Effect of “475°C Embrittlement” on the Corrosion Behaviour of Grade 2205 Duplex Stainless Steel Investigated Using Local Probing Techiques

EFFECT OF "475°C EMBRITTLEMENT" ON THE CORROSION BEHAVIOUR OF GRADE 2205 DUPLEX STAINLESS STEEL INVESTIGATED USING LOCAL PROBING TECHNIQUES

C. Örnek[1], D.L. Engelberg[1], S.B. Lyon[1], T.L. Ladwein[2]

[1] Corrosion and Protection Centre, University of Manchester, Sackville Street, M13 9PL, UK

[4] Aalen University of Applied Sciences, Beethovenstraße 1, 73430 Aalen, Germany

ABSTRACT

The work reported in this paper correlates microstructure development after low temperature embrittlement heat treatments with pitting corrosion susceptibility in grade 2205 duplex stainless steel. Heat-treatments at 475°C for up to 255 hours were carried out and microstructures characterised using scanning electron microscopy (SEM) and micro-hardness testing. Local electrochemical measurements using an electrochemical micro-cell were carried out and the critical pitting temperature (CPT) determined. Short-duration heat treatments for up to 10 hours showed an increase in CPT, attributed to an improved electrochemical character of the ferrite. Long-term heat treatments (>50 hours) indicated a decrease in CPT due to the precipitation of other precipitates and the formation of elemental depletion zones.

INTRODUCTION

Duplex stainless steels (DSS) are prone to phase transformations when exposed to temperatures in excess of 250°C [1]. Microstructure changes are typically accompanied by embrittlement and the loss of corrosion resistance, affecting the endurance and performance of these alloys. 475°C embrittlement is related to the formation of Cr-enriched α"-phase and Cr-depleted α'-phase, though other secondary precipitates such as G- and R-phase can also form [1-4]. Extensive work exists in the literature about the effect of ageing treatment on mechanical properties [5-8], however, the effect of low temperature embrittlement heat treatments and spinodal decomposition on corrosion properties of duplex stainless steels is not clear. In this paper microstructure development and hardness of 475°C embrittlement were compared to critical pitting temperatures in chloride-containing environment, determined using an electrochemical micro-cell technique.

EXPERIMENTAL

Solution annealed grade 2205 duplex stainless steel plate material was used for all tests with the chemical composition given in Table 1. Coupon samples with dimensions of ca. 15mm x 10mm x 10mm were heat treated at 475°C ± 5°C for 5, 10, 20, 50, and 255 hours, followed by a water quench.

Table 1: Chemical compositions of material used

Grade	C	Si	Mn	P	S	Cr	Ni	Mo	N	Fe
2205	0.016	0.40	1.50	0.021	0.001	22.4	5.80	3.20	0.180	bal.

Macro-hardness tests were carried out with a Vickers indent (HV30), using the mean of 10 indentations. Micro-hardness measurements were performed on stress-free surfaces with a Struers micro-hardness tester (HV0.01). Ferrite and austenite microhardness values were measured and the mean of 20 - 25 indentations is reported. All micro-hardness indentation diameters were smaller than 9.1 µm, placed in the centre of a crystallographic phase region, with each indentation encompassing less than 75% of the area of each phase region. The results should, however, only be considered as a trend of the change in hardness for each phase, since an effect of the indentation size with respect to the finite phase region size cannot be excluded. A SEM was used to measure the dimensions of the indents, and errors are calculated as the standard deviation with respect to the mean.

The CPT of all coupon samples was probed with an electrochemical microcell as shown in Figure 1. The tip of the electrochemical microcell was a polymer tube (PE) with an area of 0.125 cm^2. The working electrode was placed onto a Peltier element for temperature control with a temperature control accuracy of ±0.1°C. The CPT was determined in 5°C temperature intervals, starting from room temperature (RT) up to the temperature where stable pitting was observed. A Gamry Reference 600 potentiostat with an Ag/AgCl reference electrode and a Pt counter electrode were used for all measurements. The electrolyte was a 3 wt.-% NaCl solution. The Open Circuit potential (OCP) was measured for 3 minutes, followed by a potentiodynamic scan from -300mV to +1500mV vs. OCP using a scan rate of 1 mV/s. The CPT was defined as the temperature where the current density showed a steep increase of at least two orders of magnitude with respect to the measured passive current density (before reaching the trans-passive region). All tests were repeated three times to confirm repeatability.

RESULTS

Macro- and micro-hardness measurements are summarised in Figure 3. The increase in macro-hardness with aging times indicates changes in the microstructure; given the heat treatment conditions this can be attributed to the occurrence of 475°C embrittlement. A significant increase after 255 hours of ageing was observed. A similar trend was observed in the micro-hardness measurements. Aging of

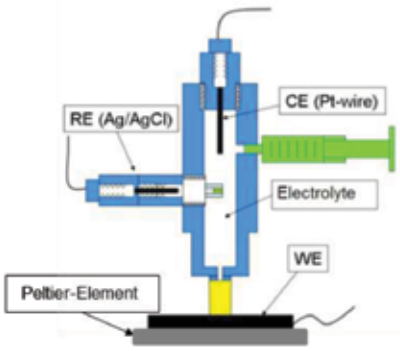

Figure 1: Local probing electrochemical microcell (WE = working electrode, CE = counter electrode, RE = reference electrode) [9]

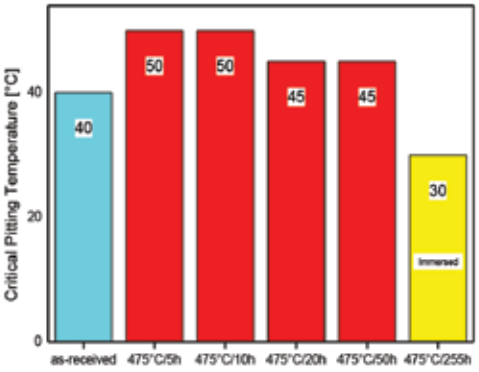

Figure 2: Critical pitting temperatures for grade 2205 aged at 475°C

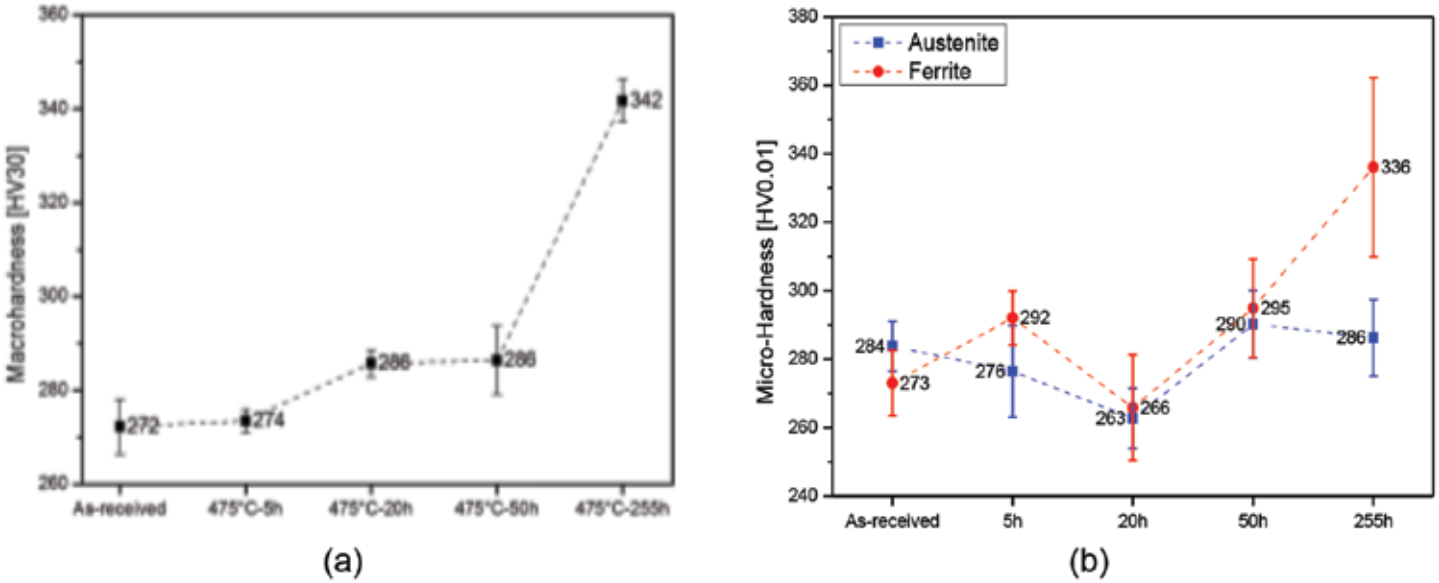

Figure 3: (a) Macrohardness of bulk material, (b) microhardness of austenite and ferrite; dashed lines in both diagrams indicate possible trend.

up to 50 hours at 475°C seems not to cause significant hardness changes, but an increase in the micro-hardness of the ferrite after 255 hours is noticeable. Interestingly, the austenite did not show an increase in hardness.

The CPT of all heat-treated samples is shown in Figure 2. The as received grade 2205 microstructure had a CPT of 40°C. A CPT increase from 40°C to 50°C with 5 and 10 hours aging was observed, with a slight drop after 20 and 50 hours aging to 45°C. The 255 hours heat-treated condition could only be tested in fully immersed conditions, and a CPT of 30±3°C was determined.

Micrographs of the surface attack after CPT testing of the as-received material is shown in Figure 5a-b, and the 5 hours aged sample in Figure 5c-d. In the as-received microstructure the austenite seemed to protrude in all micrographs, indicating a proportionally higher dissolution rate of the ferrite. Interestingly, after 5 hours of aging the opposite trend was observed, indicating a higher dissolution rate of the austenite. The EBSD map in Figure 5d confirms the protruding microstructural features in Figure 5c as ferrite. The dissolution behaviour of both phases seemed to be balanced after 20 hours ageing. After longer ageing times of 50 hours and 255 hours, larger attack on the ferrite is again observed, with the corresponing image of the 255 hours aged sample shown in Figure 4b. However, the austenite showed small pits which might be due to de-alloying effects [10]. In the microstructure after 255 hours aging, the presence of a spinodal decomposition could even be observed at high resolution in the SEM, shown in Figure 4a.

DISCUSSION

The hardness increase indicates the occurrence of 475°C embrittlement with ageing in excess of 50 hours, well-possibly attributed to phase transformation reactions in the ferrite (Figure 4a). After 5 hours aging the corrosion behaviour of the ferrite seems to be enhanced as the micrograph in Figure 5 points to a lesser corrosion attack on ferritic sites, in parallel to an increase in the CPT (Figure 2). Tavares et al. observed comparable results in which the CPT of super duplex grade 2507 increased by 15°C from 72°C to 87°C in 1 M NaCl for samples aged for 8 hours, and the CPT then decreased after 12 hours aging to 63°C [11]. It is believed that spinodal

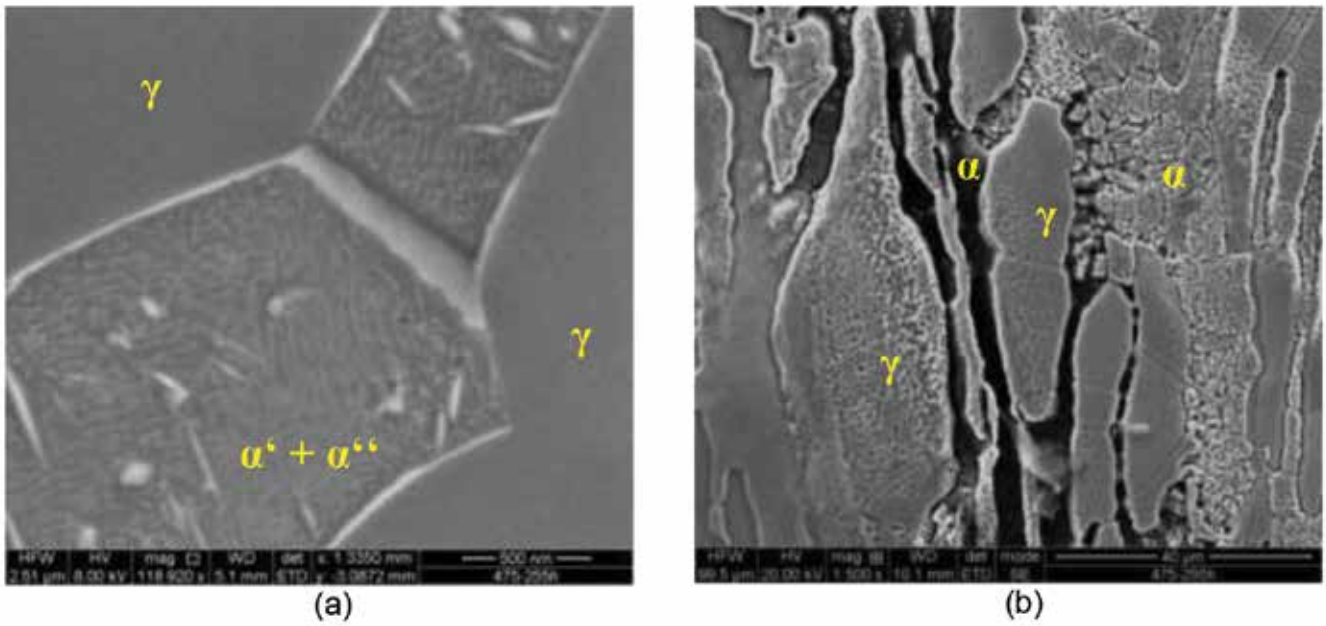

Figure 4: Microstructure of 475°C/255h: (a) spinodal decomposition in the ferritic region, (b) main attack occurred on the ferritic regions with slight pitting-like attack on the austenite.

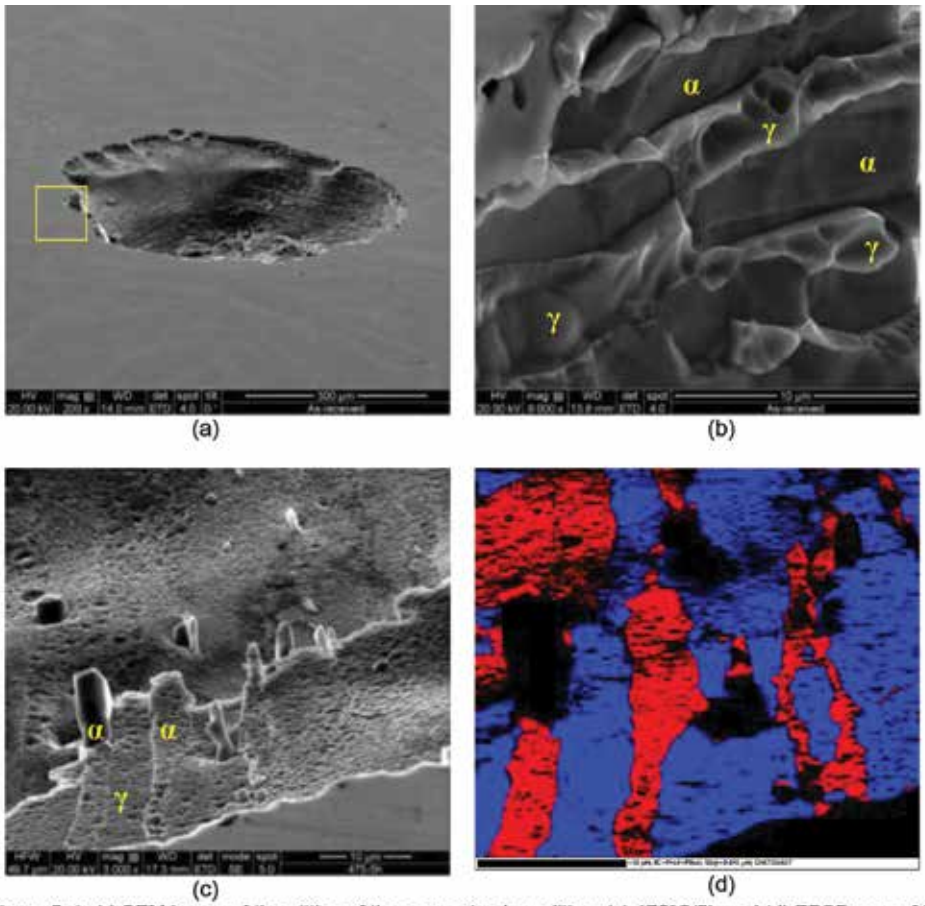

Figure 5: (a-b) SEM image of the pitting of the as-received condition, (c) 475°C/5h and (d) EBSD map of the region shown in (c), with blue representing the austenite, red the ferrite, and black non-indexed points

Figure 5: (a-b) SEM image of the pitting of the as-received condition, (c) 475°C/5h amd (d) EBSD map of the region shown in (c), with blue representing the austenite, red the ferrite, and black non-indexed points.

decomposition in the early aging conditions let to an improvement of the corrosion properties due to a better passivation behaviour, and precipitated secondary phases deteriorated the electrochemical properties. Seemingly, this effect reversed after 20 hours of aging, as the CPT decreased. SEM (and TEM investigations, not reported here) on the 5 and 20 hours aged specimens showed a spinodally-decomposed microstructure in the ferrite, and after 50 and 255 hours aging other types of precipitates were also observed (Figure 4), with the spinodal microstructure consisting of Cr-enriched α''-phase and Cr-poor α'-phase visible as fractal background contrast in the ferrite in Figure 4a. However, once more precipitates were formed with longer ageing treatments the corrosion behaviour decreased rapidly. TEM and SEM analysis could clearly show at least three different precipitates =10 µm; BC+Pred+Pblue; Step=0.041 µm; Grid731x637 in the ferrite and at the ferrite/austenite interphase, ranging in sizes between about 40 to 250 nm. EDX measurements confirmed that some were enriched in Cr and Mo, with elemental depletions adjacent to their locations, which is believed to be the reason for the observed decrease in CPT. The size and number of those precipitates increased after 255 hours of aging, possibly causing micro-galvanic effects within the ferrite. The latter may also be augmented by elemental depletion adjacent to these precipitates, inducing an increased corrosion susceptibility of the ferrite.

CONCLUSIONS

Macro-hardness measurements (HV30) indicated microstructure embrittlement after 255 hours aging at 475°C. Micro-hardness measurements (HV0.01) showed an increase in hardness of the ferrite, with no significant change in the austenite.

An increase in CPT for short-term aging treatments up to 10 hours at 475°C was observed, followed by a drop after 255 hours aging.

The dissolution characteristics indicate that the ferrite is associated with the change in corrosion resistance for both short- and long-term aging treatments.

Spinodal decomposition is believed to enhance the corrosion properties for aging times up to 10 hours, with other precipitates affecting the corrosion resistance due to the formation of elemental depletion zones.

ACKNOWLEDGEMENTS

The authors are grateful for the provision of grade 2205 plate material by Rolled Alloys.

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