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Sulphide stress cracking of a valve stem of duplex stainless steel

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ABSTRACT

The present paper describes a failure investigation of a double disc valve stem made of duplex stainless steel 329 (UNS S32900). The valve stem which operated in moist H_2S environment at 128 °C in a heavy water plant had undergone cracking during operation. The microstructure of the stem material showed precipitates of σ-phase at ferrite/austenite boundaries and elongated oxide inclusions. The formation of σ-phase had occurred during the manufacturing stage of the stem. The crack propagation was more favourable in the ferrite phase and along the ferrite/austenite boundaries where precipitates of σ-phase were formed. It was concluded that the valve stem failed by sulphide stress cracking due to hydrogen embrittlement of ferrite phase. Recommendations to avoid such failures are also suggested.

1. Introduction

Duplex stainless steels (SSs) are widely used as material of construction in various chemical industries owing to their superior strength and corrosion resistance as compared to austenitic stainless grades. Duplex stainless grades have dual microstructure with almost equal fraction of both ferrite and austenite phases.

Although, duplex SSs are more resistant to stress corrosion cracking (SCC) than austenitic grades [1], they are not completely immune to this type of failure. Especially, when there is a source of hydrogen, theses alloys show high susceptibility to hydrogen embrittlement, which are well documented [2–7]. The ferrite phase present in duplex SSs suffer more extensive embrittlement than the austenite phase in the presence of hydrogen. Similarly, it is well known that steels as-well-as ferritic or martensitic grades of stainless steels are readily embrittled by hydrogen, in contrast to austenitic SSs [8]. Cracking of susceptible metals such as high strength steels and even duplex SSs have been reported in hydrogen-containing environment [9]. One such failure of duplex SS 329 caused by sulphide stress cracking (SSC) is analyzed in the present paper.

SSC is a form of hydrogen embrittlement cracking [9] that occurs in an environment containing H_2S and water under the combined action of corrosion and external tensile stress. Hydrogen induced cracking (HIC) e.g., blistering, fissuring, and step-wise cracking observed in carbon and low alloy steels is different from SSC in that it does not require an application of externally applied tensile stress [9, 10]. HIC involves recombination of atomic hydrogen to molecular hydrogen at weak internal interfaces (e.g. inclusions, and laminations) in the material resulting in generation of pressure or stress which is enough to crack the material. On the contrary, SSC is a solid-state embrittlement reaction resulting from the interaction between the metal lattice and the atomic hydrogen [9]. Hydrogen ions are the product of corrosion processes, which pick up electrons from the corroding metal forming hydrogen atom. Some of these hydrogen atoms can diffuse into the metal and embrittle its crystalline structure. H_2S environment is considered to be highly aggressive with respect to SSC and hydrogen embrittlement because of two reasons: one is that H_2S increases the corrosion rate

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Fig. 1. The image of the failed valve stem showing corrosion attack and axial cracks (indicated by arrows) at several locations.

of metals in aqueous solutions and the other is that it poisons the hydrogen recombination/evolution reaction leading to increased absorption of atomic hydrogen into the metal.

Duplex stainless steel has another problem in that the ferrite phase is not stable and transforms to various embrittling phases when exposed at temperatures greater than 300 °C. Spinodal decomposition consisting of phase separation of ferrite into Fe-rich α and Cr-rich α′ occurs in the temperature range 300–500 °C [11]. At still higher temperatures in the range 600–1000 °C [12], intermetallic phases such as σ and chi can form. These phases (σ and chi) can even precipitate during the production of the component especially when the cooling rate is low after solution annealing or welding. These intermetallic phases lead to degradation in mechanical properties and corrosion resistance of duplex SSs and hence, limit their service life [1].

2. Background

A double disc valve stem (diameter 62 mm) made of duplex SS 329 (UNS S32900) in a heavy water plant failed due to cracking during operation. The photograph of the failed stem is presented in Fig. 1 that shows a long longitudinal crack (indicated by arrows). There were several other cracks as well as patches of corrosion attack on the cylindrical surface of the stem. The stem was used in a moist H_2S gas environment at pH = 4 and at a temperature and a pressure of 128 °C and 19 Kg/cm^2 respectively. The valve stem was in service for 30 years.

3. Material

The chemical composition of the failed stem was analyzed and the result is presented in Table 1. Some deviation in the chemical composition was observed (Ni, Mn and P contents are higher) compared to the standard grade of duplex SS 329 as per ASTM A240 [13]. The average ferrite content of the stem rod as measured by a ferritscope was 66%.

4. Stereo microscopic examination

The cylindrical surface of the failed stem was examined at higher magnifications using a stereo microscope. Fig. 2a shows corrosion attack on the surface as several shallow pits. One of the cracks on the cylindrical surface of the failed stem rod is shown in Fig. 2b. It appears that the corroded regions or pits on the surface are joined together to form a large crack.

5. Microstructural examination

Samples cut from the failed stem were polished to a finish of 1 µm. The microstructure of the stem was revealed after electrolytic

Table 1
Chemical composition (wt%) of the failed stem, which is compared with the standard composition of duplex SS 329 as per ASTM A240 [13].

Element	Stem rod	SS 329 as per ASTM A240
Cr	25.4	25–28
Ni	5.3	2.0–5.0
Mo	1.7	1.0–2.0
Mn	1.35	1.0 max
Si	0.27	0.75 max
C	0.08	0.08 max
P	0.05	0.04 max
S	0.03	0.03 max
Fe	Bal.	Bal.

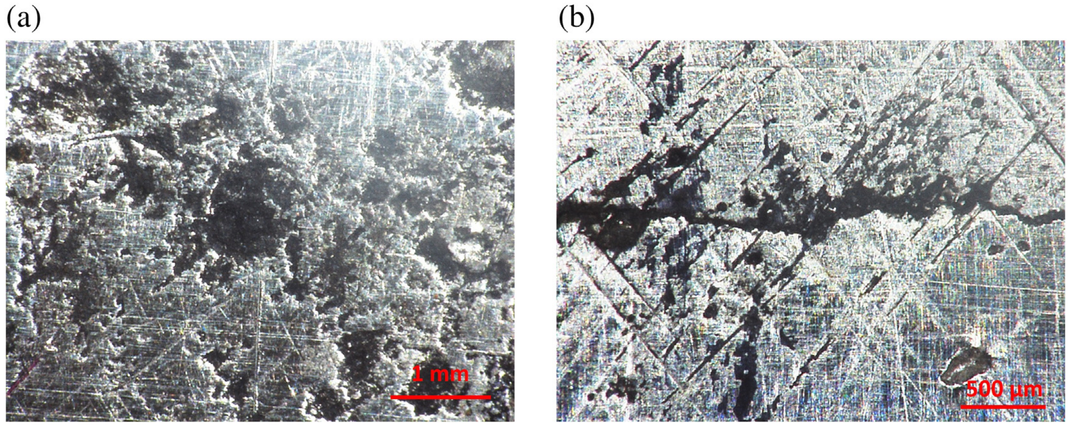

Fig. 2. Stereo micrographs of the cylindrical surface of the failed stem showing (a) corrosion attack in the form of wide and shallow pits and (b) one of the several cracks.

etching in KOH solution (45 g KOH + 60 ml water) at 2.5 V for few seconds.

A typical etched microstructure of stem away from the crack is shown in Fig. 3a consisting of austenite islands (light-color etched) in ferrite matrix (dark-color etched). In addition, small-sized precipitates of red/orange color are also observed which are mostly concentrated at the ferrite/austenite boundaries and within the ferrite phase. These precipitates were identified as σ-phase based on their red/orange color after electrolytic etching in KOH solution as per ASTM standard E407 [14]. Such a distribution of σ-phase at ferrite/austenite boundaries is also reported in literature [15]. The stem material also contained large inclusions which were of almost spherical shape when viewed on the transverse section. However, when examined on the longitudinal section, these inclusions were found to be elongated along the axis of the stem. A typical elongated inclusion on the as-polished longitudinal surface is shown in Fig. 3(b).

Fig. 4 is the montaz of optical microscopic images of the cross-section of stem showing the full length of a crack. The crack is observed to be initiated at the surface and has propagated to the transverse direction of the stem, i.e., in a direction perpendicular to the axis of the stem. There is not much branching of the crack. In general, the cracks were very wide and their typical propagation through the duplex phases of ferrite and austenite on the etched microstructure is shown in Fig. 5a. The optical micrograph in Fig. 5b is taken near the crack tip. It is evident that the cracks are more likely to propagate in the ferrite phase and along the ferrite/austenite boundaries where precipitates of σ-phase are located. Once the austenite phase is encountered along the crack path, either the cracks are stopped or they change their path to remain in the ferrite phase (Fig. 5b).

Scanning electron microscope (SEM) attached with energy dispersive spectroscope (EDS) was used to analyze the type of inclusion and to conclusively confirm the presence of σ-phase in the microstructure of stem material. The SEM micrograph in Fig. 6 shows the typical microstructure of duplex SS stem on the transverse section. Ferrite and austenite phases are distinguished by their color contrast (austenite is brighter than ferrite). The rounded particle at the centre of micrograph (Fig. 6) shows an inclusion in the stem. The chemical compositions of small precipitates (dark grey in color) formed in ferrite and at ferrite/austenite boundaries and that of inclusion were analyzed using point EDS and the results are presented in Table 2. The chemical compostions of individual ferrite and austenite phases were also measured and are shown in Table 2. The compositions of only major alloying elements are consisdered

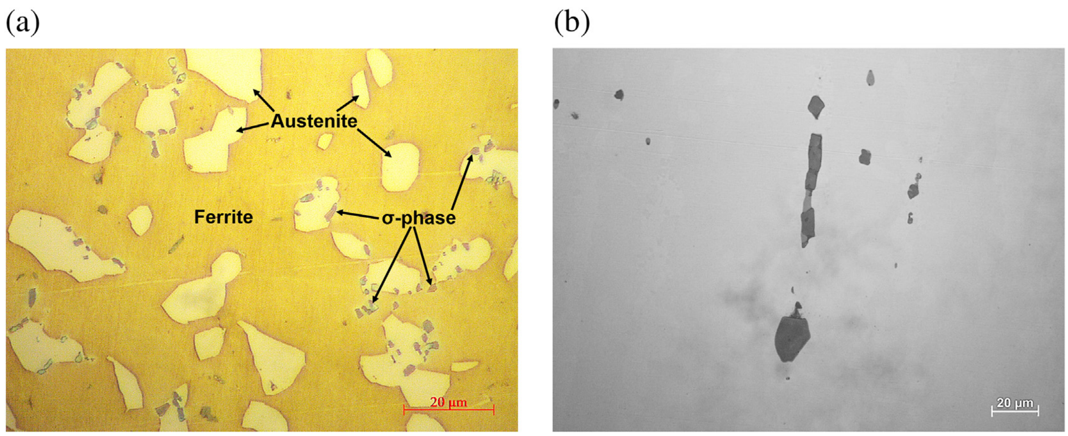

Fig. 3. Optical micrographs showing (a) the typical microstructure of duplex SS 329 stem on the transverse section after electrolytic etching in 45% KOH solution consisting of ferrite, austenite and precipitates of σ-phase and (b) elongated inclusions on the as-polished longitudinal surface.

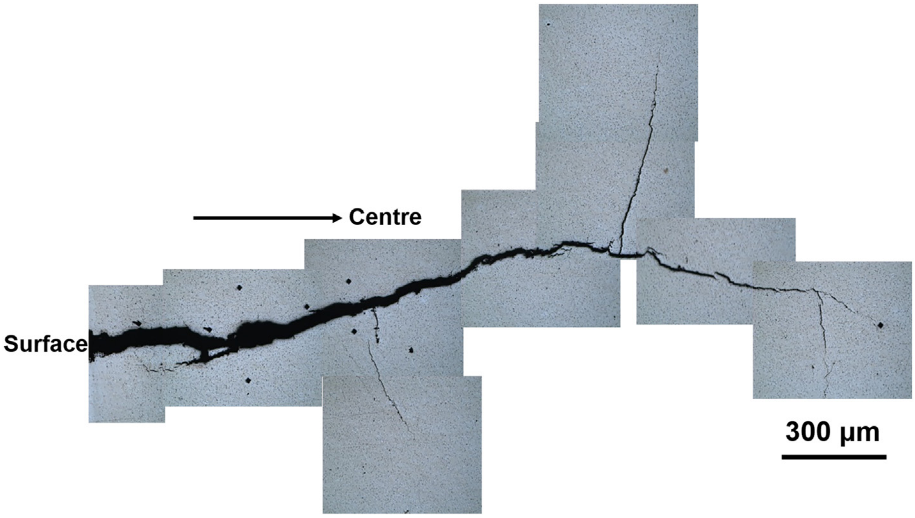

Fig. 4. Montaz of optical micrographs on the cross-section of the failed stem showing the propagation of a crack in the transverse direction starting from the surface.

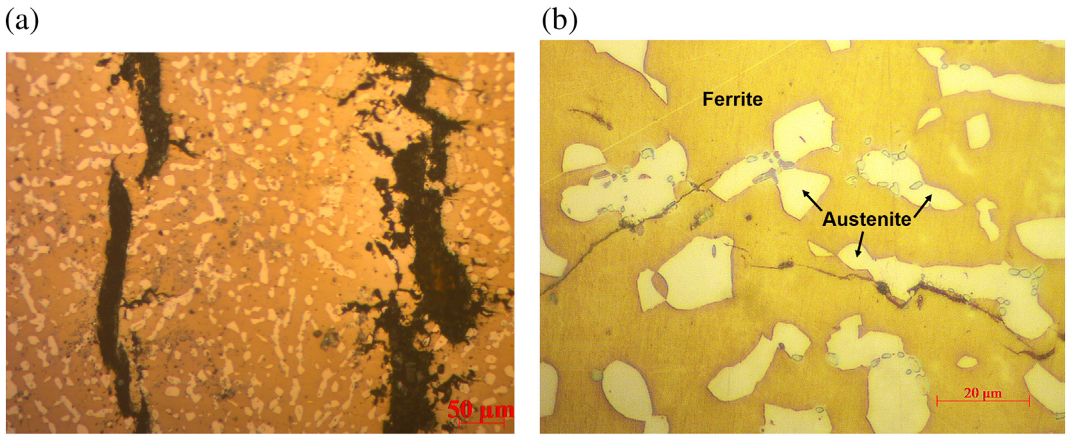

Fig. 5. Optical micrographs of the failed stem on the transverse section after electrolytic etching in 45% KOH solution showing (a) crack propagation path within ferrite and austenite phases and (b) the region near the crack tip. The cracks are more likely to propagate within the ferrite phase and along the ferrite/austenite interfaces where precipitates of σ-phase are present.

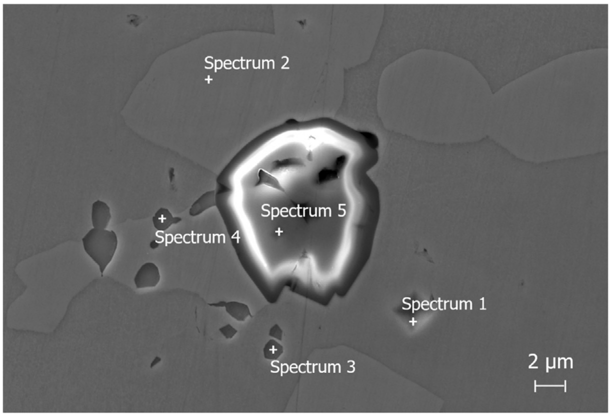

Fig. 6. SEM micrograph of the transverse section of duplex SS 329 stem showing a large inclusion. Also marked are the locations where point EDS was performed corresponding to which the compositions are presented in Table 2.

Table 2
Chemical composition (wt%) of different phases/precipitates corresponding to the EDS spectra marked in Fig. 6.

Element	Ferrite, α (spectrum 1)	Austenite, γ (spectrum 2)	Precipitate in α (spectrum 3)	Precipitate at α/γ boundary (spectrum 4)	Inclusion (spectrum 5)
Cr	26.9	22.9	56.8	49.3	32.8
Ni	3.9	6.7	2.3	2.8	–
Mo	2.7	1.1	5.7	4.6	–
Mn	1.5	1.8	1.6	1.2	20.5
Si	0.7	0.5	0.3	0.5	–
O	–	–	–	–	31.5
N	–	–	–	–	6.4
Other elements	–	–	–	–	Al: 6.3, Mg: 1.2
Fe	Bal.	Bal.	Bal.	Bal.	Bal.

here. The phases/precipitates on which point EDS were performed are marked in Fig. 6. As expected, ferrite phase is enriched with ferrite stabilizing elements such as Cr, Mo and Si and lean in austenite stabilizing elements such as Ni and Mn. The reverse is the case for austenite phase, i.e., it is enriched in Ni and Mn and lean in Cr, Mo and Si. The precipitates formed in ferrite and at ferrite/austenite boundaries are highly enriched in Cr and Mo indicating that these must be σ-phase in agreement with the optical microscopic results. Sigma-phase is comparatively richer in Cr and Mo than the matrix [1, 15]. The chemical composition of inclusion shows high contents of O, Cr and Mn (Table 2) indicating that duplex SS stem contained oxide-type inclusions in the microstructure.

6. Microhardness

The hardness of the failed stem was measured on the transverse section at a load of 500 g. The average hardness was 259 HV (27.2 HRC) which is close to the specified maximum value of 28 HRC for AISI 329 [13]. The high hardness of the stem could be related to improper solution annealing or to the presence of σ-phase in the microstructure. σ-phase is a hard and brittle phase which is known to increase the hardness and decrease the toughness of a material [1, 16, 17]. However, an increase in hardness is significant only when σ-phase is more than 5% but the toughness of the material is affected even at a low level of 1–2% of σ-phase [17].

7. Discussion

The microstructure of the failed stem of duplex SS AISI 329 showed precipitates of σ-phase within ferrite and at α/γ interfaces. Sigma-phase in stainless steels is generally formed in the temperature range of 600 to 1000 °C [12]. Since, the operating temperature of stem is only 128 °C, the σ-phase must have been formed at the manufacturing stage of stem. Sigma-phase is a hard and brittle phase which decreases toughness and ductility and increases the yield strength of a material [1, 16]. At a lower temperature of around 800 °C, sigma phase forms in a coral-like structure [12] according to the reaction $\alpha \rightarrow \sigma + \gamma_2$. The diffusion distances are smaller at such lower temperatures, so, the σ-phase is smaller in size. But at higher temperatures close to 1000 °C, σ-phase is coarser and more compact which is explained by the lower nucleation rate and higher diffusion rate at elevated temperatures [12]. The failed stem in the present study showed σ-phase which is coarse, compact and almost spherical in shape. This indicates that the stem after forging might have been annealed at a temperature closer to 1000 °C during manufacturing stage resulting in precipitation of σ-phase.

The duplex SS stem was in service in moist H_2S gas at 128 °C. H_2S environment is known to cause environmental cracking or more popularly known as SSC and hydrogen embrittlement of all types of stainless steels including duplex grades [9]. The maximum susceptibility of duplex SS to environmental cracking in H_2S is generally observed at intermediate temperatures in the range 60 to 120 °C depending on the specific alloy [9] but cracking can also occur at slightly higher temperatures such as at 128 °C in the present case.

Environmental cracking is caused when three conditions are simultaneouly present: applied stress, susceptible microstructure and corrosive environment. All of these conditions are satisfied in the present case. Because of the operation of double disc valve, axial load is exerted on the stem during service. Moist H_2S as desciribed above is highly corrosive to stainless steels and is also a source of hydrogen. It is well known that Fe-based alloys having phases with body-centred-cubic (BCC) or body-centred-tetragonal (BCT) crystal structures such as found in steels, ferritic and martensitic stainless steels are prone to hydrogen embrittlement but not the austenitic grades which have face-centred-cubic (FCC) structure [1, 8]. This is due to restricted slip capabilities in the BCC structure [8]. The susceptibility to hydrogen embrittlement increases with tensile strength or hardness of a material and therefore, it is limited to steels with a hardness of 22 HRC or greater [8]. In fact, according to NACE standard [18], a steel with a hardness value more than 22 HRC and a duplex stainless steel with a hardness value more than 25 HRC are not recommended for use in sour gas (H_2S) environment.

There are other reasons proposed for higher hydrogen embrittlement of ferrite phase apart from its BCC structure such that the diffusivity of hydrogen in ferrite is greater than that in austenite by four to five orders of magnitude and solubility of hydrogen in ferrite is lower than that in austenite [19]. In the present study, the crack propagation in duplex SS stem was observed to be more favourable in ferrite and along the ferrite/austenite boundaries where precipitates of σ-phase are present (Fig. 5b). In contrast, austenite islands acted as barriers to crack propagation. Several authors [20–22] have reported a similar observation, i.e., ferrite is more prone to hydrogen embrittlement in duplex SSs. A high propensity of hydrogen pick up and crack initiation in the ferrite phase as against austenite phase has also been shown in duplex SS in hydrogen charging experiments [23]. Therefore, it was concluded that the stem of AISI 329 had failed due to SSC by hydrogen embrittlement cracking of ferrite phase. The presence of large amount of brittle σ-phase in the microstructure of duplex SS 329 stem increased the tensile strength and hardness (27.2 HRC), hence, such a microstructure would be highly susceptible to hydrogen embrittlement or SSC. Further, higher inclusion content in the microstructure of a material, such as in the present case, is also reported to promote hydrogen embrittlement [24]. These inclusion particles act as hydrogen traps and increase the absorption of hydrogen atoms in the microstructure. However, no evidence of contribution of inclusions on propensity to hydrogen embrittlement is observed in the present study.

8. Conclusions

Large amount of σ-phase and oxide inclusions were observed in the microstructure of the failed valve stem of duplex stainless steel which operated in moist H_2S gas at 128 °C. Such a microstructure is more susceptible to environmental cracking. The valve stem failed by sulphide stress cracking due to hydrogen embrittlement of ferrite phase. The crack propagation was more favourable in the ferrite phase and along the ferrite/austenite boundaries where precipitates of brittle σ-phase are formed. Based on the morphology of σ-phase, it appears that the material of stem was annealed at temperatures closer to 1000 °C during manufacturing that resulted in precipitation of σ-phase. A well annealed duplex SS without any sigma phase would last much longer in the H_2S service at the operating conditions.

9. Recommendations

(a) Cleanliness and a suitable microstructure of a material are significant features to ensure a long service life of a component in an aggressive environment such as in moist H_2S gas. During procurement of duplex SS AISI 329 forged rod, it should be ensured that the material is free from σ-phase and does not have a high inclusion density. A fast and easy way to determine the presence of σ-phase is by electrolytic etching of polished sample in KOH solution. The measurement of impact energy by Charpy impact test also reveals the presence of σ-phase in the microstructure.

(b) Although, valve stem has failed after a long service of 30 years its tendency to hydrogen embrittlement would increase with service time as more and more hydrogen is absorbed by the material. Therefore, the ability of stem to bear a load without crack initiation would also reduce with time. Therefore, it should be ensured that there is no excess tightening of the valves resulting in overloading of the stem that otherwise brings down the time to crack initation and propagation.

(c) Super duplex stainless steels such as UNS S32205 or UNS S32750 (in a proper solution annealed condition) which have higher corrosion resistance than duplex SS grade UNS S32900 may be used for a new valve stem.

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