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TECHNICAL NOTE

Effect of Temperature on the Microstructure and Hardness of Service Exposed 25Cr35NiNb Reformer Tubes

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Abstract Premature failures of 25Cr35NiNb microalloyed steel reformer tubes are due to progressive microstructural degradation of the material during service exposure at high temperature. Limited information is available in the open literature regarding the influence of temperature on microstructure and mechanical properties of this material. Effect of temperature on the microstructure, carbide content and hardness of the steel across the wall thickness of tube exposed for 11 years is presented in this paper. No evidence of any microscopic defects was observed in specimen exposed at 650 °C, whereas micro-voids were observed along grain boundary regions in the tube exposed at 997 °C. Grain size increased with increase in service temperature. In the tube exposed at higher temperature, near the outer wall, carbides were distributed uniformly in the matrix, whereas carbides were concentrated at grain boundary near the inner tube wall, resulting in higher hardness near the outer wall of the tube.

Keywords Reformer tube · 25Cr35NiNb microalloyed steel · Grain size · Carbide content · Hardness

1 Introduction

Centrifugally cast 25Cr35NiNb austenitic stainless steel is extensively used as reformer tubes in chemical and petrochemical industries for hydrogen generation [1, 2]. During service, outside surface of the tube is heated to ~1000 °C and a constant temperature gradient is maintained across the thickness. Microstructural evolution of the prolonged service exposed tubes many times results in its premature failure due to creep deformation. Considering the safety of the plant recent efforts were being made to assess the high temperature tensile properties and remaining life of the service exposed reformer tubes [3–6]. Yan et al. [7] revealed precipitation of carbides at elevated temperatures resulting in increase in hardness of HP40Nb steel without tungsten addition. Alvino et al. [8] reported higher hardness in the steel near inner wall compared to the outer wall of the tube due to carbide precipitation. Ray et al. [5] and Swaminathan et al. [6] did not reveal any significant difference of hardness between the virgin and service exposed material. However, a systematic study regarding the microstructural evolution and concomitant degradation in properties of the steel during the service exposure has not been reported. The present study was carried out to investigate the effect of microstructure and hardness on prolonged exposure at elevated temperatures of reformer steel tube.

2 Materials and Methods

25Cr35NiNb microalloyed reformer tube having nominal thickness of 15 mm obtained from Numaligarh Refineries Ltd, India was used for the study. Table 1 shows the chemical composition of the material. One end of the 15 m long tube was exposed at 650 °C and the other end at 997 °C for 11 years. The specimens from the sections exposed at 650, 820 and 997 °C were investigated. The thickness of the service exposed tube at 997 °C was found to be 13 mm. Specimen of dimension 15 mm × 5 mm was

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Table 1 Chemical composition of microalloyed 25Cr35NiNb steel (in wt%)

C	Mo	Si	Cr	Ni	Nb	Ti	Fe
0.4	0.037	1.3	23.6	34.9	0.8	0.037	Balance

sliced from the tubes. Standard metallographic specimen preparation technique was used and etched in glyceregia solution. Microstructure was investigated under optical microscope and scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectrometer. Volume percentage of carbide precipitates and matrix grain size was determined by image analysis technique and line intercept method, respectively. Hardness across the thickness was measured using Vickers hardness indenter.

3 Results and Discussion

Figure 1a to f show optical micrographs of the sample exposed at 650, 820 and 997 °C, at near inner and outer wall surface. Microstructure in Fig. 1a reveals equiaxed grains with continuous carbide network at grain boundary regions. Figure 1b shows that grains are elongated and carbides are in discontinuous form. The average grain size at the inner and outer wall surface is determined as 67 and 73 µm, respectively. No evidence of cracks or creep cavities was observed in the samples exposed at 650 °C.

Sample near inner wall surface (Fig. 1c), reveals fragmentation of carbide network at grain boundary regions. At 820 °C, the micrograph shows presence of micro-voids near inner wall. Figure 1d reveals carbides are in the form of intermittent particles throughout the grain near outer wall surface.

From Fig. 1e, the presence of large number of voids at the grain boundary region is evident. The size and morphology of the voids indicate considerable growth after nucleation during the prolonged high temperature exposure. A gradual decrease in the density of defect from the inner wall towards the outer wall was observed. Due to the high centrifugal forces during casting, the outer surfaces of the tubes exhibit equiaxed grains and columnar grain structure for much of the wall thickness from the inner wall. Hence, under the service condition, it is usual for cracks to initiate at the inner wall regions. Similar observations were also reported by Brear et al. [9]. The carbide network can also be observed at the grain boundary regions. However, the amount of carbide network has reduced considerably compared to Fig. 1a. Figure 1f reveals microstructural evolution in the material near the outer wall surface during the exposure at 997 °C. The carbides are in the form of discontinuous particles and distributed throughout the matrix. Since, the temperature at the outer surface of the tube was higher compared to the inner surface, carbon diffuses from the Cr-rich carbides to the Nb-rich areas to form NbC in the matrix. This leads to a morphological change for grain boundary carbide network and subsequent precipitation of carbides near the outer surface of the tube. Since, the inner surface was at lower temperature, similar phenomenon was not observed. Hence, uniform and fine precipitation of particles were absent near the tube inside surface.

Figure 2a shows the SEM mircrographs of the sample exposed at 650 °C. EDX analysis revealed three types of second phase particles at the grain boundaries. The continuous dark grey phase (phase-A) is a Cr-rich carbide (Fig. 2b). The EDX spectra of the discontinuous white particles (phase-B) having an average length of ~15 µm shown in Fig. 2c indicates Nb-rich carbide. The bright fine particles (phase-C) with size of around 2.5 µm is (Nb, Ti)-rich carbides (Fig. 2d). Figure 2a also indicates higher amount of Cr-rich carbide in the alloy compared to other carbides.

Figure 3a shows the variation of grain size across wall thickness of the reformer tubes. Coarse grains are observed near outer wall and the grain size increases with increase in temperature. Similar trend was reported by De Almeida et al. [10] and Alvino et al. [8]. Since, the temperature at the outside surface is higher for prolonged time, grain coarsening occurs at regions near the outer wall.

Figure 3b shows plot of volume percentage of Nb-rich carbide versus distance across the wall thickness of the tubes exposed at various temperatures. The Nb-carbide remains almost constant across the thickness for each temperature. The amount of Nb-carbide near the inner wall surface decreased from 7 % at 650 °C to 4.3 % at 997 °C. Similar trend was observed at regions near to the outer wall of the tube.

Variation of hardness versus distance from inner wall is shown in Fig. 3c. The hardness across the tube thickness remains almost constant in the material exposed at 650 °C. The hardness of the tube decreases when the tube was exposed to higher temperatures. A variation in hardness is observed across the thickness when the tube is exposed to 997 °C. The hardness near the outer and inner wall is 252 HV and 178 HV, respectively. The increase in hardness near outer wall of the tube exposed to 997 °C is attributed

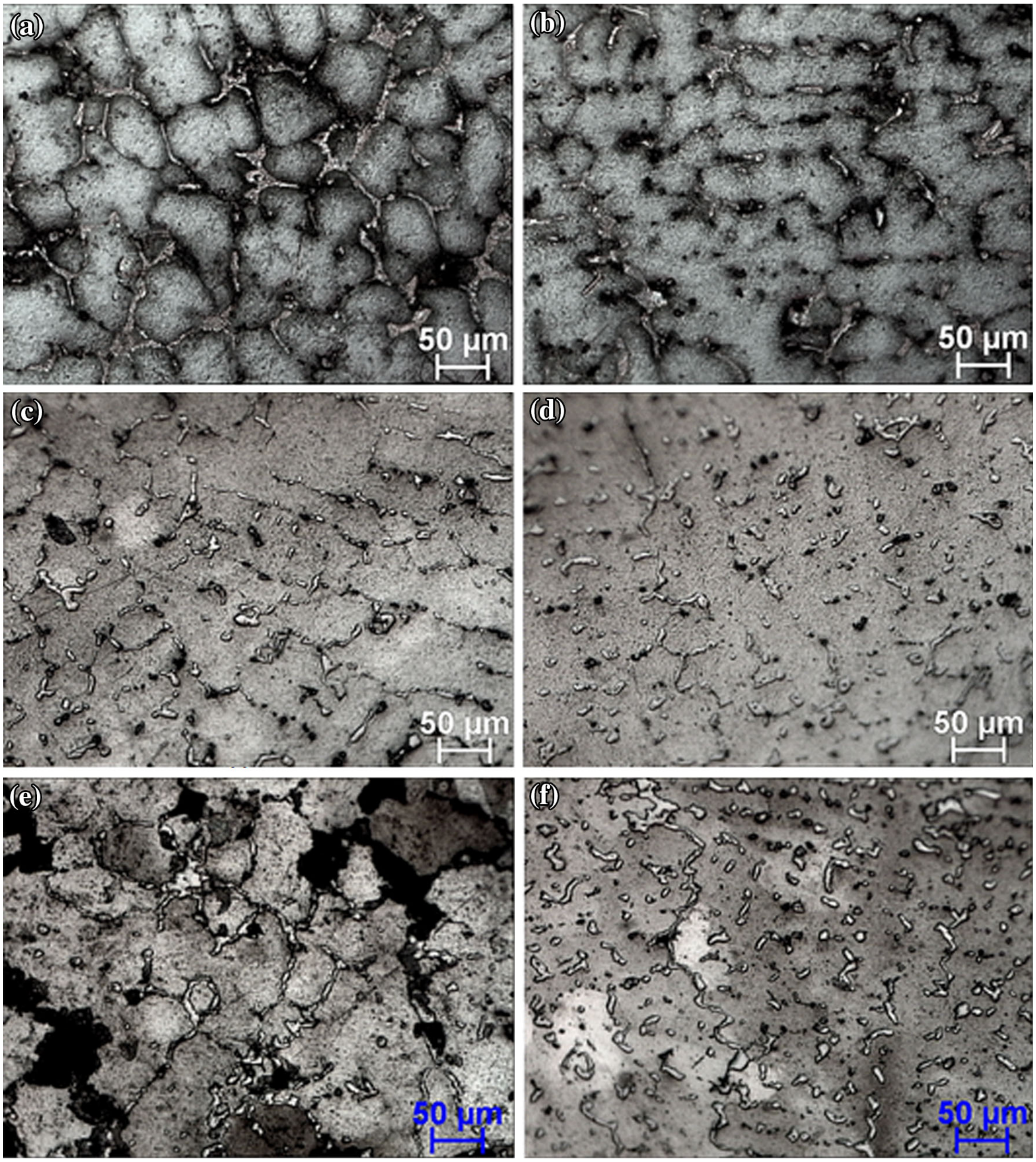

Fig. 1 Optical micrographs of specimen near **a**, **c**, **e** inner and **b**, **d**, **f** outer wall. **a** & **b** 650 °C, **c** & **d** 820 °C and **e** & **f** 997 °C

to the presence of fine carbide particles distributed uniformly in the matrix (Fig. 2f). The hardness increases with decrease in grain size.

4 Conclusion

The conclusions are as follows:

- Network of coarse Cr-rich carbide at grain boundary and growth of cracks along grain boundary is observed near inner wall of tube exposed at 997 °C. Whereas, at near outer wall, cracks are not visible and fine carbide precipitates are nucleated in the grain.
- Grain size increased with increase in temperature and distance from inner wall of the tube.
- Volume percentage of Nb-rich carbide decreased with increase in temperature and was almost constant across the thickness of the tubes.
- Hardness near inner wall decreases with increase in temperature whereas, near outer wall of service exposed tube at 997 °C shows higher hardness due to fine precipitates in the grain.

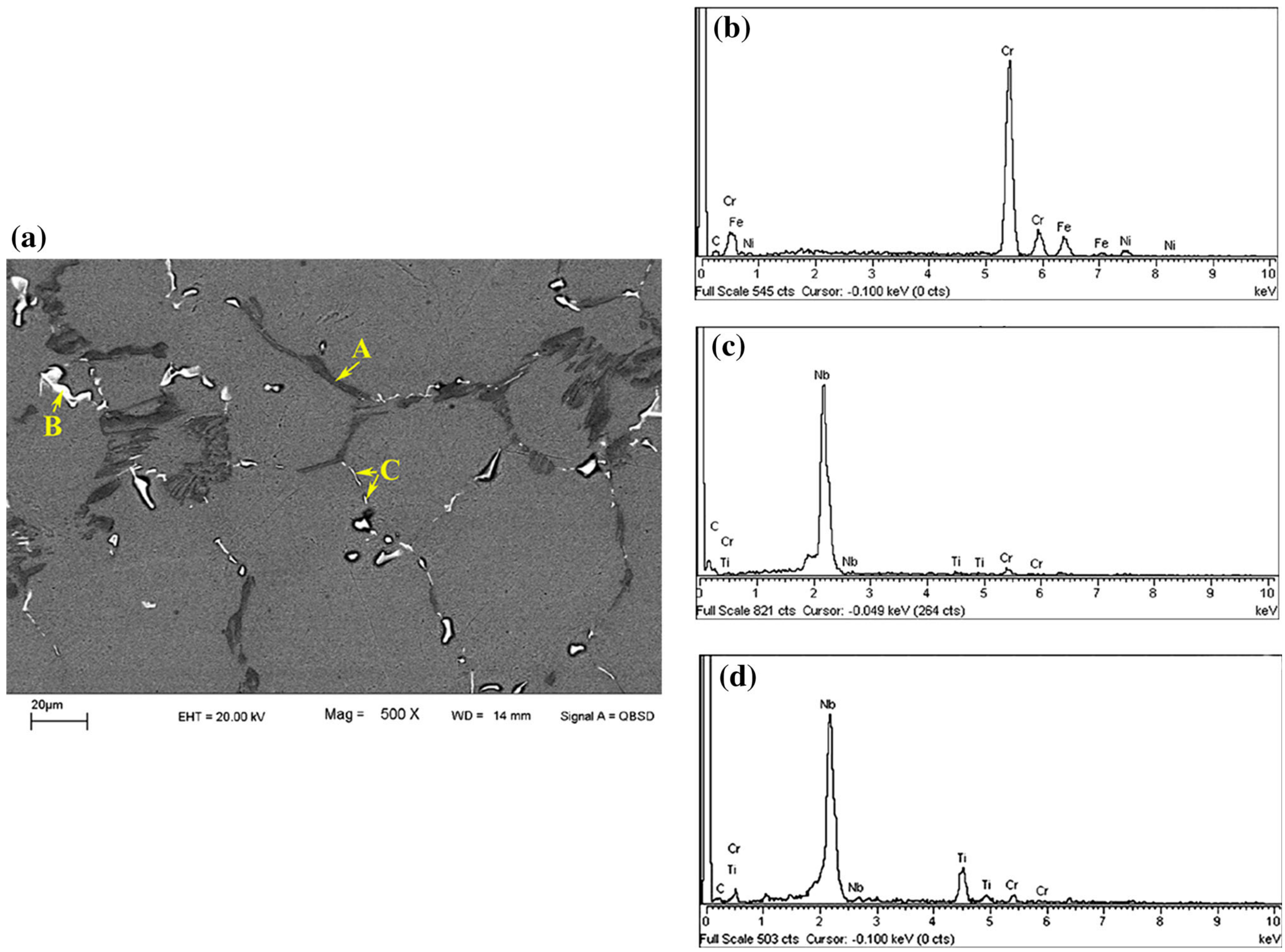

Fig. 2 **a** Back-scattered SEM image of the sample heat affected at 650 °C. **b**, **c** and **d** EDX spectra of phase-A, phase-B and phase-C, respectively

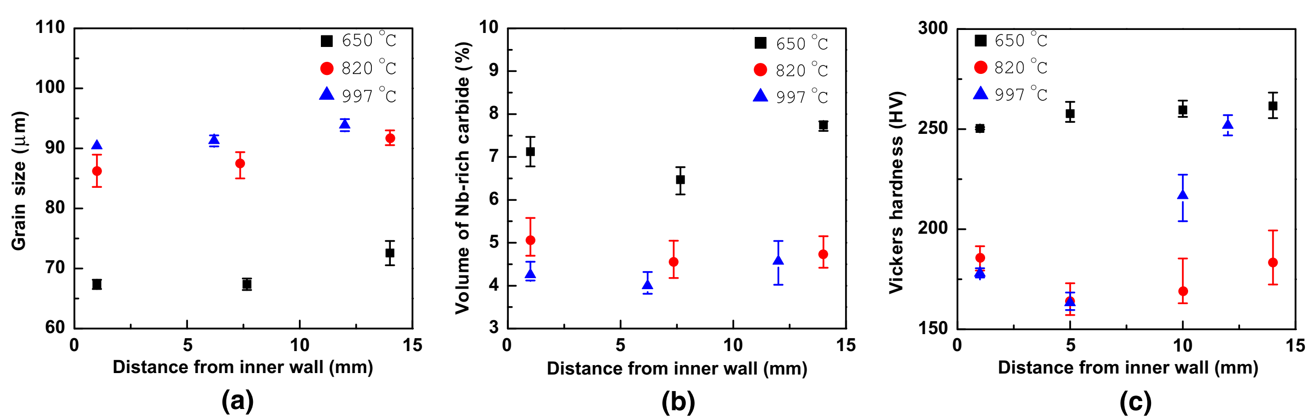

Fig. 3 Variation of **a** grain size, **b** Nb-rich carbide and **c** hardness along wall thickness of the reformer tube

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References

1. Joubert J, St-Fleur W, Sarthou J, Steckmeyer A, and Fournier B, *Comput Coupling Phase Diagr Thermochem* **46** (2014) 55.

2. Wahab A A, and Kral M V, *Mater Sci Eng A* **412** (2005) 222.
3. Jahromi S A J, and Naghi Khani M, *Int J Eng T B* **17** (2004) 183.
4. Bonaccorsi L, Guglielmino E, Pino R, Servetto C, and Sili A, *Eng Fail Anal* **36** (2014) 65.
5. Ray A K, Kumar S, Krishna G, Gunjan M, Goswami B, and Bose S C, *Mater Sci Eng A* **529** (2011) 102.
6. Swaminathan J, Guguloth K, Gunjan M K, Roy P K, and Ghosh R, *Eng Fail Anal* **15** (2008) 311.
7. Yan J, Gao Y, Yang F, Yao C, Ye Z, Yi D, and Ma S, *Mater Sci Eng A* **529** (2011) 361.
8. Alvino A, Lega D, Giacobbe F, Mazzocchi V, and Rinaldi A, *Eng Fail Anal* **17** (2010) 1526.
9. Brear J M, Church J M, Humphrey D R, and Zanjani M S, *Int J Pres Ves Pip* **78** (2001) 985.
10. De Almeida L H, Ribeiro A F, and May I L, *Mater Charact* **49** (2002) 219.