Characterization of a lean duplex stainless steel

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Abstract

The continuous improvement of the applications of duplex stainless steels (DSS) is justified mainly by their very good corrosion resistance in very aggressive environments and by their mechanical strength, often twice than that of conventional austenitic grades. Therefore more extensive applications have been suggested, like constructions, structural components, transport vehicles, etc. However for such not advanced but quantitatively important applications the base cost of the alloy is one of the more conditioning feature. An apparent way to obtain leaner alloys 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 analyzed in order to investigate the structural stability of the austenite against its possible transformation to martensite and the secondary phase’s precipitation. The detailed characterization has been performed with SEM-EDS on as received, heat treated (600-850 °C) and cold rolled alloy. A limited precipitation of chromium carbides and nitrides at the grain boundaries has been detected. The martensite formation has been revealed both in the heat treated and cold rolled material.

1. Introduction

In the last decades the applications of duplex stainless steels (DSS) became continuously more diffuse mainly by their very good corrosion resistance in very aggressive environments, like offshore, chemical, oil and gas industries. But their mechanical strength, about twice than that of austenite grades, is also interesting for more extended applications, like constructions, structural components, transport vehicles, etc.

However for such not advanced but quantitatively important applications the base cost of the alloy became one of the more conditioning feature. An apparent way to reduce the cost of these alloys 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 and nitrogen contents, to maintain the typical balanced microstructure of DSS, with about the same content of ferrite and austenite.

In the last decade several researches [1-5] have been carried out with the aim to define the composition of steel following the above criteria. The main problem seems to arise in maintaining the correct balance between ferrite and austenite, and from the stability of the austenite, against its transformation to martensite during deformation [1, 2] and harmful precipitation phenomena. In the paper such problems have been examined in a recently proposed “lean DSS”: the 2101 grade.

2. Experimental procedure.

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>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>P</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2101</td>
<td>0.03</td>
<td>0.60-0.80</td>
<td>4.0-5.0</td>
<td>22.0-22.5</td>
<td>1.0-1.5</td>
<td>0.50</td>
<td>0.035</td>
<td>0.005</td>
<td>0.19-0.22</td>
</tr>
</tbody>
</table>

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.

Cold deformations with different thickness reductions (10%, 25%, 50%, 65%, and 85%) were applied to the as received material. 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.

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, 10 s).

The martensite has been detected by OM after etching with Beraha’s reagent, SEM and TEM (bright field), by X ray diffraction (CrKα radiation) and by Moesbauer spectroscopy. The amount of transformed austenite after deformation was qualitatively quantified by image analysis. Micro hardness tests were conducted on the deformed material.

3. Results and discussion.

3.1 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>
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</tr>
</tbody>
</table>
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)

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$ % 2101</th>
<th>$\alpha$ % 2101</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal</td>
<td>50 ±2</td>
<td>50 ±2</td>
</tr>
<tr>
<td>Transverse</td>
<td>46±3</td>
<td>54±3</td>
</tr>
</tbody>
</table>

3.2. Heat-treated samples: grade 2101.

The stability of the microstructure have been investigated after isothermal aging in the temperature range 550-850°C, mainly on not-etched specimens by SEM-BSE. At the temperature of 600 °C, for treatment time shorter than 40 min, no precipitation of secondary phases has been detected, but for longer times some small dark particles were detected at the ferrite grain boundaries. They were analysed 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 40’ at 650 °C, while at 750 °C the first grain boundary precipitation has been detected after a 20 m’s treatment (Fig.1a) and can still be observed after 20 h (Fig.1b). Increasing the temperature, particles became larger and the precipitation occurs also at the $\alpha$-$\gamma$ boundaries (Fig. 1b).

3.3 Dangerous phase’s precipitation.

Our results confirm that any dangerous phases precipitation has observed, also after long time exposures in the temperature range 650-900°C, typical of the $\sigma$ and $\chi$ phases formation in the more common DSS. Indeed the reduction of the nickel and mainly of
the molybdenum contents seems to allow avoiding the precipitation of intermetallic phases, very detrimental for the toughness and corrosion resistance of conventional DSS. The microstructures obtained after solution and isothermal aging treatments have to be analyzed and discussed by comparison with the equilibrium microstructures of the Fe-Cr-Mn alloys. The results of Thermocalc calculations for the steel examined are shown in fig. 3. The diagram exhibit a large discrepancy with our results and a general pattern different from that of the more common Fe-Cr-Ni DSS [6]. Over 800°C the only phases in the microstructure of the steel should be the α-ferrite and the γ-austenite: in good agreement with the microstructure obtained after solution treatment previously described, the Thermocalc calculations forecast a microstructure with almost equivalent contents of ferrite and austenite.

The situation is different for the temperature range below 800°C, where Thermocalc calculations forecast the disappear of the γ-austenite, substituted by α-ferrite and σ-phase, following a rather complicated transformation pattern, in the temperature range 600-800°C. This is not confirmed by our results or by Lee evaluations [7] and other experimental data [8, 9]. The composition of the steel examined lies very near to the border between the regions α+γ+σ and α+σ both in the ternary Fe-Cr-Mn system and in the pseudo-binary Fe-Cr-6%Mn system of Lee at 650°C, which indicate an α-ferrite(higher)+γ-austenite(lower) microstructures, with, eventually, very low contents of σ-phase.

4 Martensitic transformation.

The increased manganese 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 in 2101, both after cold rolling and after quenching from 750-850°C, as revealed by OM (Fig.4-5), TEM (Fig.6), XRD and Mossbauer spectroscopy. Analyzing the XRD spectra, the γ peak seems to reduce during the cold deformation, in favour of the δ peak. Similarly in the Mossbauer spectra the paramagnetic peak decreases and the ferromagnetic peak grows increasing the thickness reduction during cold rolling.

The cold rolling effect was to induce the formation of lath martensite. As the deformation degree increases the amount of transformed austenite increases too (Fig. 7). The martensite formation slightly affects the hardness of the alloy. We can see a general growing in micro hardness with the deformation degree (Fig.8).
Fig. 4- Martensite laths: 2101 (750°C, 25 min, WQ)

Fig. 5- Martensite laths: 2101 (cold rolling, thickness reduction: 25%)

Fig. 6- TEM: Martensite laths: 2101 (cold rolling, thickness reduction: 85%)
5. Corrosion behaviour.
The general corrosion behaviour of the steel examined, after solution treatment, has been examined by potentiostatic tests. Some results are reported concerning the tests carried out in an aggressive medium as a chloride solution (3, 5 gr/l NaCl) at pH 3 and 7, to activate the pitting effect.
The fig. 7 show the effect of the pH value on the polarization curves: decreasing the pH decrease, as expected, the critical voltage value from -0, 2 to -0, 4 V. But at the lowest pH the corrosion current, at the same voltage, become lower in the stability range of the oxide surface film.
The curves of the fig. 8 allow to have a more direct comparison of the behaviour of the steel under examination, with that of the traditional austenitic AISI 304 and 316L and of the common duplex 2205. It is correct to remember that the medium used in the test is an aggressive chloride solution. The curves emphasize the best behaviour in such conditions of the 2205 DSS. However there is a minor difference between the lean duplex and the two austenitic grades. The stability of the protective film remain slightly better in the two austenitic, but particularly at the lowest pH value, the behaviour of the lean duplex appears very similar to that of the AISI 304.
6. Conclusions

The results obtained on two new lean Mn duplex stainless steel, with different low nickel contents, can be summarized:

- 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.
- 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 2101 grade can transform to martensite both after cold rolling and after quenching form 750-850°C.
- General corrosion behaviour in chloride environments is quite similar to that of austenitic AISI 304 grade.

References