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475 °C Embrittlement in a Duplex Stainless Steel UNS S31803

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The susceptibility of a duplex stainless steel UNS S31803 to thermal embrittlement at 475 °C was evaluated by means of mechanical tests (impact energy and hardness), magnetic measurements (hysteresis and thermomagnetic analysis) and scanning electron microscopy. The results show that the material undergoes severe embrittlement and hardening in the first 100 h. The corrosion resistance of the ferrite phase in a 10%HNO_3 + 0.05%HF solution deteriorated after 500 h of ageing. The Curie temperature (T_c) was the most sensitive magnetic property to the microstructural changes that promote embrittlement. T_c increases with ageing time due to the progressive reduction of chromium in the Fe-rich matrix during spinodal decomposition.

Keywords: *duplex stainless steel, 475 °C embrittlement*

1. Introduction

Duplex stainless steels (DSS) are widely used in chemical, petrochemical, cellulose and nuclear plants around the world[1-4]. Because of their fine austenitic-ferritic microstructure they offer an excellent combination of mechanical and corrosion resistance properties.

The best performance of wrought DSS is obtained in the solution treated condition. Nevertheless, two hardening and embrittlement processes may occur when these materials are heated: (a) sigma phase (σ) precipitation in the range of 700 °C to 900 °C and (b) precipitation of a Cr-rich phase (α’) in the range of 300 °C to 600 °C. The α’ precipitation leads to a progressive hardening and reduction of the material toughness[5-7]. This precipitation occurs by spinodal decomposition, a mechanism by which the ferrite phase decomposes into a Cr-rich phase (α’) and a Fe-rich phase. Because this reaction occurs more rapidly at 475 °C, this process is also known as “475 °C embrittlement”. However this phase separation may also occur in temperatures as low as 300 °C in exposures after thousands of hours or at 600 °C in exposures for few minutes[8], depending on the chemical composition of the steel.

Many researchers have studied and developed methods of detection and also quantification of thermal embrittlement in DSS. Tsuchiya *et al.*[9] and Evanson *et al.*[10] employed magnetic measurements and found that the hysteresis loss, residual induction and coercive force increased with ageing time in cast DSS. Controversially, Maeda *et al.*[7] have found experimentally that there is a decrease in the coercive force during the ageing of cast duplex stainless steels in the range of 350-450 °C. Kim *et al.*[11] found an increase of the Curie temperature in ferritic stainless steels aged at 370 °C and 400 °C.

Another consequence of the spinodal decomposition of the ferrite phase is loss of corrosion resistance. If the Cr content of the Fe-rich matrix becomes lower than 14 at.%, pits of corrosion may be observed by scanning electron microscopy (SEM) in the ferritic regions in samples etched with a 10%HNO_3+0.05%HF solution[9].

In the present research work, the susceptibility of a DSS S31803 to thermal embrittlement at 475 °C was evaluated by means of hardness and Charpy impact tests, magnetic measurements and SEM.

2. Materials and Methods

A 3 mm sheet of duplex stainless steel UNS S31803, with the composition shown in Table 1, was received in the solution treated condition, containing (43 ± 3)% of

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

% C	% Cr	% Ni	% Mo	% N	% S	% P	% Fe
0.032	22.38	5.32	2.55	0.1123	0.003	0.028	balance

austenite phase. The material was heat treated at 475 °C for 20, 100, 300 and 500 h.

The age hardening was measured by Brinnel hardness tests. The embrittlement was measured by Charpy tests, using subsize (2,5 mm) V-notch specimens[12]. The impact tests were conducted on a universal impact machine. The aged samples were etched with a 10%HNO_3 + 0.05%HF solution and observed by SEM.

The magnetic measurements (hysteresis and thermomagnetic analysis - TMA) were carried out in a Vibrating Sample Magnetometer (VSM) EGG PAR model 4500. The TMA data were obtained with a high-temperature oven in low vacuum atmosphere (0.1 mmHg) and under an applied magnetic field of 500 Oe. The heating rate was 5 °C/min. A barium ferrite was taken as standard for magnetic measurements.

The samples for magnetic measurements were disc-shaped with a diameter of about 3.5 mm and thickness between 0.05 and 0.20 mm. The obtained hysteresis curves were corrected for the demagnetization field as proposed by Chikazumi[13] and Cullity[14].

3. Results and Discussion

Figure 1 shows the hardness and impact energy behaviour with ageing time at 475 °C. The α' precipitation promotes strong hardening and embrittlement in the first 100 h of ageing. Figure 2 show the backscattered electrons image of the sample aged for 500 h and etched in a 10%HNO_3+0.05%HF solution. The pits observed in the ferrite phase indicate that in this condition the Cr content of the matrix is probably lower than 14 at%[9]. Even though a decrease of toughness had been detected in the first 20 h of ageing, it was only after 500 h of ageing that a pronounced decrease of corrosion resistance of the ferrite phase was observed by SEM. This fact show that some chemical and electrochemical tests[15,16], based in the loss of corrosion resistance, may not be effective in predicting the embrittlement of the steel.

Table 2 shows the magnetic properties of coercive force ($_MH_c$), residual induction (B_r) and saturation induction (B_s) obtained at room temperature in the different investigated conditions. As can be seen, B_r and B_s were not affected by ageing and the $_MH_c$ increased very slightly with ageing time. The difference between the coercive force of the sample aged by 500 h and the unaged sample was about 6%, which is very low if we consider the strong variation of mechanical properties that takes place in the same time. Besides, Fig. 3 shows that the hysteresis loops of the unaged sample and the one aged for 500 h are almost coincident. These results are in disagreement with those obtained by Tsuchiya *et al.*[9] and Evanson *et al.*[10] for cast duplex stainless steels. The former authors found a great

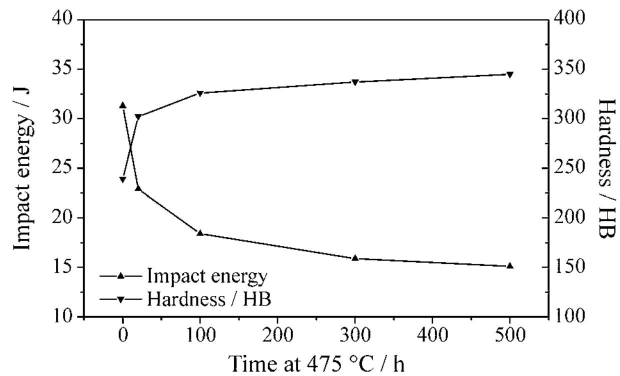

Figure 1. Impact Energy and Brinell Hardness as function of time exposure at 475 °C. (ST = Solution treated).

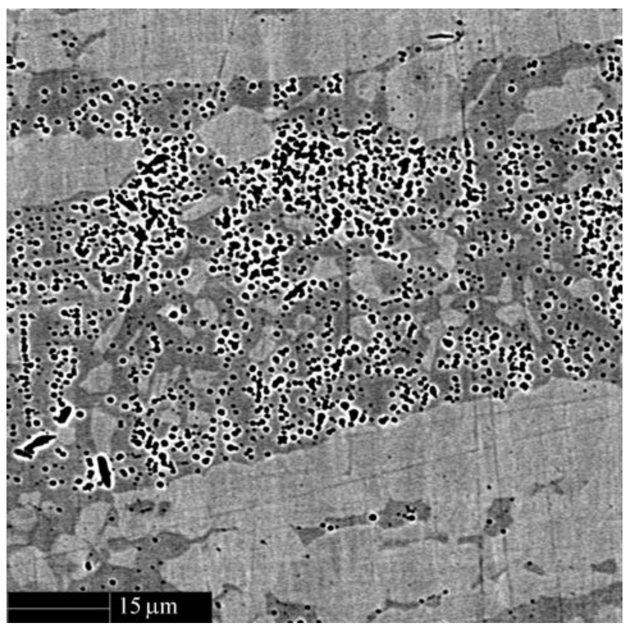

Figure 2. SEM composition image of the sample aged for 500 h at 475 °C, etched with 10%HNO_3+0.05%HF solution.

Table 2. Magnetic Properties: coercivity ($_MH_c$), residual induction (B_r), saturation induction (B_s) and magnetic transition temperature (T_c).

Condition	$_MH_c$ (Oe)	B_r (G)	B_s (G)	T_c (°C)
Solution treated	266	6590	7535	503
475 °C / 20 h	270	6800	7500	533
475 °C / 100 h	271	6776	7554	550
475 °C / 300 h	271	6740	7575	558
475 °C / 500 h	281	6882	7362	566

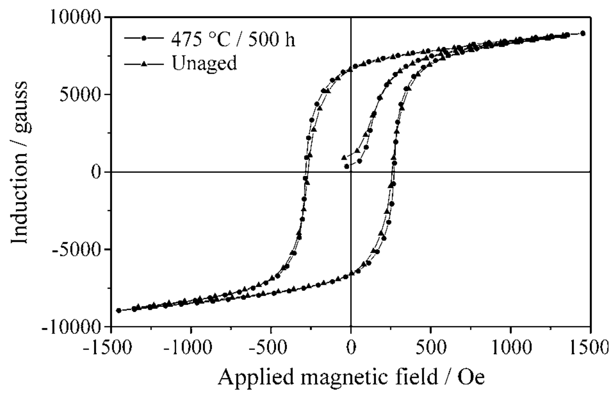

Figure 3. Comparison of the hysteresis loops of the samples solution treated and aged at 475 °C for 500 h.

change in the hysteresis loop due to ageing at 475 °C for 443 h and the latter have reported an increase in the B_r values with ageing time. Its worth mentioning that in the present work, a wrought alloy was analized, while the authors cited above studied cast DSS, which contain phase proportions and chemical compositions different from wrought alloys. The steel analysed by Tsuchiya *et al.*[9] contained only 12.5% of ferrite phase and the steels analysed by Evanson *et al.*[10] contained 12.5 to 26.1% of this phase. These two aspects, of differences in phase proportions and chemical composition, explain the discrepancies in the of B-H curves encountered in this work, when compared with the results of the other two articles.

The output of the thermomagnetic analysis (TMA) is a curve of magnetization *versus* temperature. Figure 4 shows the TMA heating curves obtained for each sample. As can be seen, the magnetic transition temperature (Curie temperature - T_c) increases with ageing time. A precise determination of the T_c can be obtained by deriving the M(T) *vs.* T curve, as shown in Fig. 5. Table 2 shows the T_c values obtained by this procedure.

The increase of T_c with ageing time at 475 °C is due to the influence of the chromium in the magnetic transition temperature of ferrite. As shown in the Fe-Cr phase diagrams available in the literature[17-18], when the amount of Cr is higher than 3 wt.%, T_c is an inverse function of the chromium content. On the other hand, the chromium content in the Fe-rich phase is progressively reduced during the ferrite decomposition. As a consequence, T_c increases with ageing time, which is in agreement with the results obtained by Kim *et al.*[11] in a ferritic alloy. However, no published work on the T_c behaviour in DSS during the ageing embrittlement was found by the authors.

The plot of T_c against ageing time (Fig. 6) exhibits a behaviour similar to the hardness variation (see Fig. 1). In Fig. 7 the impact energy and the Brinnel hardness are plotted against T_c/T_o, where T_o is the initial value of T_c (503 °C). Although additional experiments must be performed at other temperatures, it seems to be clear that the measurement of T_c may be used to detect and quantify the effects of the 475°C embrittlement on the mechanical properties of DSS. It is important to be sure, however, that the heating rate applied in the TMA is the same for all conditions investigated.

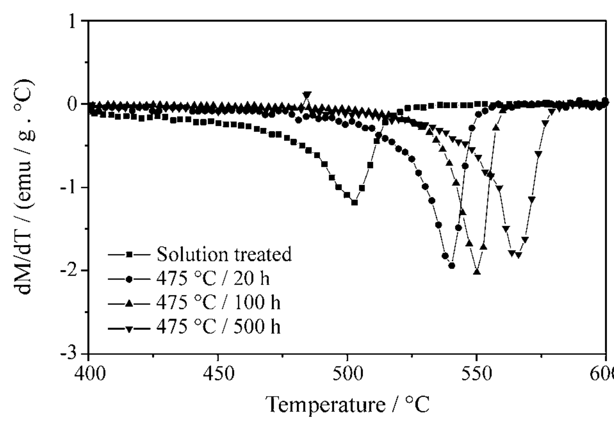

Figure 5. Curie Temperature (T_c) determination.

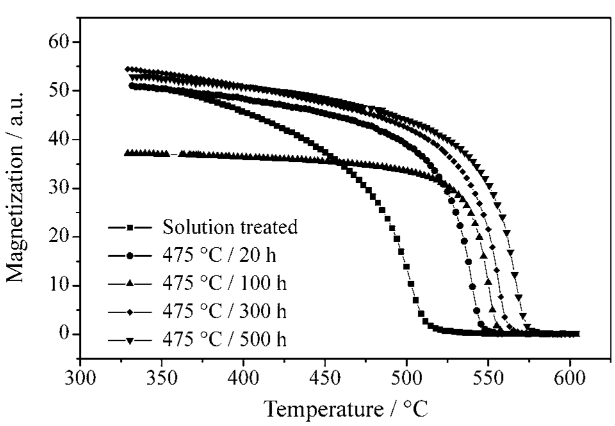

Figure 4. TMA comparative curves at increasing temperatures.

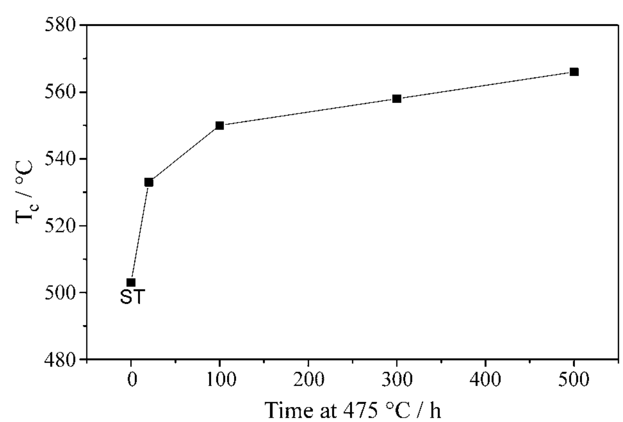

Figure 6. T_c dependence on the time of exposure at 475 °C.

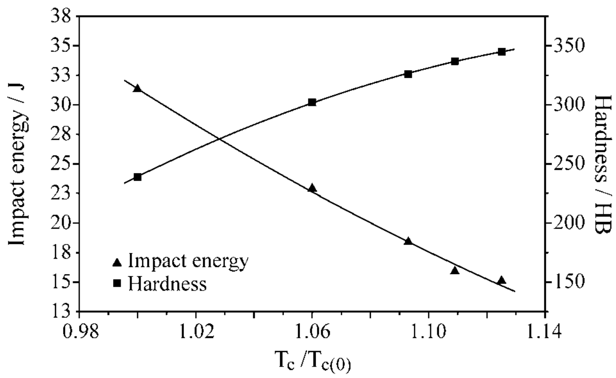

Figure 7. Mechanical properties (impact energy and Brinnel hardness) against T_c.

4. Conclusions

The studied duplex stainless steel UNS S31803 undergoes a reasonable hardening and embrittlement in the first 100 h of ageing, but is only after 500 h that its corrosion resistance to the 10%HNO_3 + 0.05%HF solution is deteriorated.

It was found that in ageing times up to 500 h the magnetic properties B_r and B_s remained nearly unaltered and the coercive force ($_MH_c$) presented a slight increase with the ageing time. There was no significant difference in the hysteresis loops of the sample unaged and the one aged at 475 °C for 500 h. On the other hand, the magnetic transition temperature (Curie temperature, T_c), measured by thermomagnetic analysis, increased with ageing time. This is due to the progressive reduction of Cr content in the Fe-rich phase during the ageing process. This phenomenon may be used to detect and quantify the effects of the α'precipitation in duplex stainless steels.

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