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An investigation of carburization resistance performance of ethylene furnace tube alloys

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Carburization tests and analysis were performed on some samples of radiant tube alloys of ethylene furnaces at three petrochemical plants. These tubes had undergone carburization in service with some losing their structural integrity. This study evaluates and compares the carburization resistance performances of some of these tubes in service and identifies the cause of their degradation. The polished surfaces of the test samples were visually observed. The depth of carburization zones for each test sample was measured. Scanning electron microscopy and energy dispersive x-ray spectroscopy were used to examine the carburization zones and the rest part of the specimens and to characterize the microstructure and elemental composition of the tubes' material. Optical microscope (Image analyzer) was used to examine the etched surface of each of the test samples. Microhardness testing was performed to determine their mechanical strength. Visual inspection revealed the sagging in some of the tubes. Metallurgical assessment indicated that the selected furnace tubes showed relative greater depths of carburized zones when compared with other tube materials tested. Microstructure of the tubes showed coarse Cr-carbide precipitation and continuous carbide networks at austenite grain boundaries.

Key words: Ethylene furnace, carburization, degradation, high temperature(s), microstructure, tubes.

INTRODUCTION

Carburization is the formation of metal carbides in a material as a result of exposure to a carbon containing atmosphere. In some cases, materials are intentionally carburized to impart a high surface hardness and wear resistance. However, in service, it can result in loss of mechanical properties over time in addition to wastage of the material.The high temperature operating conditions and the chemical reactions during operations process in an ethylene furnace has necessitated the selection of carburization resistant alloys for use. Ethylene (C_2H_4) is produced by cracking ethane (C_2H_6) in pyrolysis furnaces. The process stream in a furnace consists of a mixture of steam and ethane, which is passed through a coil of reaction tubes, externally heated to a temperature of 950 to 1150°C. The gas temperature is raised quickly and passed through the coil at a high velocity with short residence time. The temperature in the reaction tube is approximately 850°C. Cracking of ethane produces free C according to the reaction:

$$C_2H_4 \longrightarrow CH_4 + C$$

Carbon produced by the aforementioned reaction is deposited at the internal surface of the tube wall as adherent coke. The coke is removed by shutting off the hydrocarbon feed and passing air and steam through the coil. Such a process is known as decoking. Frequent decoking accelerates the thermal damage of the tubes while less frequent decoking increases the rate of carburization attack. Various other closely related investigations (Tari et al., 2009; Ul-Hamid et al., 2005; Nishiyama et al., 2003; Terry et al., 1989; Mucek, 1983; Serna and Rapp, 2003; Kasai et al., 1991) have been performed. Different other metallic materials have also been suggested. However, highly alloyed austenitic

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Table 1. Details of carburized zones.

S/No.	Description	Tube wall thickness (mm)	Carburized thickness (mm)	Percent carburized	Remarks
1	Sadaf sample 1	8.0	1.0	13	Spotty
2	Sadaf sample3	7.0	5.0	71	
3	Sadaf sample 9	7.8	2.0	26	
4	Petrokemya PK P5	10.4	4.0	38	
5	Yanpet sample Y1	7.5	3.0	40	Spotty

stainless steels have been most favoured for their carburization resistance. The objective of this investigation is to evaluate the carburization resistance performance of the selected furnace tube alloys which are of different percent material compositions. It also aims at determining their suitability in high temperature service conditions.

EXPERIMENTAL PROCEDURE

The test materials were from different furnaces in different plants: Saudi Petrochemical Company (Sadaf), Arabian Petrochemical Company (Petrokemya) and Yanbu Petrochemical Complex (Yanpet) and supplied by Saudi Basic Industries (SABIC). The nominal compositions of the tubes are:

Tube 1 to 2: 25Cr - 20Ni - Fe (HK-40);
Tube 3 to 6: 25Cr - 35Ni - Fe;
Tube 7 to 9: 35Cr - 48Ni - Fe;
Tubes 1 to 9 are from Sadaf.

Tubes from Petrokemya consist mainly of 25Cr-35Ni, except one sample from tube 8 with chemical composition of 35Cr-48Ni.The tube alloy from Yanpet is of HP grade (35Cr-45Ni). The operating temperature of the furnace is 850 to 900°C.

Specimen preparation

The samples were cut each in cross-section into 10 × 10 mm as suitable for scanning electron microscopy examination. The cut samples (cross-section) were separately mounted in molding resins, ground with silicon carbide to 600 grits, polished to 1 μm, cleaned thoroughly, rinsed in ultrasonic cleaner and dried for further observation in the SEM. Each of the samples were further etched with a freshly prepared mixture of 20 wt % nitric (HNO_3) and 4 wt% hydrochloric acid (HF).

The etchant was obtained by mixing 200 cc of concentrated 70 wt% HNO_3 with 70cc of concentrated 49 wt% HF and 670 cc of distilled water (according to NACE standard TM 0498-98-Item No. 21235). Each of the specimens was immersed for two hours at room temperature; then removed, rinsed with distilled water and dried for microscopic examination.

Visual observation and measurements

The polished surfaces of the test specimens were visually observed. The carburized zones of the specimen were apparent in each of the specimens. The depth of carburized zones revealed was measured in each of the specimens and the results obtained are presented in Table 1.

SEM examinations and micrographs

Scanning electron microscope (SEM) was used to examine the carburized zone and characterize the microstructural features of the scale and the underlying alloy. Energy dispersive x-ray spectroscopy combined with SEM was used to determine the elemental composition. Mechanical strength of the samples was compared with the Vickers microhardness tests.

Optical microscopy (Image analyzer)

Optical microscope (Image analyzer) was used to examine the etched surface of each of the specimens. The representative micrographs of the results obtained are presented in various figures as will be indicated later.

RESULTS AND DISCUSSION

Many samples were examined, characterized and analyzed. Here only few representative sample results will be presented and discussed due to space concern. The results of tube alloy sample 1 representing tube 1 to 2; tube 3 representing tubes 3 to 6 and tube 9 representing tubes 7 to 9 from Sadaf will be presented and discussed. The tubes from Petrokemya are of the same composition with those of Sadaf (4 of tube 3 to 6 type and 1 of tube 7 to 9) and hence will further be mentioned. The two tubes from Yanpet bear the same composition and are almost similar to tube 3 to 6 except for slightly lower Ni content; they will also be briefly mentioned. Table 1 shows the details of tube wall thickness (mm), the samples carburized thickness.

Tube 1: - HK-40 (25Cr- 20Ni)

In tube 1, which consists of HK-40 (25Cr-20Ni), the SEM micrograph (Figure 1) at low magnification, did not present a clear carburized zone in both specimens. However, the very narrow zone could be observed in the optical microscopy micrograph (Figure 2). This zone was measured to be 1 mm thick as presented in Table 1. The percent carburized zone is 13.The carburization effect in the sample from tube 1 can therefore be described as minimal. This is further evidenced by the microstructure as presented in Figure 3 at much higher magnification of x600 and by the EDS analysis in Figure 4 which revealed

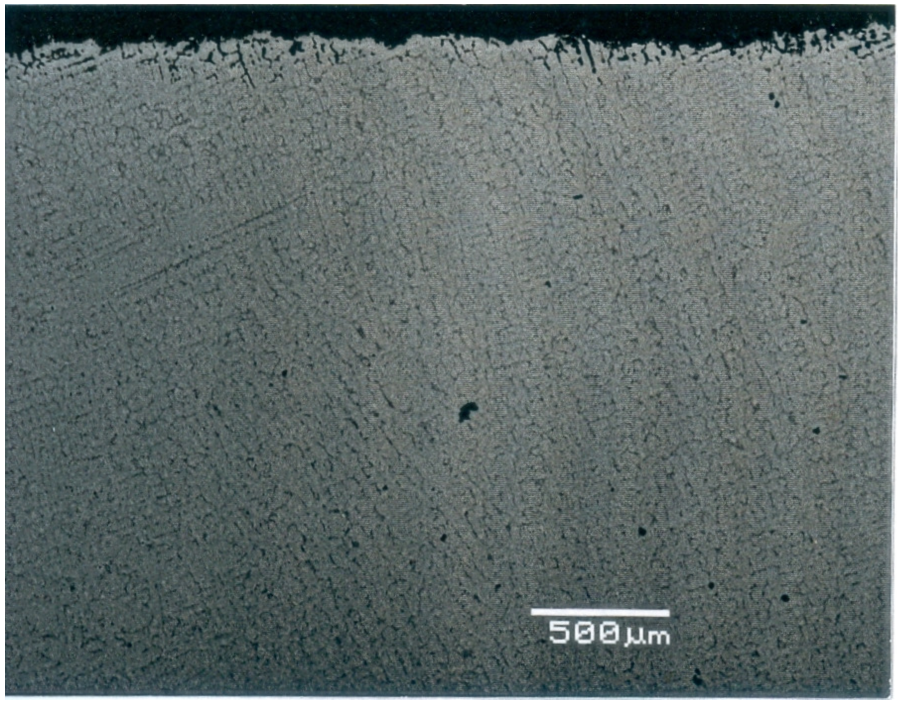
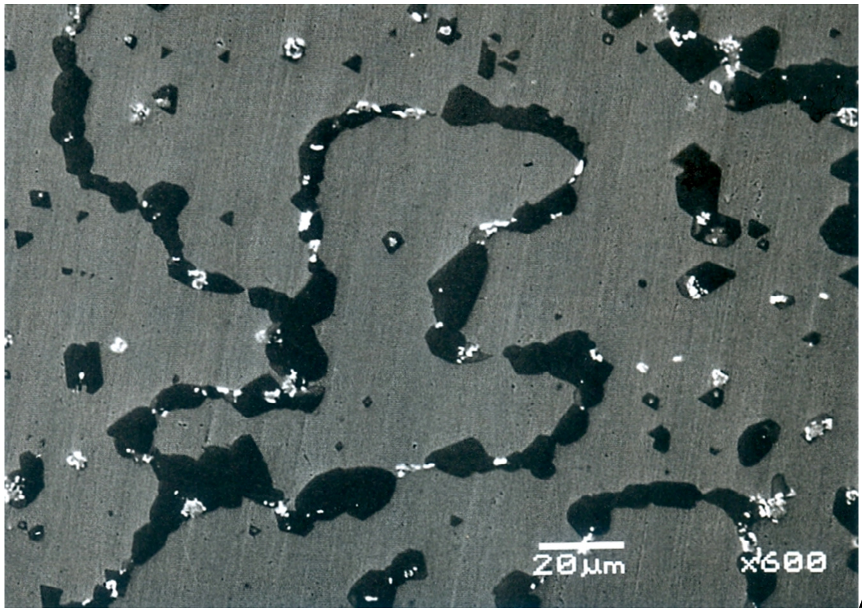


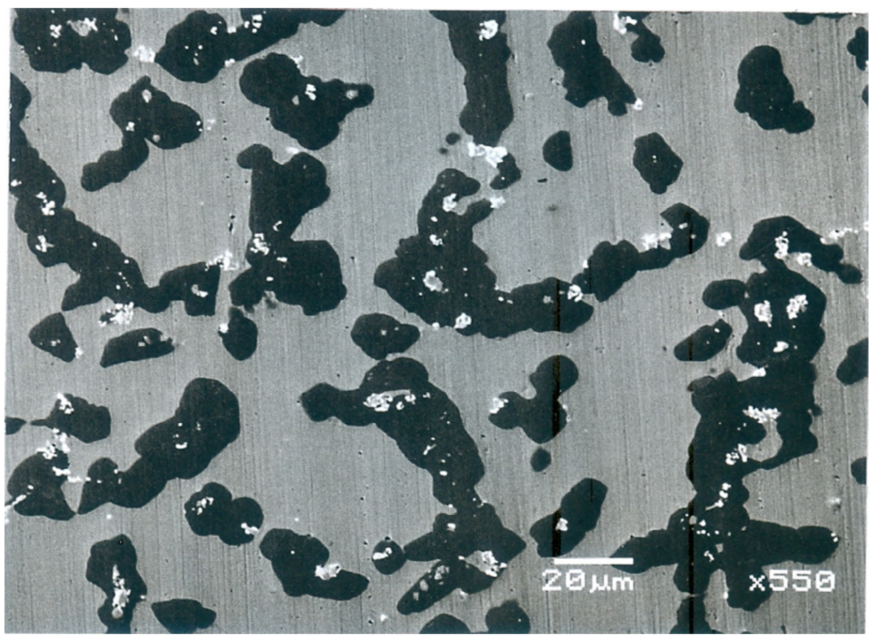
Figure 1. SEM image of tube 1 metal alloy (carburized region).

Figure 2. Optical image of tube 1 test sample.

the matrix of the sample to comprise of austenite (Fe-Cr-Ni solid solution) and the grain boundary consisted of Cr-rich carbide. In Figure 3, it can be seen that the Cr-rich carbide precipitates present within the austenite grains are coarse in size. The very low carburization observed in this sample could be due to the operating conditions of



A



B

Figure 3. SEM image of tube 1 alloy: A. uncarburized, B. carburized regions.

the furnace and/or the location of the tube in the plant.

Tube 3: 25Cr - 35Ni - Fe

Micrographs of samples obtained, at low magnification of x37 from tube 3 **(25Cr-35Ni-Fe)** are presented in Figure 5A for the SEM and Figure 5B for the optical microscopy micrographs, respectively. A wider carburized zone was obtained in the test sample. The carburized zone's thickness is 5 mm and the percent carburized is 71. This tube was made from the steel of different composition from that of tube 1. There was an increase in nickel content from 25 to 35% when compared. This could make a contribution to the increased thickness of the carburized zone. If this is the case, it means then that the more the nickel content the more the tendency towards carburization. The increased carburization could also be due to a probable difference in the temperature of operation, the location in the furnace, the frequency and other operating parameters of the furnace. The increase in carburization in this alloy is further exhibited in the

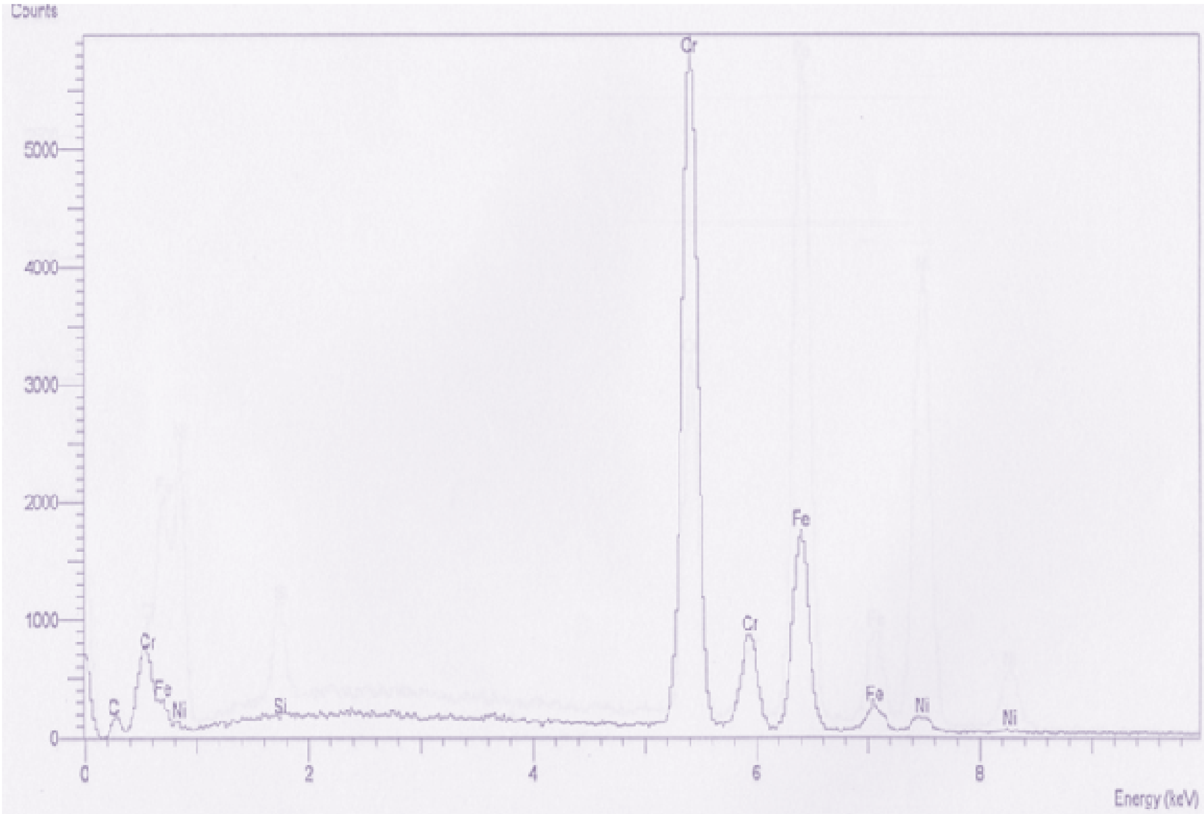


Figure 4. EDS analysis of tube 1 at the grain boundary of the carburized zone.

microstructure as presented in the micrographs in Figure 6A and B for the uncarburized and the carburized zones. Figure 7A and B shows the energy dispersive spectroscopy (EDS) analysis of the portions of Figure 6. The carbide precipitation appears relatively coarse both at the austenite grain boundaries and within the matrix itself when compared with the uncarburized region of the tube material of tube 1. This observation was corroborated by the EDS analysis where Cr concentration was determined to be 13 wt% at various regions within the austenite. The carburized region from the same sample shows high degree of carbide precipitation at the grain boundaries and the appearance of blocky carbide particles in the matrix as shown by the SEM image. The grain boundary precipitate comprised, predominantly, of Cr as shown by the EDS spectrum in Figure 7. This is presented in the form of a continuous network. The white precipitates adjacent to the grain boundaries are Nb rich as shown by the EDS spectrum.

In tube 3 the carbide precipitation appears relatively coarse both at the austenite grain boundaries and within the matrix. The depletion of Cr within the matrix indicates a tendency of Cr to diffuse and form Cr - rich carbides at the austenite grain boundaries and/or coarse pre-existing carbides within the austenite. Diffusion of Cr is enhanced at an elevated temperature. The higher the temperature, the greater the carburized zone; and coarser the carbide. It was observed in the results obtained during the microhardness test that carburized zones of the materials gave higher hardness values (HV 316) than the uncarburized (HV 216) regions. Increased hardness at the carburized zone can be attributed to the high degree of carbide precipitation and also to C pick-up due to the carburizing environment.

Hardness measurements combined with the microstructural observations suggest that carburization attack led to the formation of a surface hardened layer of reduced ductility. Formation of this layer further corroborates the inability of the alloy to form a continuous protective oxide scale at its surface. Typical microstructure of heat resisting austenitic casting steels consists of austenite matrix and carbide precipitates. Use of varying contents of Cr and Ni in these alloys allows control of properties such as strength at elevated temperature and resistance to carburization and hot gas corrosion. Nickel imparts the alloys with an increased resistance to carburization attack, thermal shock and thermal fatigue; while chromium provides increased corrosion and oxidation resistance, (ASM Metals Handbook, 1990). In the carburized region of the tube 3 steel alloy sample, the white precipitates adjacent to the grain boundaries are Nb-rich as shown by the EDS spectra

A

B

Figure 5. Micrographs of tube 3 alloy: A. SEM, B. Optical images of carburized zone.

in Figure 7A and B as written earlier. Relatively small additions of Nb to heat resistant castings can increase their resistance to thermal shock. Furthermore, Nb acts as a carbide stabilizer by forming MC-type carbides which present massive carbide precipitation at the grain boundaries. Also, visual examination has revealed that tube 3 was clearly sagged and significant plastic deformation during service was observed. The tube showed the most severe degradation of all the samples studied in this investigation. This phenomenon was also evidenced as earlier indicated by the SEM/EDS examination where the microstructures of these tubes showed relatively coarse blocky carbides within the austenite matrix and continuous carbide networks at the grain boundaries. These observations suggest that the alloy had been exposed to an excessively high temperature during service. The hardness of carburized zone was also found to be higher in tube 3 as compared to the other tube material. These results indicate higher precipitation and carbon pick-up by the alloy. Deposition of coke at the inner pipe wall also promoted carbon deposition and precipitation of secondary carbides within

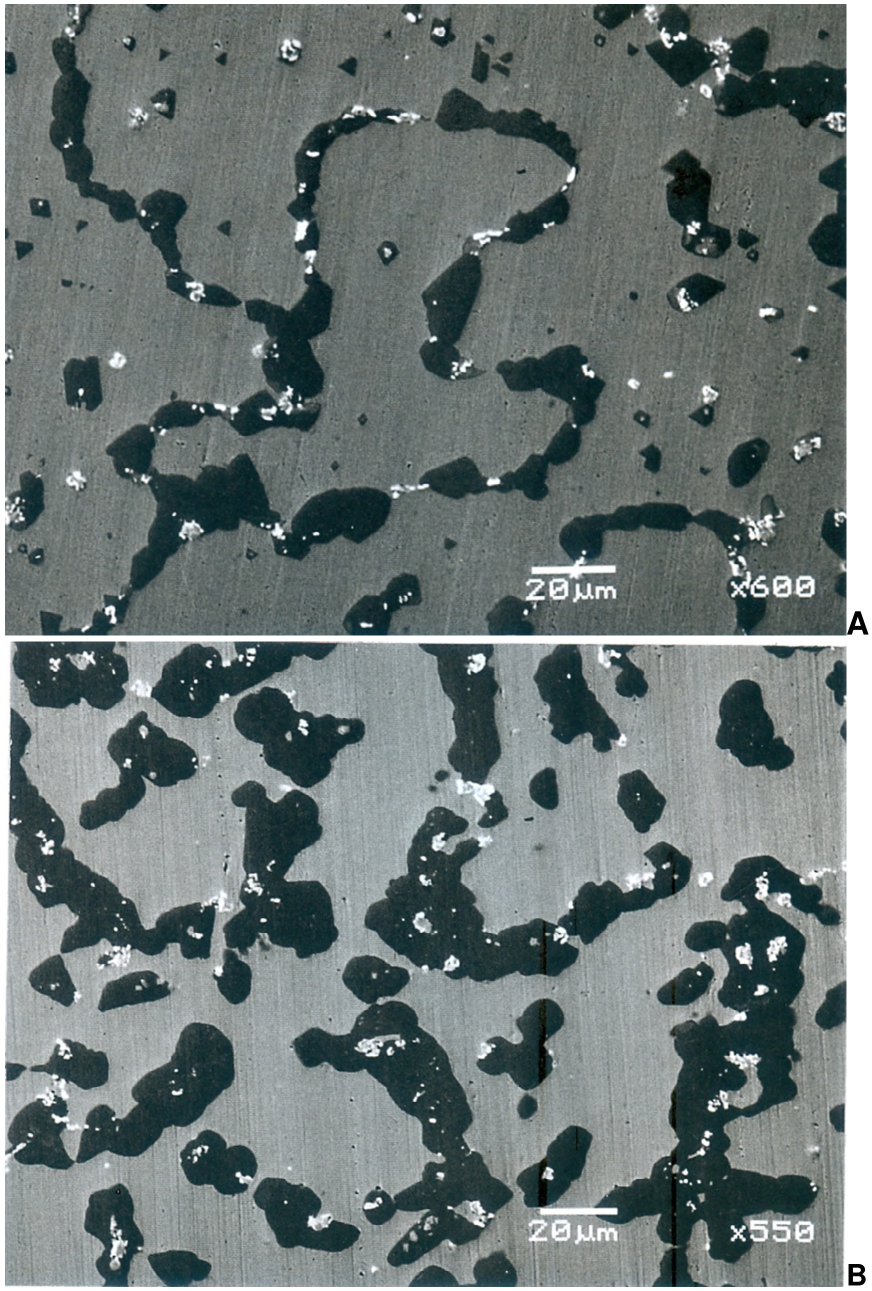


Figure 6. SEM images of tube 3 alloy: A. uncarburized, B. carburized zones.

the alloy matrix.

Tube 9: 35Cr-48Ni-Fe

This tube has the nominal composition of 35Cr-48Ni-Fe. The SEM at the low magnification of x37 and the optical micrographs are presented in Figure 8A and B. The carburized thickness for the test sample is 2.0 mm and the percent carburized is 25. The microstructures obtained at the higher magnification of x600 for the test sample of this tube are presented in Figure 9A and B for the uncarburized and the carburized zones. The microstructures comprise of dark Cr-rich and white Nb-rich precipitates along with greyish precipitates which are comparatively richer in Ni as shown in the EDS spectrum and elemental composition of Figure 9C.

When compared with tube 3, it is apparent that the alloy of tube 9 gave better carburization resistance performance. This result could not be said to be due to much higher chromium and nickel content alone; it could also be due to the furnace condition operating parameters,

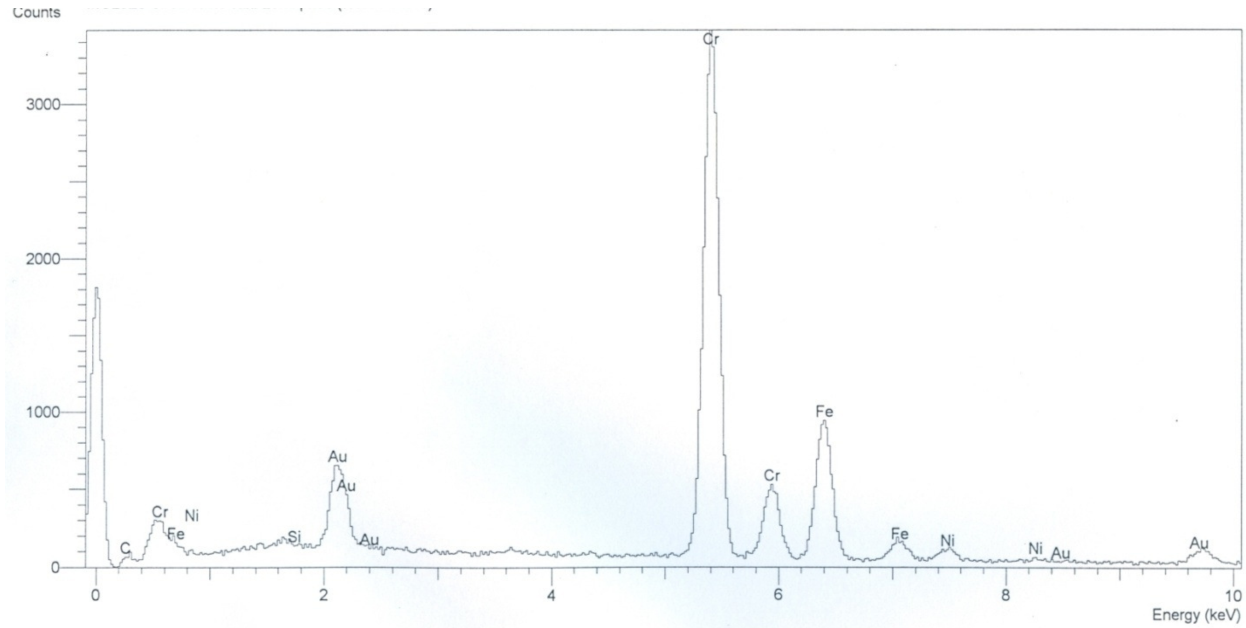


Figure 7. EDS analysis of the grain boundary portion of tube 3 carburized zone.

particularly the temperature and the location within the furnace. This plausible assertion could be corroborated with the better carburization performance of tube 1 which also had far lower Ni content than the alloy of tube 3 and far less Cr and Ni contents than alloy of tube 9.

Tubes from Petrokemya and Yanpet

The other tubes used are from Petrokemya and Yanpet (Figures 10 and 11). As mentioned earlier, the tubes from Petrokemya bear the same composition with those of tube 3 from Sadaf and one sample was the same in composition with tube 9 already reported and discussed earlier. The only difference could be in the operating conditions that could affect their carburization resistance. This is evidenced in the results presented in Table 1 with reference to different/varied carburized thickness and percent carburized values obtained with the samples from Petrokemya. The carburized thickness varied from 0.5 to 4.2 mm and the percent carburized zone from 4 to 40. The very high carburization resistance of a sample marked PK 5 with the same composition of 35Cr and 48Ni-Fe as others is very difficult to explain. Its location within the furnace which could affect the temperature at that point of location; this could be a plausible factor for the striking carburization resistance performance. The same sample in pass 5 had a carburized thickness of 4.0 mm and percent carburized of 38. The sample marked PK P8A of the same composition with tube 9 earlier, and located in pass 8 had a carburized thickness of 4.2 mm and percent carburized zone of 40. The SEM and optical micrographs for sample PK 5 at very low magnification (x37) are presented in Figure 10A and B, respectively. The tubes from Yanpet are of the same composition (35Cr-45Ni-Fe), with the same carburized thickness (3 mm) and the same percent carburized value of 40. They were used in the same temperature range of 850 to 900°C range. Their carburization resistance performance, depending on the operating parameters, compared favorably with some of Sadaf and Petrokemya tubes. The representative micrographs (SEM and optical) are presented in Figure 11A and B, respectively.

SUMMARY AND CONCLUSION

In this study, all the furnace tubes examined showed carburization attack but to varying degrees. The representative tube 3 had the highest percent carburized of 71 and the highest measure of carburized thickness of 5.1 mm, respectively. Tube 1 and had very low carburization and together with tube 9 that represented alloys of other composition. Tube 9 was highly alloyed ore than the tubes 1 and 3. In general, the carburized characteristic of the steel samples did not follow a particular pattern neither did it follow the alloying form/composition and could not, therefore, be used largely to discuss the carburization resistance or susceptibility of the tube steels. The operating parameters and frequency of use could be a significant factor in the carburization factor resistance of the tube alloys. The microstructure of all the tube alloys tends to

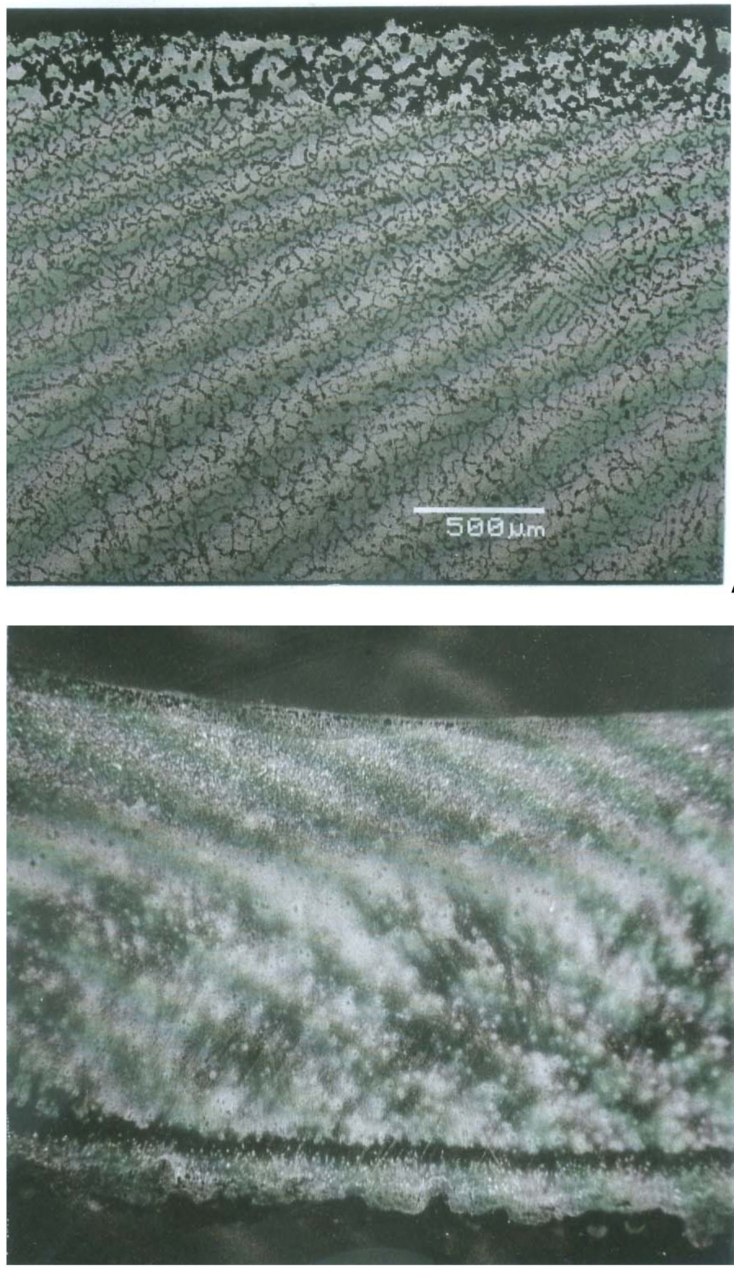


Figure 8. Micrographs of tube 9 alloy: A. SEM image, B. Optical image.

be similar. In fact, the tubes were randomly made of the same alloy in three different groups though with slight compositional difference(s) among the groups. The grain boundaries of the carburized zones were more enriched with chromium due to its diffusion at high temperatures and its combination with carbon to form chromium carbide. Deposition of coke at the inner wall also promoted carbon diffusion and precipitation of secondary carbides within the alloy. All the tube steel alloy materials investigated underwent carburization attack due to an exposure to excessively high temperature during service but at varying degrees. The carburization attack was very much less visible in tube 1 alloy. It was most severe in 3. The specific reason for this adverse carburization resistance performance of the tube is not known. There was no information about the plant process temperature, pressure, length of exposure, expected service life, operating medium, location and orientation of tubes within the furnace. Tube 9 also suffered moderate carburization susceptibility as indicated by the results and the alloy resistance was better than what was obtained for the tube alloys used in furnaces in Petrokemya and

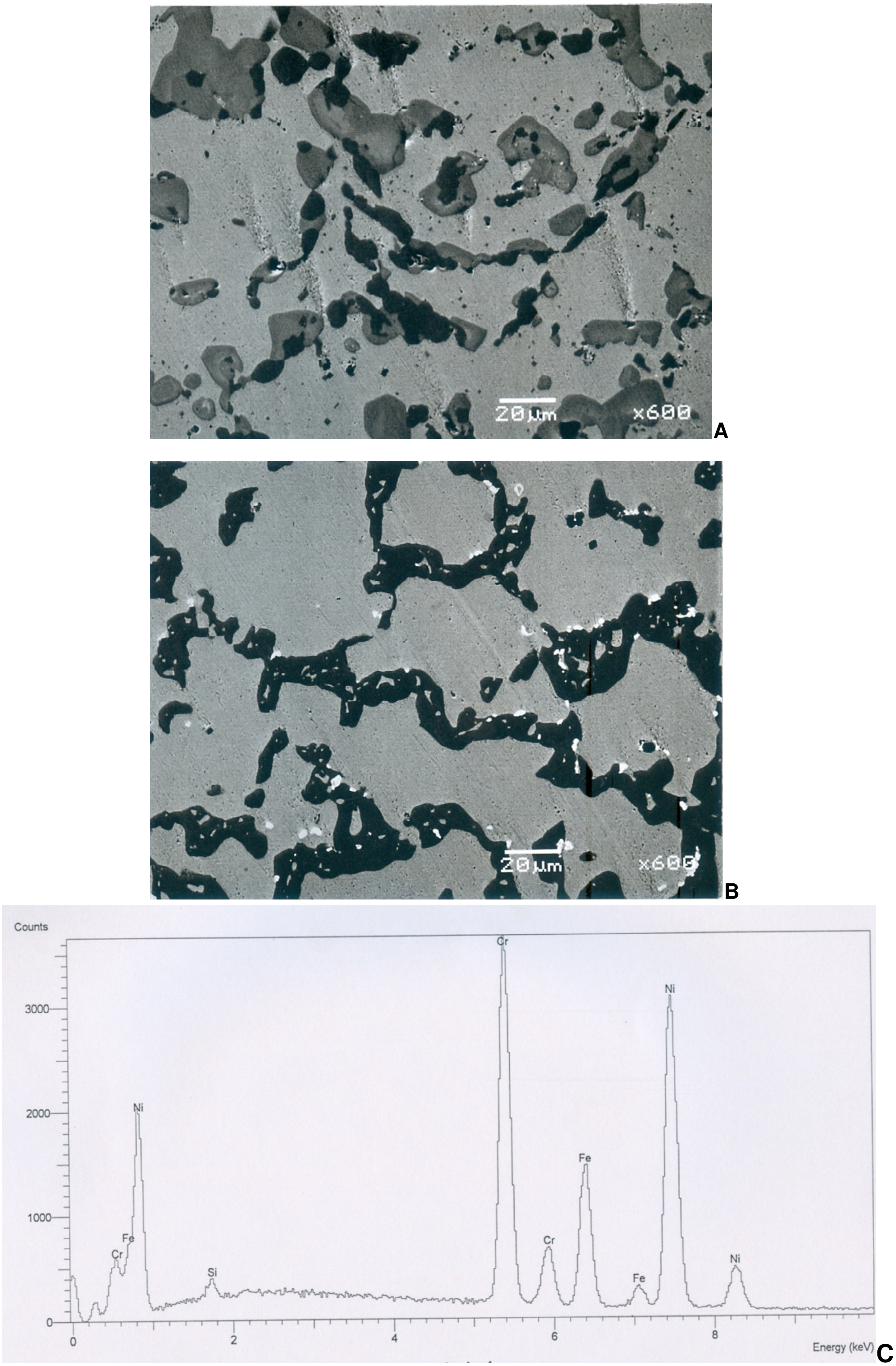
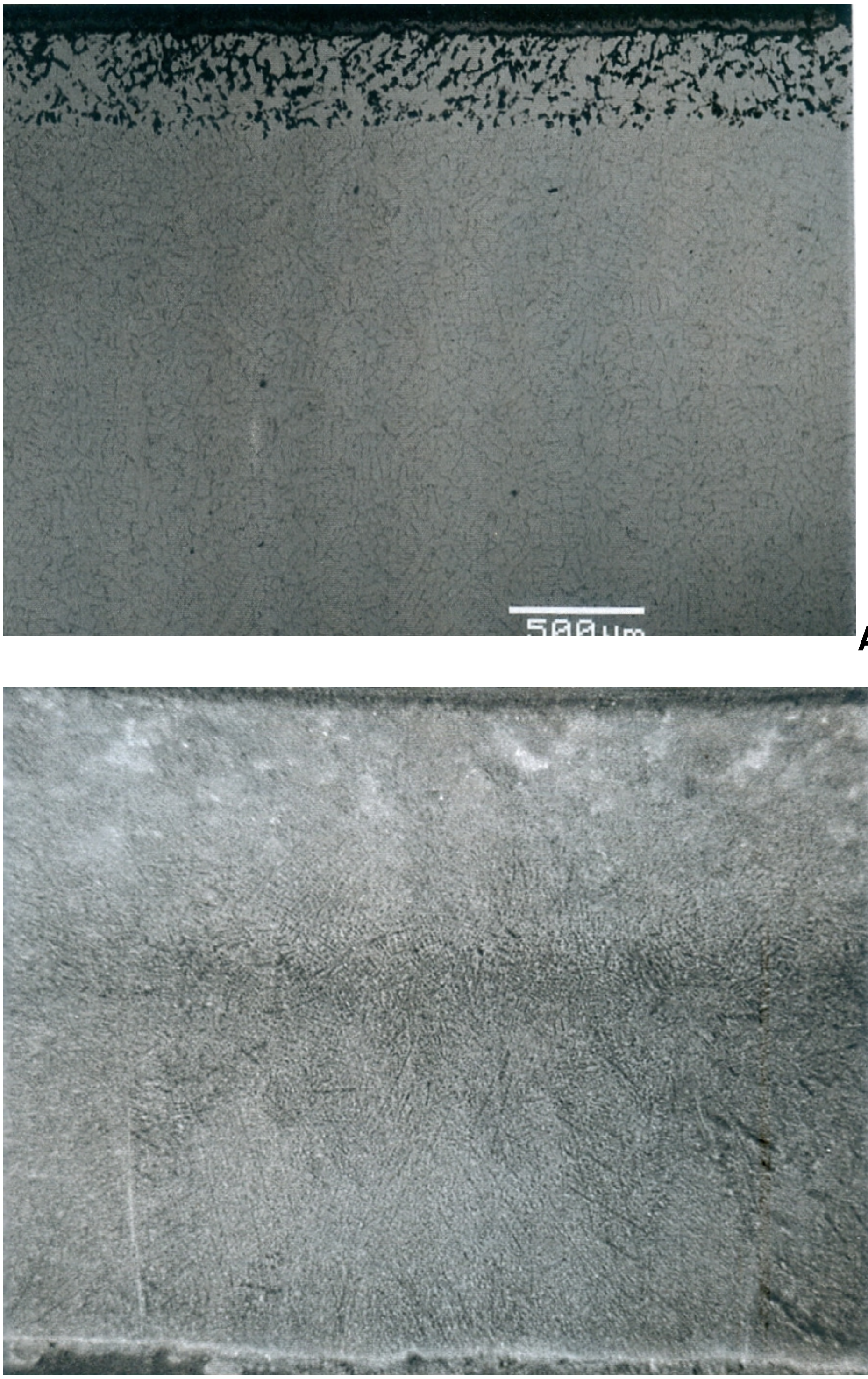


Figure 9. SEM micrographs of tube 9 sample: A. uncarburized zone, B. carburized zone, C. EDS analysis of the grain matrix of tube 9 alloy sample.



A

B

Figure 10. A. SEM image of Petrokemya tube 5 showing carburized zone, B. optical image.

Yanpet plants. The temperature of operation in ethylene furnaces should be controlled closely to avoid overheating during ethylene production as well as decoking.

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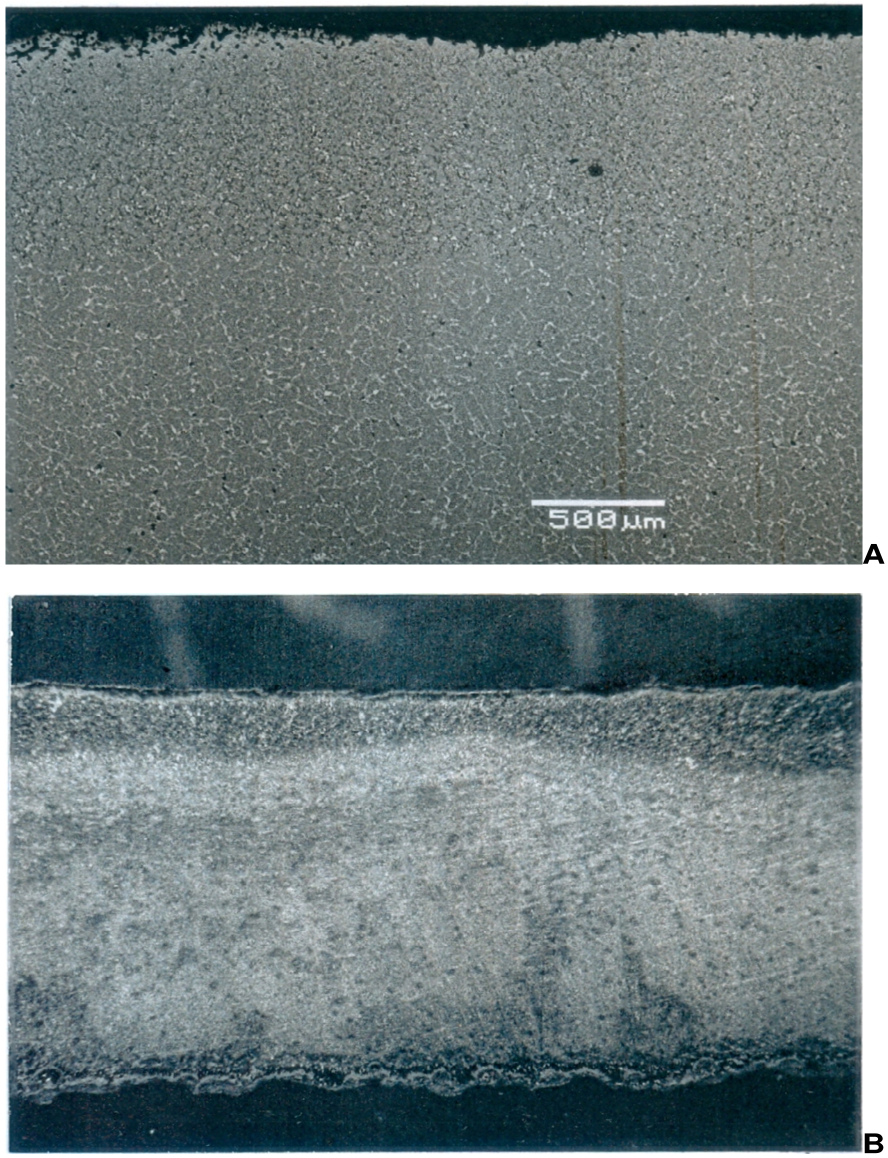

Figure 11. Micrographs of Yanpet tube alloy: A. SEM image, B. optical image.

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