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Abstract

Plastic deformation by cold rolling produces important changes on microstructure of the duplex stainless steel UNS S31803. Structure refinement and martensitic transformation were detected and analyzed by microscopy, X-ray diffraction and magnetic measurements. True deformations in the range of 0.92–3.38 were applied. The maximum amount of α' martensite was 30.2% obtained with the maximum deformation applied (3.38). The annealing at 400 °C promotes a further increase of α' martensite content, as observed before in austenitic metastable steels. Hardness against deformation curves of AISI 304L and duplex steel were compared and analyzed. The stability of the martensite phase with temperature was investigated by magnetic measurements, and it is found that the reverse reaction $\alpha' \rightarrow \gamma$ starts between 500 and 520 °C.

Keywords: Duplex stainless steels; Martensitic transformation

1. Introduction

Duplex stainless steels (DSS) are corrosion resistant alloys for special applications in the chemical, petrochemical and nuclear industries. Due to the higher contents of chromium, molybdenum and nitrogen they present high corrosion resistance. The grain refinement promoted by the duplex structure and the alloying elements provide higher mechanical strength than austenitic and ferritic grades such as AISI 304 and AISI 430, respectively.

Many workers [1–6] have already studied the effects of plastic deformation in austenitic stainless steels. The formation of deformation induced martensites in metastable austenitic stainless steels such as AISI 304 and 316 have been extensively reported. In these steels two martensitic phases may be formed: ε martensite (hcp, paramagnetic) and α' martensite (bcc, ferromagnetic). Mangonon and Thomas [1] studied the transformations during the tensile test of an AISI 304 steel and found that the ε martensite is formed in the beginning of deformation and reaches a peak value at about 5% of tensile strain. After this the ε phase decreased to almost zero at 20% of plastic strain. The martensite α' (bcc, ferromagnetic) increased continuously with strain and at high plastic deformations this was the only martensitic phase present in the steel. Similar results were reported by Seetharaman and Krishnan [2] deforming an AISI 316 steel by rolling and tension test.

The sequence of transformation $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ was so proposed to metastable austenitic steels deformed by uniaxial tension and rolling. However, the direct transformation $\gamma \rightarrow \alpha'$ is also possible through dislocation reactions [6].

The susceptibility to deformation induced martensite transformation increases with the decrease of stacking fault energy (SFE) [2,6,7]. It explains the lower metastability of the AISI 316 (SFE $\approx 50\,mJ/m^2$) when compared to the AISI 304 (SFE $\approx 18\,mJ/m^2$).

An increase of the α' martensite volume fraction due to heat treatment at 400 °C after deformation was reported by many authors [1,8,9] in metastable austenitic steels. However, the explanation for this increase remains unclear.

The austenite to martensite transformation in duplex stainless steels (DSS) are much less studied than in austenitic grades. Reick et al. [10] measured the stacking fault energy value in the

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Table 1
Chemical composition (wt.%) of the material

Cr	22.3
Ni	5.44
Mo	2.44
C	0.02
N	0.160

austenite of a 2205 DSS and quantified the martensite increase by X-ray diffraction. Despite of the low SFE (10 mJ/m^2), the austenitic phase did not present a very high work hardening rate as should be expected.

In the present work the microstructural effects produced by cold rolling in a duplex stainless steel UNS S31803 (2205) were investigated. Specially, the martensite formation by deformation was studied by X-ray diffraction and magnetic saturation measurements.

2. Experimental

The duplex stainless steel UNS S31803 (composition shown in Table 1) was received as plates of 2.5 mm in thickness. In the as received condition the material presented a microstructure with 55% of austenite and 45% of ferrite. The material was cold rolled from 2.50 to 1.00, 0.50, 0.25, 0.18, 0.13 and 0.11 mm. An AISI 304L steel was also deformed and analyzed for comparison. Sample identifications, true deformations and reductions are shown in Table 2. Heat treatments at 400 °C for 1 h were carried out after deformation. Samples deformed till 0.18 mm were heat treated in the 400–690 °C range to investigate the stability of the martensite phase.

Magnetization saturation and coercive force were measured in a vibrating sample magnetometer (VSM) EGG-PAR model 4500 with maximum applied field 400 kA/m, time constant 10 ms and total measuring time 30 min.

X-ray diffraction was carried out in a diffractometer PHILIPS®, model X'Pert Pro, in step scan mode with step size of 0.02°, time per step of 3 s and angular interval 35–105°. Radiation Co Kα (1.7890 Å) without monocromator was used with 40 kV and 40 mA. The measurements were made at room temperature in continuous sweeping mode. Spinner was used to minimize the effect of preferential direction. In order to keep the beam completely on the sample for low incident angles a divergence slit of 1° was used.

Metallographic samples were prepared with conventional polishing and etching with hot (90 °C) Murakami's etchant (10 g of potassium ferricianet, 10 g of potassium hydroxide, 100 ml distillated water). Electrolytic etching in 10% acid oxalic solution was also tried. Quantitative metallography to determination of volume fractions was performed using the Image Tool software [11]. Chemical compositions analysis was carried out in a scanning electron microscope ZEISS equipped with EDS. Microhardness tests with 100 g (HV100) were also performed.

Table 2
Samples identification

Sample identification	Thickness	True deformation through thickness	Reduction (%)
A (ST)	2.500	0	0
B	1.00	−0.92	60.0
C	0.550	−1.51	78.0
D	0.270	−2.23	89.2
E	0.180	−2.63	92.8
F	0.130	−2.96	94.8
G	0.110	−3.12	95.6
H	0.085	−3.38	96.6

3. Results

The first effect produced by cold rolling the duplex stainless steel samples was the fabulous structure and grain refinement, as observed by comparing the microstructures of samples A, C and D, shown in Figs. 1–3, respectively.

The second important effect produced by the cold rolling is the deformation induced martensitic transformation. Fig. 4 shows the X-ray diffractograms of the samples A, C, D and G. Martensite ε′ was not observed in the DSS. Martensite α′ has the same crystallographic parameters of ferrite (here called δ). Fig. 4 shows the increase of the α′ reflections with cold deformation. In agreement, Fig. 5 shows the magnetization curves of samples A, C–E, G and H. The magnetization saturation increase with cold deformation confirms the α′ generation by the γ → α′ reaction. Fig. 6 shows the m_s *versus* deformation behaviour of samples. As observed before in austenitic steels [1,8,9], a heat treatment at 400 °C after deformation causes an increase of the α′ martensite content of about 2–6%.

Murakami's etching provides a very good contrast between the light and dark regions, but does not reveals the grain bound-

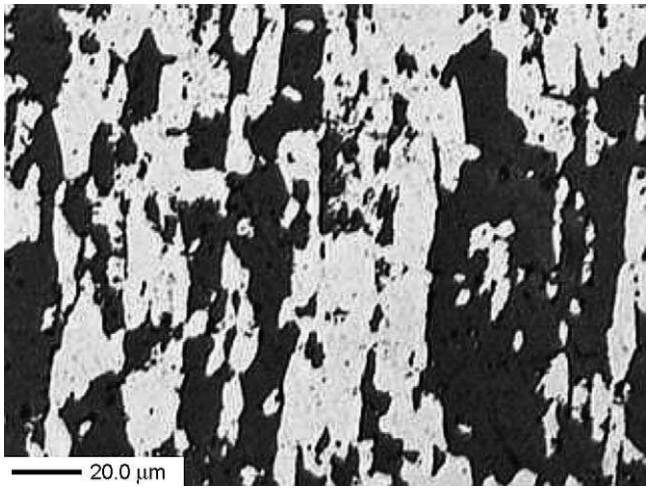

Fig. 1. Microstructure of the solution treated sample (Murakami's etch).

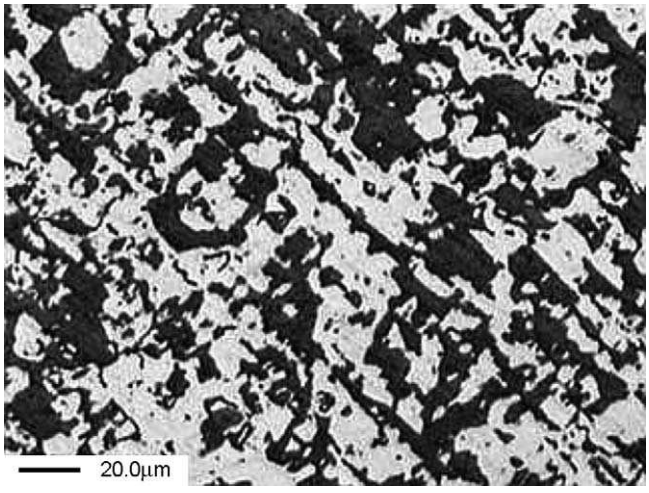

Fig. 2. Microstructure of sample C ($\varepsilon = -1.51$, $r = 78.0$) (Murakami's etch).

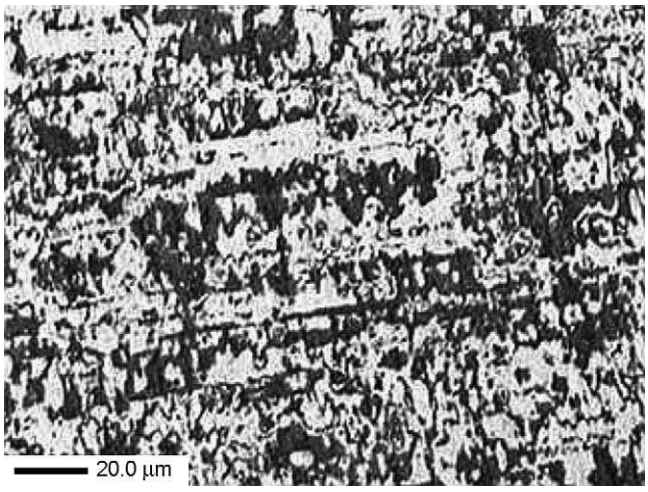

Fig. 3. Microstructure of sample E ($\varepsilon = -2.63$, $r = 92.8$) (Murakami's etch).

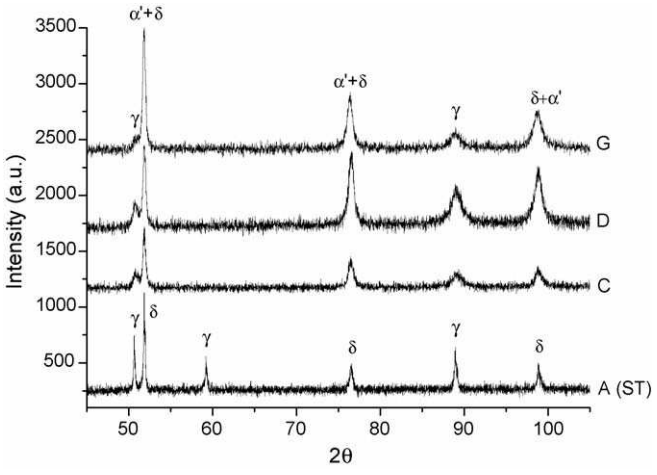

Fig. 4. X-ray diffractograms of samples A, C, E and G.

aries neither the martensite phase. Indeed, Table 3 shows that the volume fractions of the dark and light phases do not change with the increase of deformation. The effect of the etching on the martensite α′ is the same as in the previous austenite. It

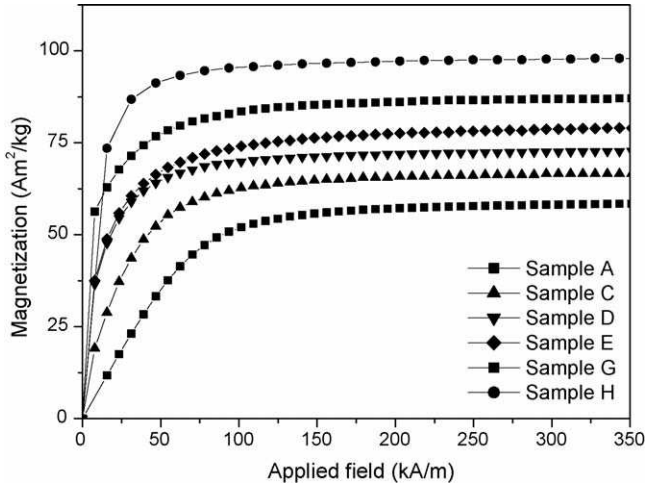

Fig. 5. Magnetization curves of samples A, C–E, G and H.

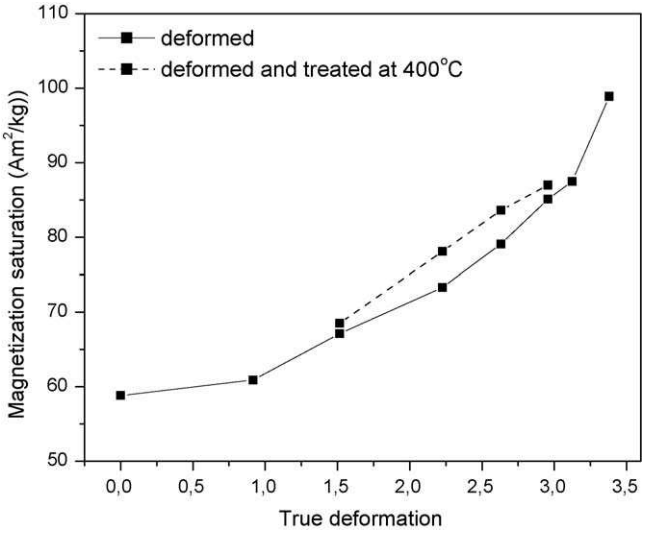

Fig. 6. Microstructure of sample C electrolytic etched in 10% oxalic acid solution.

Table 3
Volume fraction of dark and light areas

Sample	Dark areas	Light areas	Martensite volume fraction, $C_{\alpha'}$
A	51.4 ± 2.7	48.6 ± 3.2	0.00
C	48.4 ± 4.8	51.6 ± 4.8	0.06
D	52.2 ± 4.6	47.8 ± 4.6	0.10
E	48.7 ± 4.7	51.3 ± 4.7	0.15

also indicates that they have the same chemical composition, as already determined in the case of austenitic stainless steels [1]. The electrolytic etch with 10% oxalic acid solution (Fig. 7) only reveals grain boundaries of the deformed structure. The martensite quantification in the DSS could not be done by metallography with the etch solutions used in this work.

The quantification of martensite α′ was so performed by X-ray diffraction and magnetic saturation measurements.

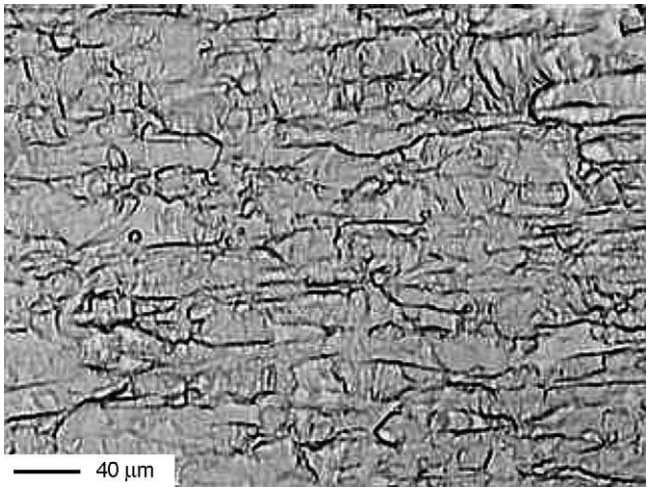

Fig. 7. Amount of martensite α′ *vs.* true deformation.

Table 4
Average chemical composition measured by EDS in sample E

Region	Cr	Mo	Ni	Fe
Light areas (γ and α′)	21.83	2.18	5.85	Balance
Dark areas (δ)	23.02	3.00	4.45	Balance

Quantification by X-ray diffraction was carried out by the direct comparison method described in [12], considering the same scattering factors in both phases. In the cold rolled samples the amounts of ferrite (δ) plus martensite (α′) were quantified. Since they have exactly the same reflections it is impossible to separate them. The amount of α′ was then obtained subtracting the amount of δ present in the solution treated sample (0.45 or 45%) from the δ + α′ content.

Quantification by magnetization saturation was based on the equation proposed in an earlier work [13]:

$$C_{\alpha'} = \frac{m_s\,(\mathrm{A^2\,m/kg})}{133\,\mathrm{A^2\,m/kg}} \quad (1)$$

where $C_{\alpha'}$ is the martensite volume fraction, m_s the magnetization saturation value of the sample analyzed. The value 133 A^2 m/kg is the intrinsic saturation magnetization of the ferrite phase of the UNS S31803 DSS as determined in [13]. In this study the same value (133 A^2 m/kg) was adopted for the martensite α′. This assumption is reasonable considering that the m_s value is mainly function of the chemical composition and the two phases (α′ and δ) present similar Cr, Ni, Mo and Fe contents, as determined by EDS (Table 4).

Fig. 8 shows the results of martensite α′ quantifications. X-ray diffraction and magnetization saturation results are very close. Fig. 9 compares the curves of amount of austenite transformed into martensite by deformation against true deformation of the UNS S31803 duplex steel and the AISI 304L austenitic steel. In this comparison the curves were constructed with the magnetization saturation data. The martensite fraction of the AISI 304L steel samples were determined considering the intrinsic m_s value

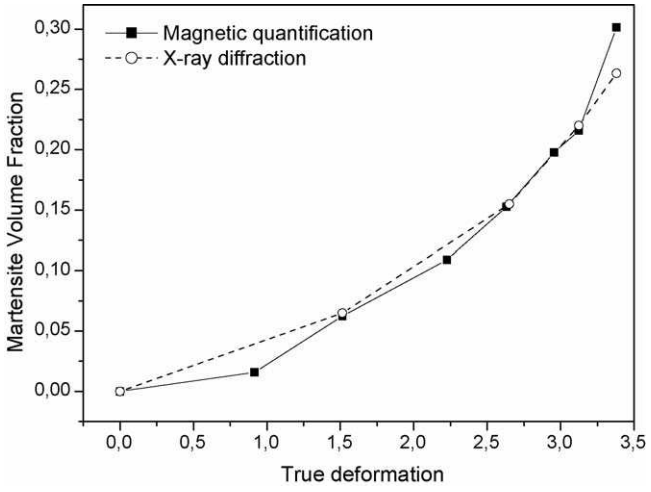

Fig. 8. Coercive force *vs.* amount of true deformation.

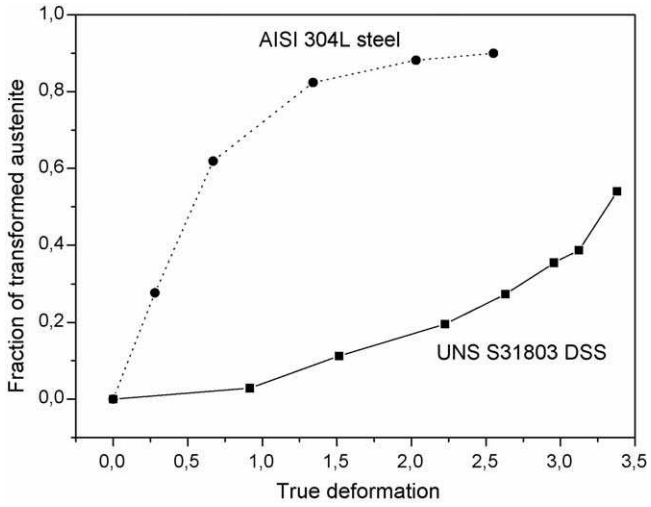

Fig. 9. Comparison between the amount of transformed amount in the UNS S31803 duplex steel and AISI 304L austenitic steel.

of the α′ phase as 160.4 A^2 m/kg, as proposed by Mangonon and Thomas [1]. Despite of its lower stacking fault energy, as measured by Reick et al. [10], the austenite phase of the duplex steel is less metastable than the austenite of the AISI 304L steel.

The dependence of the martensite fraction with deformation presented in Fig. 9 is quite different in both steels. In the austenitic 304L steel behavior can be described by an exponential decay law, while in the DSS, an exponential increase could by fitted. Differently from the results presented by Reick et al. [10] the martensite fraction of the DSS does not reach a saturation value in the range of deformation investigated. A maximum amount of 30.2% of martensite α′ was obtained in the most deformed condition (sample H).

Fig. 10 shows a comparison between the microhardness increase with deformation in the AISI 304L and in the UNS S31803 duplex steel. The percentages of transformed austenite are also indicated in the figure. In the case of the DSS, the

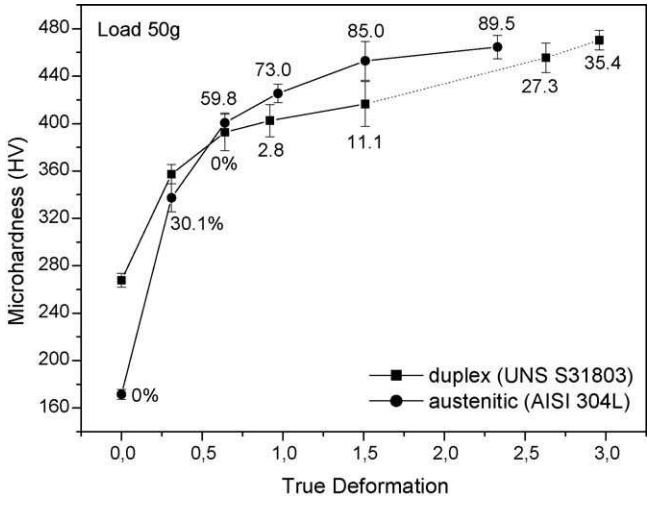

Fig. 10. Comparison between the microhardness evolution of the austenite phase in the UNS S31803 duplex steel and AISI 304L austenitic steel.

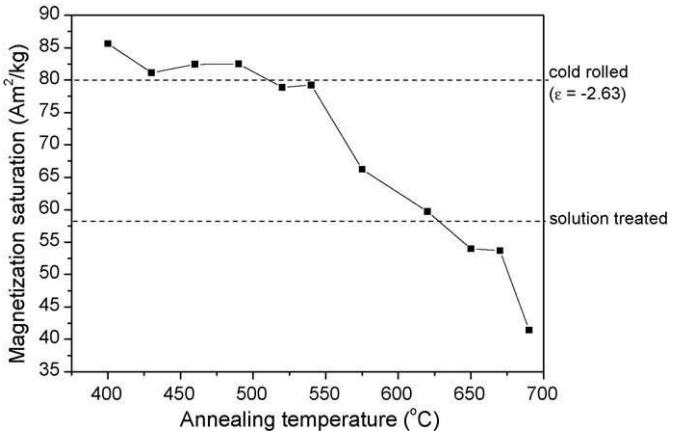

Fig. 11. Magnetization against annealing time in the sample cold rolled with $\varepsilon = 2.63$.

indentations were initially made in the light regions, which were initially austenitic and then partially transformed into martensite. However, as the increase of deformation produces finer microstructures, the microhardness measurements of the individual phases become more difficult. As a consequence, the two last points of the curve of the DSS in Fig. 9 are from light and dark regions. Now analyzing the results of Fig. 9, it is clear that the AISI 304L presents a higher initial work hardening rate due to its higher metastability. However, a pronounced increase of microhardness of the DSS is observed in the last two points. Such change of slope can be related to the observed increase of martensite content. However, this hypothesis must be confirmed by further experiments, since the two last points of the curve can be influenced by the ferrite phase and grain boundaries effects.

The stability of the martensite phase was investigated by isothermal annealing and magnetic measurements (Fig. 11) in samples previously deformed till 0.18 mm, and so containing about 15% of α'. The results presented in Fig. 11 show that the martensite reversion starts between 500 and 520 °C where the magnetization saturation (m_s) becomes smaller than the value of the cold rolled sample. The temperature of the finish of the reversion should be that where the magnetization saturation becomes as low as the value of the solution treated sample (58.8 A^2 m/kg), which means about 620 °C. However, the m_s becomes lower than 58.8 A^2 m/kg in the sample annealed at 650 °C and a further decrease is then observed in the annealing at 690 °C. The explanation for this behavior is that above 600 °C the paramagnetic sigma phase can be formed in duplex stainless steels [14]. Further experiments must be conducted to study how and from which temperature sigma phase precipitates in the cold worked DSS containing α' martensite.

4. Conclusions

Microstructure changes produced by cold rolling in a duplex stainless steel UNS S31803 were analyzed in this work. Plastic true deformations in the range of 0.92–3.38 were applied at room temperature. A strong grain refinement is observed with the increase of deformation.

Deformation induced magnetic martensite (α') was quantified by X-ray diffraction and magnetization saturation measurements. The results obtained by these two methods were very close and revealed that the amount of α' increases exponentially in the range of deformation analyzed. The maximum amount of this phase was 30.2% in the most deformed sample ($\varepsilon = 3.38$). Despite of its reported lower stacking fault, the austenite of the duplex stainless steel is less metastable than that of the AISI 304 L steel.

The annealing at 400 °C promotes an increase of 4 to 6% in the α' martensite, as observed before in metastable austenitic stainless steels. Experiments with isothermal annealing at different temperatures showed that the reverse reaction $\alpha' \rightarrow \gamma$ starts between 500 and 520 °C in the DSS containing about 15% of α'.

As suggestion for future works, further analysis of the martensite formation in duplex stainless steels using transmission electron microscopy (TEM) is required.

Acknowledgements

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