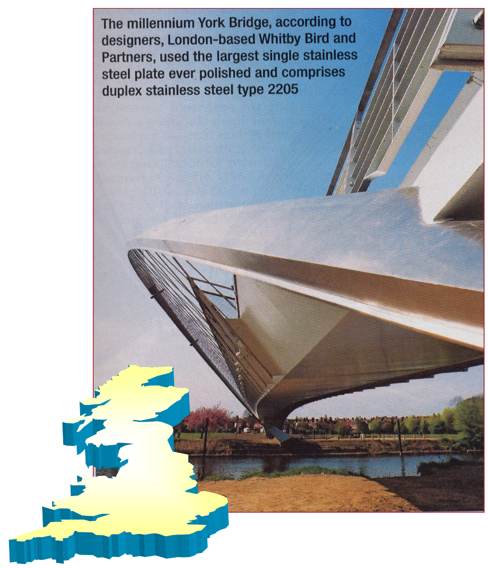
Figure 25 : Material selection chart for FGD scrubbers systems systems**.(42)**

9-4 Building and construction / bridges.

Due to their cost advantages when considering weight savings aspects (high mechanical properties) and maintenance cost savings (21/23%Cr providing more corrosion resistance than 304 grades) , lean duplexes are more and more considered for structural applications. Typically the Eiffel tower should have been build up from lean duplex (ex :2304). At least 30% weight savings, tons of painting, millions of hours for maintenance could be considered. The same story can be considered for the golden gate bridge of San Francisco but 2205 duplex should than be considered for marine environments purposes. Recently, the millennium bridge in York has been designed and builds with

2205 duplex. In front of Guggenheim museum in Bilbao a 2304 footbridge has been erected. Several Asian applications are also reported.
Reinforced duplex bars are now specified for corrosion free bridge even in marine environments. Duplex grade 2205 has show no pitting corrosion and a complete passive behaviour over more than 900mV polarisation (rel. to OCP) in Ca(OH)2 , pH 12.6, NaCl saturated solutions whereas austenitic steel with 2.5 Mo suffered from pitting. **(44,45)** The market for duplex reinforced bars is evaluated to millions of tons!
Experimental work has confirmed that duplex grades can be used in the most critical cases for design and construction (orthotropic deck/ Massina, Soreboelt bridges) Cost calculation for solid duplex bridges compared to carbon steel result in an increase of 20% of the erection and building costs (including the welds). **(46,47)** Savings are expected from lower maintenance costs.
More recent investigations confirm the advantages of stainless steel in fire conditions. Higher temperature can be considered without damages as well as more safety margins. Having 30 minute instead of 20 minutes to escape a building can make the difference! Once again duplex grades offer cost savings answers**.(48)**





Figures 26&27:
Evolution of mechanical properties with temp**.(48)**
York millennium bridge made out of 2205 duplex plates.

9.5- Other Applications:
Other interesting successful duplex applications have been reported at the Grado conference. For some of them 20/30 years of positive experience are available.
Pulp and paper industry is obviously one of them. Digester, pulp storage tanks, drums, bleaching equipments… paper machines are made out duplex. The uses of lean duplex are more and more considered for the less corrosive conditions. This includes the uses of lean duplex in liquor tanks and suction roll **(2,3,49).** Interesting machining properties for the lean 2101 duplex grade have been reported**.(50)**
Urea plant is a very specific market for duplex grades even having 50%ferrite! Specific grades have been developed for the urea-carbamate stripper and condenser. Austenitic 25Cr 22Ni 2Mo can be replaced by highly alloyed duplex grades**.(36,38)**

In the end, one of the most versatile and successful uses of duplex grades remain the chemical tanker applications. The 2205 alloy is now the standard grade, able to be considered to carry most of the chemicals**.(51)** For the less corrosive applications (barges) 2304 is now also considered.
In more complex chemical Industries, duplex stainless steels have also been considered. A key_note lecture covering the uses of superduplexes in organic solutions has been presented**.(52).**

FIG.28

FIG.29

FIG.31

FIG.30

Figure 28 : Chemical tanker.
Figure 29 : Pollution control equipments made out of UR 52N+ / UNS32520/ 2507Cu.
Figure 30 : Arco project
Figure 31 : Chemical tanker.

10- MISCELLANEUS.

Some authors which contributed to the Grado conference are not referenced in this paper. Please accept my apologise! I had no time to summarize all the work presented although the papers were of good quality. This concerns particularly the so-called complementary products which in reality are of key importance!

10- CONCLUSIONS.

The paper as outlined part of the tremendous high quality of the scientific contributions made at the Duplex '07 Grado conference, organised by the AIM. I would first present my gratitude for the work done by the whole team and more specifically to professor Nicodemi. It has been an honour for me to co chair with him the event.
Without doubt creativity is still there and new grades and applications are now emerging.
Among them the so-called lean duplexes targeting to replace austenitics 304 and 316. Ni price increase is the best argument to modify the habits! The cost savings start to be very attractive although more has to be done by stainless steel producers to reduce production costs and increase availability. More is also needed to clarify the real properties of each grade and optimise material selection. Among the lean duplex grades PREN value can move from 22 to 32**!(53)** Differences higher than that between 304 and 316 grades! Negative effects of very low Ni additions when considering crevice propagation and slight negative effects on pitting corrosion of Mn additions are reported in the literature. How behave lean duplexes in solutions containing small amount of chlorides in the 50/90°C temperature range? Are the grades totally immune to corrosion?

Without doubt when properly specified, the compromise between high strength, improved corrosion resistance and low alloying elements content must be a strong insensitive for success. Huge market applications are targeted and a two digit growth for duplex in the future is expected. If thin gauges are available, further strong increase of the demand s expected since most of the actual existing applications covers the heavy plate applications (> 6 mm.).
For the most critical conditions some "hyperduplexes" have been recently designed. They are considered for "niche" markets mainly in seamless applications.
After years, the positive advantages, on corrosion resistance but also and mainly on structure stability, of nitrogen applications has been confirmed. The newly developed duplex grades have nitrogen content more close to the solubility limit. No real negative effects on mechanical properties are reported. Improvements of the HAZ microstructure are even reported.
The newly designed duplex grades of the 2205 family presents improved microstructure stability making it possible to consider them for lower temperature applications (even -100°C for welded structures) and wider range of heat input can be considered.
Finally positive field experiences, of several decades, in most of the corrosive environments, concerning the classical 2205 and 2507 (Cu,W) grades have been presented and have confirmed the research work and convictions of the duplex pioneers.

REFERENCES:

1) J.CHARLES and S.BERNHARDSON, The duplex stainless steels: materials to meet your needs. Duplex Stainless Steels '91 Conference Beaune, France pp 3-48.
2) J.CHARLES, Why and where duplex stainless steels. Duplex Stainless Steel '97 Maastricht, the Netherlands, pp29-42.
3) J.CHARLES, 10 years later, obviously duplex grades in industrial applications look like a success story. Duplex conference 2000, Venezia, Italy pp 1-12.
4) O.DOBLE,T.HAVN, Lean Duplex Stainlss Steel for structural applications. Duplex'07, Grado, Italy.
5) J.CHARLES, Past, present and future of duplex stainless steels. Duplex'07, Grado, Italy.

6) JC GAGNEPAIN, P.SOULIGNAC, Why duplex usages will continue to grow? Duplex'07, Grado, Italy.
7) D.S.BERGSTROM,J.J.DUNN,D.R.HASEK, Benchmarking of duplex stainless steels vs. conventional stainless steel grades. Duplex'07, Grado, Italy.
8) B.HOLMBERG, M.LILJAS, Consequences on welding procedues when changing material from austenitic to duplex stainless steel. Duplex'07, Grado, Italy.
9) P FERRO, A.TIZIANI, F.BONOLLO, M.BULLA, Influence of post-welding heat treatments on corrosion properties of duplex and superduplex stainless steels – a comparison between furnace and induction heat treatment. Duplex'07, Grado, Italy.
10) V. Di COCCO, E.FRANZESE, F. IACOVIELLO, S.NATALI, Heat treatment influence on the crack propagation in a 25Cr 7Ni superduplex stainless steel. Duplex'07, Grado, Italy.
11) A.F.ARMAS,S.HERENU,S.DEGALLAIX?a;condo,F.LOVEY, Temperature influence on the cyclic behaviour of aged and unaged super duplex stainless steels. Duplex'07, Grado, Italy.
12) O.STRORZ,A.IBACH,M.POHL ,Morphology of sigma phase and its effects on the mechanical behaviour of duplex-steels. Duplex'07, Grado, Italy.
13) L.MAINES,A.MOLINARI,F.COLOMBARI,P.BURLANDO, The effect of slution annealing temperature on toughness and microstructure of a 329A duplex stainless steel. Duplex'07, Grado, Italy.
14) P.FERRO,R.CERVO,F.BONOLLO,R.BERTELLI, Set up and implementation of a numerical model of simulation of heat treatment of duplex stainless steels. Duplex'07, Grado, Italy.
15) J.O NILSSON,G.CHAI, The physical metallurgy of duplex stainless steel. Duplex'07, Grado, Italy.
16) I.CALLIARI,M.ZANESCO,E.RAMOUS,R.BERTEELLI, Microstructure and properties modifications after isothermal aging of a low nickel DSS. Duplex'07, Grado, Italy.
17)I.CALLIARI,E.RAMOUS,G.REBUFFI,M.ZANESCO,G.STRAFFELINI, Investigation on the secondary phases effects on a 2205 DSS, fracrure toughness. Duplex'07, Grado, Italy.
18) R.DAKHLAOUI,C.BRAHAM, A.BACZMANSKI, S.WRONSKI, K.WIERBANOSKI, E.C.OLIVER, Analyze Of phase's mechanical behaviour of duplex stainless steels by X-ray and neutron diffraction. Duplex'07, Grado, Italy.
19) M.G.MOSCATO, M.C.MARINELLI, S.DEGALLAIX,.I.ALVAREZ-ARMAS, Short crack initiation during low-cycle fatigue in UNS 32750 duplex stainless steel plate. Duplex'07, Grado, Italy.
20) S.SIEURIN, R;SANDSTRÖM, E.M.WESTIN,M.LILJAS, Fracture toughness of welded commercial duplex stainless steel. Duplex'07, Grado, Italy.
21) O.HECHLER,M.FELDMAN at al, Fatigue of welded details made of duplex stainless steel. Duplex'07, Grado, Italy.
22) L.WARD, B.GIDEON, D.CARR at al, Residual stress determination of duplex stainless steel welds and their susceptibility to intergranular corrosion. Duplex'07, Grado, Italy.
23) V.VIGNAL,D.KEMPF, H.PELLETIER, J.PEULTIER , Micromechanical behaviour of duplex stainless steels; effects of the microstructure on the surface microstrains and local stress-strain laws. Duplex'07, Grado, Italy.
24) F.FANICA, B.BONNEFOIS, JC.GAGNEPAIN ? Welding duplex stainless steels : recent improvements developments. Duplex'07, Grado, Italy.
25) M.SERRIERE, A.FANICA, B.BONNEFOIS, JC GAGNEPAIN, Mechanical and corrosion properties of superduplex UNS 32520 after PWHT. Duplex'07, Grado, Italy.
26) K.A.JOHANSSON, O.STRANDMYR, G.E.EIE, O.HAGERUP, 25 years with duplex, from Tommeliten to Gjoea. Duplex'07, Grado, Italy.
27) T.CASSAGNE, F.BUSSCHAERT, Experience with duplex stainless steels in oil and gas production. Duplex'07, Grado, Italy.
28) L.MARKEN, G.RORVIK, I.M.KULBOTTEN, Duplex and superduplex stainless steel in Norwegian petroleum industry. Duplex'07, Grado, Italy.
29) S.COELHO, I.ABUD, C.BARBOSA, R.CENTENO, Corrosion resistant alloys for ultra deep water petroleum production application. Duplex'07, Grado, Italy.
30) I.HANNAH, S.PATERSON, Reducing risk of hydrogen induced stress cracking (HISC) in duplex stainless steel for subsea applications. Duplex'07, Grado, Italy.
31) R.JOHNSEN, B.NYHUS, S.WASTBERG, New improved method for HISC testing of stainless steels under cathodic protection. Duplex'07, Grado, Italy.
32) EE.SKAVAS, S.KARLSEN, S.C.A. SEKNE, T.G.EGGEN, Crevice corrosion of 25Cr duplex tubes in subsea umbilicals. Duplex'07, Grado, Italy.
33) L.ROMMERSKICHEN, S.LEMKEN, R.HOFFMANN, Lean duplex grades as longitudinally welded pipes for linepipes in the oil and gas industry.. Duplex'07, Grado, Italy.
34) S.JACQUES, J.PEULTIER, P.SOULIGNAC, Desalination plants – why using duplex stainless steels. Duplex'07, Grado, Italy.
35) M.YAMASHHITA, S.MATSUMOTO, N.HIROHATA, Corrosion resistance and properties of duplex stainless steels. Duplex'07, Grado, Italy.

36) M.L.NYMAN, U.KIVISAKK, M.HOLMQUIST, K.GORANSSON,Performances of SAF2707HD (UNS32707) in severe chloride containing environments. Duplex'07, Grado, Italy.
37) P.STENVALL, M.HOLMQUIST, Weld properties of Sandvik 2707HD. Duplex'07, Grado, Italy.
38) Y.KOBAYASHI, N.KOIDE, Corrosion resistance of duplex stainless steels in hypochlorite solutions. Duplex'07, Grado, Italy.
39) G.HINDS,A.TURNBULL, Stress Corrosion cracking of duplex stainless steels in evaporative conditions. Duplex'07, Grado, Italy.
40) J.R.SAITHALA, J.D.ATKINSON, Stress Corrosion behaviour of duplex stainless steels in dilute chloride solutions at 130°C. Duplex'07, Grado, Italy.
41) J.R.SAITHALA,J.D.ATKINSON, Effects of temperature and chloride concentration on the pitting behaviour of zeron 100, 2205,and Ferallium alloy 255 duplex stainless steels. Duplex'07, Grado, Italy.
42) J.PEULTIER, J.C.GAGNEPAIN, P.SOULIGNAC, Duplex and superduplex stainless steel grades for wet desulfurisation systems. Duplex'07, Grado, Italy.
43) R.L.RICHARD, 20+ of successful FGD experience with superduplex (UNS32550)at the Gibson generation station. Duplex'07, Grado, Italy.
44) T.SOURISSEAU, E.CHAUVEAU, B.DEMELIN, C.BOURGIN, A comparison of the performance of 1.4362 and 1.4404 stainless steel grades for concrete reinforcement.
45) M.J. CORREIRA, M.M.SALTA, I.T.E.FONSECA, J.TELEGGDI, Corrosion resistance of duplex stainless steels in Ca(OH)2 saturated solutions. Duplex'07, Grado, Italy.
46) A.FANICA, E.MAIORANA, UNS S 32205 for bridge construction : an experience of application. Duplex'07, Grado, Italy.
47) G.ZILI, F.FATTRINI, E.MAIORANA, Application of duplex stainlesss steel for welded bridge construction in aggressive environment. Duplex'07, Grado, Italy.
48) R.BERTELLI, R.CRISTEL, Stainless steelfire resistance : low nickel DSS preliminary results. Duplex'07, Grado, Italy.
49) D.EYZOP,J.SJÖSTRÖM, O.KÄLLGREN, 304SRG : a growing market for paper mill suction rolls. Duplex'07, Grado, Italy.
50) C.BERGKVIST, J.OLSSON, machining in the new duplex grade LDX 2101-easier than expected. Duplex'07, Grado, Italy.
51) S.JACQUES, G.HAGI, "Tour Pomerol" chemical tanker : eight years experience with duplex EN 1.4462. Duplex'07, Grado, Italy.
52) A.J.INVERNIZZI, L.BENEDITTISS.P.TRASALTI, Corrosion behaviour of duplex SAF 2507 in aquous acid organic solutions. Duplex'07, Grado, Italy.
53) L.PEGUET, A.GAUGAIN, Pitting and crevice corrosion behaviour of ferritic and duplex stainless steels in hot chloride environments. Duplex'07, Grado, Italy.