A NEW EUROPEAN 200 SERIES STANDARD TO SUBSTITUTE 304 AUSTENITICS?

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Abstract

A new grade of the 200 series has been defined for the European market as a candidate alternative to austenitic grade EN 1.4301 (AISI 304). It has been designed for certain applications at the lower end of the corrosion resistance range of this reference material. A new chemistry has been proposed to ensure adequate properties as there had been disappointment in the European market with poorly defined imported products. The new grade is designed to reduce the nickel content (to min 4.5%) while still stabilising the austenitic phase with combined copper (min. 1%) and relatively low nitrogen and carbon contents. A minimum of 16.5% Cr combined with 0.1% N and 1% min. Cu provide the required corrosion resistance properties while copper additions make it possible to improve drawability. The grade was recently assigned a material number by VDEh (1.4618 – X9CrMnNiCu 17-8-5-2). The paper presents mechanical properties of the grade including drawability and corrosion resistance characteristics. Experimental data of the newly designed grade are compared to the existing 200 grades as well as to stainless steels of the 300 and 400 series. It is concluded that the newly designed grade has mechanical properties slightly superior to those of EN 1.4301 (AISI 304) and equivalent to those of EN 1.4310 (AISI 301) grade. In terms of corrosion resistance, the grade is close to that of grade EN 1.4301 (AISI 304), upgrading the classical 200 series.

Introduction

For more than 50 years manganese additions have been considered as a replacement of nickel in austenitic stainless steels. As a result, reductions in alloy surcharge, particularly at times of nickel prices peaks, can be expected. This has resulted in the development of the so-called 200 series. The grades are known to have complementary nitrogen additions in order to further stabilize the austenitic phase. Copper additions have also been successfully considered in order to provide a stable austenite. With copper additions, nitrogen additions can be reduced providing softer manganese austenitic grades.

The grades had only limited applications - with a few exceptions, such as India - until the end of the last century. They were selected mainly for their combination of high strength and ductility. More recently large amounts of type 200 stainless steels have been produced in Asia. The grades show modified chemical compositions – low chromium additions, extra low nickel additions ... – and in some cases high residual elements like sulfur which are known to have detrimental effects on localized corrosion resistance (pitting, crevice).

The lack of international standards and references for those grades has been pointed out recently. Grades in coils or finished products have been imported into Europe without clear references.

They are called equivalent to 304 regardless of their chemistry. In some cases they have been labeled 18-10 grades or even 300Mn series.

For a European 200 series to be viable, a certain amount of standardization was required. Providing technical information was made a priority to avoid misunderstandings and improper use of poorly defined type 200 stainless steels. There was an urgent need to avoid damage to the excellent image of stainless steels.

In order to fulfill these requests, a working group with representatives of the main European flat stainless steel producers was created under the umbrella of Euro-Inox. The main conclusions are presented in this paper.

History and current developments in the 200 series

The 200 series of stainless steels was developed in the early 1930s. Although the first chemical analyses investigated were of the 205 kind (Ni content close to 1% and stabilization of the austenitic phase by simultaneously high manganese and nitrogen additions - see figures 1 and 2), the first grades which received the AISI label in the mid-fifties were the 201 and 202 grades (Ni content around 4 to 6 % and nitrogen additions lower than 0.25 %). They became more popular out of the urge to conserve the nickel during the Korean War. In that time, nickel uses were mainly restricted to military applications. The Tenelon grade / AISI 214 grade with less than 2% Ni and about 0.35%N was produced at the end of the fifties. The Mn-austenitic grades containing Mo to improve the corrosion resistance properties appeared in the mid-sixties both in the US and Europe.

Simultaneously Mn and Cu containing grades were developed which made it possible to produce 4 to 6 %Ni austenitic grades (AISI 211 and 203) with relatively low nitrogen content (< 0.06 %). Equivalent drawing properties to 304 could be achieved. Due to a new Ni shortage phenomenon, the grades started to be popular in the early 70's. With the new AOD technology, nitrogen additions in the 200 series were made easier and more cost-effective (Table 1). Once again nickel shortage ended and with high availability, Ni prices went down again. For more than 30 years, grade 304 was the standard of the stainless steel family at an average yearly growth of 5 to 6%.

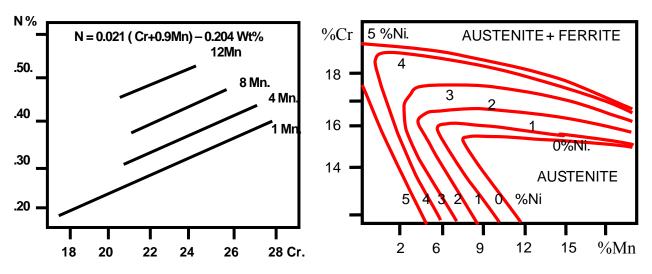


Figure 1. Effects of %Cr and %Mn on N solubility

Figure 2. Aust. stability at 1075°C (Franks)

The 200 series still had marginal applications in the eighties and nineties. With the new century, a new period of high volatility of nickel price started. Asia and particularly China became a major consumer of stainless steel. Part of the tonnage was produced locally, the remaining being imported mainly from India.

Туре	Standard	Cr	Ni	Mn	Ν	С	S	OTHERS
201	S20100	16.0 - 18.0	3.5 - 5.5	5.5 - 7.5	0.25MAX	0.15MAX	0.030MAX	-
201LN	S20153	16.0 - 17.5	4.0 - 5.0	6.4 - 7.5	0.10 - 0.25	0.03MAX	0.015MAX	Cu 1.0MAX
202	S20200	17.0 - 19.0	4.0 - 6.0	7.5 - 10.0	0.25MAX	0.15MAX	0.030MAX	-
204L	S20400	15.0 - 17.0	1.5 - 3.0	7.0 - 9.0	0.15 - 0.3	0.03MAX	0.030MAX	
	S20430	15.5 - 17.5	1.5 - 3.5	6.5 - 9.0	0.05 - 0.25	0.15MAX	0.030MAX	Cu 2.0 - 4.0
205	S20500	15.5 - 17.5	1.5 - 3.5	14.0 - 15.5	0.32 - 40	0.12 - 0.25	0.030MAX	
214	S21400	17.0 - 18.5	1.0MAX	14.0 - 16.0	0.35MIN	0.12MAX	0.030MAX	
216	S21600	17.5 - 22	5.0 - 7.0	7.5 - 9.0	0.25 - 0.5	0.08MAX	0.030MAX	Mo 2.0 - 3.0
	S24000	17.0 - 19	2.25 - 3.75	11.5 - 14.5	0.2 - 0.4	0.08MAX	0.030MAX	
	S32001	19.5 - 21.5	1.0 - 3.0	4.0 - 6.0	0.05 - 0.17	0.03MAX	0.030MAX	Cu 1.0MAX
	EN 1.4371	16.0 - 17.0	3.5 - 5.5	6.0 - 8.0	0.15 - 0.20	0.03MAX	0.015MAX	-
	EN 1.4372	16.0 - 18.0	3.5 - 5.5	5.5 - 7.5	0.05 - 0.25	0.15MAX	0.015MAX	
	EN 1.4373	17.0 - 19.0	4.0 - 6.0	7.5 - 10.5	0.05 - 0.25	0.15MAX	0.030MAX	

Table 1. Chemical analyses of different 200 series grades.

The continuous pressure to obtain low cost grades resulted in the development of cheaper stainless steels with lower and lower amounts of alloying elements such as nickel and even chromium. Due to low cost and sometimes less performing manufacturing routes grades with very high sulfur and carbon were sold on the market. Such productions moved from a marginal level to hundreds of thousands of tons. Typical 200 series chemistries including more recently developed grades are presented in Table 2. As observed some of the grades (X1, X2) have very low Cr and high sulfur contents.

Table 2. Typical chemistries of 200 series (X1, X2 samples issued from Asian market).

Country	Cie	Usual name	UNS	Cr	Ni	Mn	Cu	С	Ν	S (ppm)	Rp0.2	Rm	Mid
Europe	U&A	16-4Mn	S20100	16,3	4,1	6,5		0,09	0,16	40	400	770	39,99
	U&A	16-7Mn †	S20400	16	1,6	7,5	2,9	0,05	0,19	< 10	390	710	28,92
	KTN	H400		18	3,8	6,8		0,035	0,16	7	450	770	48,35
USA		Nitronic 30	S20400	16	2,5	8,5		0,02	0,17		390	830	101,8
		Nitronic 19D*	S32001	20	1,6	5	0,5	0,02	0,13		500	850	105,8
	Allegheny	219	S21904?	21	6	9		0,03	0,25		460	780	-114
S.Amer.	Acesita	P201A	-	15,2	1,1	9	1,7	0,1	0,1	<10	370	870	95,36
	Acesita	P202A	-	15,1	4	7,2	1,6	0,06	0,05	<10	310	730	71,87
	Acesita	P300A †	S20400	16,1	1,5	7,4	2,9	0,05	0,18	3	370	745	35,89
Asia	Jindal	J1	-	15	4	7	1,6	0,06	0,05	60	300	700	74,88
	Jindal	Л	-	16,1	4	7,1	1,7	0,06	0,07	31			46,85
	Jindal	J4	-	15,5	1	10	1,6	0,09	0,14	60	470	820	74,99
	Jindal	J4	-	15,9	1	9,7	1,6	0,1	0,15	82			62,73
	NTK	D10	-	17,5	4,8	3,7	2,8	0,06	0,15	10	355	675	-36,5
	X1	-	-	15	1,1	9,6	1,7	0,1	0,14	123			74,7
	X2	-	-	11,3	1,1	12,8	0,08	0,13	0,045	60			176,2

The new 200 European grade: 1.4618

The newly developed type 200 grade is designed to obtain an optimum compromise between cost reduction (lower nickel), high formability properties (reduced C, N additions but with Cu) and corrosion resistance properties as close as possible to 304 (16.5% Cr min; 4.5% Ni min). Table 3 presents the 1.4618 specification, which has been agreed by the main European stainless producers. The grade meets the 201-1 "rich side" of the AISI 201 specification. As observed, the grade can be considered as a "soft" representative of the 200 series. In the second half of 2007, more than 1,000 tons issued from industrial melts were delivered to European and American markets. Typical mechanical properties of those production lots are

presented in Table 4. The grade behaves like a 301 austenitic steel, i.e. mechanical properties (YS) are slightly higher than those of grade EN 1.4301 (AISI 304).

Table 3. VDEh 1.4618 specification.

Steel number	1.4618
Steel name	X9CrMnNiCu17-8-5-2
Chem. Composition in % by mass	$C \leq 0.10, Si \leq 1.00, Mn 5.50-9.50, P \leq 0.070, S \leq 0.010, Cr 16.50-18.50, Ni 4.50-5.50, Cu 1.00-2.50, N \leq .15$
YS 0.2% (MPa)	220
UTS (MPa)	520-850
El 80 % min.	40
KV 20 °C (Joules)	100

The composition of the grade starts from he requirements of EN 1.4372 and AISI 201. Copper addition is necessary for metallurgical reasons in order to obtain mechanical properties close to those of grade EN 1.4301 (AISI 304). Its mechanical properties are in accordance with the AISI 201-1 "rich side", but are too soft for the EN 1.4372 or AISI 201-2 "lean side". It will be included at the next revision of EN10088 under the number 1.4618 and for the time being certificates can be supplied from the mills according to ASTM A240 grade 201-1 and the agreement of the customer upon copper addition.

Table 4. ASTM and European Standard equivalences.

	UNS	Туре	С	Mn	Р	S	Si	Cr	Ni	N	Cu
ASTM A240	S20100	201	0.15	5.5-7.5	0.060	0.030	1.0	16.0-18.0	3.5-5.5	0.25	
EN 10088-2	1.4372	X12CrMnNiN17-7-5	0.15	5.5-7.5	0.045	0.015	1.0	16.0-18.0	3.5-5.5	0.05-0.25	
	1.4618	X9CrMnNiCu17-8-5-2	0.10	5.5-9.5	0.07	0.010	1.00	16.5-18.5	4.5-5.5	0.15	1.00-2.50
-											

0.03-0.065 5.6-6.4 0.035 0.0020

520-850

				UTS	min	YS	min	E%	min	Harc	In. Max	KV ep>	10 mm
	UNS	Туре		ksi	MPa	ksi	MPa	2" 50 mm	80 mm	HB	HRB	L	Т
ASTM A240	S20100	201-1 "rich side"		75	515	38	260	40		217	95		
		201-2 "lean side"		95	655	45	310	40		241	100		
EN 10088-2	1.4372	X12CrMnNiN17-7-5	С		750-950		350		45				
			Н		750-950		330		45			100	60

220

330

0.5 16.6-17.2 4.4-5.0 0.070-0.110 1.4-1.8

40

50

100

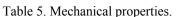
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1.4618	X9CrMnNiCu17-8-5-2	
	Typical values 2B	

1.4618 201.1 Cu

Mechanical Properties

Table 5. Mechanical properties.										
Producer	TEMP.	Thickness	Rp0.2	Rp1.0	Rm	A8)	r			
	°C.	mm.	Мра	Мра.	Мра	%				
	20	0.4	304		663	58	0.9			
ТК	20	0.5	309	660		55	0.87			
	20	2.5/4.5	345		653	50				
	20	1/2	318	351	652	50				
OUTOKUMPU	150	1	218	252	530	50				
OUTOROMPO	350	1	174	210	494	39				
	350	0.6	186	215	508	38				
	330	0.0	100							
ArcelorMittal	20	3	325		645	56	0.93			



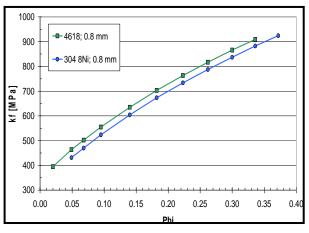


Figure 3. Rp0.2 versus cold reduction (3048Ni)

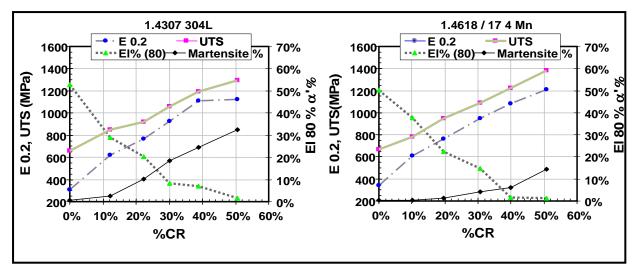


Figure 4. Austenitic stability and mechanical properties versus cold reduction.

When cold worked, grade 1.4618 has less α -martensite than grade EN 1.4307 (AISI 304L) for a given deformation. Mechanical properties remain very similar even if the 1.4618 grade shows slightly higher mechanical properties in the cold worked state, compared to EN 1.4307 (AISI 304L). Figure 5 illustrates that 1.4618 is a much softer grade than EN 1.4372 (AISI 201) whereas ferritic grade 1.4509 (441) behaves differently.

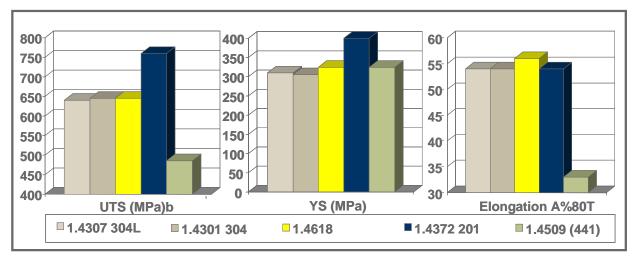
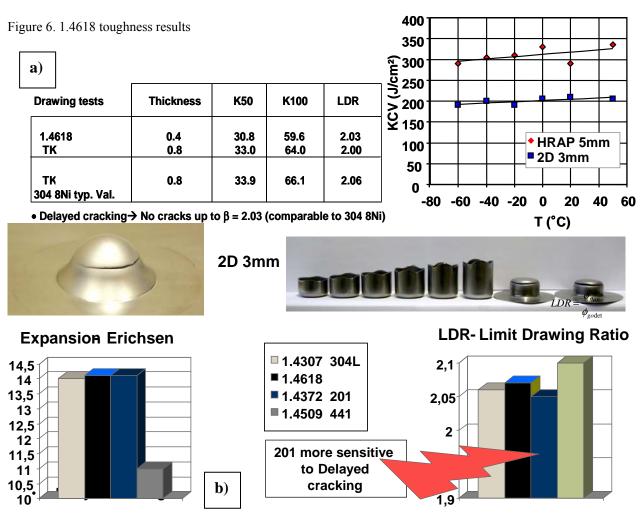
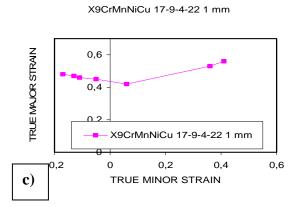


Figure 5. Room temperature tensile properties of several austenitic and ferritic stainless steels.



 \diamond no cracks (Swift cup b = 2.05); Bending test: No defect (bending radius 4 mm)



% FLD data - 705-1 Th : 1.0 mm						
% Width [mm]	Minor strain (e2)	Major strain (e1)				
20	-0,17	0,48				
40	-0,13	0,47				
60	-0,11	0,46				
100	-0,05	0,45				
120	0,06	0,42				
140	0,36	0,53				
200	0,41	0,56				

Figure.7. Formability results

Grade EN 1.4618 performs at least as well as grade EN 1.4307 (AISI 304L) in terms of formability. As for all austenitic structures, expansion properties are excellent. LDR values are improved when compared to the classic grade EN 1.4372 (EN201) grades. This is also the case for delayed cracking behaviour. Obviously the combination of minimum 1% Cu additions and optimum nitrogen content significantly improves the formability properties of grade 1.4618, when compared to the other 200 series grades.

Corrosion Resistance Properties

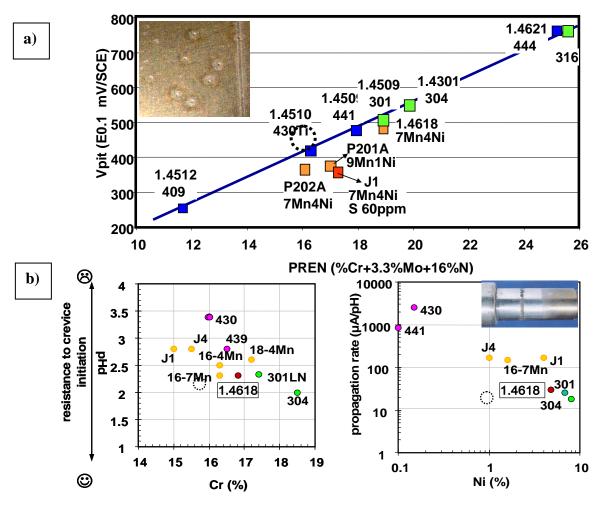


Figure 8. a) Pitting corrosion resistance properties (critical pitting potentia,pH = 7).b) Crevice corrosion resistance properties (pHd in NaCl 2M, T= 23°C sol.)

Pitting corrosion resistance of grade 1.4618 has been investigated by potentiodynamic curves performed in a 0.02M NaCl (23°C - pH 7) solution (Figure 8a). The grade behaves like grade EN 1.4310 (AISI 301), i.e. its pitting corrosion resistance is slighly lower that that of the austenitic grade EN 1.4307 (AISI 304L). This results from a slight reduction in Cr content partially compensated by N additions which enhance pitting corrosion resistance properties. Considering crevice corrosion resistance, grade 1.4618 again has equivalent properties to a EN 1.4310 (AISI 301) austenitic stainless, whose behavior is very close to that of grade EN 1.4307 (AISI 304L). Considering crevice corrosion propagation, Ni has a powerful effect in reducing the corrosion rate. At 4.5%Ni, the 1.4618 grade has much better properties than 1% Ni 200 series grades. For both pitting and crevice corrosion resistance, grade 1.4618 is the best performing grade among the 200 series grades investigated.

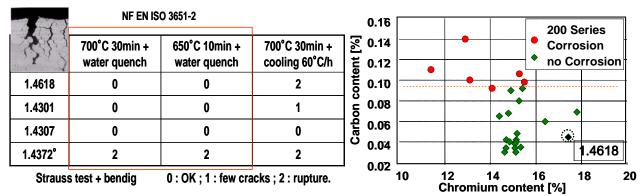


Figure 9. Intergranular corrosion resistance results. Beneficial effects of reducing C and N contents.

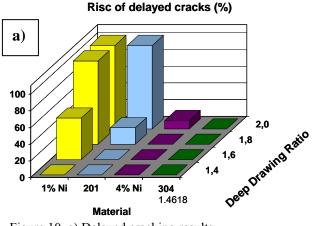
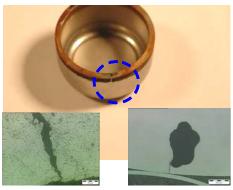


Figure 10. a) Delayed cracking results b) SCC tests on caps (salt spray tests).

Cap results after 1000 H Exposure –(ASTM B117) : Salt spray testsNbr of cup with cracks.

Grade	Drawing ratio	Nb. of cracks		
4 4204	1,83	0/3		
1.4301	1,94	0/3		
204000	1,83	0/3		
304DDQ	1,94	2/3		
1.4618	1,83	2/3		
	1,94	3/3		



b)

Intergranular corrosion resistance was investigated by means of Strauss tests followed by bending tests. Drastic improvements are observed compared to grade EN1.4372 (AISI 201). Reducing nitrogen and carbon contents improves the behavior of the steel. Only sensitising treatments at 700°C for 1 hour may induce intergranular cracks after Strauss test and bending operations. In those conditions even grade EN 1.4301 (AISI 304) is sensitised. In all testing conditions grade EN1.4372 (AISI 201) has the poorest behavior.

Delayed cracking properties are also markedly improved by this chemistry. The grade performs almost like grade EN 1.4301 (AISI 304). Salt spray tests performed on caps have shown, for the most critical areas, crack propagations for grade 1.4618 which are not observed for type EN 1.4301 (AISI 304) grades. Metallographic investigations have identified that mostly cracks initiate on corroded areas (small crevice; pitts,...). This is consistent with results presented earlier showing a slight decrease in localised corrosion when comparing grade 1.4618 to grade EN 1.4301/304L.

Weldability

	Without FM	Wi	th Filler Metal		
Welding process	Typical Thickness	Thickness	Filler Wire rod		Protective Gas
			wire roa	coil	
Spot welding Seam weld	< 2 mm < 2 mm				
TIG	< 1.5 mm	> 0.5 mm	ER 308 L (Si) W.Nr 1.4370 ER 347 (Si)	ER 308 L (Si) W.Nr 1.4370 ER 347 (Si)	Argon + 5 % Hydrogène Argon + Hélium
PLASMA	< 1.5 mm	> 0.5 mm	ER 310	ER 308 L (Si) W.Nr 1.4370 ER 347 (Si)	Argon Argon + 5 % Hydrogène Argon + Hélium Argon + 2 % C02
MIG		> 0.8 mm		ER 308 L (Si) W.Nr 1.4370 ER 347 (Si)	Argon + 2% 02 Argon + Hélium Argon +3%C02+ 1 %H2
S.A.W.		> 2 mm		ER 308 L ER 347	
Électrode		Repairs'	E 308 E 308 L E 347		
Laser	< 5 mm				Helium Restricted : Argon - N2

Table 6. Typical 1.4618 welding conditions.

Typical welding conditions for grade 1.4618 are presented Table 6. The grade behaves almost like grade EN 1.4301 (AISI 304). No specific welding parameters have to be used in most of the cases. EN 1.4301 (AISI 304) or EN 1.4310 (AISI 301) welding products may be used.

Conclusion

Extensive data of the newly designed 1.4618 grade have been presented. It is concluded that the grade for a 200 series grade has an optimum chemical composition to obtain mechanical and corrosion resistance properties equivalent to those of grade EN 1.4310 (AISI 301). Deep drawing properties can be obtained without significant sensitivity to cold cracking phenomena. The grade has a weld ability equivalent to those of grade EN 1.4301 (AISI 304). The grade is designed to offer to end-users a 200 series grade able to replace 304-like grades in a wide number of cases. Nevertheless, for the most severe conditions, 1.4618 grade is slightly more sensitive to corrosion phenomena than 304 grade.

The grade has been jointly developed with ArcelorMittal Stainless, ThyssenKrupp Stainless, Outokumpu and Acerinox under the umbrella of Euro-Inox.

Acknowledgements

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