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Rejuvenation of service exposed ammonia cracker tubes of cast Alloy 625 and their re-use

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ABSTRACT

This study is an extension of a previous study undertaken to rejuvenate ammonia cracker tubes of Alloy 625 alloy that have been service exposed in heavy water plants for their full service life of 100,000 h. The service exposure caused significant microstructural modifications and deterioration in mechanical properties, and a solution annealing treatment of 2 h at 1160 °C rejuvenated all properties similar to those of the virgin alloy. The present study reports the evolution of microstructure and mechanical properties of a full service exposed centrifugally cast Alloy 625 tube that was put into service again for 55,000 h after receiving a rejuvenation treatment. During the second service, microstructural modifications, increase in strength and loss of ductility were on the lines of the work reported earlier. However, it was encouraging to observe that degraded properties after the second service life remained within the bounds of those of virgin and full service exposed tubes. The good performance of the rejuvenated tube during the second service life has been attributed to good control of operation parameters that limited the precipitation of grain boundary carbides during the first service life, which otherwise would have had a direct bearing on premature failure of tubes during their second service life.

1. Introduction

Alloy 625 is a nickel–chromium–molybdenum alloy with significant amount of niobium. Nominal composition of the alloy (in wt%) is: Cr – 20% to 23%; Fe – 5%; Mo – 8% to 10%; (Nb+Ta) – 3.15% to 4.15%; Al – 0.4%; Ti – 0.4%; Co – 1%; Mn – 0.5%; Si – 0.5%; P and S – 0.015% each; C – 0.1% and the balance is nickel (single figures refer to the maximum limit). It possesses high strength, excellent fabricability and joining, good oxidation resistance and outstanding resistance to stress corrosion cracking as well as pitting. These properties make it an excellent material for chemical industries for applications such as bubble caps, tubing, reaction vessels, distillation columns, heat exchangers, transfer piping, valves, etc. In nuclear industries, the alloy finds application as reactor-core and control-rod components of light water reactors. It is also one of the candidate materials for advanced reactor concepts because of its high allowable design strength at elevated temperatures, especially between 650 and 750 °C [1].

In ammonia based mono-thermal heavy water production plants, Alloy 625 tubes are the primary containment of cracker units where pressurised ammonia gas is cracked into a synthesis gas ($3H_2+N_2$). Cracker tubes are approximately 90 mm in diameter, 8 mm in wall thickness and 12 m long (~effective heating length) and are housed inside a rectangular furnace fired by multiple radiant-type burners to heat them from outside. These tubes are designed for a service life of 100,000 h at 717 °C temperature and a pressure of 14.5 MPa (Table 1). However, these tubes are operated at temperatures varying from about 550 to 650 °C and at a pressure of around 14 MPa. Although virgin tubes are in solution annealed condition, service exposure results in significant hardening due to the precipitation of various phases [2–7]. This has caused premature failure of some tubes due to embrittlement caused by the precipitation of carbides and intermetallic phases [7-9]. Precipitation behaviour of these phases can be understood on the basis of their time-temperature-phase (TTP) diagram (Fig. 1) discussed in detail elsewhere [7,10]. The life of service-exposed tubes is extended by giving a re-solution annealing treatment at 1160 °C for 2 h [7–9,11]. In spite of the precipitation of embrittling phases, tubes of wrought Alloy 625 have been found to successfully complete their designed life of 100,000 h in operating plant conditions [7], and the present study would established that centrifugally cast Alloy 625 tubes, which offer significant cost benefits, perform equally well under plant conditions.

There are limited studies on creep properties of Alloy 625 [8,9,12]. Its creep resistance improves significantly upon reducing

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Table 1
Operating and design parameters of cracker tubes of cast Alloy 625.

Operating pressure	14.0 MPa
Design pressure (rupture)	14.5 MPa
Design pressure (elastic)	15.7 MPa
Operating temperature	550-650 °C
Design temperature	717 °C
Lifetime basis	100,000 h
Minimum stress to rupture at design temperature	82 MPa
Permissible creep at design temperature and pressure	1%

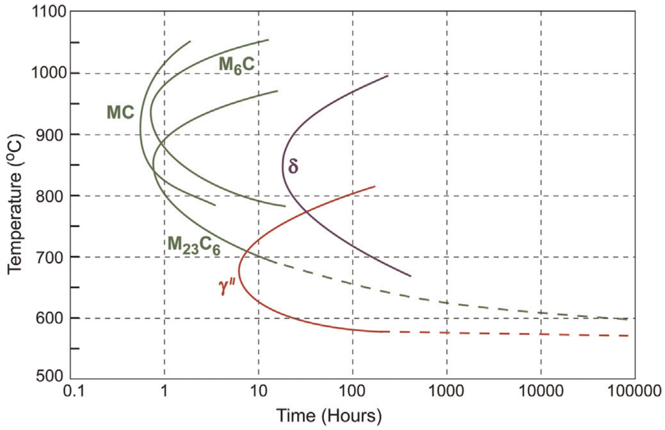

Fig. 1. Time-temperature-phase transformation diagram of the phases precipitating in Alloy 625 (redrawn after reference [10]).

the grain size [12]. Mathew et al. [8,9] have carried out extensive creep studies on samples of “rejuvenated” Alloy 625 and experimentally evaluated its creep life over a wide range of temperatures (650–900 °C) under iso-stress condition at a fixed stress of 105 MPa. They considered the stress of 105 MPa after multiplying a safety factor of 1.5 to a hoop stress of 70 MPa equivalent to 14 MPa of operating pressure of cracker tubes. Iso-stress rupture life plot at 105 MPa exhibits a linear behaviour with two slops with a slope change at a temperature of about 800 °C and corresponding to least rupture ductility. On the basis of this data, they predicted a creep rupture life of about 75,500 h at 720 °C. Mathew et al. [8] also analysed rupture life of the “rejuvenated” alloy as a function of applied stress using the Larson–Miller parameter (LMP), given by $LMP = T(C + \log t_r)$, where t_r is the rupture life and T is the test temperature in Kelvin. Mathew et al. [8] have shown that the rupture life of the rejuvenated alloy falls within a scatter band of ± 20% of that of the virgin material. Considering a value of $C = 20.7$ in the LMP equation [13], they have predicted its service life to be about 81,500 h at 720 °C at a stress of 105 MPa. This value is close to that predicted by the iso-stress analysis. The authors have suggested dislocation creep to be the rate controlling deformation mechanism at 720 °C [8].

The two slop linear behaviour of iso-stress rupture life plot suggests of complex microstructural changes occurring in the tested temperature range. Mathew et al. [8,9] have also investigated microstructures of creep tested samples. The alloy exhibits extensive formation of acicular δ-phase within grains under most of the test conditions. Though the δ-phase is considered to be a stable phase, it dissolves gradually at temperatures between 850 and 875 °C. As the creep-test temperature increases from 750 to 875 °C, amount of the δ phase decreases with its complete absence at 875 °C. The morphology of δ precipitates changes significantly with increasing temperature. The number density of δ-phase precipitates decreases but their size increases at higher ageing temperatures. Sample creep tested at 700 °C forms γ″-phase. $M_{23}C_6$ carbide precipitates envelop grain boundaries at most of the temperatures studied. When the microstructural data observed by Mathew et al. [8,9] is mapped over the TTP diagram (Fig. 1), the observed phases fall within expected phase fields suggesting that the creep stress does not appear to have any effect on their evolution. It is therefore not unreasonable to consider that creep damage in Alloy 625 occurs predominantly in the form of microstructural changes rather than mechanical damage in the form of cracks and cavities.

Over a decade ago, an extensive research programme has been initiated primarily to study the effect of microstructural modification on mechanical properties during service with an aim to rejuvenate service exposed tubes for their re-application in cracker units. A part of this study on the “modifications in microstructural and mechanical properties in a service exposed wrought Alloy 625 ammonia cracker tube removed after 100,000 h of service” has been reported recently [7]. According to this study, precipitation of $Ni_2(Cr,Mo)$ and/or γ″ phases during service causes considerable hardening throughout the cracker tube while precipitation of grain boundary carbides and δ phase causes a significant reduction in toughness. Thickness of the grain boundary carbide film has been found to increase from top to bottom sections suggesting of a monotonous increase in the temperature witnessed by the cracker tube [7]. This study established that a solution treatment of the service exposed alloy at a temperature of 1160 °C for 2 h successfully dissolves all the precipitates as well as grain boundary carbides that form during service and rejuvenate alloy properties. However, the study remains incomplete as it is not clear if the rejuvenated tubes would perform similar to those of virgin tubes, particularly with respect to carbide precipitation. This is because the slow rate of the formation of grain boundary carbides in nickel-base superalloys is attributed to the entrapping of carbon into primary carbides of MC type (where M can be Nb, Ta and/or Ti) and the carbon has to disintegrate first from MC carbides to form grain boundary carbides [14]. Primary carbides form during the solidification process and are very stable and decompose very slowly at elevated temperatures only [14]. However, grain boundary carbides that form during the service dissolve easily during the rejuvenation (solution) treatment releasing carbon in the austenite matrix, which may increase the carbon content above the solubility limit of carbon. This carbon in the rejuvenated alloy would be freely available in the alloy for easy precipitation of grain boundary carbides during the next service and would make rejuvenated tubes vulnerable to premature failures as reported in reference [15]. Therefore, it is necessary to ascertain that dissolution of grain boundary carbides formed during the service does not increase the content of dissolved carbon in the austenite matrix significantly. One direct way to understand this is by ensuring that degradation in properties of a rejuvenated tube during its second service life remains similar to those in the service aged virgin alloy.

Objectives of the present study are:

(1) to characterize microstructural and mechanical properties of a full-service exposed cracker tube of cast alloy re-exposed for 55,000 h (for the second time) after receiving a rejuvenation (solution) treatment;
(2) to compare its properties with those of a virgin cast Alloy 625 tube as well as with a full service aged cast Alloy 625 tube.

This study demonstrates that rejuvenation of cracker tubes would be effective when there is a good control over service temperature during their previous life.