INVESTIGATION ON LOW NI DUPLEX STAINLESS STEEL GRADES

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Abstract

Different stainless steels (SS) can provide a very wide range of mechanical properties with the advantage of no need for surface protection. Duplex stainless steels (DSS), in particular, with twice the mechanical strength of conventional austenitic and ferritic SS, have a potential use in constructions. The DSS grades have been improved and, parallel with development towards higher grades for corrosive conditions, there is a great interest in leaner composition. A useful way to reduce the cost is to reduce the Ni content and to compensate with manganese and nitrogen additions. In the present paper the structural and mechanical properties of two low Ni duplex grades are compared in order to investigate the structural stability of the austenite as it may convert to martensite and the secondary phases precipitation. The detailed characterization has been performed with SEM-EDS and Charpy test on as received and on thermally treated (600-850°C) specimens. A few precipitates of chromium carbides and nitrides at the grain boundaries have been detected in both grades. The martensite structure has been noted only in 2101 type DSS. As concerns the impact toughness the behaviour of 2101 grade is quite similar to that of other DSS, while the 2304 has no drastic drop of toughness. Their corrosion properties in aggressive chloride environments are quite similar to that of austenitic AISI 304 grade.

Introduction

The good corrosion resistance of duplex stainless steels justify their applications in very aggressive environments, typical of chemical, offshore, oil and gas industries while their mechanical strength enables interesting applications both for constructions and transport vehicles, offering the advantage of reduced maintenance costs, being unnecessary the surface protection.
The base cost of the alloy is becoming a conditioning feature in diffuse and quantitatively important applications, in medium level aggressive environments. A great interest to develop lean grades of DSS aimed at the reduction of the cost, maintaining the basic good properties: mechanical strength, weldability, formability and good even if not extreme, corrosion resistance is growing.
An apparent way to reduce the alloy's cost is to reduce the content of the most expensive alloy components: nickel and molybdenum. Such reduction could be compensated by the increase of the manganese a nitrogen contents, to maintain the typical balanced microstructure of DSS, with both ferrite and austenite.
In the last decade research [1-4] has been carried out with the aim to define the composition of steel following the above criteria. Several different magnetic measurements were applied successfully to characterize the properties and the microstructure of duplex stainless steels [5, 6]. The main matters arise in maintaining the correct balance between ferrite and austenite contents and in the stability of the austenite against its transformation to martensite during cold forming

as a result of plastic deformation [1, 2]. For some years duplex grades with low Ni or Mn-N substitution for Ni have been proposed and are currently used, but a lack of information exist on structural stability after deformation or thermal treating.
The present paper is aimed to analyse the microstructure of two typical lean DSS.

Experimental

The as received materials were wrought rods (30 mm) previously solubilised (1050°C, 30 min), with chemical compositions lying in the ranges of Table 1.

Table 1. Chemical composition (%wt.).

Grade	C	Si	Mn	Cr	Ni	Mo	P	S	N
2101	0.030	0.60-0.80	4.0-5.0	22.0-0.5	1.0-1.5	0.50	0.035	0.005	0.19-0.22
2304	0.03	0.56	1.4	23.2	4.3	0.18	0.027	0.001	0.10

Isothermal "short" ageing treatments of specimens, were carried out at temperatures 550-850°C for 15-90 min and "long" treatment were carried out at 670 °C for 15-200 h.
The volume fractions of ferrite and austenite in a solution treated sample have been measured on 3 longitudinal and 3 transversal sections (20 fields for each section) by image analysis on light micrographs at 200×, after etching with the Beraha's reagent (reaction time, 10s).
The martensite which has been detected by OM and SEM, after etching with Beraha's reagent and by X ray diffraction (CrKα radiation).
Different phases have been observed by SEM examination of polished samples, using the backscattered electron (BSE) signal, on the basis of atomic number contrast effect: the ferrite appears slightly darker than austenite, while the secondary phases would appears lighter. The SEM operated at 25 kV; the BSE detector was set to maximize the atomic number contrast, allowing ferrite, austenite and other phases to be identified.
Instrumented Charpy–V impact specimens were prepared in the standard form of 10×10×55 mm. Impact test was carried out at room temperature, on samples treated at 550-650-750 and 850°C for 15-45-90 and 120 min.

Results and discussion

Solution treated material

The banded structure of elongated γ islands is observed in the longitudinal section, while the isotropic structure of ferrite and austenite grains is displayed on the transverse section. No secondary phases were detected. The values of volume fractions of ferrite and austenite, measured on longitudinal and transverse sections (200×), are reported in Table 2.

Table 2. Austenite (γ) and ferrite (α) % vol. in longitudinal and transverse sections.

	γ %2101	γ %2304	α %2101	α %2304
Longitudinal	50 ±2	56 ±2	50 ±2	53 ±3
Transverse	46±3	44±3	54±3	47±5

Table 3 reports chemical composition of ferrite and austenite measured with EDS-analysis, expressed as partition coefficients.
The Ni and Mn austenite enrichment and Cr ferrite enrichment are evident, the partition coefficients are quite similar to that observed in the common Cr-Ni-Mo grades.

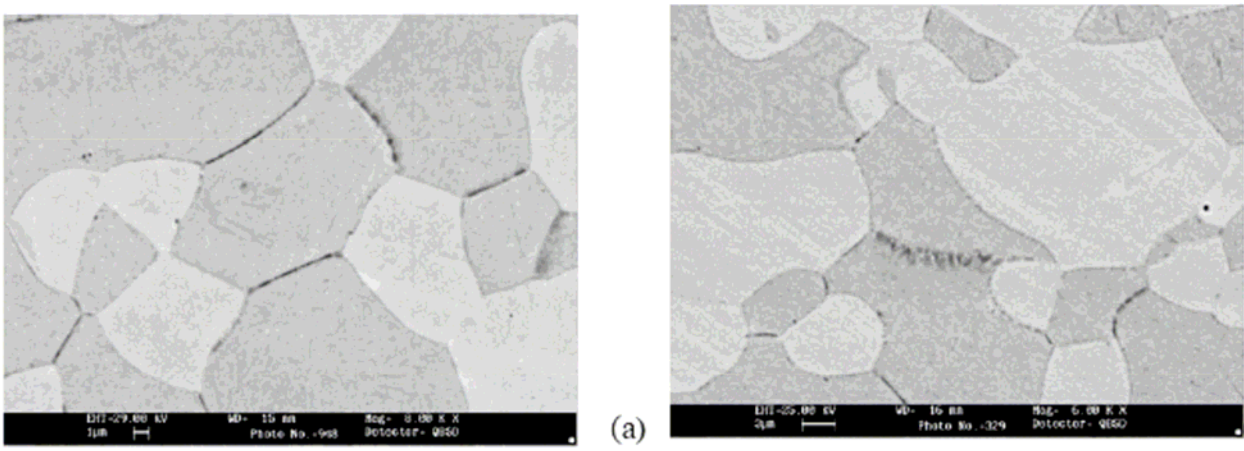
Table 3. Austenite and ferrite compositions. (Wt %, EDS)

	α/γ 2304	α/γ 2101
Cr	1.23	1,14
Mn	0.75	0,84
Ni	0.59	0,62

Heat-treated samples

Microstructure of 2101 grade DSS

The microstructure has been investigated mainly on not-etched specimens by SEM-BSE; the ferrite is darker than austenite. At the temperature of 600°C, for treatment time < 40 min no precipitation of secondary phases has been detected, for longer times some small dark particles were detected at the ferrite grain boundaries. They were analyzed by SEM-EDS (close to the resolution limit) and an enrichment of Cr was observed at the grain boundaries so the precipitates were identified as chromium nitrides.
The same grain boundaries precipitation was observed after soaking times longer than 40min at 650°C, while at 750°C the first grain boundary precipitation has been detected after a 20 min treatment (Figure1a) and can still be observed after 20 h (Figure1b). Increasing the temperature, particles became larger and the precipitation occurs also at the α-γ boundaries (Figure 1b).



(a) (b)

Figure 1. SEM-BSE micrographs of sample treated at 750 °C for 45 min (a) and 20 h (b)

The shortest times for grain boundary carbide precipitation lies in the temperature range 650-750°C, as already observed [3].
No σ and χ phases have been detected, neither for very long thermal treatments in the 650-900 temperature range. This could be related to the low Ni and Mo contents.
In addition the Ni content may induce the instability of the austenite, as suggested in previous researches, which report of a probable transformation to martensite during cold forming (1). Moreover the martensite formation has been confirmed (2) in some low-Ni DSS after cold rolling and annealing (1040°C, air quenched).
We have detected different amount of martensite laths (Figures 2 and 3) in treated and rapidly quenched from 750-850°C samples. Different cooling rates have no significant effect on the amount of final martensite.
The X-ray diffraction spectra evidenced that the ferrite peaks increase as the amount of martensite increases.

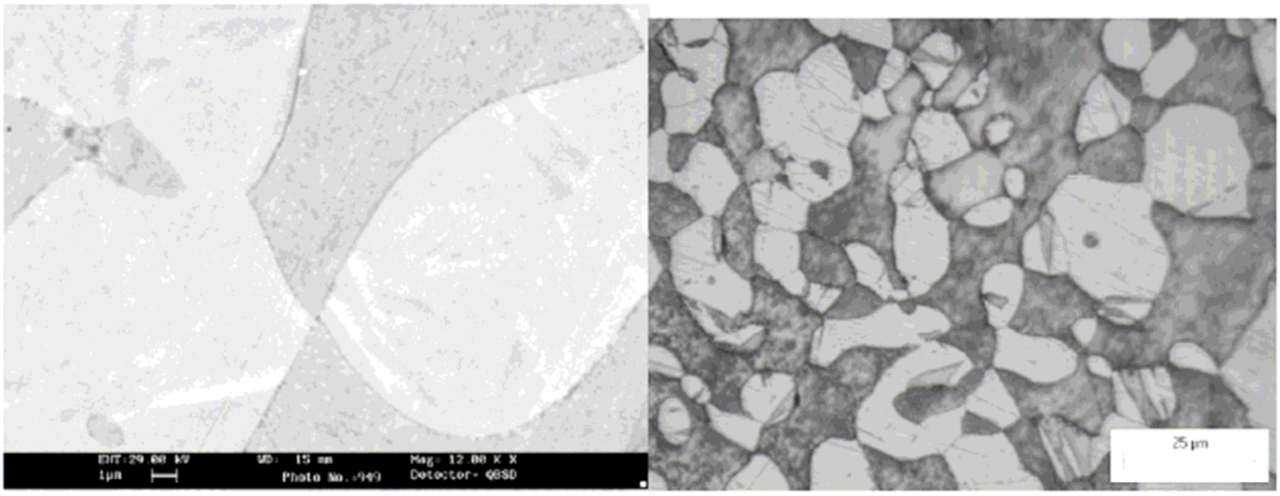


Figure 2. SEM-BSE and OM micrograph (750 °C, 25 min, WQ): martensite laths.

Microstructure of 2304 grade DSS

The microstructure of the 2304 grade DSS is not affected by the heat treatment at 600°C and no secondary phases or alpha-ferrite spinodal decomposition have been noted. A moderate precipitation of carbo-nitrides has been detected after long treatments (100 hours) at 670°C and after 45 min at 750°C.
In Figure 3 the SEM-BSE micrographs of the specimen treated for 90 min and 20 hours are reported. The carbo-nitride precipitation is evident just below the austenite grain boundary, as it has moved towards the austenite (ferrite) giving the precipitation inside the austenite grains.
A similar grain boundary precipitation was observed after long times (10 hours) treatment at 850°C but the kinetics are slower than at 750°C. On the other hand the main effect of the heat treatment in the range 600-850°C is the increasing of the austenite volume fraction, with values ranging from 44±1% of the as received sample to 62±2% of the sample treated at 850°C for 15 hours, accompanied by a decreasing of the Cr content in the austenite and by its increasing in the ferrite. This Cr enrichment and the very low amount of Mo seem to stabilize the ferrite and the secondary phases formation is not favoured.
The austenite of this grade appears to be stabile, indeed no austenite to martensite transformation has been detected after heat treatment. Probably the Ni (4.3%) and N (0.18%) contents are high enough to stabilize the austenite avoiding the structural transformation evidenced in the 2101 grade DSS.

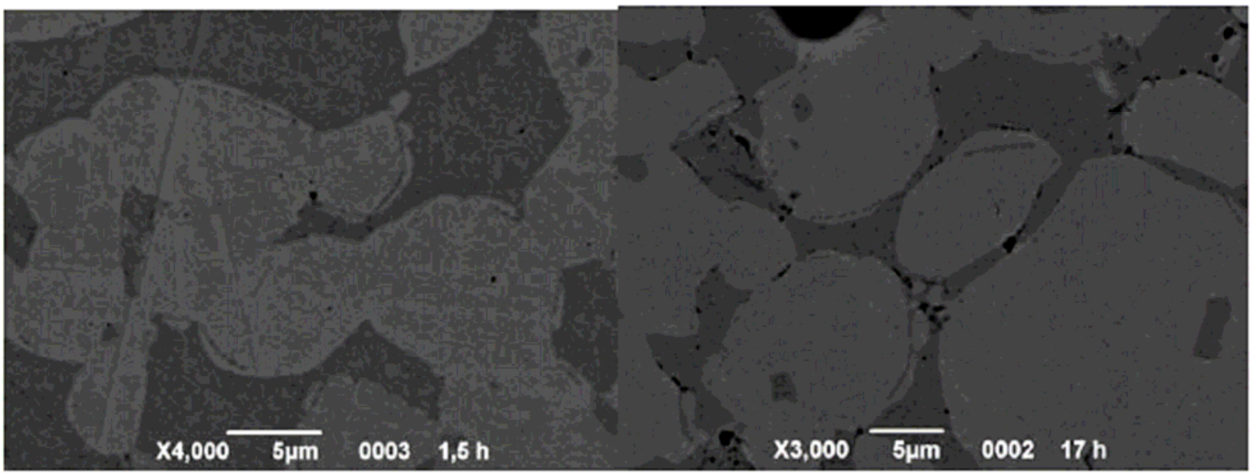


Figure 3. SEM-BSE micrographs: 750°C for 90min(left) and 20 hours(right)

Impact toughness

The effect of heat treatments on toughness of both the grades was studied by Charpy impact tests carried out at room temperature.

As shown in Figures 4 and 5, the steels have different impact toughness properties: the 2101 grade has the ductile and fragile behaviour, while the 2304 has no the fragile behaviour.

The 2101 is ductile until 20-40 minutes of isothermal treatment at 600-650°C, corresponding to first stages of the carbides-nitrides precipitation, where the impact energy drops down at about 50 J. The critical times for precipitation lie around 750°C, in good agreement with (3). However the impact energy is never lower than 30 J, also after very long soaking times, of several hours. The presence of some laths of martensite on the impact toughness has not yet been investigated. The 2304 grade DSS is always ductile, with the impact energy values never lower than 200 J.

At this stage of the research we may conclude that the presence of nitrides at the austenite grain boundaries has no remarkable effects on the toughness of the 2304 steel.

The sample was treated at 550°C (1), 650°C (2), 750°C (3), 850°C (4), for 15 min (A), 45 min (B), 90 min (C), 120 min (D).

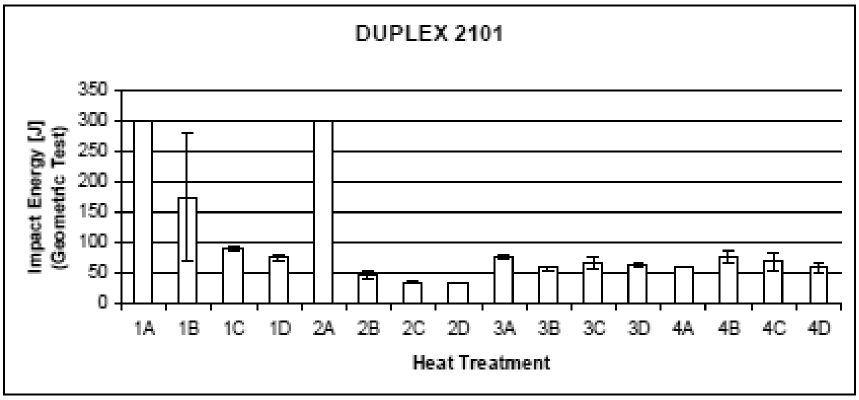


Figure 4. Impact energy of 2101 versus time/temperature of treatment

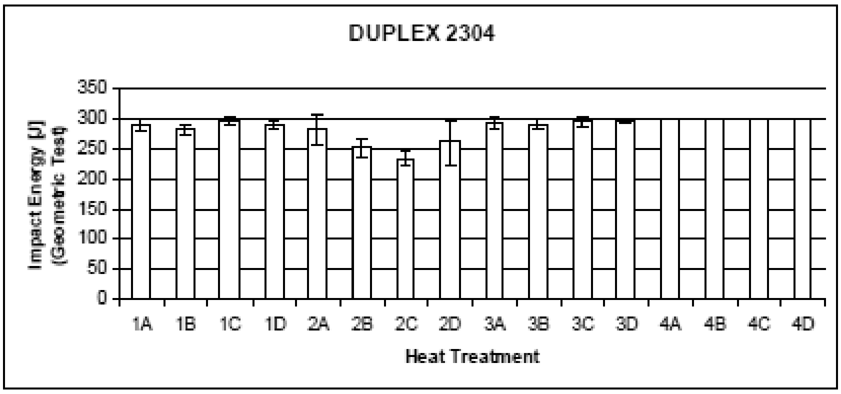


Figure 5. Impact energy for 2304 grade DSS versus time/temperature of heat treatment

Conclusions

Some results about the study of two duplex stainless steels with different low nickel contents were presented:

- The relatively low nickel and molybdenum contents make the precipitation of intermetallic phases more sluggish than in conventional duplex stainless steels, and no sigma related phases precipitation has been detected, also after long time isothermal aging treatments, in both the grades

- Precipitation at the grain boundaries of chromium nitrides has been observed after isothermal treatment in the temperature range 600-750°C, with different kinetics
- The austenite of the 2101 type DSS is quite instable, and a diffuse transformation austenite-martensite has been evidenced, while the austenite of the 2304 DSS is more stable and no martensite has been detected.
- The impact toughness after solution treatment is very good in both grades,
- The impact energy after isothermal treatment in the 2101 grade is never lower than 30 J, while in the 2304 is never lower than 200 J,
- General corrosion properties in chloride environments are quite similar to that of austenitic AISI 304 grades.

References

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