High ductility low-nickel duplex stainless steel for lighter transport vehicles

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Among 19-21% Cr, low-nickel, manganese and copper added 50% α-50 % γ duplex stainless steel compositions, tensile ductility proved to be optimum (~ 45 % elongation) when austenite phase is thermally stable at room temperature and at a given level of instability during cold working: 10% conversion of initial austenite to α'-martensite per 0.1 deformation (mean rate). A selected alloy, 0.020C - 0.5Si - 3.7Mn - 0.9Ni - 19.8Cr - 0.4Cu - 0.150N is insensitive to embrittlements by sigma-phase or spinodal α–α' decomposition. High tensile properties (450 MPa Y.S., 660 MPa T.S., 45%EL) are obtained after annealing; the alloy is hardenable by temper-rolling, leading to the same levels of elongation, at a given level of Y.S., as austenitic AISI 301L (EP 1-4318) stainless steels. TIG welding under argon + 3% N_2 produces a duplex (35% γ - 65%α) weld with tensile, bending, and biaxial stretching properties equivalent to base annealed strip. Corrosion resistance (pitting, ...) is slightly better than that of AISI 304. This alloy should be well fitted to structural applications such as railway carriages, bus frames, car bodies, ... allowing significant weight gains.

INTRODUCTION: DUPLEX STAINLESS STEELS, A NEED IN TRANSPORT VEHICLES

Transport vehicles, such as railway carriages, bus frames, are often made of stainless steel, mainly because of the large gap between S.S. and carbon steels, in respect to corrosion and durability.

Ferritic S.S. such as 1-4003 or 1-4589 offer a moderate resistance to corrosion and structures often need to be painted, to save the initial aspect ; their mechanical properties are roughly equivalent to those of structural carbon steels.

Austenitic S.S such as 1-4318 (301L) or 1-4371 (201L) don't need painting and may be temper-rolled to different tensile levels, such as 450 MPa YS/45% El, 800 MPa YS/25% El, 1200 MPa YS/12%El ....., according to the difficulty of cold-forming operations and to the level of remaining ductility required for shock-absorption.

A comparison with carbon steels in a yield stress versus elongation diagram (figure 1) clearly shows the advantage of austenitic SS for weight saving, if Y.S. is considered to dimension the structure for a given necessary level of cold ductility, Y.S. being also in direct relation with the endurance limit.

However, austenitic SS suffer from their expensive high-nickel content ; temper-rolling hardening is eliminated from HAZ of welds, which may become the weakest places, so that some of the weight advantage of temper-rolled austenitic SS cannot be used.

Highly alloyed duplex stainless steels, such as 1.4462 (UNS-S31803) containing 22Cr - 5,5Ni - 3Mo - 0,140N have been proposed or studied for static building [1] [2] and transport industry [3] [4] [5].

Despite the advantage of a high T.S., their development is probably slowered by the cost induced by the high nickel and molybdenum levels, and by the difficulties due to sensitivity to embrittlements by sigma phase or α–α' spinodal ferrite decomposition at medium temperature.

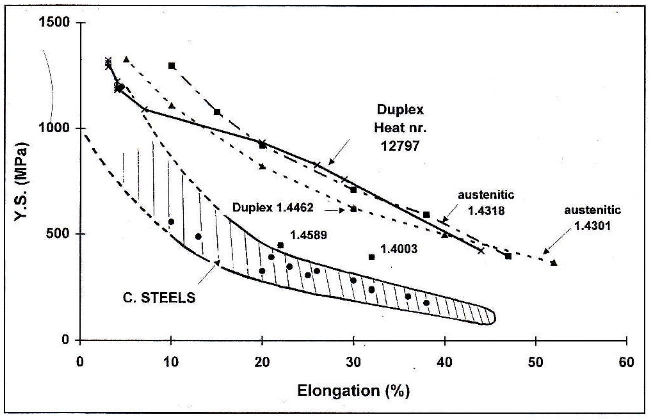

Fig. 1 - Yield stress vs elongation.

Fig. 1 - Tensione di snervamento vs. allungamento.

Low-nickel duplex stainless steels as NITRONIC 19D [6] have been proposed for car modular frames, especially as cast parts [7] ; when hot and cold-rolled, their tensile properties [6] are a bit lower than those of 1.4318 austenitic SS, compared at the same elongation potential.

For building light structures, the best would be a duplex stainless steel, in which welds with high tensile resistance may be obtained, with a higher tensile ductility than the existing ones.

The following experimental program was launched to reach this goal.

EXPERIMENTAL PROCEDURE

Heats, hot and cold working

13 laboratory 25 kg heats were cast (table 1).

They contain 18.9 to 21.3 Cr, .033 max C, signifiant variations in Si (0.5 to 1%), Ni (0.5 to 0.9%), Cu (0.04 to 0.9%), nitrogen (0.130 to 0.170%) and Mn (3.7 to 4.1%). After reheating at 1240°C, they were forged in 50 x 50 mm bars, reheated to 1240°C and forged in 20 x 120 mm flat bars or

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heat nr. / mass	12640	12639	12638	12637	12729	12731	12758	12757	12760	12794	12797	12855
C %	0.033	0.031	0.025	0.028	0.030	0.030	0.033	0.032	0.033	0.030	0.019	0.023
Si %	1.05	0.48	0.52	0.54	1.06	1.10	0.49	0.57	0.54	0.51	0.49	0.50
Mn %	4.07	3.79	3.75	3.72	3.89	3.99	3.82	3.85	3.76	3.87	3.73	3.86
Ni %	0.82	0.81	0.81	0.09	0.82	0.82	0.84	0.53	0.84	0.83	0.87	0.62
Cr %	21.2	20.7	19.9	18.9	21.2	20.2	19.9	19.0	19.9	19.9	19.8	19.3
Mo %	0.037	0.036	0.036	0.035	0.211	0.212	0.206	0.211	0.209	0.201	0.209	0.202
Cu %	0.39	0.39	0.39	0.04	0.40	0.40	0.38	1.02	0.33	0.41	0.40	0.948
P %	0.018	0.017	0.018	0.017	0.017	0.017	0.016	0.018	0.016	0.013	0.016	0.015
N2 %	0.170	0.136	0.150	0.132	0.167	0.166	0.143	0.155	0.136	0.145	0.147	0.159
V %	0.103	0.097	0.094	0.091		0.072	0.081	0.078	0.860	0.068	0.076	0.092
Al ppm					100	100	70	70	70	50	90	100
S ppm	37	35	35	34	6	4	12	10	10	10	8	5
B ppm									14	20	13	16
O2 ppm										44		62
Ca ppm										24	33	23
Ti ppm										100	60	

Table 1 - Laboratory heats.

Tab. 1 - Temperature delle prove di laboratorio.

Heat Nr	Initial austenite %	Y.S. MPa	T.S. MPa	Elongation at rupture EL %	ε homog. (*)	Part of austenite converted to martensite % (*)	Conversion rate % / ε = 0.1
12637	42	433	855	24	0.20	78	39
12638	52	501	817	43	0.32	52	16
12639	41	471	714	40	0.29	12	4
12640	43	520	773	33	0.22	0	0
12729		479	735	33			
12731	42	484	737	36	0.21	2	1
12757	53	473	800	45	0.34	43	13
12758	44	454	718	45	0.30	25	8
12760		465	786	46			
12794	46	456	732	47	0.31	35	11
12797	41	439	697	45	0.31	32	10
12855	49	456	733	44	0.32	33	10
(*) : ε homog. = rational deformation at Fmax							

Table 2 - Tensile test results.

Tab. 2 - Risultati delle prove di tensione.

16 mm octogons. 20 x 120 mm flat bars were ground to 18 x 120 mm, reheated to 1240°C and hot rolled to 2.2 mm thick hot-bands in 5 passes (intermediate reheating at 8 mm), with exit at 600-700°C and air-cooling. After annealing 1 mn at 1100°C in salt bath, air-coooling and pickling, the bands were cold-rolled on a laboratory mill into 1 mm - thick strips, each pass starting at room temperature. Strips were annealed at 1040°C (1 mn) in salt bath and air-cooled.

2.2 Sample examination and testing

Magnetic phase content was measured by saturation magnetization using a SERMAG 35-13M sigmameter. Reference specific magnetization (for a 100% ferro-magnetic structure) was calculated by a formule readjusted from [8]:

$$4_{\pi}I_S = 2.17 - 0.0275 \times Cr\% - 0.033 \times Ni\% - 0.026 \times Mo\% \\ - 0.061 \times Si\% - 0.060 \times V\% - 0.026 \times Mn\% \\ - 0.023 \times Cu\% - 0.12 \times C\% \quad \text{(Tesla)}$$

Magnetic phases may be ferrite and martensite, either «quenched» or generated during cold-working of austenite. Metallographic structures were revealed by Beraha (HCl + $K_2 S_2 O_5$) etching or by a modified Villela etching, containing 10 g/l picric acid: martensite platelets appear among austenite islands in some of the annealed specimens.
Room temperature mechanical testing was done on flat ISO 12,5 x 50 specimens in quasi static usual speed.

HIGH TEMPERATURE PHASE EQUILIBRIUM

Ferrite contents were evaluated, on hot-rolled specimens after the following treatments in salt bath (water-quench) : 40 mn at 1000°C ; 30 mn at 1050°C ; 20 mn at 1100°C ; 15 mn at 1200°C ; 10 mn at 1280°C. Figure 2 shows a usual decrease of ferrite content as equilibrium temperature decreases. After cold-rolling and annealing at 1040°C, the duplex structures contain 45 to 60% ferrite (table 2).
Microstructures (figure 3) exhibit banded areas of austenite, containing, for heat nr 16637, a significant amount of martensite platelets (figure 3a) ; other heats contain no or only traces of martensite.

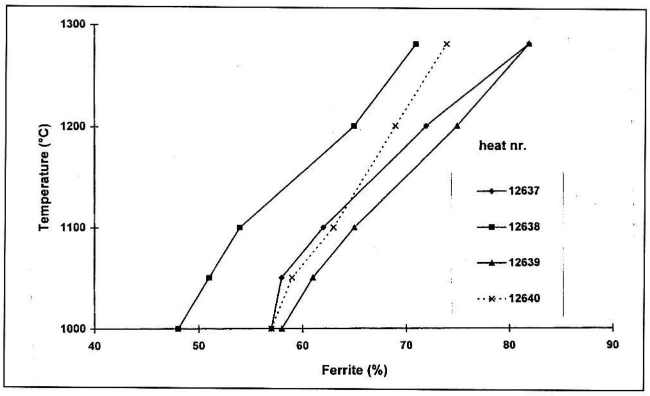


Fig. 2 - Ferrite content at high temperature.

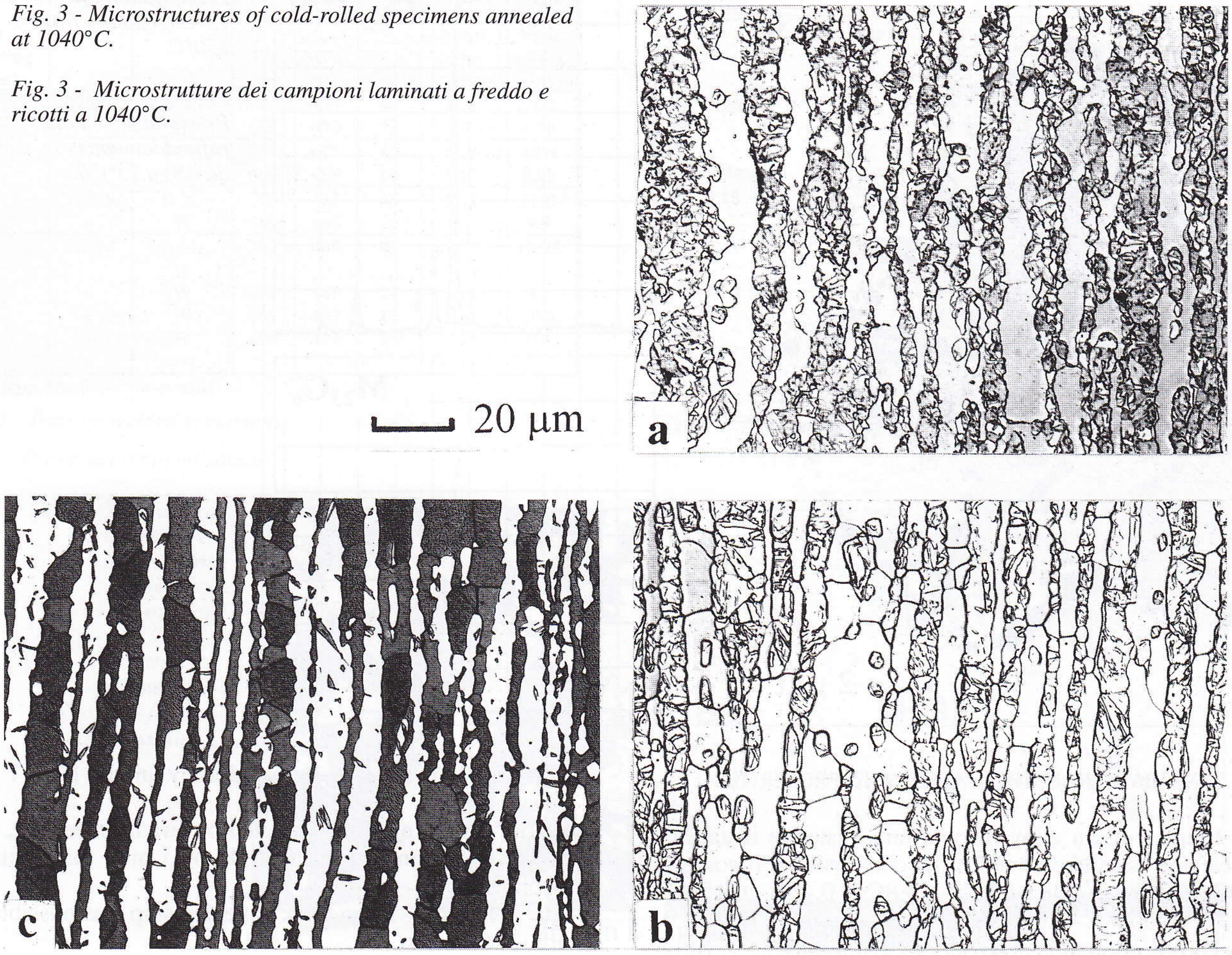
Fig. 2 - Contenuto di ferrite ad alta temperatura.

TENSILE PROPERTIES

Room temperature tensile properties are reported in table 2 . Elongation at rupture varies widely (24 to 47%), without so

Fig. 3 - Microstructures of cold-rolled specimens annealed at 1040°C.

Fig. 3 - Microstrutture dei campioni laminati a freddo e ricotti a 1040°C.



large variations of Y.S. (430 to 520 Mpa) or T.S. (700 to 850 Mpa).
Martensitic transformation during cold deformation was measured by magnetic measurement of the homogeneously deformed part of the specimen, and comparison with the initial value, from which the part of austenite converted to martensite, in % of initial austenite, is established (table 2). The austenite to martensite mean conversion rate is then obtained by dividing by the rational homogeneous deformation (table 2). It varies from 0 to 39% (per ε = 0.1).
Figure 4 describes the relation between tensile characteristics and the martensite formation rate. Optimum elongations, of about 45%, are obtained when the conversion rate is about 10% (per ε = 0.1).

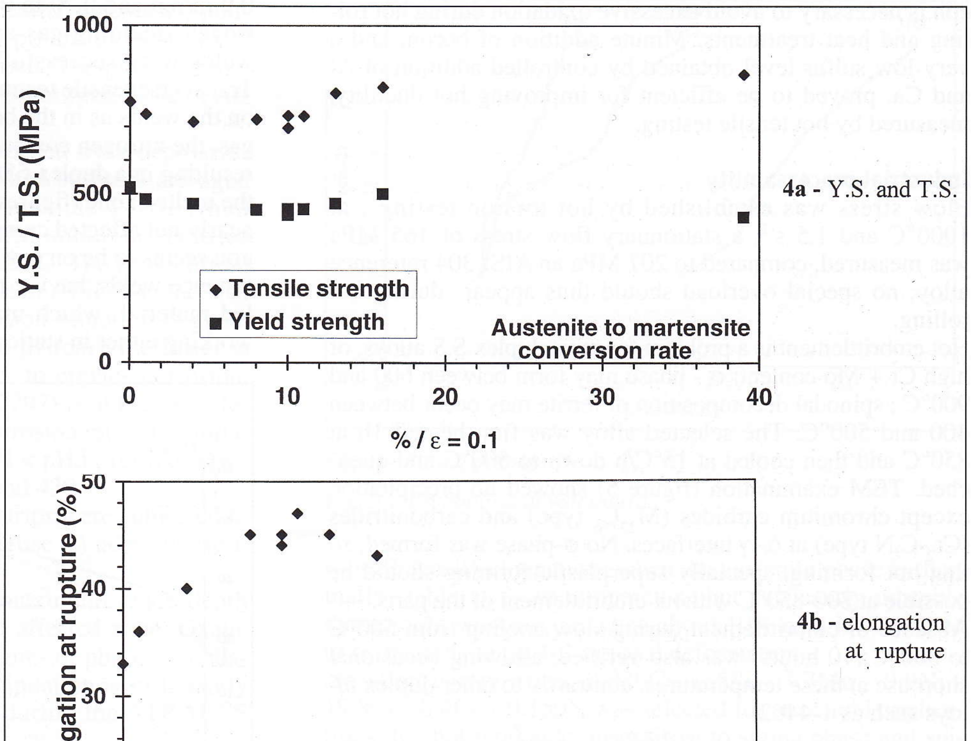


Fig. 4 - Tensile properties vs austenite to martensite conversion rate.

Fig. 4 - Proprietà di tensione vs. rate di conversione da austenite a martensite.

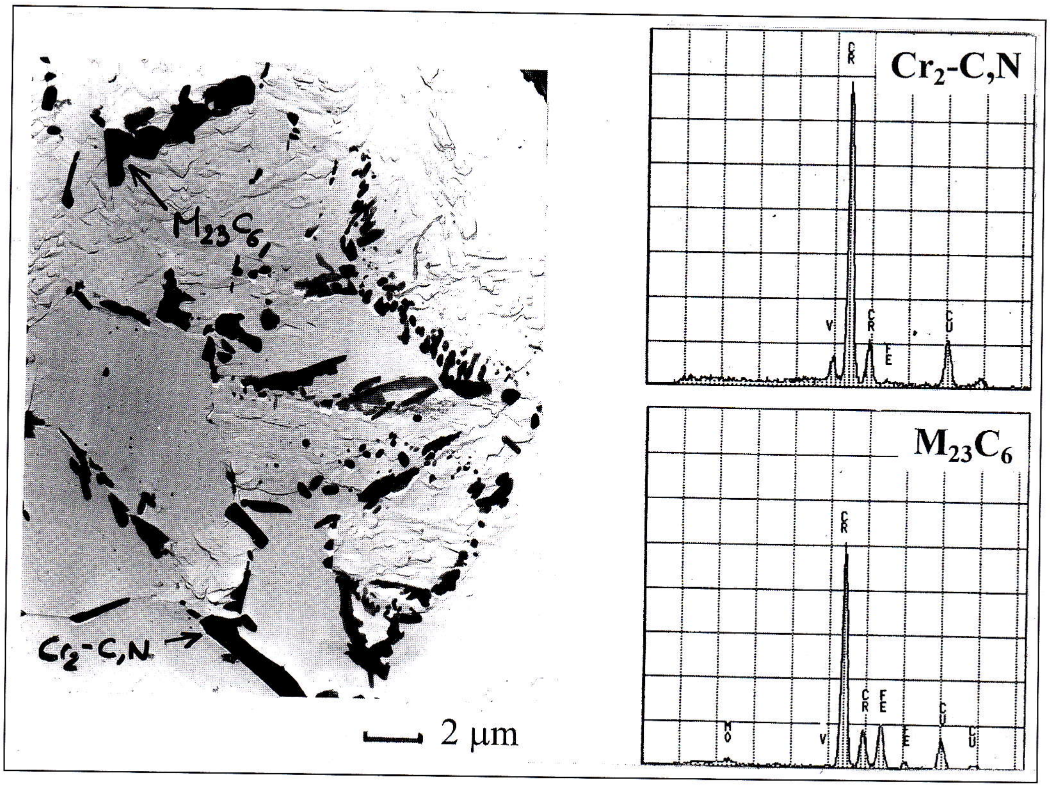


Fig. 5 - Precipitation after 15°C/h cooling from 850°C.

Fig. 5 - Precipitazione dopo raffreddamento da 850 a 15°C/h.

CANDIDATE INDUSTRIAL ALLOY AND PROPERTIES

From figure 4-b, an alloy of optimum austenite instability was selected as candidate industrial composition. It contains 0.020C - 0.5Si - 3.7Mn - 0.9Ni - 19.8Cr - 0.4Cu - 0.150N - 0.0013B - 0.0008S - 0.009Al - 0.0033Ca (heat nr 12797).

A low carbon content is necessary to avoid interphase carbide precipitation and sensitization. A small quantity of nickel is generally usefull for resistance to crevice corrosion. Silicon is necessary to avoid excessive oxidation during hot rolling and heat treatments. Minute addition of boron, and a very low sulfur level obtained by controlled addition of Al and Ca, proved to be efficient for improving hot ductility, measured by hot tensile testing.

Industrial processability

Flow stress was established by hot torsion testing ; at 1000°C and 1.5 s^{-1}, a stationnary flow stress of 165 MPa was measured, compared to 207 MPa an AISI 304 reference alloy; no special overload should thus appear during hot rolling.

Hot embrittlement is a problem for most duplex S.S alloys, of high Cr + Mo content: σ - phase may form between 600 and 900°C ; spinodal decomposition of ferrite may occur between 400 and 500°C. The selected alloy was first heated 1h at 850°C and then cooled at 15°C/h down to 500°C and quenched. TEM examination (figure 5) showed no precipitation except chromium carbides ($M_{23}C_6$ type) and carbonitrides (Cr_2-C,N type) at α–γ interfaces. No σ-phase was formed, so that hot forming, specially superplastic forming should be possible at 800-850°C without embrittlement of the parts.

Absence of embrittlement during slow cooling from 500°C to 300°C (10 hours) was also verified, allowing occasional short use at these temperatures, contrarily to other duplex alloys such as 1-4462.

Alloy final properties

Formability. Tensile properties of annealed and cold-rolled specimens are found in the temper-rolling curve (figure 6); and positionned in a Y.S. vs elongation diagram (figure 1), where the curves of the selected alloy and of 1-4371 are at the same level.

Biaxial stretching was evaluated by Erichsen testing, resulting in 10.95 mm Erichsen height on 1 mm- thick annealed specimens.

180° bending of 1 mm thick annealed ship was possible on a radius of 1 mm.

Welding. 1 mm-thick annealed strips were TIG-welded at 0.9 m/mn and 0.70 to 0.76 KJ/cm with argon + 1 to 5% nitrogen shielding gas and pure argon back protection. All welds were successfully bent to 180° on a 1 mm radius. Transverse tensile testing gave nearly the same Y.S. and T.S. on the welds as in the base metal (table 3). For 3% N_2 in the gas, the nitrogen content of the weld is increased to 0.160%, resulting in a duplex 65% ferrite - 35% austenite structure in the melted zone (figures 7 and 8a) and the Erichsen height is nearly not affected compared to the base metal. 3% N_2 in argon seems to be on optimum value to obtain ductile high resistance welds, having the same yield strength as the annealed material, which may be relevant for many structures working either in static or dynamic conditions.

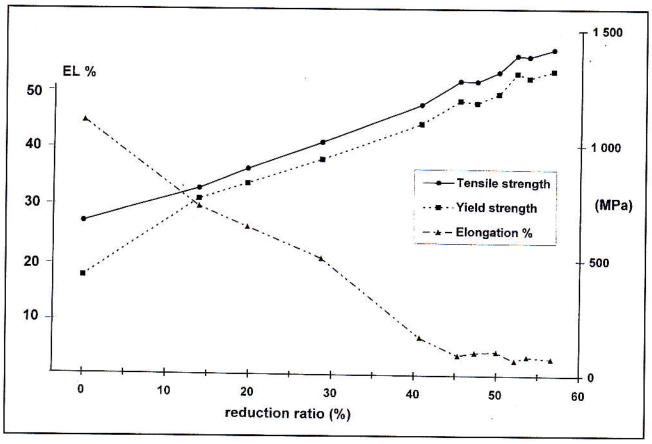


Fig. 6 - Tensile properties of cold-rolled specimens.

Fig. 6 - Proprietà di tensione di campioni laminati a freddo.

% N_2 in shielding gas	heat nr	position	T.S. MPa)	Y.S. MPa)	EL %	Erichsen height	
						front (mm)	back (mm)
2	12638	B.M.	800	479	43	11.2	11.2
	«	W	655	470	13	9.3	8.75
2	12758	B.M.	774	467	45	11.0	10.8
	«	W	665	460	13	8.45	8.85
2	12760	B.M.	786	465	46	11.0	10.8
	«	W	700	465	20	9.4	9.5
	12794	B.M.	730	460	45	10.95	10.95
1	«	W	680	460	17	9.15	9.2
3	«	W	661	457	12	10.9	10.6
5	«	W	695	475	15	9.25	9.3

B.M. = Base Metal - W = weld

Table 3 - Tests on welded specimens.

Tab. 3 - Prove su campioni saldati.

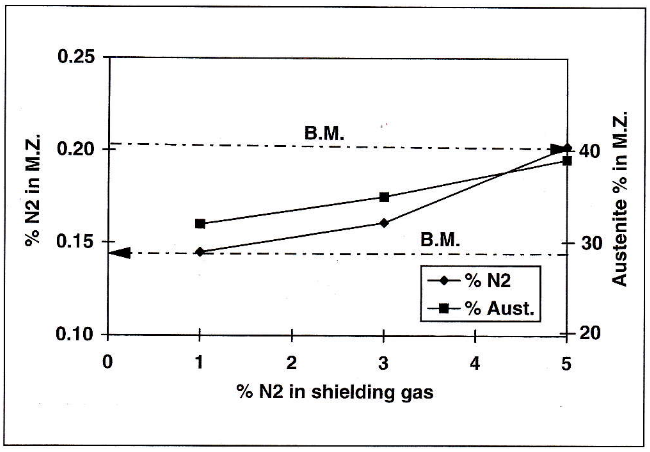


Fig. 7 - Effect of N_2% in shielding gas.

Fig. 7 - Effetto di N_2% in gas schermante.

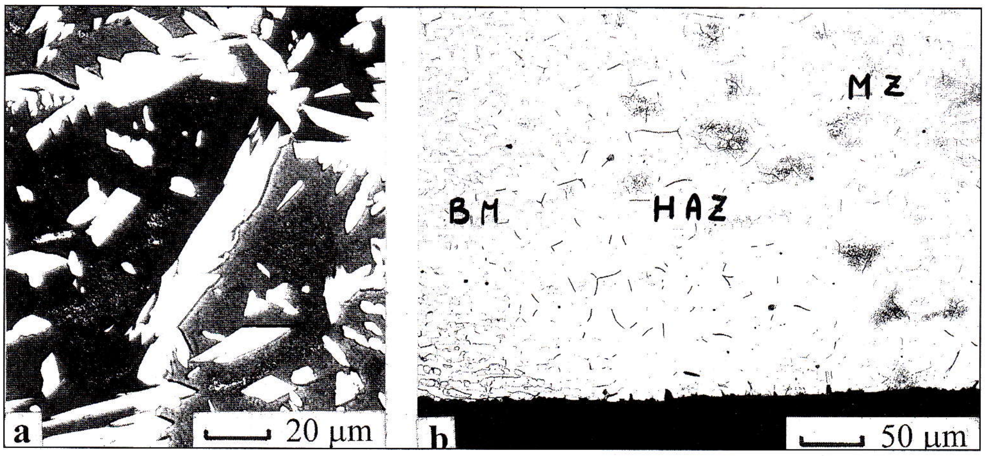


Fig. 8 - TIG welded microstructures 8a - melted zone (Beraha) 8b - HAZ (oxalic).

Fig. 8 - Microstrutture saldate TIG: 8a - zona di fusione 8b - HAZ (ossalico).

Corrosion resistance. Pitting resistance was evaluated in NaCl 0.5M, pH 6.6 at 23°C on annealed specimens, polished with grit-1200 SiC paper. A potentiokinetic (100 mV/mn) statistical method [9] was used. The pitting probability of the selected alloy (figure 9) is between those of AISI grades 304 and 316L.

Crevice corrosion resistance is approched by a depassivation pH method [9]: grit-1200 polished surfaces are aged 24h in air. A potentiokinetic testing (scan rate = 10 mV/mn) is performed in a deaerated NaCl-2M solution, acidified with HCl 0.1M and thermostated at 23°C. The peak current (i_{crit}) vs pH curve is compared to those of AISI 304 and AISI 430. The resistance to crevice corrosion initiation is given by the depassivation pH (pHd) at 10 µA/cm^2; the lower is the pHd, the higher is the resistance to crevice corrosion. The selected duplex alloy (heat nr 12797) is at the same level of pHd as 304 (figure 10). The corrosion rate after initiation is in relation with the slope at pH < pHd ; for the selected alloy, it is between those of 304 and 430.

TIG-welds on 1 mm-thick annealed strips were subjected to a " STRAUSS " (ASTM A262 - practise E) corrosion test. No cracks are seen after bending.

After further transverse polishing, maximum crack depth was evaluated to 20 µm, in the heat affected zone. Oxalic electrolytic reveals a few grooved grain - or phase- boundaries in the H.A.Z. (fig. 8b) ; this precipitation is sufficiantly discontinuous to avoid deep atack during the STRAUSS corrosion test.

CONCLUSIONS

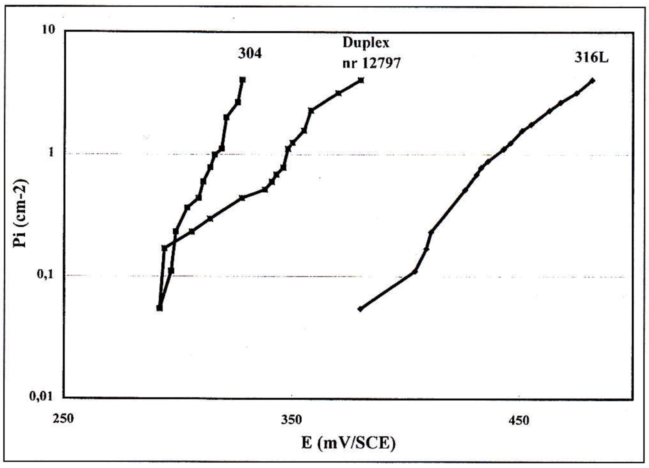


Fig. 9 - Pitting probability.

Fig. 9 - Probabilità di vaiolatura.

Several low nickel manganese added duplex stainless steel compositions were studied. Ductility proved to be optimum (≈ 45% tensile elongation) when the austenite phase is thermally stable at room temperature but suffisantly unstable during cold working, i.e when about 10% of it is converted to α' martensite per 0.1 rational deformation.

An alloy composition, 0.020C - 0.5Si - 3.7Mn - 0.9Ni - 19.8Cr - 0.4Cu - 0.150N was selected for structural applications. It's hot-workable, insensitive to sigma phase and spinodal decomposition embrittlements, hardenable by temper-rolling. Typical tensile properties are, when annealed, 450 Mpa Y.S., 660 Mpa T.S., 45% EL, and, when cold-worked, 930 Mpa Y.S., 1010 Mpa T.S., 20% EL. or 1200 Mpa Y.S., 1320 Mpa T.S., 4% El. Y.S. vs elongation is as hi-

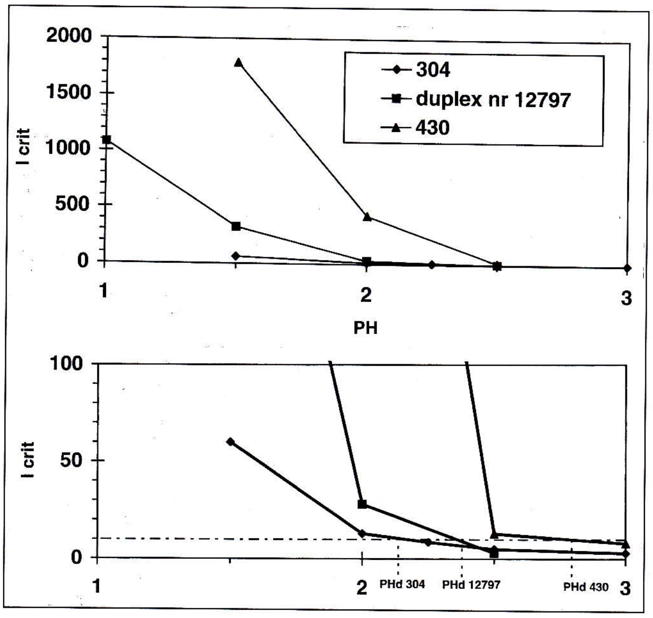


Fig. 10 - Crevice corrosion evaluation.

Fig. 10 - Valutazione della corrosione interstiziale.

gh as for 1.4318 (AISI 301L) austenitic steel and higher than for usual duplex stainless steels.

The alloy may be TIG - welded, best under argon + 3% nitrogen; the weld assembly has as high tensile and formability properties as the base annealed metal, which may be useful for structural building.

Corrosion testing proved the alloy to be more resistant to pitting than 304; it also performs good corrosion resistance in crevice; its TIG-welds are resistant to intergranular corrosion, according to the STRAUSS test (ASTM A 262-E).

This low-nickel duplex stainless steel may be a good candidate for substituting 1-4318 (301L) or 1-4371 (201L) austenitic alloys for building lighter structures such as railway carriages, car modular frames, bus frames.

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ABSTRACT

ACCIAI INOSSIDABILI DUPLEX A BASSO TENORE DI NICHEL ALTAMENTE DUTTILI PER AUTOVEICOLI PIÙ LEGGERI

Per le strutture dei veicoli da trasporto, come i "frame" dei vagoni ferroviari, degli autobus o gli "space frame" delle automobili, è stata sviluppata una nuova classe di acciai che presenta un'alta resistenza allo snervamento, elevata duttilità, buona saldabilità e proprietà meccaniche equivalenti sia nel materiale di base che in quello saldato.

E' stato dimostrato che una gamma di leghe contenenti 18-22% Cr, 2-4% Mn, 0,1-1% Ni, 0,05-4% Cu, 0,4-1,2% Si, 0,1-0,3% N calibrate per ottenere, dopo ricottura a 1000-1150°C, una struttura bifasica ferritico-austenitica (circa 50%-50%) mostra un massimo allungamento quando l'austenite, mediante deformazione a temperatura ambiente, può essere trasformata in martensite nella giusta proporzione, in un range fissato secondo un indice di stabilità dell'austenite.

Per un ulteriore approfondimento è stata selezionata una lega 0,020C-0,5Si-3,8 Mn-0,8Ni-19,8Cr-0,4Cu-0,150N. Dopo ricottura a 1040°C questa ha mostrato un resistenza allo snervamento di 460 MPa, una resistenza alla rottura di 750 MPa e un allungamento del 45%; la lega può essere trattata fino a ottenere 950 MPa di snervamento (1010 MPa di rottura) con un allungamento del 20%; ciò apre la strada per applicazioni altoresistenziali (di elementi strutturali, tubi, shells) con sufficiente duttilità residua, specialmente indicata per i veicoli da trasporto (vagoni ferroviari, autobus, automobili, serbatoi trasportabili...)

La saldatura TIG con Argon + Azoto si è dimostrata efficiente. Le saldature mostrano una struttura bifasica austenitica-ferritica con limitato aumento dei grani ferritici ed elevata resistenza allo snervamento (460 MPa) e senza alcuna significativa perdita di duttilità alla prova Erichsen. Ciò è importante per la formabilità dei tubi saldati e per la resistenza delle strutture saldate. La lega selezionata non è sensibile a infragilimento da fase sigma o precipitazione intermetallica, anche dopo diverse ore di esposizione a temperatura fra i 500 e gli 850°C.

La resistenza alla corrosione è assicurata dai livelli elevati di cromo e bassi valori di solfuri. Le saldature sono esenti da sensibilizzazione dei carburi di cromo per precipitazione.

Grazie alla migliore posizione rispetto agli acciai al carbonio in un diagramma Resistenza allo snervamento vs. Duttilità, la lega selezionata dovrebbe essere un buon candidato per la costruzione di strutture con buone proprietà di resistenza alla corrosione, di leggerezza e resistenza all'urto.