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Root Cause Analysis of the Carburized 35Cr-45Ni-Nb Tube in the Ethylene Furnace

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ABSTRACT

This paper focuses on the root cause analysis of cracking phenomenon of radiant tube which used in the ethylene furnaces of petrochemical plants. The tube furnace used 35Cr-45Ni-Nb alloy. The internal temperature and pressure of tube were in range of 800-900°C and 3.2 bar, respectively. The surface temperature of tube in the range 1000 - 1100°C. From the visual inspection by the Werner Caliper and Coordinate Measuring Machine (CMM), it was found that the tube dimension and surface roundness of used tube are larger than a new tube. The used tube becomes magnetized which was affected by the carburization phenomenon. The SEM micrograph of the used tube shows a large amount of area fraction of precipitated complex carbides such as $(Cr,Mn)_{23}$ C_6 and SiC when compared with new tube. The EDS result shows significantly high amount of C and Si contents in the used tube than in the new tube. The HV hardness and tensile strength of the used tube are lower compared with the new tube, because of the effect of the residual strain energy in the crystal structure, grain and particle sizes coarsening and area fraction of the carbides. The carburization phenomenon and its effect were discussed in more details through this paper.

Key words: Ethylene Furnaces, Carburizing, Carbide precipitation, Ni base super alloy, Welding

INTRODUCTION

In the ethylene production by heating hydrocarbon source in the Fire Heater Furnace at high temperature as shown in Figure 1(a). Their molecules are cracked into an ethylene monomer with a chemical structure ofC_2H_4. The dissociation reaction will occur in the tube coil which is the nickel-base alloy grade 35Cr-45Ni-Nb.Meanwhile, the soot and coke are formed as the by-product obtained from the dissociation reaction because there was incomplete combustion in tube coil. A volume fraction of coke in the used tube is effect to service life of the tube as shown in Figure 1(c) compared with the new tube figure 1(b). After long life service at high temperature the used tube contained high volume fraction of the soot and coke.

When the Fire Heater Furnace was stopped running for the maintenance, the surface temperature and internal pressure of the tube were reduced at a lower rate(equivalent ambient). The heated tube which was once enlarged would be decreased in size and volume. Some tubes, which have coke associated, cannot be decreased in to the original size. Therefore, the tube rupture was occurred. The reason of cracking phenomenon will be discussed in the following section as shown in Figure2.

Carburization phenomenon in the tube:

The coke had been occurred in the environment of carbonaceous species at high temperature. This phenomenon caused dissociation reaction and the diffusion of carbon through the matrix to combine with the alloying elements. It yielded a new inter metallic compound in the old microstructure and crystallization was taken place along the grain boundary. This process is called carburization which was reduced the mechanical properties of materials and make it susceptible to be damaged[1][2].

In the oversea industry, the damage has been occurred in ethylene tube furnace materials 35Cr-45Ni-Nb. The damage had been analyzed by various techniques.1) SEM uses for deter min in gchromumcarbi deprecipitated at the lattice of grain boundary and corrosion.2) EDS uses for deter min in gachemical compound of crystallized car bid etype M (M = Cr, Nb) at grain boundary3) Micro hardness uses for determining the hardness of the matrix and compounds [3][4][5][6] and a testing of fracture

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mechanic using Monte Carlo formula withAPI-581requirementsto assess the damage and longevity prediction[7].

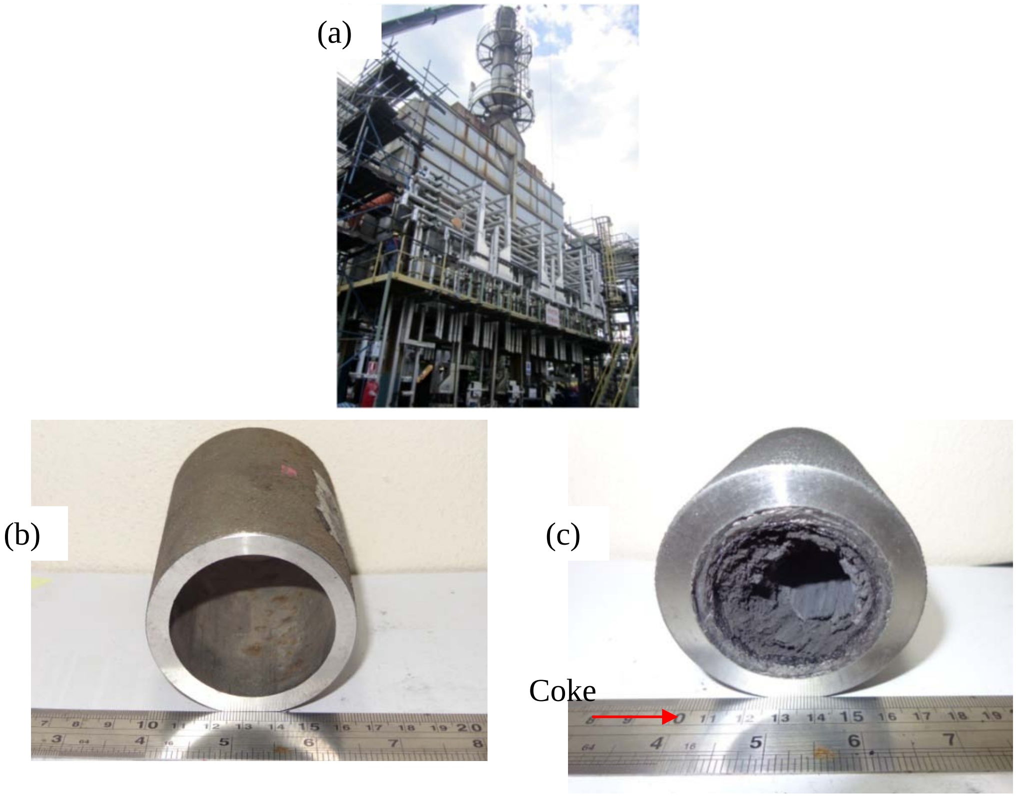

Fig. 1: The Fire Heater Furnace and tube coil of 35Cr-45Ni-Nb alloy (a)Fire heater furnace, (b) New tube and (c) Used tube with coke or soot contained

Although, there are many researches concerned on this topic, however, the scope of their studies did not cover the factor on mechanical, metallurgical and chemical properties. This paper consequently investigates the root cause of rupture of the used tube grade 35Cr-45Ni-Nb, especially its mechanical, metallurgical and chemical properties. The result of our investigation can be helpfully to use as the fundamental guidance in choosing a tube welding repair. In order to select welding electrode, Pre- heat and Post-weld heat treatment.

Materials And Methods

Materials:

New tube used in the experiment is Ni-based super alloy grade 35Cr-45Ni-Nb which is called unassigned material in the ASME-IIP art B code (Nonferrous Material Specifications). It is difficult to determine the original characteristics of its mechanical and metallurgical properties. This alloy has high quality of the cracking and creep resistances at a high temperature.

In the production of tube were used the centrifugal casting and annealing processes. The microstructure of the tube is consisted of two type of inter metallic compounds types;1) carbide $Cr_{23}C_6$which is a combination of chromium with carbon; 2) gamma double prime (γ") which is the aggregation of nickel with niobium as coherent with gamma matrix and it causes precipitates becoming the body center tetragonal (BCT) crystal or Ni_3Nb. It resists the motion of dislocation through the plane, so the plane is not disconnected. That is the reason why a new tube has creep resistance property at a high temperature.[8][9][10]

The used tube in the experiment was taken from the petrochemical industry in Thailand. It is the mechanical parts of the fire heater furnace that produced ethylene monomer. The total length of tube is 9meters,the rupture of tube is occurred when the machine is stopped running for repair. The specimen near cracking area was randomly selected to be investigated. The new tube is used as a reference. The environment of machine operation is shown below:

Material grade = 35Cr-45Ni-Nb
Operate pressure = 32 barg.
Internal temperature of tube= 800°C to 900 °C
Surface temperature of tube= 1000°C to 1100 °C

Visual examination testing (VT):

The VT is used for detecting surface discontinuities and a change of tube shape by using Werner Caliper and CMM (Coordinate Measuring Machine).[11]

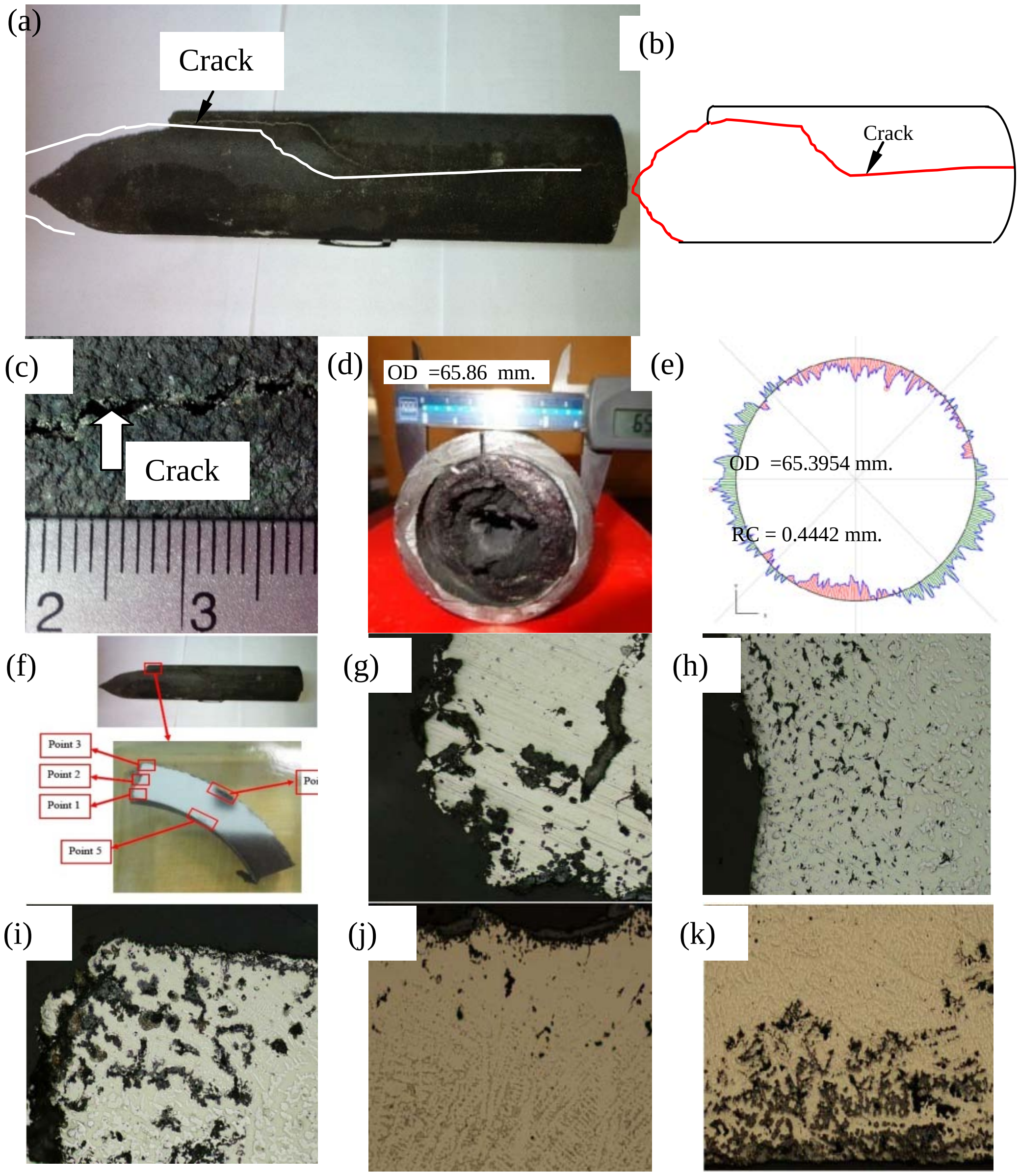

Fig. 2: Investigation of crack and microstructure on the used tube (a) cracking line,(b)2D sketch,(c) Surface tube crack,(d)measuring OD of tube,(e) Roundness circle(RC),(f) Profile of point checks, (g) Point 1:10x,(h) Point 2:10x,(i) Point 3:10x,(j) Point 4:5xand (k) Point 5:5x.

SEM and EDS (Chemical analysis):

They are used for to determine a location of elements by mapping. They are used for determining the elemental distribution on the cross sectional area of nickel, chromium and carbon compound according to the measurement of NACE Standard TM 0498-98[12][13], as shown in Figure 3.

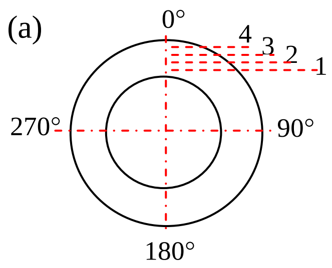

Fig. 3: Specimen Preparation for Chemical Analysis
(a) Position for scanning (b) Profile of tube of cross section.

Microstructure analysis:

The specimen was polished and etching by using 40 ml glycerol , 20 ml hydrochloric acid and 20 % nitric acid. Percent of area fraction and particle size of anintermatallic compound as analyzed the by MSQ software

Mechanical testing:

(1) Vickers micro hardness testing was taken place on cross sectional area of new tube and used tube to determine its hardness. The objective of testing is to determine the hardness of each layer of tube wall thickness that affected from the formation of anintermetallic compounds. In this test, we use a constant load of 500 g. with distance between point of 1.5 mm. (4 points per quadrant at 0,90,180,360 deg. (as in Figure4a)), accordance with standard NACE Standard TM 0498-98[12]and ASME-II Part A code (Ferrous Material Specifications), SA-370[14].

(2) The preparation of tensile specimen was cut from specimen per quadrant at 0,90,180,360 deg. as shown in Figure4b accordance with standard ASME IIA SA 370[14]and its acceptance criteria. The tensile testing machine had been accredited by Calibration ISO-17025,class 1.

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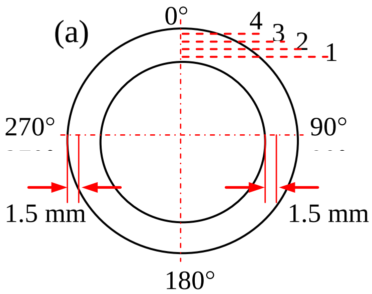


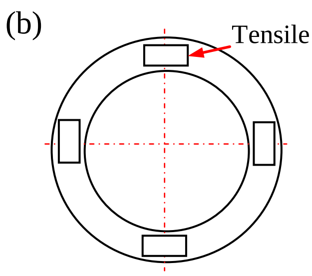


Fig. 4: Specimen preparation for mechanical testing
(a) Hardness specimen position and (b) Area Tensile specimen position.

Results:

Visual examination testing(VT):

From the result, it shows the comparison between the used tube and new tube as follows.

1) The used tube has a rougher surface than the new tube as shown in Figure 5a&5d, respectively. There are some black cubes scattered on the outer surface, and coke precipitates inside the tube.

2) Outside diameter(OD) of used tube is larger than the new tube when measured by Werner and CMM as shown in Figure 5(b-c) and Figure 5(e-f), respectively

3) Roundness circle (RC) of used tube is larger than a new tube when measured by CMM as shown in Figure 5(c) and 5(f).

SEM/EDS element analysis:

Form the microstructure of material and chemical composition from outer surface to inner the tube, the quantitative and qualitative comparison is shown below.

Quantitative comparison of the new tube and the used tube:

The EDS mapping is used to define the distribution of element in the new tube and used tube of the 35Cr-45Ni-Nb alloy. The result shows that the amount of carbon is found approximately 1.7 % with uniform distribution in all area of microstructure of the new tube as shown in Figure 6.In the used tube, there is high amount of carbon in area 1-2 than area 2-3 and area 3-4, respectively as shown in Figure 8.

The amount of carbon in the new tube and the used tube is different; because carbon in the used tube is diffused and covered all over the metal as a result of the amount of soot-covered is sufficient for gas atom to highly penetrate through the tube.

Qualitative comparison of the new tube and the used tube:

The EDS mapping is used for determining the distribution area of elements in the new tube and used tube as shown in Figure 7 and Figure 9, respectively. The result shows that there are three phases in the matrix of the new tube and used tube. The qualitative comparison can be explained as follows: As seen in the new tube (Figure 7(a))the secondary electron (SE image) which is analyzed by EDS, it is found that:

a) Light gray phase which is the matrix is probable to be an element of Ni, Fe, Si and Mn (arranged in order from most to least, respectively).

b) Dark gray phase which is line scattered across the matrix is probable to be an element of Cr and can be combined with carbon to form chromium carbide($Cr_{23}C_6$).

c) White phase which is line scattered across the matrix is probable to be an element

of Nb and can be combined with Ni to form $Ni_3Nb(\gamma'')$.

As seen in the used tube (Figure 9(a))the SEM image which is analyzed by EDS, it is found that:

a) Light gray phase is similar to the new tube.

b) Dark gray phase is probable to be an element of complex carbide such as$Cr_{23}C_6$and mixed silicon carbide (SiC).

c) White phase which is probable to be an element of Si and can be combined with C to be precipitated as silicon carbide (SiC).

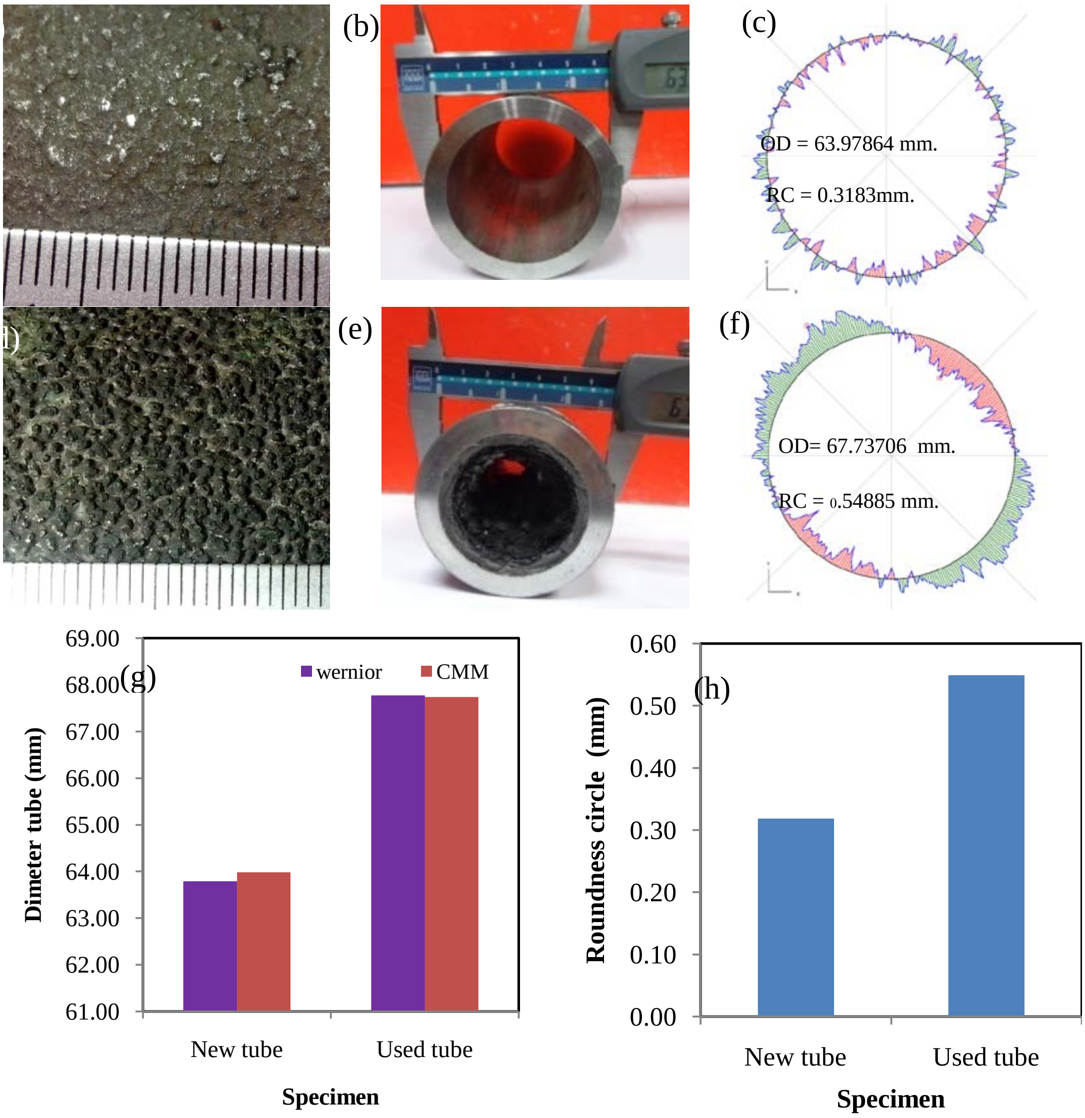


Fig. 5: Visual inspection of tube (a,b,c)Surface, OD and Roundness circle(RC) of the new tube, respectively (d,e,f) Surface,OD, Roundness circle(RC) of the used tube, respectively(g) OD measured by wernior and CMM and (h) RC measured by CMM machine.

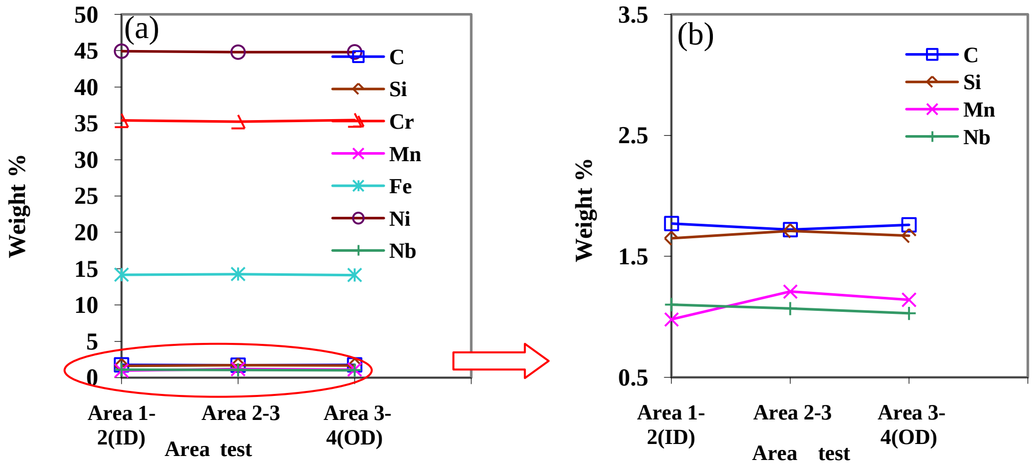


Fig. 6: EDS chemical analysis of new tube (a) All element and (b) Focusing on C, Si, Mn and Nb.

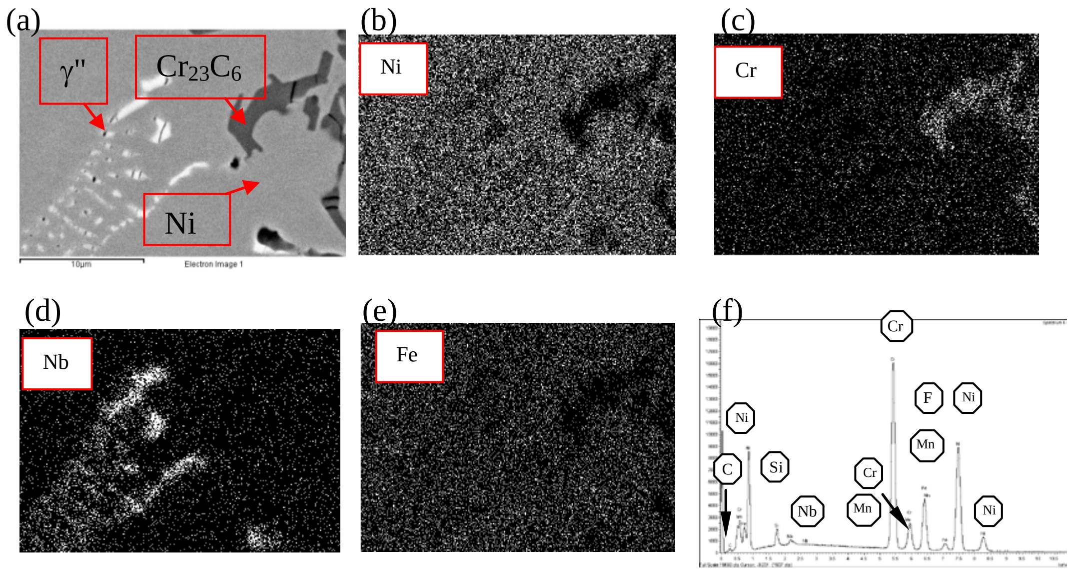


Fig. 7: EDS Mapping analysis of new tube (a) SEM image (b) Ni (c) Cr (d)Nb (e) Fe and (f) Spectrums for each element.

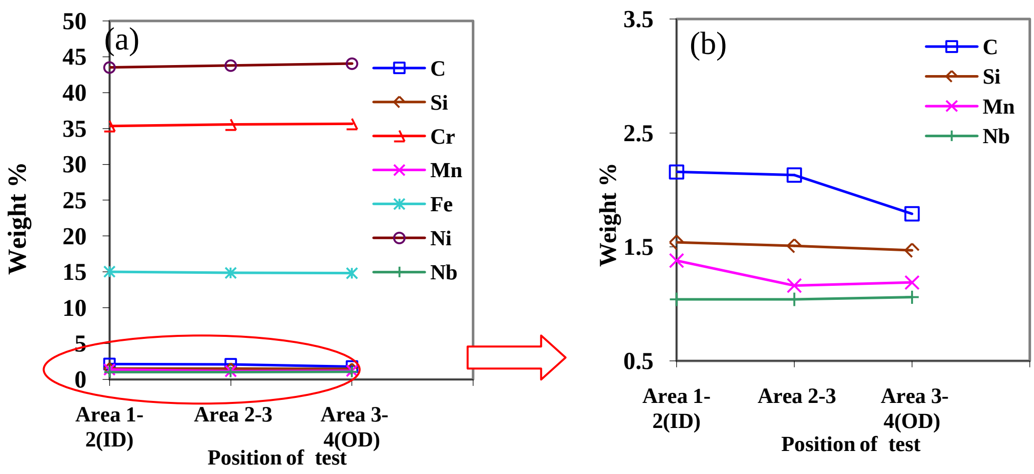


Fig. 8: EDS chemical analysis of used tube (a) All element and (b) Focusing On C, Si, Mn and Nb.

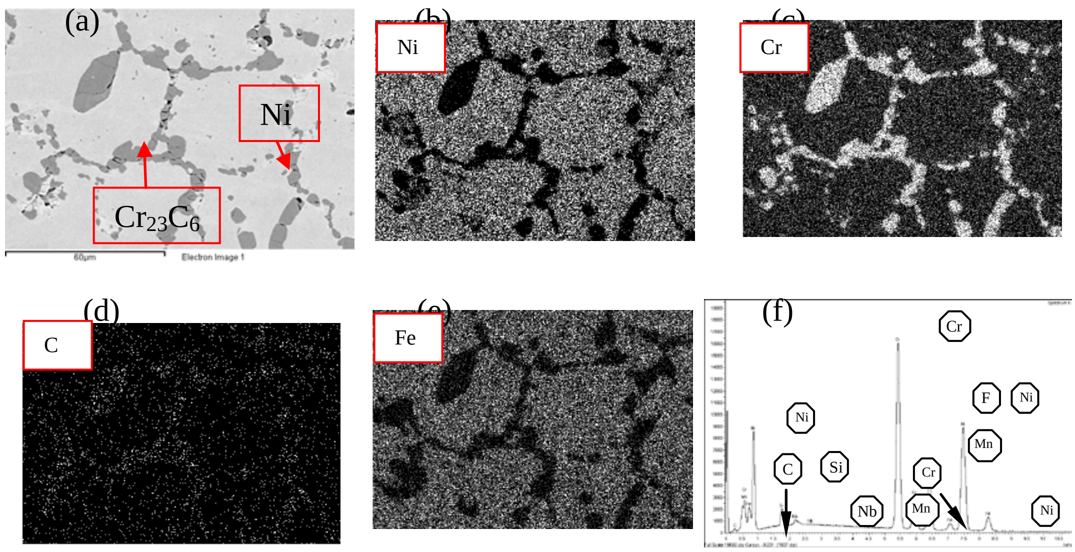


Fig. 9: EDS mapping analysis of used tube (a) SEM image (b) Ni (c) Cr (d) C (e) Fe and (f) Spectrums for each element.

Mechanical testing:

Hardness:

Figure 10 was shown the results of the new tube and the used tube by measuring from the outer layer to the inner layer of tube.

Comparison of MHV between the used tube and the new tube:

The value of hardness of the used tube is lower than the new tube because the thermal from service affected the internal energy change as explained below:

a) Chemical energy causedγ"(Ni_3Nb) to be decomposed into matrix and the grain boundary was destroyed because the inter metallic compound $Cr_{23}C_6$ was produced as shown in Figure 11(a).

b) Strain energy at high temperature caused the grain boundary(GB) to move easily and combine together to form a larger grain. Thus, the activation energy is combined with strain energy in the crystal structure and it reduced the interface energy at grain boundaries. Meanwhile, there is a combination of carbide in the applicable temperature for producing $Cr_{23}C_6$as shown in Figure 11(b).

c) Other energy sources occurred from the defect of material i.e. dislocation, inclusion grain boundary and free surface respectively.

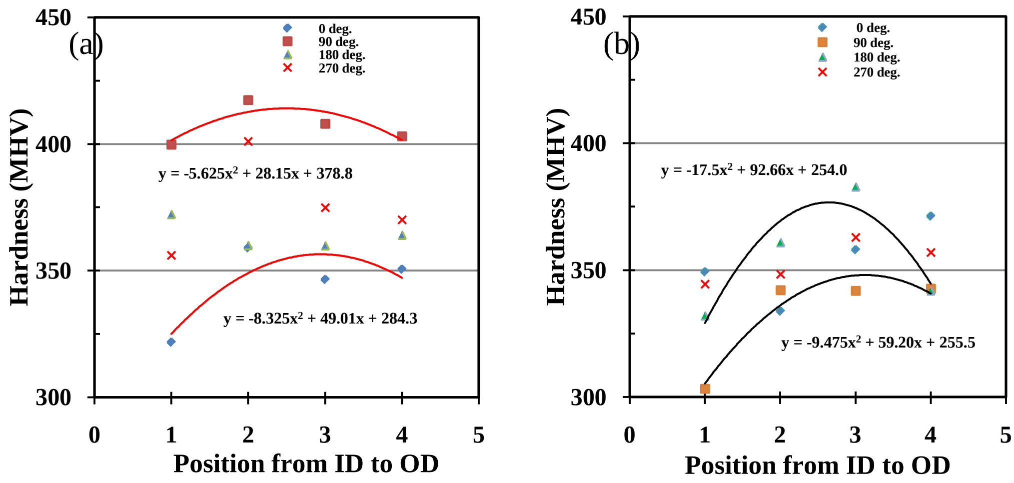


Fig. 10: MHV hardness (a) new tube and (b)used tube

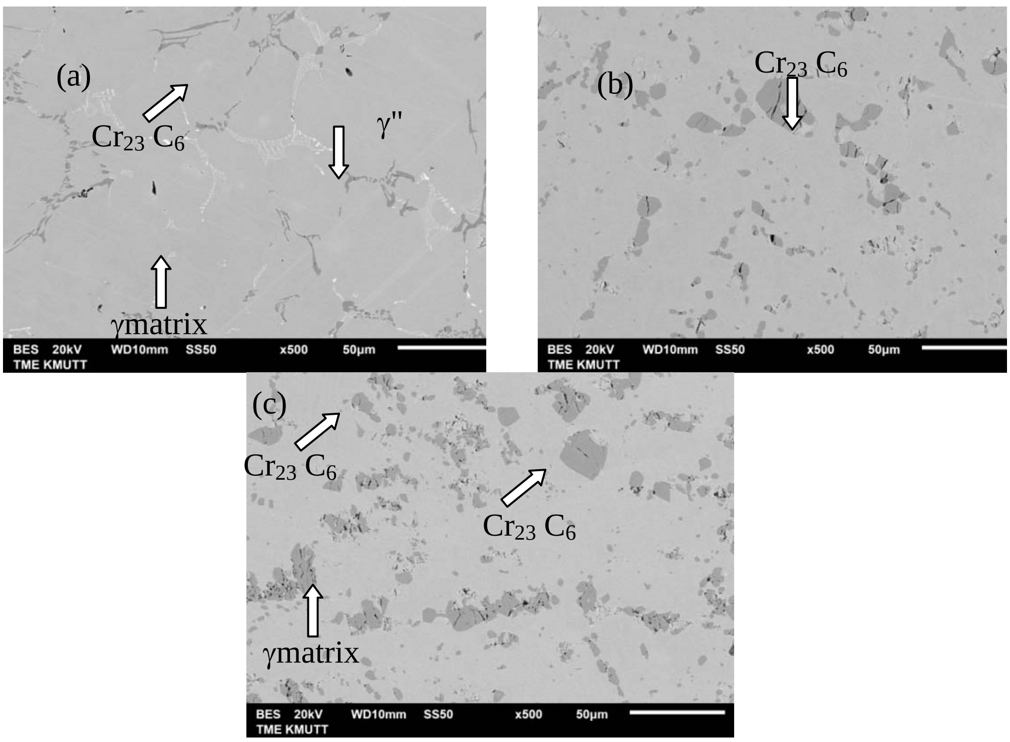


Fig. 11: SEM images of new tube and used tube taken from different position
(a) External surface of New tube (b) External surface of used tube and
(c) Internal surface of used tube.

Comparison of MHV between used tube at different layers:

MHV of the used tube has been increased to maximum and after that it is decreased because there is a chemical compound of hydrocarbon (C_2H_4) in the tube. It is arisen from incomplete combustion and the environmental condition whose temperature and pressure can produce the new element. After that, the diffusion of carbon in the form of coke penetrated through the material (see Figure 12). Its reasons might be explained as follows:

a) Particle coarsening of new tube and used tube can be seen from the microstructure in Figure 13(a) and (b), respectively. Moreover, the mean particle size(Figure 13(c)), it was founded that the coarsening grain growth in the areaID-1 more than area 3-4 measured by using the MSQ software. There is effected of service temperature of the fire heating furnace included hot spot and carburization phenomenon.

b) Degree of carburizing in tube (at cross sectional area) causes the area fraction of $Cr_{23}C_6$ and Si C), area 1-2 smaller than area 3-4 (Figure

13(d)) and the number of inter metallic compound inside the tube (1,533 particles) is greater than outside (261 particles) measured by using the MSQ software.

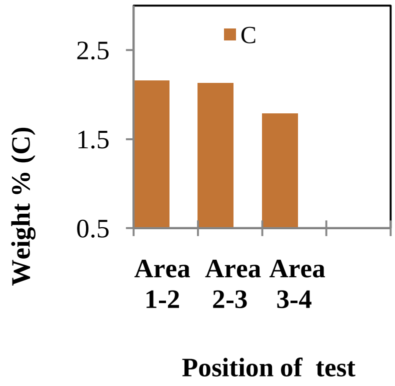
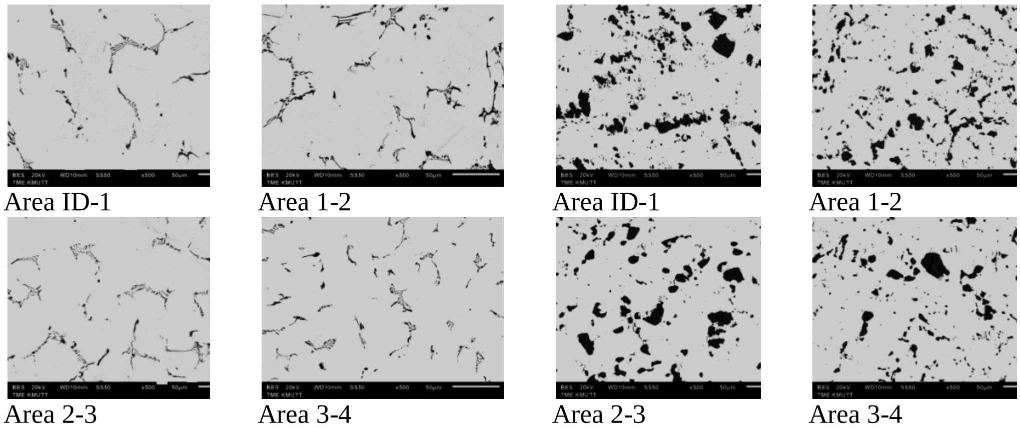


Fig. 12: Concentration of carbon in the used tube in different areas.



(a) Particle size of new tube (b) Particle size of used tube

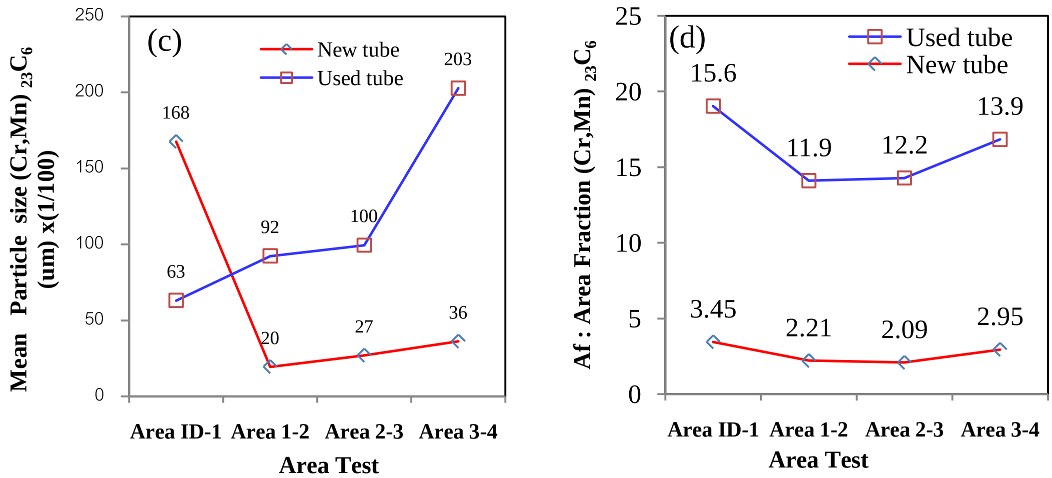


Fig. 13: The new tube and used tube were checked the area fraction and particle size of $(Cr,Mn)_{23}C_6$(a) (b) Particle size of new tube and used tube(c) Mean particle size and (d) Area fraction.

Comparison of tensile strength between the new tube and used tube:

The ultimate stress and yield stress of new tube was 513MPa and 360 MPa, respectively. The results showed that the new tube had higher ultimate strength and yield stress than those of the used tube, because more carbon had decreased the tensile strength of the used tube as shown in Figure 14. It conforms to the carburizing level as explained in section 3.3.1 and 3.3.2.

Discusion:

Form the visual examination test results, it is founded that a crack on the surface and subsurface of the used tube can be seen. The micro-crack by optical microscope (OM) has length of 1.5 mm. measured from the surface. There is coke precipitates in the tube greater than the new tube (Figure 5). It is because of the packed carbon (coke) inside the inner layer of tube had swollen during operation with high temperature and high pressure. Then carbon atom had been diffused through the matrix of inner tube. Then, it formed complex carbide such as$Cr_{23}C_6$or$SiC$and other different area fractions (Figure13(d)) to be formed in the matrix structure of inner tube.(Figure 7 and 9).

It is because the strength and hardness is decreased when compared with the new tube. The ultimate strength and yield stresses seem to be decreased. In other words, the used tube has lost the plasticity and elasticity at the inner layer of tube. Therefore, cracking is taken place because of a large amount of packed carbon in the tube. It cannot be shrunk to the same original condition while it is cooling down. Moreover, the shrinkage of tube in different quadrant causes different stress on each quadrant(Figure 5(f)).

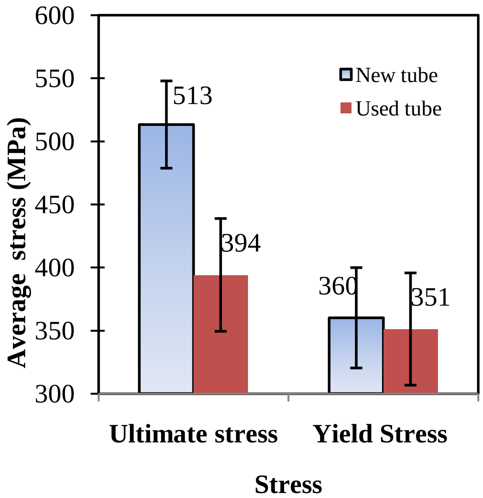


Fig. 14: Tensile stress of the new tube and used tube.

However, all of phenomenon can be changed by material, services temperature, type of gas and operating time.

In conclusion, the cause of tube rupture is carburization phenomenon because the diffusion and pressure of environment in the tube are very high. For the future work, more studies on elevation of the tube on which the coke is taken place should be done because it affects the metallurgical and mechanical properties of material. The result of study will be used as a data for repairing the tube in the fire heater furnace of petrochemical industry.

Conclusion:

5.1 The investigation root cause of tube rupture by used method; VT,SEM/EDS and mechanical. This is resulted that;

1) The tube were cracked and deformation ,depend on attachment of coke.,

2) The SEM micrograph that founded the different of area fraction of the $Cr_{23}C_6$ particle and mean particle size of precipitated chromium carbides (Cr_{23} C_6),depend on the diffusion of carbon and service temperature.,

3) The EDS founded that the different of quantitative and qualitative, carbon composition and area of element, respectively. This is effect to life time

4) The mechanical properties of tube was changed after service, confirm by the value hardness and tensile stress had decreased, in the reason of carburization

5.2 The carburization was effected to micro structure of used tube. This is depend on service operation such as services temperature, type of gas and operating time. Therefore, the operator must be carefully controlled the soot and hot spot in the tube for preventive tube rupture.

5.3 The phenomenon of carburization inert tube is relation with carbon diffusion of gas steady state.

This affected to the chemical composition, physical metallurgy and mechanical properties.

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