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Damage characterization of an ASTM A 213 grade 91 tube after 116.000 h of service in a reforming plant

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ABSTRACT

ASTM A213 T91 steel is used in power plants and petrochemical industry, for long-term service components. The improved mechanical properties of grade 91 are strictly related to its specific microstructure: a tempered martensite matrix with fine precipitates embedded in. Despite low alloy heat resistant ferritic steels, that have a well known operational experience, T91 service performances are still faintly consolidated, because this material has serviced only in a limited number of plants, since the eighties. Most of the available data were obtained by laboratory tests on relatively short term creep strength and corrosion properties.

The investigations reported in this paper represent an important opportunity to describe and better evaluate the damage evolution of the grade T91 steel after more than 100000 h of exposure in severe conditions (580 °C, 18—26 bar, combustion environment).

Our results suggest that the steel suffered by different damage forms, which appear on definite portions of the tube cross section. The main degradation forms observed, in fact, into the tube bulk are both the martensite recovery and the microstructural evolution. This latter promoted mostly Laves phase precipitation and coarsening. On the other hand, both the outer and the inner wall side, suffered mainly by severe oxidation/carburization. Especially on the outer surface, the massive carbide precipitation has caused an evident loss of ductility so that the mechanical properties of the tube appear appreciably reduced.

1. Introduction

ASTM A213 T91 steel is used in power plants and petrochemical industry for long-term service components. This 9% Cr steel shows high resistance to creep and, for this reason, the usual service temperature can be raised up to 580—600 °C, increasing performances.

The improved mechanical properties of grade 91 are strictly related to its specific microstructure: a tempered martensite matrix with fine precipitates embedded in. Two typologies of secondary phases are present: $M_{23}C_6$ carbides (where M = Cr/Fe/Mo/Mn) along grain boundaries (prior austenitic grain boundaries, packed, block, martensite laths boundaries) and finely dispersed MX type carbonitrides within laths (where M = V/Nb and X = C/N). The $M_{23}C_6$ carbides increase the creep strength by retarding the subgrain growth, while the MX carbonitrides pin down free dislocations. Despite low alloy heat resistant ferritic steels, which have a well known operational experience, T91 service performances are still faintly consolidated, because this material has serviced only in a limited number of plants, since the Eighties. Therefore, long term performance needs careful observation. At the present time, a poor number of data about T91 damage after 100.000 h of service exposure have been published [1,2]. Most of the previous work were conducted in laboratory on relatively short term creep strength and corrosion properties [3—6].

Long term service exposure triggers evolution on the

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microstructure [7–11] in terms of $M_{23}C_6$ carbides coarsening, precipitation of new secondary phases (Laves and modified Z phases) and recovery of the pre-existent martensite lath. Only MX carbonitrides remain stable and not suffer coarsening. Laves phases are Fe_2Mo intermetallic precipitates, containing also small amounts of Si and Cr, which nucleate on prior austenitic grain and subgrain boundaries, close to $M_{23}C_6$ carbides. The influence of Laves phase on creep resistance is not fully understood: their precipitation decreases the amount of Mo dissolved in the matrix, reducing solid solution strengthening; on the other hand, it increases the creep strength by precipitation hardening. However, only fine particles play a beneficial role; in fact, reached the mean diameter of Laves sub-micrometric dimensions, the effect on creep resistance is lost. Moreover, Laves phases can act as favorite site of nucleation of creep voids, due to their relatively high hardness. Modified Z phase is a complex nitride, whose chemical composition in metallic elements is approximately $50\%(Cr + Fe)$ and $50\%(Nb + V)$. This class of precipitates can be considered as precursor of Z phase and appears in the matrix after long term service in creep conditions, replacing MX precipitates and reducing solid solution strengthening. Although very detrimental effect on creep strength has been ascribed to Z phase in 12% Cr steels [9,10,12], in grade 91 steels modified Z phase precipitation starts only after 30.000–40.000 h at 650 °C, whereas at lower temperatures it does not play a significative role on long term microstructural evolution and stability. The loss of creep rupture strength of T91 steels is due also to recovery of original microstructure, preferentially near prior austenitic grain boundaries (PAGB). Crept specimens showed characteristic increasing in lath and subgrain size [9,10,13,14]. Well developed subgrains of low dislocations density in the interior are typical feature of long term exposed specimens [13]. Stress seems to promote tempered martensite recovery [14] and this microstructural evolution usually triggers creep damage. The preponderant part of creep curves of P91 steel is the tertiary stage. This can be explained as a continual degradation of creep strength resulting from microstructure evolution. In general, creep damage includes the development of voids and cracks, often along grain boundaries; however, compared with low alloy steels, martensitic steels are less sensitive to form intergranular cavities. The association of small cavities with large second phases has been frequently observed [15–17].

Corrosion may also occur during long term exposure to high temperature. The oxidation resistance of P91 grade in steam and flue gas is a potentially life limiting factor. Temperature, flue gas composition and chemical composition of the alloy (especially of Cr, Mo, Ni) play a significative role in promoting the development of a protective spinel scale or a less protective iron oxide scale with macroscopic defect such as pores and cracks [4–6]. In simulated CO_2 rich environment, samples of P91 steel were attached by oxidation and carburization simultaneously, with deleterious effects on ductility and surface: a double-layered oxide scale is formed and massive precipitation and coarsening of $M_{23}C_6$ carbides are observed. The oxidation/carburization behavior is influenced by several factors, such as temperature, pressure, alloy composition and gas composition. However, oxidation and carburization processes are not independent from each other. Furthermore, they are influenced by arrangement of chromium rich phase and oxide microstructure; in this way the formation of a more protective and diffusion repressive chromium-rich oxide layer reduce carburization and oxide growth. The mechanism for the inward transport of the carbon remains unclear, even if it is supposed a movement of corrosive gaseous components CO, CO_2, H_2O and H_2 through pores and cracks in oxide scale and the next reacting with base material [18–21].

The present work focuses on damage characterization of a grade 91 steel tube, coming from a catalytic reforming plant after over 100000 h of service life in severe conditions. Through optical, electron and transmission microscopy, as well as EDX elements mapping and microhardness measurements, the component has been deeply investigated in order to identify and point out the manifold damage founded on it.

2. Materials and methods

The tube portion, examined in this study, comes from a catalytic reforming plant. The component was designed to operate at 580 °C and 18–26 bar with naphtha and hydrogen process fluids and serviced for 116000 h. The outsider diameter and the wall thickness are 114,3 mm and 10,5 mm respectively. The chemical analysis was performed by optical emission spectroscopy OES ARL 3460 Thermofisher. Metallographic specimens for optical microscopy investigations were taken from the tube to examine both transverse and longitudinal sections. Cutting was performed by a Buehler Isomet 4000 precision saw. Specimens were mounted in an automatic mounting press and carefully polished using a series of grit papers and finished by diamond polishing. Afterwards, polished areas were etched with the Vilella's reagent and examined under a Nikon Eclipse ME600 optical microscope equipped with digital camera and software for image processing and analysis. Fegsem investigations were performed with a Fegsem Zeiss ultra Plus. The chemical composition of each precipitate was determined by electron dispersive X ray analysis EDX Inca 250 X max 50. TEM analysis was carried out with a 200 kV Scanning/Transmission Electron Microscope (STEM), JEOL 200CX. A radial profile of microhardness was performed with a manual Leitz Vickers microhardness measuring system. The indentation was made with a 200 g load. Tensile tests were carried out on a Galdabini PM 60 apparatus, equipped with a TOM-I extensimeter, according to UNI EN ISO 6892–1:2009 standard [22].

3. Results

3.1. Visual examination

Pictures of received tube are shown in Fig. 1. A red-brown oxide layer is clearly visible on the outer surface; there is no evidence, however, of significant reduction of the wall thickness.

3.2. Chemical analysis

Table 1 shows that the chemical composition of investigated material meets the ASTM A213-06 [23] compositional range.

3.3. Optical microscopy

LOM was used to identify the alloy microstructure. The serviced material shows coarsened carbides and defined grain boundaries in the bulk (Fig. 2), whereas both external and internal surfaces have a complex microstructure, with multiple layers of different appearances. On the outer wall side, (Fig. 3a–b) the most external layer can be identified as an oxide, with a thickness ranging between 500 and 1000 μm. Under this layer, a very thin (30–50 μm) zone without precipitates can be distinguished as a grey-white line, followed by a portion of bulk material, of 1100–1200 μm thickness, showing a dense network of large precipitates. At the end, under this zone, the typical microstructure of serviced bulk material can be observed. The inner surface (Fig. 3c–d) shows a similar pattern, even if the oxide layer and the precipitation-rich zone appear appreciably thinner (50–100 μm).