INFLUENCE OF THE INTERMETALLIC PHASES PRECIPITATION ON THE CORROSION BEHAVIOUR OF A DUPLEX STAINLESS STEEL

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The effect of the intermetallic phase precipitation on the sulphide stress corrosion cracking resistance of a duplex stainless steel has been studied. Maximum embrittlement was observed in samples treated at 825° C having been associated with the precipitation of sigma phase. Specimens sensitized at 675° C for short period of time just showed a slight sulphide attack and only chromium carbides were observed in the metallographic examination. Longer exposure times produced the precipitation of intermetallic phases and the failure of the specimens. Scanning electron microscope analysis of the fracture surfaces of these specimens helps to explain the reasons of this behaviour.

INTRODUCTION

Duplex austenitic-ferritic stainless steels are increasingly used in these corrosive environments because of their good combination of mechanical and stress corrosion cracking properties that cannot be achieved by fully austenitic or fully ferritic stainless steels (1). Modern wrought duplex stainless steels are characterised by a two phases structure which consists of a mixture of about 50% volume of face centered cubic austenite islands in a matrix of body centered cubic ferrite grains. The optimum combination of properties is accomplished when a duplex microstructure with near equal proportions of austenite and ferrite is obtained by control of their chemical composition and thermomechanical processing (2).

However, this initial balanced microstructure can be substantially modified as neither the austenite nor the ferrite are fully stable and changes can occur during isothermal or anisothermal heat treatments. Most of these transformations are concerned with the ferrite, as elements diffusion rates are approximately 100 times faster than in austenite due to the less compact lattice of the body centered cubic crystal structure (3). Among the different phases which have been identified are various carbides, chromium nitrides, σ, χ, R, π, ε, τ, α' or G intermetallic compounds and the secondary austenite which is formed inside the ferrite (3-5).

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Several previous papers have demonstrated the marked influence of the microstructural changes on the mechanical properties (1,4-7) and corrosion resistance (1,4,5,7) of various duplex stainless steels. Nevertheless, to the authors' knowledge, no study that relates the precipitation of these phases with the sulphide stress corrosion cracking behaviour of the material and the operating failure mechanisms has been published.

The aim of this paper is to investigate the effect of the intermetallic phases precipitation, promoted by different heat treatments, on the sulphide stress corrosion resistance, the fracture topography of the broken specimens and the operating failure mechanisms of a duplex stainless steel.

EXPERIMENTAL PROCEDURE

The material chosen for the present study was a 13.5 mm thick hot rolled plate of a duplex stainless steel conforming to ASTM A240 type UNS 31803, whose chemical composition is (%wt) C 0.017, Si 0.41, Mn 1.48, P 0.028, S 0.001, Cr 22.1, Ni 5.6, Mo 3.0, N 0.13, remainder Fe. The as received mechanical properties in the longitudinal direction were as follows: 0.2% yield strength 553 MPa, ultimate tensile strength 782 MPa and elongation 37%. Material in this condition will be referred as AR. Coupons from this plate were heat treated in a small laboratory furnace at various temperatures in the range from 475 to 900° C for a variety of times up to 24 hours to produce the precipitation of the various brittle phases. These samples were identified as A/B where A indicated the treatments temperature and B the sensitization time.

Sulphide stress corrosion (SSC) tests were carried out at room temperature on round specimens machined from these heat treated coupons in their longitudinal direction. These tests were performed following NACE standard TM-01-77. The environment for these tests was prepared using high purity reagents and adjusting the pH of the solution to 3 before starting the tests. Specimens were introduced in this solution and loaded with a stress equivalent to 100% of the material yield strength by means of CORTEST deformation rings. The maximum testing time was fixed at 720 hours, considering that those samples which exceed this time do not show susceptibility to sulphide stress cracking. Those specimens which failed before the scheduled time were examined in a scanning electron microscope in order to analyse the operating failure mechanisms.

RESULTS AND DISCUSSION

Table 1 exhibits the effect of the various sensitization heat treatments on the time to failure in the SSC test. Maximum embrittlement was detected in samples which were treated at 825° C. No sample treated at this temperature passed the test, failing all them before the scheduled time. These results are in very good agreement with the previously performed fracture toughness tests where a loss of more than 95% of the initial AR toughness was observed in samples treated at this temperature for a period as short as 2 hours (6). This behaviour was attributed to σ phase precipitation clearly evident in the microstructure. An increase in the exposure time to 4 hours increases the amount of σ

phase in the microstructure and reduces the time to failure to only 2 hours. However, when a certain volume fraction of σ phase (around 20%) is precipitated the effect of an additional increase in the sensitization time is scarcely noticeable, reaching a near constant value in the time to failure. Once again, a good agreement with the fracture toughness tests results where a saturation in the embrittlement was found (6) is observed.

TABLE 1- Effect of the sensitization heat treatments on the SSC resistance.

Refer.	time (h)	Refer.	time (h)	Refer.	time (h)	Refer.	time (h)
AR	> 720	900/2	> 720	900/4	496	825/2	326
825/4	2	825/24	1.8	750/2	> 720	750/4	> 720
750/8	> 720	750/20	60	675/2	> 720	675/8	401
675/25	380	475/2	> 720	475/4	> 720	475/24	> 720

Scanning electron microscope examination of the fracture surfaces of these specimens showed the presence of long splits, relatively narrow, orientated parallel to the rolling direction, that is perpendicular to the main fracture plane. Figure 1 exhibits one example of them. Fracture surfaces are near completely free of corrosion products indicating that there has not been a strong corrosive attack. The use of higher magnification revealed the brittle character of the walls of these cracks that is evident in the micrograph of figure 2. An almost completely identical fracture topography was observed in fracture toughness specimens heat treated to the same condition as it is seen in figure 3 (6). All these similitudes between fracture toughness and sulphide stress cracking tests points towards a failure induced for the embrittlement of the material with little or no action of the corrosive environment.

Samples treated at 900° C exhibited a similar behaviour but longer exposure times are required for ferrite decomposition to σ. Some controversy seems to exist with the results of another work (3) where precipitation of σ phase at 900° C after just two minutes was reported. A plausible explanation could be based in the differences in composition between the steels studied in both papers as a marked influence of the alloying elements on the shape of the transformation curves and the position of their "noses" has been claimed (8).

Specimens sensitized at 675° C for a short period of time pass the test without failure just showing a slight sulphide attack. Metallographic examination of these specimens does not reveal any evidence of σ phase in the microstructure due to its slower formation at this temperature. However, a precipitation of small particles was observed at the austenite - ferrite interfaces. These particles were identified by means of WDS spectrometry as chromium carbides with a small amount of molybdenum in their composition. This identification agrees with those reported by other authors (4,5) and has been associated with the high mobility of carbon to these interfaces which are enriched in carbides forming elements (4). As a consequence of this precipitation a chromium depletion in the neighbourhood of the grain boundaries was induced favouring the above mentioned sulphide attack. Longer exposure times at 675° C produce a more copious carbide precipitation, the first evidence of intermetallic compounds, identified as σ, principally, and χ phases (7) and the failure of the SSC specimens before the scheduled time. As both phases coexist it is difficult to study their effects individually (3). The embrittlement of specimens treated at 750° C is lower than that of coupons treated at 825° C for the same period of time due to the slower rate of precipitation of σ phase at this temperature. However, long time sensitized samples exhibited lower toughness and shorter failure times than 675° C ones. In these samples a preferential nucleation of σ phase around previously precipitated carbides is observed.

Several significant differences were found between fracture toughness and sulphide stress cracking results of samples treated at 675° C for long periods of time. Although a certain loss of toughness is observed when the exposure time increases from 2 to 12 hours, associated with the precipitation of σ and χ phases, a near constant value, very similar to that measured in 825° C, is then reached and the fracture topography of the long term sensitized fracture toughness specimens is near identical to that found in those treated at 825° C (6) having been attributed to brittle phases precipitation.

On the other hand, SSC specimens machined from samples sensitized at 675° C always exhibit longer times to failure than those treated at 825° C for the same period of time and no saturation in the embrittlement is evident at least for the period of time analysed in the present paper. Furthermore, SSC specimens are covered by corrosion products pointing towards the action of a sulphide attack favoured by the chromium depletion in the neighbourhood, as it is shown in the micrograph of figure 4. Moreover, the decrease in chromium and molybdenum due to this brittle phases precipitation facilitates the formation of pits at the surface of the specimens promoting the initiation of the sulphide attack.

Finally, samples treated at 475° C, where α' phase which is formed between 300 and 525° C, must be present although, due to its extremely small size was not detected by optical or scanning electron microscopy. No failure of SSC specimens was observed and just a slight decrease in toughness after 24 hours of sensitization was reported (6). Much longer exposure times are required to produce a significant embrittlement and the failure of the SSC specimens.

CONCLUSIONS

a.- Isothermal decomposition of ferrite produces various phases which leads to a certain embrittlement of the steel. The more marked effect was observed in samples treated at 825° C due to σ phase precipitation with little or no action of the corrosive environment. Fracture topography of these specimens is very similar to that found in the fracture toughness ones treated in the same condition.

b.- Samples treated at 900° C exhibited a similar behaviour but longer exposure times are required before so marked embrittlement is produced. Those specimens sensitized at 750° C seems to behave in an intermediate way between 675 and 825° C ones.

c.- Samples treated at 675° C for short period of time passed the tests without failure. These specimens just showed a slight sulphide attack that has been associated to the chromium depletion produced by carbide precipitation. Longer exposure times increased the volume fraction of chromium carbides and induced σ and χ phases precipitation. As a consequence SSC failed before the scheduled time although times to failure were longer than those in 825° C treated samples.

d.- Fracture surfaces of these specimens revealed the presence of pits and corrosion products pointing towards a sulphide stress corrosion cracking mechanism associated to the depletion in chromium and molybdenum in the neighbourhood of brittle phases formed during the sensitization treatment. Marked differences with the fracture toughness specimens were observed.

e.- Samples treated at 475° C where α' phase is present did not showed failure of SSC specimens and just a slight decrease in toughness was observed. Longer exposure times are required before a noticeable embrittlement is produced.

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Figure 1. Fracture surface of a sulphide stress corrosion specimen

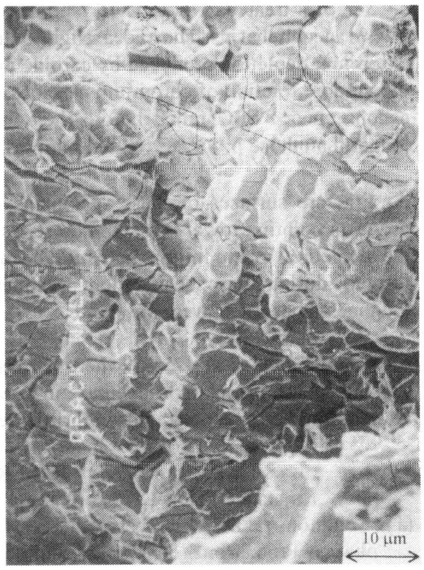

Figure 3. Fracture toughness test specimen

Figure 2. Brittle character of the crack walls

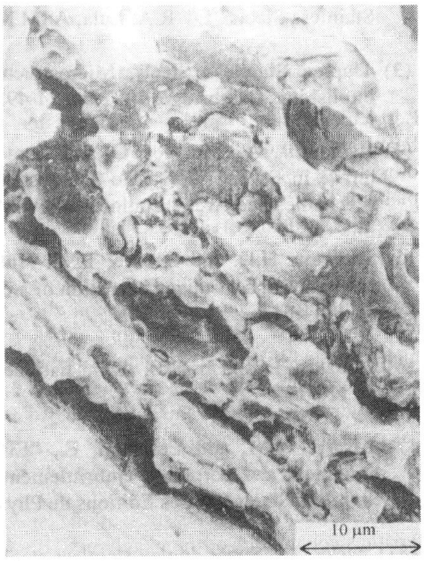

Figure 4. Corrosion products on the fracture surface