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The Effect of Service Time on Carbide Volume Fraction and Hardness of Catalyst Tube Materials

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Abstract. The effect of service time on secondary carbides formation in reformer furnace tubes has been studied to obtain a relationship between carbide volume fraction, service time, and hardness. Tube material is Kubota KHR35CT which is part of ASTM A297 HP class. The study was performed by examinations of microstructural evolution and hardness. The microstructures were examined using optical and scanning electron microscopes of the new tube, and the other tubes that had been in service for 17,500; 96,300 and 113,800 hours at 850°C. Carbide volume fraction was measured using image analyzer. Carbide volume fraction of the new tube is 7.72%, and increased to 8.86% after 17,500 hours, 9.54% after 96,300 hours, and 10.95% after 113,800 hours. The increase in carbide volume fraction to 8.86 % did not affect the hardness substantially because the hardness only increases from 191 to 198 BHN. However, increasing exposure times to 96,300 and 113,800 hours decreased the hardness to 170 and 173 BHN respectively. These decreases in hardness may be corresponding to the coarsening and agglomeration of carbide particles due to longer exposure time at 850°C.

Keywords: catalyst tube, creep, degradation, microstructure, carbide precipitate.

1. Introduction

Cast alloys of ASTM A297 HP are widely used for radiant tube in reformer furnace to produce hydrogen gas as a result of endothermic reaction between light hydrocarbon and water vapor. The main degradation mode of reformer tubes is creep because they are being operated at high temperatures (up to 1000°C) and internal pressures. In some cases other degradation modes such as overheating and thermal shock [1,2] may also contribute to shorten the service life. Therefore, the tube material shall have high creep resistance and long service life.

The primary reformer in ammonia plant of Pusri Unit 3 has a capacity of 1100 MTPD and consists of 378 catalyst tubes of Kubota KHR35CT that arranged in nine harps of 42 tubes each. The tubes are vertically installed and hanged on the spring at the top and to expand downwards. The light hydrocarbon feeding gas and steam enters from the top end at a temperature of 400°C and pressure of 455 psig, and flowing down through the catalyst in individual tubes before coming out of the tubes at 850°C and pressure of 443 psig. The endothermic reforming reaction



takes place in the catalyst tubes. The heat is supplied from 200 arch burners and 10 tunnel burners in the furnace. The heat is transferred to the catalyst tubes through radiation to maintain metal temperature at 850°C.

The microstructure of ASTM A297 HP alloy consists of austenitic dendrite surrounded by eutectic carbides. The primary carbides were precipitated at the grain boundaries during solidification and fine secondary carbides were precipitated in the matrix at service temperature [3,4]. High temperature strength of the tube was obtained from these precipitates [5,6]. Embrittlement and reduction of strength might occur when these precipitates coarsened or agglomerated. Further microstructure degradation may involve the formation of creep cavities, cavities coalescence, micro-cracking and final propagation of cracks [1,3].

The present work will discuss about the microstructure evolution and its effect on the hardness at various service time of reformer furnaces.

2. Materials and Methods

Nine tubes samples, consists of a new tube and eight used tubes from Primary Reformer Pusri Unit 3 Row-J harp with different service time are shown in Table. 1. Figure 1 shows the location of samples taken from each tube for laboratory analysis

Table1. Tube samples from primary reformer Pusri-3

Identity	Service time (hours)
New (N)	0
T8	17500
T11	17500
T2	96300
T12	113800
T18	113800
T22	113800
T37	113800
T42	113800

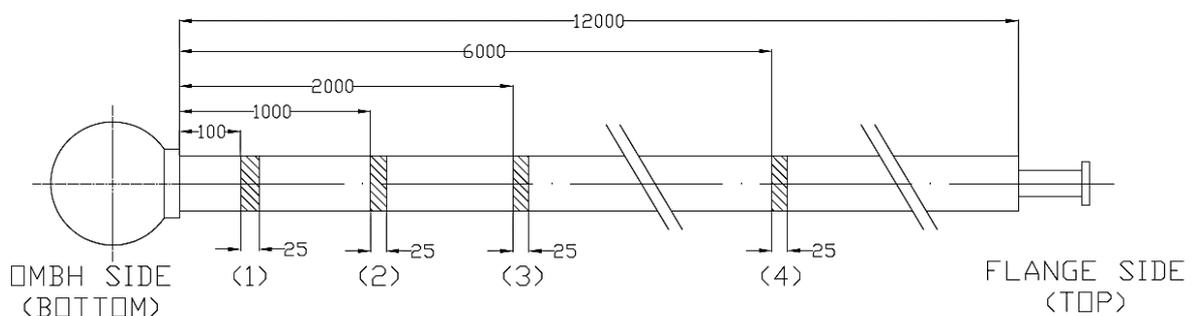


Figure 1. Tube dimensions and location of sampling

Tubes materials have been exposed to high temperature at various time, there is a possibility that some of the tubes has been degraded by creep. Safety limit for creep expansion on this catalyst tube is 6% [7]. To verify the status of each tube; circumferential dimensions were measured to obtain data about deviation from the new tube dimensions. Figure 2 shows the measurement data. It can be seen that most of the tube was expand less than 1%, however small portion of the tubes were expanded higher but still below 2%.

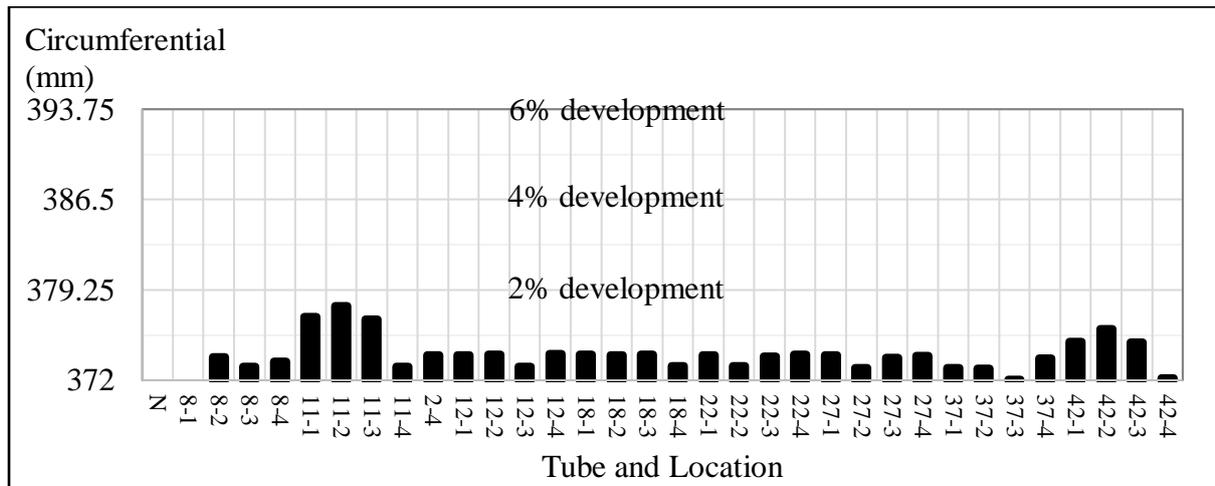


Figure 2. The circumferential tubes expansion

Chemical compositions of each tube were examined using optical emission spectroscope ARL 3460. Table 2 shows chemical composition of each tube and comparison to ASTM A297 HP and Kubota KHR35CT specifications. All of chemical composition fulfills ASTM A297 HP specifications except nickel content is slightly higher. Some of the tubes have carbon content slightly lower than minimum requirement for Kubota KHR35CT.

Table. 2. Chemical Composition of Tubes (weight %)

Service Time (hours)	Identity	%Cr	%Ni	%Nb	%Ti	%Mn	%Si	%P	%Mo	%C
	ASTM A297 HP	24-28	33-37	-	-	2.0 Max	2,5 Max	<0,04	0,5	0,35-0.75
	KHR35CT	24-27	33-37	0,4-1.0	Add	2.0 Max	1,5 Max	<0,03	0,5	0,45-0.55
Measured										
0	New	24.87	36.98	0.45	0.07	0.84	0.82	0.02	0.01	0.40
17500	T8	25.16	37.52	0.44	0.09	0.84	0.95	0.02	0.01	0.39
17500	T11	24.95	37.31	0.44	0.04	0.96	0.72	0.01	0.01	0.47
96300	T2	25.57	35.31	0.43	0.03	0.73	0.74	0.02	0.01	0.42
113800	T12	24.42	36.97	0.52	0.04	0.88	0.72	0.02	0.01	0.42
113800	T18	25.16	38.10	0.50	0.05	0.89	0.87	0.01	0.01	0.41
113800	T22	24.39	36.40	0.45	0.05	0.97	0.83	0.02	0.01	0.40
113800	T37	24.67	38.07	0.46	0.07	0.80	0.80	0.02	0.01	0.40
113800	T42	25.36	38.63	0.43	0.07	0.87	0.80	0.01	0.01	0.47

*%Fe: Rem

Microstructures of 2 × 1.4 × 2 cm specimens were performed on cross section perpendicular to the tube axis using light microscope Nikon Eclipse MA2000 and scanning electron microscope JEOL JSM 6510A. Volume fraction of carbides from un-etched specimens was quantified at outer, middle and inner wall section using Image-J software. Brinell hardness measurements were conducted by Mori Testing Machine using 1500 kN load following JIS Z 2243:2008 standard on specimens from the center thicknesses of tube wall.

3. Results and Discussion

3.1. Microstructure of as cast material

Kubota KHR35CT tubes were manufactured by centrifugal casting and the microstructures consist of dendrites and directional grains. Referring to Fe-Cr-Ni phase diagram [8], the primary phase (matrix) of tube sample is austenite. At temperature over 700°C, carbide-former element will strongly tie up carbon and there will be no free carbon detached from structure [3]. Chromium content is the highest among other carbide forming elements, therefore chromium carbides will be present extensively in the dendrites structure along grain boundaries. Niobium and titanium elements will form secondary carbides in the matrix [1,5,6,9,10]. Figure 3 shows the microstructure of as cast tube. It can be seen that the matrix material was free from secondary carbides precipitates.

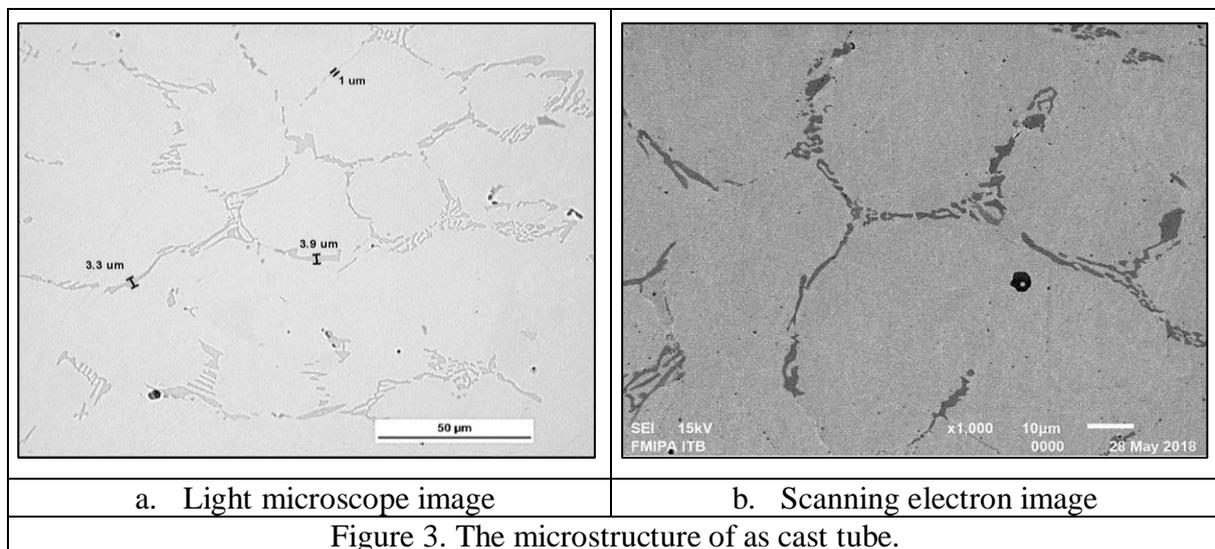


Figure 3. The microstructure of as cast tube.

3.2. Microstructure after long term services

Figure 4 shows optical and SEM micrographs of sample after 17,500 hours of services. Dendrites boundaries are thin and discontinuously ordered with fine precipitates in the matrix. On the SEM images (Figure 4), the grey area is chromium carbides, the black and white area are TiC and NbC respectively [1,9].

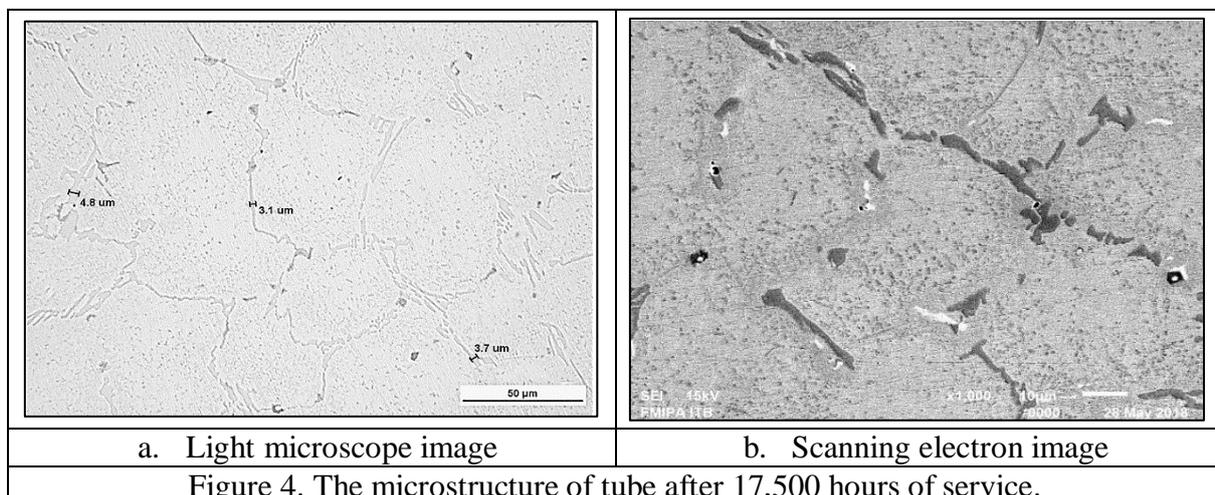
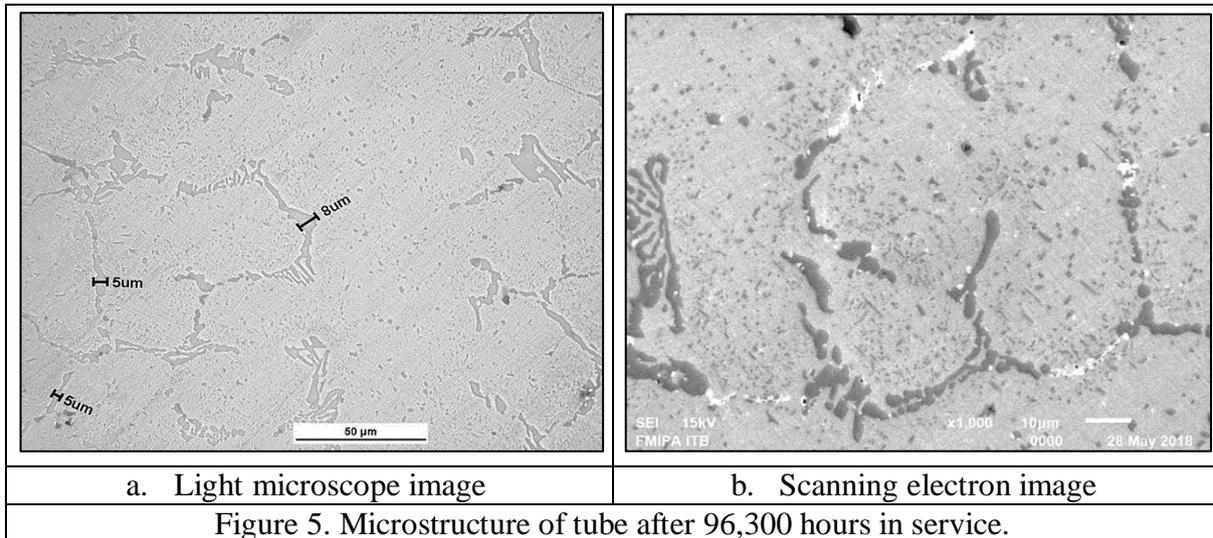
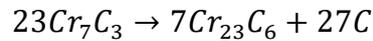
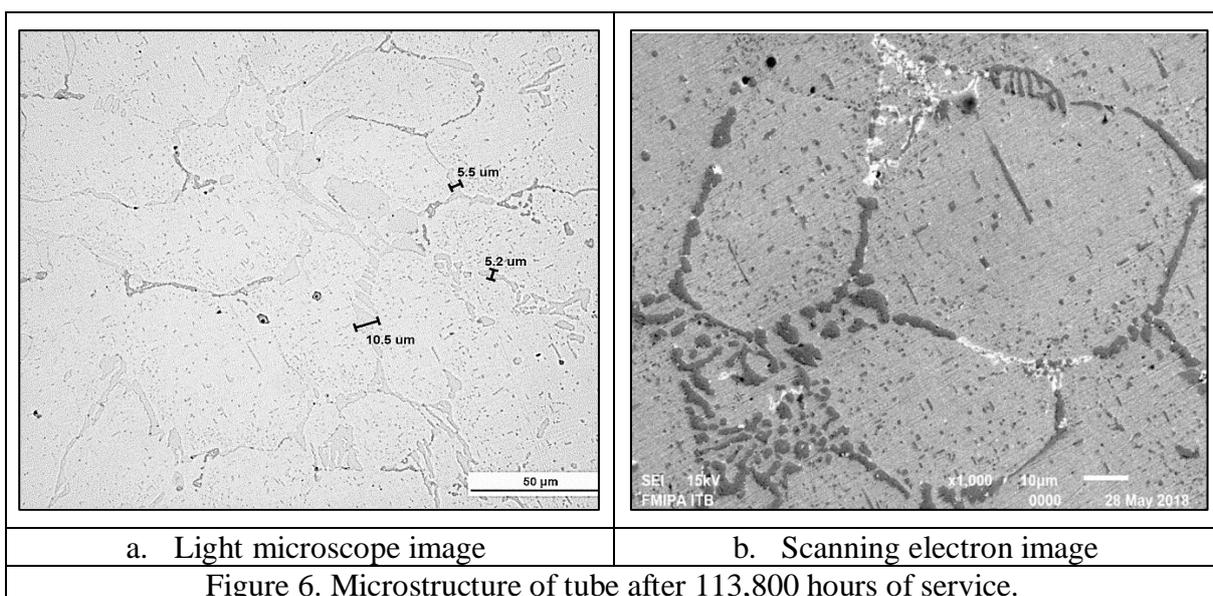


Figure 4. The microstructure of tube after 17,500 hours of service.

After 96,300 hours of service (Figure 5), precipitates in matrix are coarser than that of 17,500 hours. Volume fraction of fine precipitate Cr_7C_3 in matrix was decreased at this stage and thickening of dendrite boundaries by primary carbides was also evident. The thickening of primary carbides is due to the formation of Cr_{23}C_6 carbides along grain boundaries above 700°C [3,4]. The carbides formation reactions is,

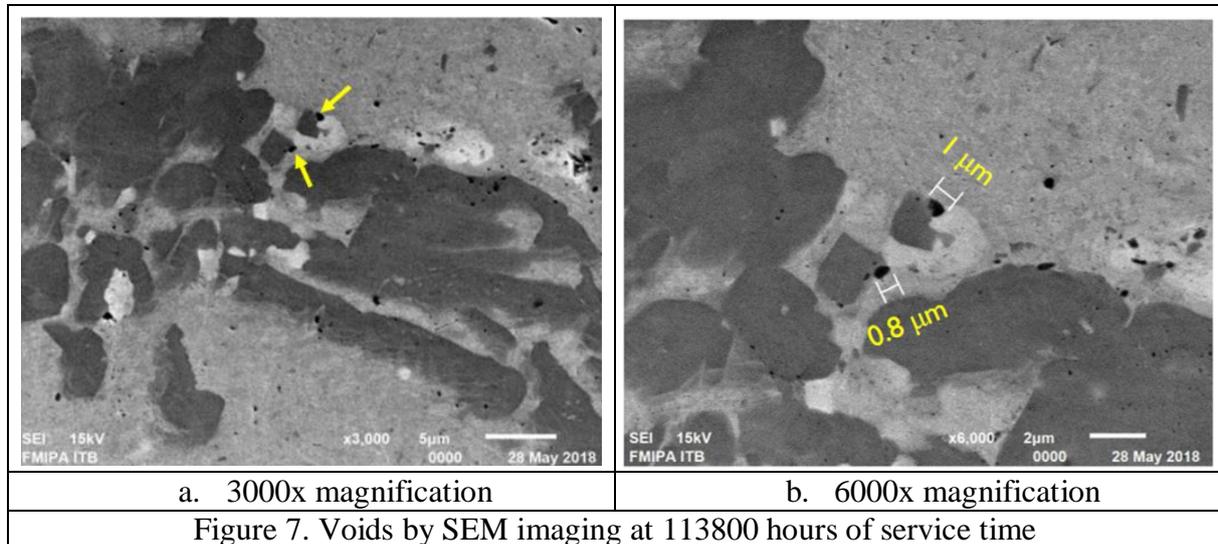


The microstructure after 113,800 hours of service is shown in Figure 6. It can be seen that the dendrite boundaries were thicker than that of 96,300 hours, and continuous. Thickening of the dendrites boundaries is due to coarsening and agglomeration of primary carbides. Precipitates in the matrix become less distributed, and also coarsening. At this stage, more white area of G-phase (Ni-Nb-Si) [6] is present on some part of the boundaries. The microstructures at several times of services in this paper are consistent with the observation by Almeida et. al [6] and Liu et. al [1].



The voids are observed after long term services (Figure 7). The formation of voids indicated that creep deformation by grain boundary sliding mechanism were active. The presence of voids

can be seen clearly at the dendrites boundaries of primary carbides. The same results are also observed by Wahab et.al [11].



a. 3000x magnification

b. 6000x magnification

Figure 7. Voids by SEM imaging at 113800 hours of service time

3.3. Effect of service time on carbides

Precipitation of Cr_7C_3 in Fe-Cr-Ni alloy steel occurred primarily at dislocation in matrix at 500°C [4] and slowly dissociated at 700°C . Above this temperature, formation of more stable Cr_{23}C_6 , TiC and NbC in several locations such as dendrite boundaries, area near boundaries, and matrix occurred. Fine and unstable Cr_7C_3 precipitates have higher chromium concentration than coarse and stable Cr_{23}C_6 precipitates, so that diffusion of chromium atoms occurred from fine Cr_7C_3 to coarser Cr_{23}C_6 precipitates, until fine precipitate dissolve completely and coarse precipitate agglomerate. From diffusion criteria, time of service is proportional to cubic of precipitate radii (r^3) while the precipitate growth is inversely proportional to r^2 [4]. Fine precipitates not only have higher growth rate but also form at shorter time. When service time is very long enough, fine precipitate dissolve slowly and coarse carbides grow up, agglomerate and have lower growth of precipitate than fine precipitate. This can be seen in Figure 8.

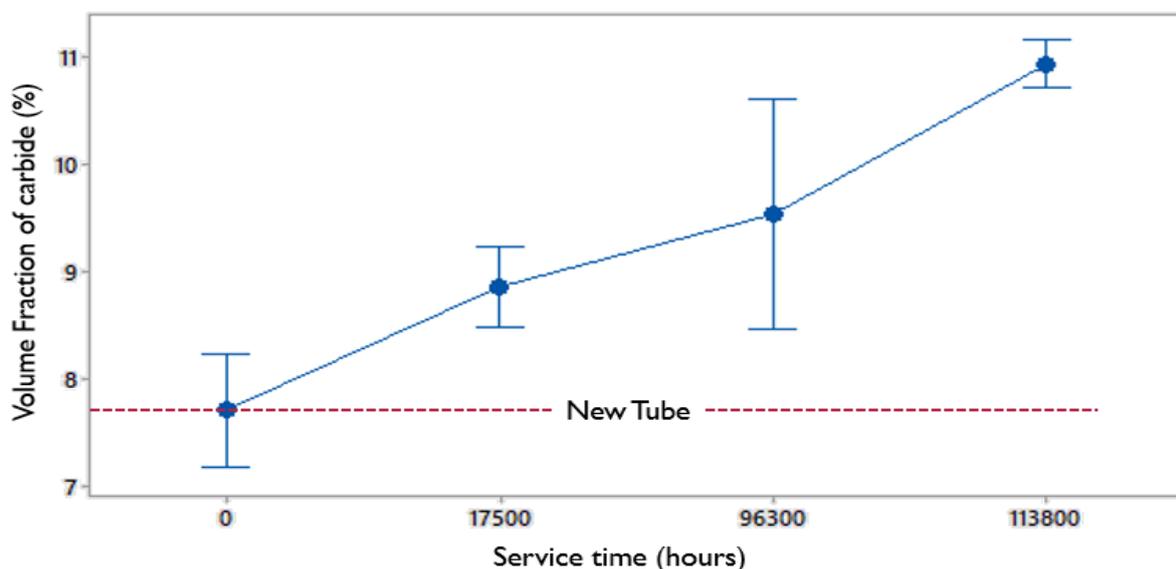


Figure 8. The plot of volume fraction of carbides against service time of tubes.

Volume fraction of carbides in the new tube is 7.72% and increased to 8.86% after tubes had been in service for 17,500 hours. Precipitates were fine and density was high especially in the matrix, as seen in Figure 4. After long time exposure, the carbide content was increased to 9.54% at 96,300 hours of service and to 10.95% at 113,800 hours of service respectively. Precipitates were coarse and density was low because nucleation rate was very low compare to growth rate (Figure 5-6).

3.4. Mechanical properties of tubes at various service time

Creep resistance of high temperature alloys rely upon development of carbides in the structure. Kubota KHR35CT has primary chromium carbides and also small additions of strong secondary carbide-forming elements, particularly titanium and niobium. Small amount of titanium and niobium will form very fine secondary precipitates in the matrix to hinder the dislocations movement.

Plastic deformation of material occurred because of dislocations movement. These dislocations on precipitation strengthened alloys could cut and-or bow at precipitates [4]. If precipitates are fine, wide interparticle spacing, and soft enough, dislocation will cut the precipitates. For coarse and hard precipitates, dislocation will be bowing just before passing precipitates to produce a dislocation loop and leaved a back stress (Orowan Stress). This stress is inversely proportional to inter-precipitate spacing. For large precipitate, this stress is low because interspacing is wider than fine precipitate.

During dislocation cutting, the stress will arise with increasing precipitate size and proportional to square root of precipitate size. When dislocation is bowing, the back stress will decreased with increasing precipitates size. These two mechanisms will present during precipitates-dislocation interaction as shown by the pink line in Figure 9. The maximum strengthening effect is achieved at transition from dislocation cutting to bowing mechanism at optimum size of precipitate (r^*).

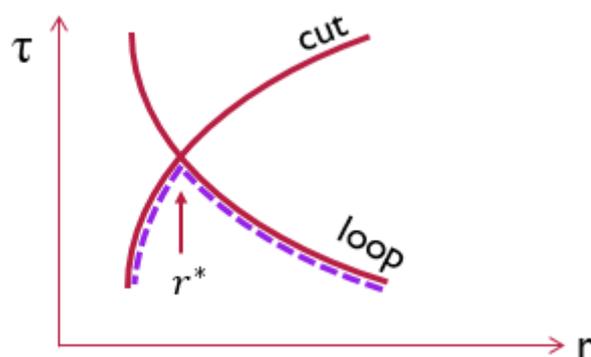


Figure 9. Transition of strengthening on precipitated alloys.

The effect of service time on material hardness is shown in Figure 10. At shorter service time (0 to 17,500 hours), the hardness only arises from 191 to 198 BHN. The precipitates resistance to dislocation motion is still lower due to low volume fraction of fine precipitates and relatively wide interparticle spacing. The carbides were coarsened and agglomerates (Figure 5-6) when the tube had been service for longer time (after 96,300 and 113,800 hours), where dislocation bowing is dominant and dislocation resistance decreased significantly as shown by decreasing in hardness from 198 to 170 BHN. It can also be seen that the hardness is almost constant at 170 BHN after 96,300 hours of service.

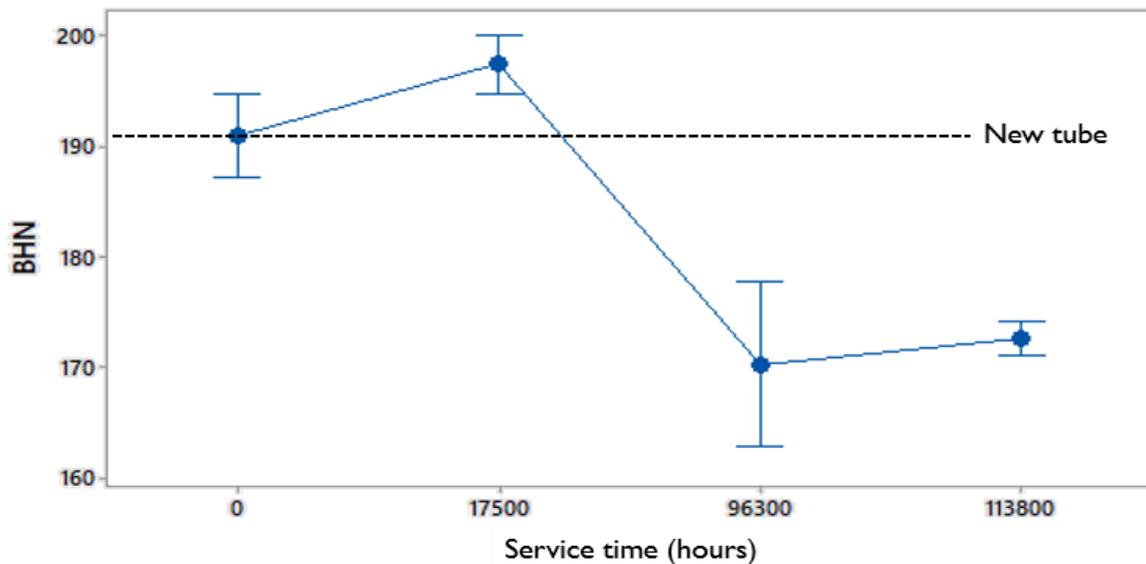


Figure 10. The effect of service time at 850°C on the hardness

4. Conclusions

- a. Carbide volume fraction in new tube is 7.75% and increases linearly to 10.95% after 113,800 hours of service at 850°C.
- b. The hardness of the new tube is 198 BHN and decreased to 170 BHN after 96,300 hours of service at 850°C.
- c. Beyond 96,300 hours of service time, the hardness is almost constant at 170 BHN.

5. Acknowledgements

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