1. Introduction

Driven by required mechanical and corrosion resistance of a stainless steel, the duplex stainless steels (DSS), usually composed by equal ferrite and austenite volume fractions due to the right alloy elements balance, were developed\(^1\)\(^2\).

The typical DSS structure is generally composed of 40%-45% of ferrite (\(\alpha\)) and 55%-60% of austenite (\(\gamma\)), obtained after solution-treatment between 1,000\(^\circ\)C and 1,200\(^\circ\)C, and followed by water quench. However, in these steels may occur the formation of deleterious phases, affecting both mechanical and corrosion resistance of the material. Between 700\(^\circ\)C and 900\(^\circ\)C, it may occur the sigma phase formation by eutectoid decomposition of original ferrite, generating also secondary austenite (\(\gamma_s\)), or by direct formation from ferrite and austenite, forming respectively secondary ferrite (\(\alpha_s\)) and secondary austenite (\(\gamma_s\))\(^3\).

Ahn and Kang\(^4\), studying a UNS S31803 DSS and its modifications with tungsten additions, reported that between 650\(^\circ\)C and 900\(^\circ\)C, \(\chi\) (chi) and \(\sigma\) (sigma) precipitation occurs; nevertheless, the \(\chi\) phase formation was registered at about 100 seconds for UNS S31803 DSS, but it is transformed to \(\sigma\) and austenite for ageing times higher than 2,000 seconds. The same authors also reported that the microstructure of UNS S31803 presents \(\sigma\) and austenite when aged for 30 hours, which was determined by quantitative analysis on
backscattered electron microscopy (BSE) images. However, due to the difficulty of differentiation between σ and χ on aged DSS, it is common practice the designation of them as intermetallic phase.

Some researches\cite{5-8} report that during the ageing treatment of UNS S31803 between 700°C and 900°C from 10 minutes to 1,032 hours σ phase formation occurs by direct formation from ferrite, resulting in massive chromium and molybdenum impoverished ferrite. Another significant σ phase formation reaction is the eutectoid decomposition of ferrite which results in σ with lamellar or divorced morphology. It was also observed that σ growth occurs simultaneously by ferrite and austenite consumption.

The influence of short ageing treatments were evaluated on UNS S31803 steel\cite{9} using an aluminum bath to ensure the efficient heating of the samples during the heat treatment. It was observed that between 800°C and 900°C for ageing times up to 5 minutes, σ phase formation occurs on α/α or α/γ, with preferential growth inside ferrite. The highest value of σ volume fraction was registered in about 2% after 5 minutes of ageing at 850°C. Recent studies of this research group\cite{10} shows that in UNS S32750 DSS σ volume fractions are higher than 30% when aged at 850°C and higher that 20% when aged at 900°C.

Considering those facts, the main objective of this paper is to evaluate the mechanisms of intermetallic phase formation between 1 minute to 5 minutes for ageing temperatures from 850°C to 950°C, in isothermal heat treatments of small dimensions specimens ensuring fast heating of these ones.

2. Experimental Procedure

The studied material (UNS S32750) has the chemical composition given in Table 1, and was obtained as 20 mm diameter round bars. Solution heat treatment was conducted for 10 min at 1,100°C with subsequent cooling in water.

The solution-treated material was isothermally aged at 850°C, 900°C and 950°C for 1 minute, 3 minutes or 5 minutes, followed by water quench. To ensure fast heating to the aging temperatures, specimens of reduced size (discs of 3 mm of thickness and external diameter of 20 mm, with a central hole of 3 mm) were immersed in a molten aluminum bath conditioned on a refractory crucible, in a muffle furnace equipped with solid state relay controllers.

After the heat treatments the specimens were abraded using silicon carbide (SiC) papers to a 220-grit finish before mounting in thermostetting plastic, parallel to the rolling direction. The mounted samples were metallographic prepared in a semi-automatic grinding and polishing machine, with final polishing provided by 1 μm diamond abrasive, using ethyl alcohol as lubricant.

Then, the metallographic specimens were analyzed by Scanning Electron Microscope (SEM), from which were obtained five backscattered electron (BSE) images for each aged sample. The scanning electron microscope adjustment was standardized for each specimen. Among other parameters, were adjusted: the accelerating voltage applied to the electron beam (maintained at 20 kV); electric current emitted by the filament (maintained at 100 μA); and the image brightness and contrast were maintained constant. This microscope adjustment ensures that the shade and design of the phases are the same for all collected samples, avoiding differences in identification and quantification of the phases. The sample images were analyzed using an image analysis software for the phase’s quantification.

3. Results

Fig. 1a presents the BSE image of a solution treated sample, in which it is observed the austenite and ferrite grains (outlined by a small relief due to the polish procedure) and small black dots probably related to nitrides. In Figs. 1b to 1d corresponding to the samples aged at 850°C for 1 minute, 3 minutes and 5 minutes, it is noted that with increasing ageing time occurs an increase on intermetallic volume fraction (showed in white).

The intermetallic and nitride volume fractions were obtained by the analysis of five BSE images similar to those shown in Figs. 1 and 2, resulting in the values presented in Figs. 3 and 4. The nitride volume fraction did not exceed 0.4% and remained constant for all samples, considering the standard deviations of the measurements.

4. Discussion

In Fig. 1a, which presents the BSE image of the solution treated sample, it was observed small black dots that are probably related to chromium nitrides. Qualitative energy dispersive spectroscopy (EDS) quantitative analysis indicates that this precipitates are related to chromium and

\begin{table}[h]
\centering
\caption{Chemical composition of the material (%wt)}
\begin{tabular}{cccccccc}
\hline
Cr & Ni & Mo & Mn & N & C & Si & Cu & Fe \\
\hline
24.95 & 6.91 & 3.79 & 0.43 & 0.263 & 0.015 & 0.26 & 0.083 & Bal. \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Microstructure of UNS S32750 DSS (a) solution-treated sample; and aged at 850°C for (b) 1 min, (c) 3 min, and (d) 5 min. Backscattered electron images (BSE). The same behavior could be observed in the samples aged at 900°C and 950°C.}
\end{figure}
aluminum nitrides, the latter added in small amounts in steel manufacturing in order to promote steel deoxidization.

Figs. 1b–1d showed that in the samples aged at 850°C the use of BSE images allows the distinction between intermetallic phases (corresponding to the white phases on the images) and nitrides (black precipitates). The different colours of intermetallic phases and nitrides enable the use of these images for automatic quantitative analysis such as those proposed in this paper. However, it was not observed different levels of light gray that may be an indication of the presence of $\chi$ and $\sigma$ phases, and differentiation between them was not possible in this work. For this reason, the lighter phases in Figs. 1 and 2 are treated as “intermetallic phases”.

From Fig. 3 analysis it is evident that the maximum intermetallic volume fraction was registered after 5 minutes of ageing at 900°C reaching an average value of 7.5%. By comparing the three studied temperatures it is also observed that after 5 minutes of ageing at 900°C the maximum intermetallic volume fractions are reached, showing that in initial stages of ageing, the mechanisms of intermetallic phase formation are temperature dependent, and do not represent the global trend of the higher intermetallic phase kinetics (in particular $\sigma$) at 850°C, as reported in previous researches [3,7,8,10].

As previously reported, maximum nitride volume fraction did not exceed 0.4%, and it remained constant for all sample conditions. In Fig. 4 it is observed the nitride volume fraction on solution-treated sample, and hence it can be assumed that the nitride volume fractions are independent from the ageing heat treatment, if we consider (i) the small nitride volume fraction; (ii) the small number of analyzed fields; and (iii) the high values of standard deviation.

5. Conclusions

The conclusions of this paper can be summarized as follows:

- The use of scanning electron microscopy (SEM) allows the differentiation between intermetallic phases and nitrides, enabling the use of these images in automated quantitative analysis of duplex and superduplex stainless steels;
- for the aged samples were registered measurable intermetallic phase volume fractions from 1 minute of aging between 850°C and 950°C. However, it is not possible the differentiation between $\sigma$ and $\chi$ phases;
- the observed nitrides were probably formed on the steel manufacturing stages, considering that there are no significant changes on its volume fraction during ageing heat treatment.
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