INVESTIGATION OF CARBURIZATION EXTENT FROM THE INNER DIAMETER (ID) OF ETHYLENE FURNACE TUBES USING NON-DESTRUCTIVE EXAMINATION (NDE) APPLIED ON THE OUTER DIAMETER (OD)

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

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ABSTRACT

This research project is to investigate the possibility of measuring the depth and location of carburization and metal dusting on the inside of ethylene pyrolysis tubes using nondestructive tools applied to the outer surface. A carburization test was conducted in a specially designed and manufactured HK-40 alloy tube.

Ethylene pyrolysis is considered the most important process in the petrochemical industry for producing petrochemical products. Some furnace tubes used for ethylene pyrolysis often suffer severe high-temperature corrosion since the tube surfaces are heated up to about 1,100 °C in contact with steam-hydrocarbon gas mixtures. Simultaneous carbon deposition on the tube surfaces (i.e. coking) can deteriorate the mechanical properties of the tube materials and may result in a failure of the furnace tubes in the form of carburization or metal dusting.

This investigation consists of four separate experimental practices to detect and assess the carburization and metal dusting damage. It involves a) impulse testing to study changes in natural elastic wave frequencies, b) metallographic evaluation, c) resonant ultrasound spectroscopy (RUS), and d) computational modeling to simulate guided wave and ultrasonic phased array technique.

The collaboration of the results of these experiments demonstrated the possibility that ultrasonic phased array can offer an efficient and economical practice to determine the remaining services life of the ethylene furnace tubes.

The elastic responses (frequency shift and mode shape changes) of the HK-40 alloy tube was studied due to changes in material properties that result from carburization and metal dusting, a severe form of carburization. Natural frequency analysis was conducted as measured at different locations of the HK-40 alloy tube before and after the carburization test. A shift in natural frequencies was observed and is understood to be due to a reduction in shear wave speed in the carburized samples. This shift seems to correlate to the extent of carburization and forms the basis for a new nondestructive evaluation method. Extensive metallographic examination of transverse and longitudinal cross section samples cut out of the HK-40 alloy tube after carburization using optical macrograph, scanning electron microscopy and energy dispersive X-
ray were used to quantify the carburization extent as compared to the corresponding shift in natural frequencies.

Computational modeling using a finite element analysis program (COMSOL) was used to simulate different scenarios of alternating the material properties, depth and shape of carburization and metal dusting. The simulations revealed strong reflections from relatively high defect depth to tube thickness ratio based on exciting a guided wave. Relatively small defects were very weak in terms of wave reflection amplitude. Hence, phased array technique was utilized in the simulation to enhance the use of guided wave by amplifying the low peak amplitude of the reflected wave from defects.

The research reported provides a new approach to advanced nondestructive testing to evaluate the remaining life of ethylene furnace tubes and other application tubes suffering carburization and metal dusting.
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DEDICATION

To all my family members, thank you so much for supporting me during my study.
CHAPTER 1: INTRODUCTION

1.1 Introduction

Ethylene is a major building block and the largest by volume for the chemical industry globally. Ethylene is produced commercially primarily by two processes. The main process is steam cracking (steam pyrolysis) of hydrocarbon feedstock (ethane, propane, butane, and naphtha). It is also produced through petroleum refining (separation from refinery gas streams) [1]. Typical process feature of an ethylene process is short residence time in the furnace. End of 2012 worldwide production is about 156 million ton/year [2].

A hydrocarbon feed stream is preheated, mixed with steam and further heated to 500 to 700 °C. The stream enters a fired pyrolysis furnace (known as cracker, cracking furnace), where under controlled conditions the feedstock is cracked at 800 to 850 °C into smaller molecules within a residence time of 0.1 to 0.5 s. After leaving the radiant coils of the furnace the product mixtures are cooled down instantaneously in transfer line exchangers (TLE) to preserve the gas composition. This quenching time is a crucial measure for severity control of the final products.

The production of ethylene is one of the most energy intensive processes in the chemical industry because furnace tubes must be decoked every 10 to 80 days (depending on feedstock, furnace type, and severity of operation) to preserve tube life [3]. Decoking is started with steam after lowering the temperature to about 800 °C and is continued with a steam-air mixture up to about 1100 °C. The combination of in-service operation and decoking cycles have reduced the tube life of outlet coils by four to six years [4].

The internal surface of the coil is exposed to high temperature hydrocarbons. This chemical system favors the deposition of carbon on the surface of the tubes. Coke formation is particularly damaging to the overall process because it accumulates on the inner wall of the tubes and eventually leads to process inefficiencies (localized increases in tube wall temperatures, poor heat transfer, increased pressure drop, reduction of inner tube diameter, and tube plugging) and tube failure [5]. The tube failure modes initiated by catalytic coke formation are: thermal shock, stress rupture, thermal fatigue, and carburization.

Since the 1950’s there have been a lot of developments in ethylene pyrolysis furnace to increase capacity, improve yield and thermal efficiency and reduce downtime for maintenance.
The areas of developments were in term of material improvement and tube size and shape design [6].

For a successful ultrasonic testing, a key element is the selection and exciting a single mode. In general, a transducer can excite all of the modes, which present within its frequency bandwidth, yielding in a signal that is very complex to interpret. Indeed, even with a single mode, great care is required for the correct identification of the reflections from defects and from normal tube features such as welds and cracks. Hence, it is essential to design the transducers and the signal to excite only the preferred mode. Then, since defects and normal tube features can convert energy to other modes, it is important also to be able to receive the signals in a precise setup [7].

1.2 Justification of Conducted Research

Wrought and cast heat resistant tube alloys used for ethylene pyrolysis furnace have a non-magnetic property feature. Due to carbon diffusion, carburization causes the change of this characteristic to be magnetic. Measuring magnetic permeability has been used for several years to estimate the degree of carburization of the tubes. Quantifying equipment used currently ranges from the hand held magnet to the more technologically sophisticated instruments such as multi-frequency eddy current instruments. While the latter can be helpful in evaluating not only the degree of carburization but its pattern as well [8]. Unfortunately, all of these existing tools are point to point inspection which is time consuming.

Hence, there is a high demand for advancement in nondestructive evaluation tools for measuring the degree of carburization with reasonable time during shutdown period of the furnace.

1.3 Scope and Objective of the Overall Research Program

The main focus of this research is to investigate the use of nondestructive testing which can be applied on the outer surface of the tube to measure the depth of carburization and metal dusting in the inner side of the tube. The overall objective of the conducted research is to address the following technological and fundamental questions:

1. What is the specific nature of the microstructure resulting from carburization and metal dusting and its potential role in causing tube failure?
2. Does ultrasonic testing provide adequate information of carburization location along the tube length instead of single spot analysis/inspection?

3. Would it be possible to: a) detect the depth and location of carburization or metal dusting using ultrasonic techniques? b) Establish a prediction of the tube service life?

4. What technique could be used to detect early stage of carburization and/or metal dusting?

1.4 Organization of the Thesis

The thesis is organized into ten chapters. The first Chapter, Introduction, covers general overview about the research topic. It justifies the research work and states the objectives of the conducted research.

Chapter two, Literature Review, summarizes previous studies of carburization and metal dusting in petrochemical plants. In addition, it covers the different techniques carried out in the field of nondestructive testing.

Chapter three, Experimental Procedure, describe the methodology and tools implemented to conduct the experiments in the following chapters.

Chapter four, Metallographic Examination, report the observations of the thorough examination of material microstructure degradation due to carburization and metal dusting. Optical macrographs, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were used in this examination along with macro hardness testing.

Chapter five, Natural Frequency Analysis, study the effect of heat treatment, carburization, and metal dusting on the natural elastic vibrational frequencies of the HK-40 alloy tube. Comparisons between readings of different vibrational modes in multiple locations were conducted along with simple simulation modeling for solid examination.

Chapter six, Resonant Ultrasound Spectroscopy, covers examination of multiple small samples before and after the carburization test to investigate if a correlation between carbon uptake and material elastic properties could be achieved.

Chapter seven, Finite Element Analysis, present the computational modeling using COMSOL for different scenarios of carburization and metal dusting. It includes an investigation
of using phased array techniques to detect location and depth of carburization and metal dusting in the early stage.

Chapter eight, Summary of Results and Discussion, summarizes, interrogates and discusses the overall outcome and correlates them together.

Chapter nine, Conclusion, summarizes the key findings of the conducted experiments and modeling in achieving significant outcome for advancing nondestructive practices.

Chapter ten, Future Work, is a suggestion for the specific topic of nondestructive evaluation of carburization and metal dusting of pyrolysis tubes to achieve full utilization of the proposed technique to assess the more complicated tube configuration.
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Ethylene (C$_2$H$_4$) is generated by cracking Ethane (C$_2$H$_6$) in a pyrolysis furnace. Cracking (or pyrolysis) furnaces are used to produce olefins such as ethylene and propylene, which are subsequently used to make the commodity materials such as polyethylene and polypropylene. They are operated at high temperature to promote endothermic reactions.

The process stream in a furnace consists mainly of a mixture of steam and ethane, passed through tubes that externally heated to the temperatures of 850 - 1150 °C. The temperature of the gas is raised quickly, and it is passed through the tube at a high velocity with a short residence time of 0.1 to 0.5 s. These tubes sometimes are called millisecond tubes [1].

The simplest reaction form of the decomposition of Ethane into Ethylene is

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (2.1)$$

The cracking reaction for ethylene can be written as

$$C_2H_4 \rightarrow CH_4 + C \quad (2.2)$$

and is accompanied by carbon formation

$$CH_4 \rightarrow C + 2H_2. \quad (2.3)$$

The last two reactions show that the process of producing ethylene generates free carbon. To slow the latter reaction, steam is added to the hydrocarbon feedstock [9].

The hydrocarbon-steam mixture is heated by passing it through tubes that are suspended within a firebox. These tubes usually are around 100 millimeter in diameter, 10 millimeter in wall thickness and about 10 meter long [10].
2.2 Tube Design and Material of Construction Development

Since the 1950’s there have been a lot of developments in ethylene pyrolysis furnace to increase capacity, improve yield and thermal efficiency and reduce downtime for maintenance. The areas of development were in term of material improvement and tube size and shape design.

The first group of the materials was HK-40 cast alloys based on 25 percent chromium and 20 percent nickel by weight. Late 1980’s saw the introduction and then the enhancement of HP alloys which has a modified composition mainly consisting of 25 percent chromium and 35 percent nickel. The alloys currently sweeping the industry are based on a composition of 35 percent chromium and about 45 percent nickel by weight. In each major advancement in the chemical composition of the alloys, there has been an increase in the chromium and/or nickel concentration (Table 2.1) and cost [6]. Figure 2.1 summarizes the major evolutionary in alloying elements.

Table 2.1: Commercial materials for ethylene furnace tubes along with their main compositions in weight percentages, temperature operating limit, and carbon ingress.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Main composition (wt.%)</th>
<th>Temperature Limit (°C)</th>
<th>Carbon ingress</th>
</tr>
</thead>
<tbody>
<tr>
<td>HK-40</td>
<td>25 Cr / 20 Ni</td>
<td>1000</td>
<td>1% at 1055 °C</td>
</tr>
<tr>
<td>HP Modified</td>
<td>25 Cr / 35 Ni</td>
<td>1125</td>
<td>1% at 1125 °C</td>
</tr>
<tr>
<td>35/45</td>
<td>35 Cr / 45 Ni</td>
<td>1150</td>
<td>1% at 1155 °C</td>
</tr>
</tbody>
</table>

Figure 2.2 shows the absorbed carbon percentage plotted against nickel content by weight percent. The carbon absorption percentage decreases with increasing nickel content percentage. In addition, silicon is also shown to have a strong effect in reducing the carbon ingress percentage.
Figure 2.1: Historical summary of ethylene furnace tube material development [11].

Aluminum is another alloying element that provides a strong protective layer (Al₂O₃) at elevated temperature. However, a concentration higher than 2-2.5 weight percent of both silicon and aluminum have an adverse effect involves tradeoffs in strength, aged ductility, and/or weldability that are often unacceptable. These alloys are generally restricted to about 2 weight percent of either element. This arrangement is helpful but is not a total solution to overcome the carburization damage [8].

Coatings and surface enrichment using silicon, aluminum, chromium, and combinations thereof, have been tried to control carburization of heat resistant alloys. Unfortunately, none of these practices have been successful for the long term. Vapor diffused aluminum enrichment showed promise and performed well at lower temperatures but broke down after relatively short times at temperatures above 1850-1900°F (1010-1040°C) [12].

Surface condition of the inner side of the tube was under investigation to study its effect on carburization damage. Manufacturing the tubes using centrifugally casting process produce impurities, such as metal inclusions, in the outer region (i.e. inner surface) of the tube causing very rapid coke build up and very poor tube life. It has been found that machining the inner surface of the tube to a smooth imperfection free surface improved the tube life and reduced the coke build up by almost one order of magnitude (Figure 2.3) [14].
Figure 2.2: Effect of nickel and silicon content on the resistance of Cr-Ni alloys to carburization [13].

Evolution on the design of the inner surface of the tube was a great interest of some companies. Sandvik Corporation, a Sweden company, introduced longitudinal fins to increase the internal surface area of the tube by up to 25 percent. This enlargement of the tube inner surface area improves heat transfer which leads to increase the productivity for ethylene producers (Figure 2.4) [15].

Heat transfer in smooth bored tubes is a combination of radiation, conduction, and boundary layer conditions. In a straight run of smooth bored tubes, laminar flow develops along the inner diameter surface, permitting precipitation of carbon into the inner surface of the tube. This coke build up layer is responsible for tube short run times. Kubota Corporation, a Japanese company, patented a mixing element radiant tube (MERT) technology. It allows the laminar layer to be periodically broken up with the turbulent flow in the core (Figure 2.5). This technology can extend the run length by fifty percent [16].
Figure 2.3: Carbon concentration profile of several centrifugally cast alloys in a) as-cast surface condition and b) machined surface condition after one year of field testing in an ethylene cracking furnace [14].
Figure 2.4: Finned ethylene furnace tubes manufactured by Sandvik Corporation [15].

Figure 2.5: Illustration of the thermal experience of a mixing element radiant tube (MERT) manufactured by Kubota Corporation [17].
2.3 Thermodynamics Consideration

Petrochemical and refinery environments contain gas mixtures of CO, CO\(_2\), H\(_2\), H\(_2\)O, CH\(_4\), H\(_x\)C\(_y\) (hydrocarbons), and organic compounds. The alloys are likely carburized if (a\(_c\))\(_{environment}\) > (a\(_c\))\(_{alloy}\). This carburization can proceed by one of the following reactions [18]:

\[
CO + H_2 = C(dissolved) + H_2O \quad (2.4)
\]

\[
2CO = C(dissolved) + CO_2 \quad (2.5)
\]

\[
CH_4 \rightarrow C(dissolved) + 2H_2 \quad (2.6)
\]

In equilibrium, the carbon activity in the environment can be calculated by [9]:

\[
a_{c(2.7)} = e^{-\frac{\Delta G_{0}^{\circ}}{RT}} \left( \frac{P_{CO}P_{H_2}}{P_{H_2O}} \right) = K_{(2.7)} \left( \frac{CO_{P_{H_2}}}{P_{H_2O}} \right) \quad (2.7)
\]

\[
a_{c(2.8)} = e^{-\frac{\Delta G_{0}^{\circ}}{RT}} \left( \frac{P_{CO}^2}{P_{CO_2}} \right) = K_{(2.8)} \left( \frac{P_{CO}^2}{P_{CO_2}} \right) \quad (2.8)
\]

\[
a_{c(2.9)} = e^{-\frac{\Delta G_{0}^{\circ}}{RT}} \left( \frac{P_{CH_4}}{P_{H_2}^2} \right) = K_{(2.9)} \left( \frac{P_{CH_4}}{P_{H_2}^2} \right) \quad (2.9)
\]

where;

- \(a_c\) is carbon activity,
- \(\Delta G_{0}^{\circ}\) is standard Gibbs free energy reaction,
- \(T\) is absolute temperature,
- \(K\) is reaction equilibrium constant,
- \(P\) is total system pressure.

If the environment contains CO, the carbon activity of the environment will be dominated by reaction (2.5). For this reaction, the equilibrium constant is [19]:
\[
\log K_{(2.8)} = \log \frac{P_{CO}^2}{a_c P_{CO_2}} - \frac{8817}{T} + 9.071
\]  

(2.10)

In ethylene production, the environment is rich in CH\textsubscript{4}, the carbon activity of the environment will be dominated by reaction (2.6). For this reaction, the equilibrium constant is [19]:

\[
\log K_{(2.9)} = \log \frac{P_{CH_4}}{a_c P_H^2} - \frac{4791}{T} + 5.789
\]  

(2.11)

In austenitic alloys, ingress of carbon into the alloy results in the formation of chromium carbides, principally. There are three forms of chromium carbides: Cr\textsubscript{23}C\textsubscript{6}, Cr\textsubscript{7}C\textsubscript{3}, and Cr\textsubscript{3}C\textsubscript{2}. Gibbs free energy of the formation of these carbides as a function of temperature are shown in Figure 2.6. Relative stability of these carbides, during carburization, is shown in Figure 2.7 for Cr-O-C system at a temperature of 620 °C. The figure illustrates the region where specific protective layer is formed and the region where the material is susceptible to carburization and metal dusting. At very low oxygen partial pressure and low carbon activity in the alloy, the most stable carbide is Cr\textsubscript{23}C\textsubscript{6} [19].

Figures 2.7 to 2.9 show that as the operating temperature increases, the oxygen partial pressure (x-axis) to form the protective layer (Cr\textsubscript{2}O\textsubscript{3}) is reduced. In addition, the carbon activity level (y-axis) is shifted up.

Considering the following equilibrium:

\[
\frac{23}{6} Cr_{(s)} + C_{(g)} = \frac{1}{6} Cr_{23}C_{6(s)}
\]  

(2.12)

\[
\Delta G_f^\circ = -RTln \left( \frac{a_{Cr_{23}C_6}^{1/6}}{a_c a_{Cr}^{23/6}} \right)
\]  

(2.13)

where \(a_{Cr_{23}C_6}\), the activity of the solid carbide precipitated, is assumed to be unity. Rearranging (2.13), it becomes:
Figure 2.6: Standard free energies of formation for some carbides [20].
Figure 2.7: Phase stability diagram of Cr-C-O system at 620 °C [21], reproduced.

Figure 2.8: Phase stability diagram of Cr-C-O system at 870 °C [21].
Figure 2.9: Phase stability diagram of Cr-C-O system at 1090 °C [21].

\[ (a_C)_{alloy} = e^{-\frac{\Delta G_f^0}{RT}} \left( \frac{1}{a_{cr}^{23/6}} \right) \]  
(2.14)

In this case:

\[ \Delta G_f^0 = 16,380 + 1.54 T \]  
(2.15)

\[ a_{cr} = \gamma_{Cr} N_{Cr} \]  
(2.16)

where;

\[ \Delta G_f^0 \text{ is Standard Gibbs energy of carbide formation;} \]

\[ a_{cr} \text{ is Chromium activity in the alloy.} \]
\( \gamma_{Cr} \) is Chromium activity coefficient;
\( N_{cr} \) is Molar fraction of chromium.

2.4 Diffusion Kinetics (Fick’s Second Law)

Once the compact and protective oxide layer (Cr_2O_3) on the surface had disappeared, carbon started to diffuse into the steel. Carburization at this stage can be considered as diffusion-controlled step. The accumulation equation (Fick’s Second Law of Diffusion) for an assumed constant diffusion coefficient (D) is expressed as in Equation (2.17).

\[
\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \tag{2.17}
\]

where,

\( C(x,t) \) is the element concentration at depth \( x \) (meter) after time \( t \) (seconds);
\( D \) is the diffusion coefficient (m^2/sec).

The solution of \( C(x,t) \) can describe the concentration gradient changes with time during the progress of diffusion as seen in Figure 2.10. For carbon diffusion in HK-40 alloy tube, one dimensional diffusion from ID to OD was considered. One dimensional solution of the Fick’s Second Law can reasonably be applied to this analysis with the following boundary conditions [22]:

For \( t = 0 \), \( C_x = C_0 @ 0 \leq x \leq \infty \)

For \( t > 0 \), \( C_x = C_s @ x = 0 \); \( C_x = C_0 @ x = \infty \)

where;

\( C_x \) is the carbon concretization at depth \( x \) after time \( t \);
\( C_s \) is the carbon concentration at the surface;
\( C_0 \) is the carbon concentration in the material.

Applying these boundary conditions to equation (2.17) yields the solution

\[
C(x,t) = C_0 + \left[ (C_s - C_0)(1 - erf \left( \frac{x}{4D_c t} \right)) \right] \tag{2.18}
\]

and further rearranging results in a form that is useful for simple method of analysis
\[
\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{\sqrt{4D_c t}}\right)
\] (2.19)

The carbon diffusivity \(D_c\) has been reported to range from \(1 \times 10^{-7} \text{ to } 2 \times 10^{-6} \text{ cm}^2/\text{sec}\) [23].

Figure 2.10: Concentration profile of carbon through the cross section of a tube [24].

**2.5 Carburization Mechanism**

To describe the mechanism of carburization in a reducing environment, the performance of two groups of materials must be considered: 1) alloys which are unable of developing a protective oxide scale. 2) Alloys which can develop and maintain a protective oxide scale. The mechanism of carburization in each case could be described as follows:

1) During heating the pyrolysis tubes to the desired gas reaction temperature, where the alloy is inherently protected by \(\text{Cr}_2\text{O}_3\), it is possible that an oxide phase initially forms. Carbon generated by reactions involving carbonaceous gases reacts with chromium at the alloy surface to form a carbide scale of the \(\text{M}_3\text{C}_2\) type if the carbon activity at the surface is sufficiently high. Subsequently, the more stable carbide phase overgrows the oxide phase. Depletion of chromium in the alloy substrate due to continued growth of the surface carbide scale restricts the formation of a more protective oxide scale. Due to the relatively high atomic mobility within the carbide scale, carbon can penetrate into the
alloy with minimal restriction yielding massive precipitation of carbide phases which result in degrading the mechanical strength of the alloy (Figure 2.11) [25].

2) Alloys inherently protected by Al₂O₃ can develop and maintain a protective oxide scale even under reducing conditions. In the early stages of the reaction and prior to developing a continuous oxide scale, some carbon can penetrate into the alloy which may yield in precipitation of a small amount of carbides. Consequently, a continuous protective scale is developed which acts as an active barrier toward carbon diffusion into the alloy. Hence, massive precipitation of carbide phases is prevented. To conclude, an alloy protected by Al₂O₃-base scale is expected to be extremely resistant to a carburizing environment [26].

![Figure 2.11: Schematic representation of the microstructure evolution for carburization mechanism [27].](image)

Depending on the oxygen partial pressure and the carbon activity of the gas, three cases have to be considered:

### 2.5.1 Case One: The Carbon Activity is below One and the Oxygen Partial Pressure is Relatively High.

A protective chromia scale is formed if the oxygen partial pressure is greater than the equilibrium partial pressure for chromium oxide formation (approximately 10⁻²⁰ bar). Carburization of chromia-forming alloys should not take place under these conditions. However, carburization may occur if carbon penetrates along grain boundary cracks and voids of the oxide scale into the material or if the oxide scale spalls due to mechanical stresses [4]. Furthermore, scales of chromium oxide become non protective at very high temperatures, too. Under the
typical conditions of ethylene and propylene cracking above 1050 °C a transition of oxides to carbides is to be expected [8]. Even though stainless steels should be stable under these operating conditions, nickel-base alloys and iron - nickel - chromium alloys (i.e. silicon or aluminum) are often preferred [13].

2.5.2 Case Two: The Carbon Activity is below One and the Oxygen Partial Pressure is Low

If the carbon activity is below one but the oxygen partial pressure of the gas is lower than the equilibrium partial pressure for the formation of chromium oxide, protective chromia scales cannot be formed and carbon can penetrate into the material without any inhibition. Hence chromia-forming materials suffer severe carbon pick-up under these conditions. The rate of carburization depends on the carbon diffusion into the material and on the solubility of carbon in the material. Silica-forming materials and alumina-forming materials should form protective oxides scales at much lower oxygen partial pressures than chromia-forming materials.

2.5.3 Case Three: The Carbon Activity is Higher than One

If the carbon activity exceeds one, so-called metal dusting is frequently observed. Metal dusting is a specific corrosion mechanism which is characterized by a complete degradation of the metal into a dust of metal, metal carbides and coke (Figure 2.12). The process of metal dusting and carburization has been studied intensively by Grabke and co-workers for both iron base alloys and nickel-base alloys [26], [28]–[30].
Figure 2.12: Schematic representation of the microstructure evolution for metal dusting mechanism [6].
CHAPTER 3: EXPERIMENTAL PROCEDURE

3.1 Introduction

The following Section discusses the carburization process, design of the HK-40 alloy tube, material of construction, equipment, test matrices, and testing methodology to perform the carburization test. The primary purpose of this testing is to expose the tube under investigation to a carburizing environment to nondestructively examine the tube and to detect the depth and location of any structural changes in the form of carburization or metal dusting.

3.2 Design and Material of Construction

HK-40 alloy is an austenitic Fe-Cr-Ni alloy that has been a typical heat resistant material for over forty years. Table 3.1 shows the chemical composition in weight percent of HK-40 alloy. Tubes made out of this material are manufactured using centrifugal casting process.

Table 3.1: Chemical composition of HK-40 alloy in weight percent.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min %</td>
<td>0.35</td>
<td>23</td>
<td>19</td>
<td>0.4</td>
<td>0.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Max %</td>
<td>0.45</td>
<td>27</td>
<td>22</td>
<td>1.5</td>
<td>1.5</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

A special designed tube was manufactured by Duraloy Technologies Corporation to comply with the testing furnace dimensions. The experimental HK-40 alloy tube is 42 inch long with an outer diameter of 3.5 inch and inner diameter of 3 inch (Figure 3.1). An insert assembly consisting of a flange and two internal tubes; the long one is to allow air accessing the full length of the HK-40 alloy tube and the small one to allow for thermocouples access to the hot reaction zone of the tube, was manufactured (Figure 3.2).

3.3 Risk Assessment

Pack carburization test has been preferred over gas carburization practice due to simplicity, risk concerns of hazardous gas emission such as carbon monoxide (CO₂), and less
expensive laboratory equipment. Personal protective equipment were utilized all the time as some of the equipment requires a high voltage supply.

3.4 Carburization Test

There are two carburization tests which were conducted. The primary test was HK-40 alloy tube testing. The second test was a supplemental test for nine HK-40 small samples located inside the HK-40 alloy tube to be examined later with resonant ultrasound spectroscopy which discussed in details in Chapter six.

3.4.1 HK-40 Alloy Tube Testing

Pack carburization test was performed using a 22 inch tube long heat treatment (clam splitting) furnace from HEAVY-DUTY Corporation with a maximum operating temperature of 1010 °C. An existing tube was occupied in the furnace and was used as heat normalizing tube, referred to heat chamber tube from now on, to assure uniform heat distribution along the HK-40 alloy tube (Figure 3.3).

The inner side of the HK-40 alloy tube was cleaned with water, dried and then filled with pack carburizer granulate, trade name is # 3 GRANULAR CHARCOAL from HEATBATH Corporation, (Figure 3.4). The level of the carbon granular was about 75 percent of the tube volume after laying down the tube in a horizontal position (Figure 3.5).

Water cooling coil was used in the left side of the heat chamber tube. Both ends of the heat chamber tube were covered by a ceramic fiber insulation (Aluminum Silicate fiber) to maintain heat. The HK-40 alloy tube was inserted inside the heat chamber tube. Thermocouples were connected to a multiple channels data acquisition devise with digital screen to reveal temperature readings (Figure 3.6).

The furnace was running for 48 hours keeping the flange open to allow any moisture and/or burned inclusions accompanied the carbon granular to come out. A suctioning flexible hose was attached to the open side of the flange to exhaust safely all the unwanted gas.
Figure 3.1: Drawing of the HK-40 alloy tube used for the carburization test.
Figure 3.2: Drawing of the insert used along with the HK-40 alloy tube for the carburization test.
Figure 3.3: Clam spitting furnace used for carburization test occupied with heat chamber tube.

Figure 3.4: Granular charcoal from HEATBATH Corporation.
The flanges then closed and the furnace run for 1000 hours continuously at 1010 °C. The surface temperature profile of the HK-40 alloy tube furnace was recorded at three different locations. Location one, two and three were at 10, 17 and 25 inch from the end cap of the HK-40 alloy tube (Figure 3.7). Variation of the temperature along the HK-40 alloy tube is most likely either due to the furnace elements deficiency or that the heat chamber tube was oxidized at some locations or both. After running for 1000 hours, the furnace was then shut down and left for two days to allow for cooling.

3.4.2 HK-40 Alloy Samples Testing for Resonant Ultrasound Spectroscopy

Nine samples were cut from an as cast extra material of HK-40 alloy provided by the manufacturer into three groups labeled 1, 2 and 3. Each group consists of three samples with different dimensions consistent on each group (Figure 3.8). A thermocouple (Heavy duty type K, Inconel sheath from OMEGA) was attached to each combustion boat to get accurate temperature readings. The combustion boats were located at three different positions inside the tube while filling the granular charcoal. Further details are discussed in Chapter 6.

The temperature recordings of the three combustion boats are show in Figure 3.9. The variation in the temperature is related to the same reason stated above.
Figure 3.6: Pack carburization test setup where the HK-40 alloy tube is inside the heat chamber tube. Both sides of the chamber tube were insulated to maintain heat. Water coil for cooling was used in the left side of the heat chamber tube. Thermocouples were connected to multichannel digital temperature reading devise.
Figure 3.7: Temperature profile at different locations of the HK-40 alloy tube. Location 1, 2 and 3 are at 10, 17 and 25 inch, respectively, from the end cap of the tube.

Figure 3.8: A picture of three different size samples from one group setting in Alumina combustion boat.
Figure 3.9: Temperature profile of the three groups of the combustion boats.
CHAPTER 4: METALLOGRAPHIC EXAMINATION

4.1 Introduction

Microstructure analysis of equally spaced cross sections of the tube was conducted to investigate the material features and integrity after the pack carburization test discussed in Chapter three. Examination of microstructural features of the base metal, scale, carburized zones were characterized using optical micrograph and scanning electron microscope (SEM). Their chemical compositions were analyzed using energy dispersive X-ray spectroscopy (EDS). Hardness test was conducted along the top and bottom strips of the HK-40 alloy tube to estimate the effect of carburization on the mechanical strength after carburization.

The level of carbon granular filled in the HK-40 alloy tube was shown in Figure 3.5. The tube was cut to transverse and longitudinal sections (Figure 4.1). Each transverse section is half inch in length while the longitudinal cross section is eight inch in length and one inch in thickness. The transverse section demonstrates more understanding of circumferential responses of the material while the longitudinal section demonstrate more understanding of the changes along the HK-40 alloy tube where temperature varies.

Four strips with one inch thickness of each longitudinal cross section were cut from the HK-40 alloy tube representing a cross section of the top side, left side, right side and bottom side for macrostructure analysis.

4.1.1 HK-40 Alloy Tube Sample Preparation

The samples were cut using automatic abrasive cutting blade with extensive coolant to avoid overheating. Then, the samples cross sections were grinded using 240, 400 and 600 grit, in sequence. After that, the samples were polished using diamond cloth. NACE standard TM0498-2006 suggested using a freshly prepared etchant consist of 20 weight percent nitric acid (HNO₃) and four weight percent hydrofluoric acid (HF). The etchant was made by mixing 200 cm³ of concentrated 20 weight percent HNO₃ with 70 cm³ of concentrated 49 weight percent HF and 670 cm³ of distilled water. The samples were immersed in the etchant solution for two hours facing upwards and then rinsed with a distilled water before drying [31].
4.1.2 Transverse Cross Section # 1 and Longitudinal Cross Section # 1

Transverse cross section # 1 is located out of the furnace region nine inches from the left side of the tubes. The temperature reading is below 650 °C.

Figure 4.2 shows an etched cross section with higher magnification at 12, 3, 6 and 9 o’clock position. The macrostructure revealed no sign of carburization or metal dusting effect on the HK-40 alloy tube.

Four strips of longitudinal cross section # 1 along with the temperature profile are presented in Figure 4.3. About one inch from the left side was out of the furnace. Temperature reading after that was recorded to be about 920 °C while the end of the right section was about 890 °C. The macro structure of the top strip (A-E) revealed a lengthy carburized zone (about three inches) while the other strips required higher magnification for thorough investigation.

Figure 4.4 showed the inner surface of the longitudinal cross section # 1. Strip A-E which represents top side of the HK-40 alloy tube showed a greenish color along dark brownish color along the carburized zone observed in Figure 4.3. The other strips have some random spots of the greenish and browsing color with a majority of the gray base metal color.
Figure 4.2: Transverse cross section # 1 of the HK-40 alloy tube located nine inch from the end cab of the tube, left side, (representing temperature below 650 °C) with higher magnification optical macrographs of four sides in as etched condition.
Figure 4.3: Side view of four strips of longitudinal cross section #1 of the HK-40 alloy tube after pack carburization test located 9.5 inch from the left side of the HK-40 alloy tube representing top, right, bottom and left side (as etched condition) (Carburization time is 1000 hours, Temperature range: 910 to 950 °C).

Figure 4.4: Top view of inner surface diameter of the four strips of longitudinal cross section #1 representing top, right, bottom and left side located 9.5 inch from the left side of the HK-40 alloy tube (as received) (Carburization time is 1000 hours, Temperature range: 910 to 950 °C).

Figure 4.5 (A, B, and C) represent an optical macrograph of three different spots of strip A-E (top side of the HK-40 alloy tube). Two different distinct layers were observed on the three macrographs. The first layer from the inner surface was very dark followed by a brighter color layer that varies in depth.
Figures 4.6 to 4.8 are higher magnification optical macrograph of strips B-F, C-G, and D-H, respectively. Very shallow carburization layers were observed with a second brighter layer adjacent to it.

Figure 4.5: Optical macrograph of the carburized zones along strip A-E (top side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 910 to 950 °C).

Figure 4.6: Optical macrograph of the carburized zone at the left edge of strip B-F (left macrograph) and at the center (right side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 910 to 950 °C).

Figure 4.7: Optical macrograph of the small carburized zone near left edge of strip C-G (bottom side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 910 to 950 °C).
Figure 4.8: Optical macrograph of a very shallow carburized layer of the left side of strip D-H (Carburization time is 1000 hours, Temperature range: 910 to 950 °C).

4.1.3 Transverse Cross Section # 2 and Longitudinal Cross Section # 2

Figure 4.9 showed an etched transverse cross section with four higher magnification optical macrographs. The upper two macrographs showed a deep carburization which presents the top side of the HK-40 alloy tube. The lower macrographs represent the bottom side and right side of the HK-40 alloy tube. The bottom side showed a lower carburization layer compared to the top side macrographs with an indication of scale flaking from its inner surface. Carburization layer of the right side is also smaller in depth compared to the top side macrographs.

Figure 4.10 revealed fours strips representing top side (E-I), left side (F-J), bottom side (G-K) and right side (H-L) of the HK-40 alloy tube. Strip E-I showed two wide (about one inch each) relatively deep carburization located at the center of the inner diameter. Strip F-J showed one wide carburized zone (about one inch) at the left side of the strip with additional two very small spots of carburization. Strip G-K revealed a very shallow uniform carburization layer. Strip H-L showed two different zone of carburization defect.

Figure 4.11 showed the inner surface of the four strips, different coloring were observed on each strip. A greenish color on the right side of strip E-I were observed while the other strips revealed some brownish and gray color on the surface.

Optical macrographs of three spots of strip E-I (top side of the HK-40 alloy tube) are presented in Figure 4.12 (A, B, and C). Two distinct layers of carburization were observed. The first layer from the inner diameter is very dark in color while the second following layer was brighter and significantly varying in depth.
Figure 4.9: Transverse cross section # 2 of the HK-40 alloy tube located 17.5 inch from the end cab of the tube, left side, (representing temperature around 910 °C) with higher magnification optical macrographs of four sides (as etched condition) (Carburization time is 1000 hours).

Figure 4.13 (A and B) represent two optical macrographs of strip F-J (right side of the HK-40 alloy tube). A uniform shallow dark layer with a localized spot at one area was observed. A second brighter color layer varying in depth following the darker layer was noticeable.

Figure 4.14 revealed a macrograph with a very shallow dark layer of carburization flowed by a second brighter color layer of the bottom side of the HK-40 alloy tube (strip G-K). Figure 4.15 revealed a macrograph with a small flake peeling off the inner surface of the left side
of the tube (strip H-L) followed by dark layer of carburization with a very shallow bright in color second layer.

Figure 4.10: Side view of four strips of longitudinal cross section # 2 of the HK-40 alloy tube after pack carburization test located 18 inch from the left side of the HK-40 alloy tube representing top, right, bottom and left side (as etched condition) (Carburization time is 1000 hours, Temperature range: 880 to 910°C).

Figure 4.11: Top view of inner surface diameter of the four strips of longitudinal cross section # 2 representing top, right, bottom and left side located 18 inch from the left side of the HK-40 alloy tube (as received) (Carburization time is 1000 hours, Temperature range: 880 to 910°C).
Figure 4.12: Optical macrograph of the carburized layers along strip E-I (top side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 880 to 910 °C).

Figure 4.13: Optical macrograph of the spot carburized area along a very shallow carburized layer of strip F-J (right side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 880 to 910 °C).

Figure 4.14: Optical macrograph of the a very shallow carburized layer of strip G-K (bottom side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 880 to 910 °C).
Figure 4.15: Optical macrograph of the random carburization concaved area of strip H-L (left side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 880 to 910°C).

4.1.4 Transverse Cross Section # 3 and Longitudinal Cross Section # 3

Figure 4.16 showed an etched transverse cross section with four higher magnification optical macrographs. The upper macrograph showed a uniform shallow carburization layer. The right and left macrograph revealed a scale flacking out of the inner surface with small random carburization layer beneath the scale. The bottom macrograph showed no sign of any defect or color changing.

Figure 4.17 revealed different features of defect compared to figures discussed in previous Sections. Strip I-M (top side of the HK-40 alloy tube) revealed two very small pitting located at the right side from the center. Strip J-N (left side of the HK-40 alloy tube) showed two deep adjacent pitting located at the center. Strip K-O (bottom side of the HK-40 alloy tube) showed no indication of defects or changing in color. Strip L-P (right side of the HK-40 alloy tube) revealed a small size pitting located at the center of the strip.

Figure 4.18 present a surface view of the inner diameter confirming the findings discussed in the Figure 4.17. There are pitting distributed randomly in the center of strip I-M, J-N, and L-P but not K-O. About two inches from the right side of the strips were out of the furnace zone.

Optical macrograph in Figures 4.19 and 4.20 revealed the existence of pitting without any carburization layer around it. However, optical macrograph in

Figure 4.21 is a macrograph that revealed a deep uniform layer with brownish color around the observed pit.
Figure 4.16: Transverse cross section # 3 of the HK-40 alloy tube 19 inch from the end cab of the tube, left side, (representing temperature around 880 °C) with higher magnification optical macrographs of four sides in as etched condition (Carburization time is 1000 hours).
Figure 4.17: Side view of four strips of longitudinal cross section # 3 of the HK-40 alloy tube after pack carburization test located 26.5 inch from the left side of the HK-40 alloy tube representing top, right, bottom and left side (as etched condition) (Carburization time is 1000 hours, Temperature range: 860 to 880 °C).

Figure 4.18: Top view of inner surface diameter of the four strips of longitudinal cross section # 3 representing top, right, bottom and left side located 26.5 inch from the left side of the HK-40 alloy tube (as received) (Carburization time is 1000 hours, Temperature range: 860 to 880 °C).
Figure 4.19: Optical macrograph of a spot carburized area of strip M-I (top side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 860 to 880 °C).

Figure 4.20: Optical macrograph of a spot carburized area of strip J-N (right side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 860 to 880 °C).

Figure 4.21: Optical macrograph of a spot carburized area of strip L-P (left side of the HK-40 alloy tube) (Carburization time is 1000 hours, Temperature range: 860 to 880 °C).
4.1.5 Transverse Cross Section # 4

Transverse cross section # 4 is located out of the furnace region 34.5 inches from the left side of the tubes. The temperature reading is below 650 °C. Figure 4.22 shows an etched cross section with higher magnification at 12, 3, 6 and 9 o’clock position. The macrostructure revealed no sign of carburization or metal dusting effect on the HK-40 alloy tube.

Figure 4.22: Transverse cross section # 4 of the HK-40 alloy tube located 34.5 inch from the end cab of the tube, left side, (representing temperature below 650 °C) with higher magnification optical macrographs of four sides in as etched condition (Carburization time is 1000 hours).
4.2 Microstructural Investigation

The corrosion morphology and structure were studied using JEOL JSM-7000F Field Emission Scanning Electron Microscope (FE-SEM) with EDAX Genesis EDS, EBSD capabilities. Secondary electron imaging (SEI) mode was used unless otherwise specified.

4.2.1 Base Metal

An etched cross sectional sample was investigated under optical microscope to study the microstructure of the base metal near the inner and outer surface. Figure 4.23 showed a relatively large equiaxed grain with some columnar grains. Over etched grain boundaries of dendritic columnar grain structure that carried out lighter solute to the inner surface during centrifugal casting. Figure 4.24 showed columnar grains aligned in the diameter direction of the HK-40 alloy tube.

![Optical micrograph revealing the relatively large equiaxed microstructure of HK-40 alloy base metal near the inner diameter surface, as etched.](image)

Figure 4.23: Optical micrograph revealing the relatively large equiaxed microstructure of HK-40 alloy base metal near the inner diameter surface, as etched.
Another sample in the as polished condition was examined using scanning electron microscope (SEM). Figure 4.25 revealed primary carbide along the grain boundaries with some secondary carbide within the matrix.

![Optical micrograph revealing the columnar microstructure of HK-40 alloy base metal near the outer diameter surface, as etched.](image)

Figure 4.24: Optical micrograph revealing the columnar microstructure of HK-40 alloy base metal near the outer diameter surface, as etched.

Energy dispersive X-ray map was conducted to examine the form of carbide exist in the grain boundaries. Figure 4.26 is a color modified micrograph of the base metal of a HK-40 alloy that elementally identifies and reveals that the carbide is mainly chromium carbide rich in chromium with some oxygen carbide due to exposure to air during sample preparation.

Chemical composition of the base metal under investigation was analyzed with energy dispersive X-ray spectroscopy (EDS). This analysis is considered as a semi quantitative analysis and do not reflect exact weight percent. Figure 4.27 along with Table 4.1 showed the elements peak with their weight percent.
Figure 4.25: Backscatter SEM micrograph of HK-40 alloy base metal showing the primary carbides along the grain boundaries and secondary carbides, as polished.

Figure 4.26: Energy dispersive X-ray map showing elemental distribution (C, O, Si, P, S, Cr, Mn, Fe, and Ni) of the base metal of HK-40 alloy tube.
Figure 4.27: Energy dispersive X-ray spectra of the HK-40 base metal.

Table 4.1: Chemical composition of HK-40 tube base metal using energy dispersive X-ray spectra.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (wt.%)</th>
</tr>
</thead>
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<tr>
<td>C</td>
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<td>O</td>
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</tr>
<tr>
<td>Si</td>
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<td>P</td>
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<tr>
<td>S</td>
<td>0.185</td>
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<td>Cr</td>
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4.2.2 Carburized Zone

This Section examines two different metallographically prepared samples in the as polished condition representing a lightly and heavily carburized zone. Figure 4.28 is a backscattered SEM micrograph showed the first sample with adherent scale having a distinct line to flake out of the metal base. Multiple intergranular branches beneath the scale was observed. Figure 4.29 is a secondary electron SEM micrograph with higher magnification of the intergranular branching of carbon which is tracing the primary carbides.

![Image](image.png)

Figure 4.28: Backscattered SEM micrograph of a light carburized zone sample, as polished.

The second sample were carburization layer was dense is shown in the secondary electron SEM micrograph in Figure 4.30. Thick adherent scale was observed. This observation indicates the large amount of carbon diffused within the matrix. Small branches of intergranular attack were obvious beneath the scale. Figures 4.31 and 4.32 showed from secondary electron SEM micrographs the propagation of carbon through grain boundaries and then diffuses within the grain. Energy dispersive X-ray map was conducted for Figure 4.32. It revealed the presence of high amount of carbon compared to Figure 4.26. This result is a strong indication that the primary carbide transformed from the initially existing Cr$_{23}$C$_6$ to Cr$_7$C$_3$. 
Figure 4.29: Secondary electron SEM micrograph underneath a shallow carburized layer on HK-40 alloy, as polished.
Figure 4.30: Secondary electron SEM micrograph of a heavily carburized zone of a HK-40 alloy sample, as polished.
Figure 4.31: Secondary electron SEM micrograph underneath a heavily carburized layer of a HK-40 alloy tube, as polished.

Figure 4.32: Secondary electron SEM micrograph of carbon attacking grain boundaries of a HK-40 alloy tube, as polished.
Figure 4.33: Energy dispersive X-ray map using color to indicate the elemental distribution (C, O, Si, P, S, Cr, Mn, Fe, and Ni) in a micrograph of a carburized zone of HK-40 alloy tube.

Different spots at the carburization layer (Figure 4.34 to 4.38) were examined monitoring the variation of carbon and chromium weight percent (Table 4.2 to 4.6), respectively, using energy dispersive X-ray.

Figure 4.34: Energy dispersive X-ray spectra of point 1 in Figure 4.30.
Table 4.2: Chemical composition of Figure 4.34 using energy dispersive X-ray spectra.

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<td>Si</td>
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<td>P</td>
<td>0.132</td>
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<td>S</td>
<td>0.252</td>
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<td>Ca</td>
<td>0.407</td>
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<td>Cr</td>
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<td>Mn</td>
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<td>Fe</td>
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Figure 4.35: Energy dispersive X-ray spectra of point 2 in Figure 4.30.
Table 4.3: Chemical composition of Figure 4.35 using energy dispersive X-ray spectra.

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<tr>
<th>Element</th>
<th>Concentration (wt.%)</th>
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<td>Mn</td>
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<td>Fe</td>
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<td>Total</td>
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Figure 4.36: Energy dispersive X-ray spectra of point 3 in Figure 4.30.
Table 4.4: Chemical composition of Figure 4.36 using energy dispersive X-ray spectra.

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<th>Element</th>
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<td>Ni</td>
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Figure 4.37: Energy dispersive X-ray spectra of point 4 in Figure 4.30.
Table 4.5: Chemical composition of Figure 4.37 using energy dispersive X-ray spectra.

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<td>Cl</td>
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<td>Cr</td>
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<td>Mn</td>
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<td>Fe</td>
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<td>Total</td>
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Figure 4.38: Energy dispersive X-ray spectra of point 5 in Figure 4.30.
Table 4.6: Chemical composition of Figure 4.38 using energy dispersive X-ray spectra.

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4.2.3 Metal Dusting

This Section examines one of the samples with pitting defect. The sample was metallographically prepared to be investigated using scanning electron microscopy (SEM). Figure 4.39 is a backscattered SEM micrograph showing two pitting indications adjacent to each other. No indications of second layer or branching were observed. The pits were not filled with any corrosion product. It was empty and the dark color is an indication of inclined surface. Figure 4.40 is a higher magnification photograph of Figure 4.39.

Multiple points inside the pit were examined in terms of chemical composition changing using energy dispersive X-ray. The results are listed though Figures 4.41 to 4.44 with their elemental analysis Tables 4.7 to 4.10, respectively.

Table 4.7: Chemical composition of Figure 4.41 using energy dispersive X-ray spectra.

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<td>Si</td>
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Figure 4.39: Backscattered SEM micrograph of two pitting adjacent to each other of the HK-40 alloy tube, as polished.

Figure 4.40: Secondary electron SEM micrograph with higher magnification of the big pit observed in the HK-40 alloy tube, as polished.
Figure 4.41: Energy dispersive X-ray spectra of point 1 in Figure 4.40.
Figure 4.42: Energy dispersive X-ray spectra of point 3 in Figure 4.40.

Table 4.8: Chemical composition of Figure 4.42 using energy dispersive X-ray spectra.

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Figure 4.43: Energy dispersive X-ray spectra of point 4 in Figure 4.40.

Table 4.9: Chemical composition of Figure 4.43 using energy dispersive X-ray spectra.

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Figure 4.44: Energy dispersive X-ray spectra of point 5 in Figure 4.40.

Table 4.10: Chemical composition of Figure 4.44 using energy dispersive X-ray spectra.

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<th>Element</th>
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<td>S</td>
<td>0.185</td>
</tr>
<tr>
<td>Cr</td>
<td>24.561</td>
</tr>
<tr>
<td>Mn</td>
<td>1.313</td>
</tr>
<tr>
<td>Fe</td>
<td>48.638</td>
</tr>
<tr>
<td>Ni</td>
<td>17.027</td>
</tr>
<tr>
<td>Total</td>
<td>100.000</td>
</tr>
</tbody>
</table>
4.3 Hardness Measurements

Macro hardness test was conducted in two strips of the HK-40 alloy after carburization. The first strip represents the top side of the HK-40 alloy tube while the other strip represents the bottom side. Each strip is about twenty inch long. Measurements were taken along two longitudinal spots, one third away from the inner diameter and one third away from the outer diameter.

Left side of the graph represents the high temperature exposure of the HK-40 during carburization. Measurements were taken for the length of the strips exposed to carburization which is about 20 inch (508 mm) long. All measurements of the Rockwell hardness testes were measured either in HRB or HRC scale. However, they are all converted to HRA for consistency in comparison.

The base metal hardness is about 55 HRA. The hardness profile of the top strip Figure 4.45 showed an increase from the less hot zone (right side), where temperature was about 820 °C, to the very hot zone (left side), where temperature were, 920 °C, of the HK-40 alloy tube.

The hardness profile of the bottom side of the HK-40 alloy top showed a decrease in hardness compared to the base metal and then dramatic increase towards the very hot zone which is related to carbide formation or some level of carburization (Figure 4.46).

4.4 Results and Discussion

The microstructure of the centrifugally cast material consist of dendrite grains aligned in the diameter radial direction of the tube. It consisted of relatively large columnar centrifugally dendrite coming to an abrupt end on the inner surface. This last to solidify metal has lighter solutes which promote some features of equiaxed structure between the dendrites. The grain boundaries constituted of Cr-rich carbides.

The left side of the HK-40 tube, where temperature was about 960 °C, exhibited severe carburization while other areas lost their structural integrity in terms of pitting in the 860 °C zone. The scale formed on the surface of the tube was adherent and there was evidence of flaking. No cracking in the tube walls were noticed. It is observed that there are signs of two carburization layers. First is the formation of adherent carburization layer, second is solid solution precipitation within the matrix. The carbide first formed at grain boundary and then advances within grain matrix.
Figure 4.45: Rockwell hardness profile of the top strip starting from end side of the HK-40 alloy tube.

Figure 4.46: Rockwell hardness profile of the bottom strip starting from end side of the HK-40 alloy tube.
The space and time of the initiation and growth of carburization is random and non-uniform in nature. Carburization takes place as an internal reaction due to the high diffusivity of carbon. Nickel is not a carbide forming element, so presumably it would tend to remain in solid solution in the matrix. Energy dispersive X-ray map revealed that carbide transformation in HK-40 alloy during high temperature service from the initially existing $\text{Cr}_2\text{C}_6$ to $\text{Cr}_7\text{C}_3$.

These examples show that not only the degree of carburization vary dramatically around the circumference of the HK-40 alloy tube but also over a very short distance along the length of the tube. Thus, temperature alone is not a determining factor. Surface condition should be considered another major factor. This non-uniformity also presents a problem in interpreting the results of measurements of the degree of carburization.

The hardness profile of the top surface in not in agreement with the hardness profile for the bottom surface. This situation is because the top surface was carburized much more than the bottom surface. Hence, the bottom surface was softening yielding to a lower hardness value compared to the base metal. The hardness then jumped in value due to the starting of carburization attack at the very end portion of the HK-40 alloy tube inside furnace. The hardness increases because of the contribution made by the presence of massive amount of chromium carbide which is hard intermetallic compound or carbon ingress in the matrix.
CHAPTER 5: NATURAL FREQUENCY ANALYSIS (NFA)

5.1 Introduction

Natural elastic wave frequency and mode shapes are functions of the material microstructure and properties, geometry and boundary conditions. Any homogenous alteration of the material microstructure and properties will result in changing the natural frequency but not the mode shapes. On the other hand, any changes in the boundary conditions or shape of the structure will result in changing in natural frequencies and mode shapes [32][33].

The present work experimentally investigates sensitivity of the natural elastic wave frequency of the tube response due to carburization and metal dusting. In addition, simulation using COMSOL was utilized to study the responses due to carburization and metal dusting separately.

5.2 Impulse Testing

The natural elastic wave frequency of the HK-40 alloy tube was excited by dropping a ball bearing of 1/4 inches diameter onto the closed end of the HK-40 alloy tube using a small tube with a height of 12 inch (305 mm) (Figure 5.1). Time domain response of the HK-40 alloy tube was measured using three 100 kHz piezoelectric transducers connected with a specially designed delay that has a concave shape to match the HK-40 alloy tube surface (Figure 5.2). The transducers were placed 6, 12 and 24 inches (152, 305, and 610 mm) from the closed end of the HK-40 alloy tube. The purpose of the transducer located at 6 inch is to provide the trigger signal to an oscilloscope. The other transducers were located at the bottom side and top side of the HK-40 alloy tube to reveal the readings at these locations. An average of three readings was taken on each test to minimize the percentage of error. The time signals were converted to frequency domain using Fast Fourier Transformation (FFT) (Figure 5.3).

Initially, the HK-40 alloy tube was tested to find out its natural frequency in the as cast condition. Then, the tube was heat treated for 48 hours at 850 °C allowing reformation or growth of primary carbides and recrystallization of the grains [34]. The impulse test was repeated at 12 and 24 inches (305 and 610 mm) on both sides (bottom and top) to study the natural frequency
responses to minute change in the microstructure of the tube material. Finally, the impulse test was carried out at different locations on the HK-40 alloy tube after being carburized for 1,000 hr.

Figure 5.1: Impulse testing setup showing the transducers positioning to measure the natural frequency in the as cast, heat treated, and carburized condition of the HK-40 alloy tube. The flange was attached to the floor while a small tube was used on the closed end of the HK-40 alloy tube to drop the ball bearing.

It is recognized that the attachment of the transducers and contact with the floor can alter the natural frequency of the tube. However, the impulse testing will measure relative changes between the untreated (as cast), heat treated, and carburized condition. Therefore, the transducers were attached in the same position in all the three cases.
Figure 5.2: Drawing of the concave delay line to be coupled with the 100 kHz transducer to match the HK-40 alloy outer diameter surface.

Figure 5.3: Example of Fast Fourier Transformation (FFT) from time signals (top) to frequency domain (bottom).
5.2.1 As Cast Condition

The natural frequency of the HK-40 alloy tube was measured in the as cast condition at 12 and 24 inch (305 and 610 mm) from the closed end. The natural frequencies are identical on both measurements (Figure 5.4). The blue lines represent the results measured at 12 inch (305 mm). The red lines represent the results measured at 24 inch (610 mm). Both measurements were on the bottom side of the HK-40 alloy tube. The most dominant and reproducible modes of vibration are the ones with highest peaks. Therefore, anything less than forty was ignored. Hence, the signals in consideration are 2050, 4100, 12401, 13951, 15502, 16752, 17602, 18152 and 18452 kHz.

![Figure 5.4: Natural frequency of the HK-40 alloy tube in the as cast condition measured at 12 and 24 inch (305 and 610 mm) from the closed end.](image)
5.2.2 Heat Treated Condition

After heat treatment for 48 hours at 850 °C, the HK-40 alloy tube was tested again. The results show no difference between the natural frequency of the HK-40 alloy tube readings at 12 and 24 inch (305 and 610 mm) on both sides. Since top and bottom side measurements are identical, reading on bottom side was used to present the comparison (Figure 5.5). It is expected the material underwent minor changes in terms of primary carbide reformation or growth and recrystallization of grains as seen by the small changes on some of the peaks. However, the natural frequency of the tube did not reflect any changes of the heat treatment effect.

![Graph showing natural frequency of HK-40 alloy tube after heat treatment](image)

Figure 5.5: Natural frequency of the HK-40 alloy tube after heat treatment measured at 12 and 24 inch (305 and 610 mm) from the closed end (bottom side).
5.2.3 Comparison of the Natural Frequency between the As Cast and Heat Treated Condition

A comparison between the natural frequency of the HK-40 alloy tube in the as cast and heat treated condition were analyzed (Figure 5.6). Since there is no difference observed earlier between the 12 and the 24 inch (305 and 610 mm) locations or measurements between the top and bottom side of the HK-40 alloy tube, a single comparison between the same locations is sufficient.

The strongest signals of the natural frequency are almost identical. There is a slight variation in frequency of the very low peaks which could be related to coupling condition between the transducer and the surface of the tube. The frequencies of interest remain the same.

Figure 5.6: Natural frequency of the HK-40 alloy tube as cast compared to heat treated measured at 12 inch (305 mm) from the closed end (bottom side).
5.2.4 Natural Frequency of the HK-40 alloy tube (Carburized Condition)

The following Sections examine the change of the natural frequency between the top and bottom side of the carburized HK-40 alloy tube at 12 and 24 inches.

5.2.4.1 Readings at 12 inch (305 mm) (Bottom Compared to Top)

This Section is comparing the readings between the top and bottom side of the HK-40 alloy tube at 12 inch (305 mm) from the closed end. There are two mode shape changes between the two, 10380 and 15250 kHz. On the other hand, the shift in the in the natural frequencies is very minimal. This small shift indicates that there may be a slight change in the material microstructure and properties between the top side and the bottom side of the HK-40 alloy tube at 12 inch (305 mm) but they are not significant (Figure 5.7).

![Figure 5.7: Natural frequency of the HK-40 alloy tube after carburization test measured at 12 inch (305 mm) from the closed end (top and bottom side).](image-url)
5.2.4.2 Readings at 24 inch (610 mm) (Bottom Compared to Top)

This Section is comparing the readings between the top and bottom side of the HK-40 alloy tube at 24 inch (610 mm) from the closed end. There is a significant difference between the natural frequencies readings between the two sides. Figure 5.8 shows multiple mode changes. These natural frequencies are 4030, 5900, 7730, 9300, 11180, 16480, 17350 and 17880 kHz. These variations in readings confirm that there are structural change between the top side and the bottom side at 24 inch (610 mm).

![Figure 5.8: Natural frequency of the HK-40 alloy tube after carburization test measured at 24 inch (610 mm) from the closed end (bottom and top side).](image)

Figure 5.8: Natural frequency of the HK-40 alloy tube after carburization test measured at 24 inch (610 mm) from the closed end (bottom and top side).
5.2.5  Comparison of the Natural Frequency between As Cast and Carburized Condition:

The following Sections examine the change of the natural frequency between the carburized and as cast condition on top and bottom side of the HK-40 alloy tube measured at 12 and 24 inches.

5.2.5.1  Readings at 12 inch (305 mm) (bottom side)

A comparison between the natural elastic wave frequency of the tube in the as cast and carburized condition measured at 12 inch (305 mm) at the bottom side of the tube were analyzed (Figure 5.9). There is a significant variation between the two readings.

Obviously, the first two readings of the natural frequency of the HK-40 tube in the as cast condition were diminished, namely, 2050 and 4100, in addition to 15502 kHz. This situation indicates that there is some mode shape changes related to structural changes on the tube.

There is a slight shift on some of the natural frequency of the as carburized condition. This observation indicates that speed of sound (C) of the tube in the carburized condition is lowered. The primary reasoning is that the ratio of the elastic moduli (E) over the density (ρ) is lowered according to the following:

\[ C = \frac{\sqrt{E}}{\sqrt[3]{\rho}} \] (5.1)

This observation could be due to a decrease in the tube elastic moduli, or an increase in the tube density or a combination with a predominant effect of the density change leading to a lower value of the ratio. The density change is consistent with carburization products. The observation is summarized in the following Table.

Table 5.1: Change in percentage of the natural frequency of the HK-40 alloy tube between the as cast and carburized condition.

<table>
<thead>
<tr>
<th>As cast</th>
<th>Carburized</th>
<th>Condition</th>
<th>% of change</th>
<th>Average of change</th>
</tr>
</thead>
<tbody>
<tr>
<td>12401</td>
<td>12180</td>
<td>Lowered</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>13951</td>
<td>13650</td>
<td>Lowered</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>16752</td>
<td>16350</td>
<td>Lowered</td>
<td>2.40</td>
<td>2.11 %</td>
</tr>
</tbody>
</table>
Figure 5.9: Natural frequency of the HK-40 alloy tube as cast compared to after carburization measured at 12 inch (305 mm) from the closed end (bottom side).

5.2.5.2 Readings at 24 inch (610 mm) (bottom side)

A comparison between the natural frequencies of the tube in the as cast and carburized condition measured at 24 inch (610 mm) at the bottom side of the HK-40 alloy tube were analyzed (Figure 5.10). There is a significant variation between the two readings.

In addition to the diminished natural frequencies of the 12 inch (305 mm) readings discussed on the previous Section, (i.e., 2050, 4100 and 15502 kHz), one more natural frequency disappeared which is 16752 kHz. On the other hand, some natural frequencies peaks rose up which are: 5900, 9300 and 11180 kHz. This observation indicates that there is in an additional mode shape change that took place at the 24 inch (610 mm) compared to the 12 inch (305 mm).

Frequencies 12404 and 13951 but not 16752 kHz shifted again. However, the percentage of change is not the same as the one for the 12 inch (305 mm). This shift is an indication that the material microstructure and properties are not consistently changing over the whole length of the tube. Table 5.2 summarizes the percentage change of the natural frequency shift.
Figure 5.10: Natural frequency of the HK-40 alloy tube as cast compared to after carburization test measured at 24 inch (610 mm) from the closed end (bottom side).

Table 5.2: Change in percentage of the natural frequency of the HK-40 alloy tube between as cast and carburized condition.

<table>
<thead>
<tr>
<th>As cast</th>
<th>Carburized</th>
<th>Condition</th>
<th>% of the change</th>
</tr>
</thead>
<tbody>
<tr>
<td>12401</td>
<td>12250</td>
<td>Lowered</td>
<td>1.22</td>
</tr>
<tr>
<td>13951</td>
<td>13776</td>
<td>Lowered</td>
<td>1.25</td>
</tr>
</tbody>
</table>
5.3 COMSOL Simulation

As a supplemental analysis to the previous laboratory test, the multi physics simulation program COMSOL was utilized to simulate carburization and metal dusting separately studying changes to natural frequency. The model was an axisymmetric 2-D (Figure 5.11). The simulation is much simpler compared to the analysis conducted in the following Section. There is no meshing required. It only requires the material properties, boundary conditions and shape of the tube to perform the analysis.

![Image of simulation](image-url)

Figure 5.11: Simple axisymmetric two dimensional analysis (2-D) of the HK-40 alloy tube using COMSOL simulation.

5.3.1 Natural Frequencies of the HK-40 Alloy Tube with no Defect

Figure 5.12 shows the predicted natural frequency of the HK-40 alloy tube. At first look, it is almost similar to natural frequencies measured on the previous section. However, there are some differences as the test previous test conducted has some human errors. The present analysis does not take in consideration the weld on the end cap of the tube, any variation of material properties due to manufacturing, the presence of the transducers, and the contact with the floor. Moreover, the following simulations represent a small carburization and metal dusting defect. Hence, the simulation is not in cast comparison with previous analysis. It is just a supplemental analysis to help interpret the impulse test conducted earlier.
Figure 5.12: Natural frequency of the HK-40 alloy tube with no defect using COMSOL software with two dimensional axisymmetric model.
5.3.2 Metal Dusting (Pitting) Defect

A small pitting defect located at 12 inch (305 mm) from the closed side of the HK-40 alloy tube was included in the model. Figure 5.13 shows the natural frequency of the HK-40 alloy tube with pitting.

Comparing the two readings, the following natural frequency appeared on the readings with pitting: 6303, 11721, 15734 and 17243 kHz. Natural frequency at 13620 and 15987 kHz disappeared from the original reading (Figure 5.12). These changes in natural frequency indicate there are some mode changes due to structural change. No shift on natural frequency was observed.

Figure 5.13: Natural frequency of the HK-40 alloy tube with pitting located at 12 inch (305 mm) from the closed end using COMSOL software with two dimensional axisymmetric model.

5.3.3 Carburization Defect

A small carburization defect located at 24 inch (610 mm) from the end side of the HK-40 alloy tube was included in the model. Figure 5.14 shows the natural frequencies of the HK-40 alloy tube with carburization.
Comparing the two readings, the following natural frequencies appeared on the readings with carburization: 6313, 8592, 11733, 15992 and 17282 and 17673 kHz. Natural frequency 13620 was disappeared from the original reading (Figure 5.12).

Two of the natural frequencies were shifted to the left side. These shifts are 15209 became 14942 and 16688 became 16566 kHz. The shift indicates that whole tube speed of sound is reduced compared to the no defect condition.

![Graph showing natural frequencies](image)

Figure 5.14: Natural frequencies of the HK-40 alloy tube with carburization located at 24 inch (610 mm) from the end of the tube using COMSOL software with two dimensional axisymmetric model.

5.4 Result and Discussion

The natural frequencies test was very helpful in detecting material microstructure and properties changes or structural changes in the tube. Both the experiment and the model indicate that changes due presumably to carburization and metal dusting can be detected by monitoring changes in the natural frequency of the tube.

However, the natural frequency analysis above does not quantify the amount of changes. It is not sensitive to recrystallization or carbide reformation due to heat treatment. It predicted the variation of the material properties between the top side (where carburization were extensive)
and the bottom side (no carburization) measured at 24 inch (610 mm). It also shows a variation between the top side (where metal dusting took place) and the bottom (no metal dusting) as shown in the metallographic examination Section.

It could be used as useful tool to express if there is a significant changes taking place on the tube or not in terms of structural changes or material properties change. Unfortunately, it will neither tell the location nor the amount of changes.
CHAPTER 6: RESONANT ULTRASOUND SPECTROSCOPY (RUS)

6.1 Introduction

Resonant ultrasound spectroscopy is a laboratory testing method to infer fundamental material properties such as elastic moduli. The natural frequencies depend on the object density, dimensions and elastic moduli. The real power of resonant ultrasound spectroscopy is the ability to work backward and determine the these parameters from the analysis of the resonance frequencies of the samples in consideration[35] [36].

NACE standard TM0498-2006, suggested two methods for measuring carburization extent, namely, combustion analysis measurement method and chemical etching measurement method. Mass gain, which is an old testing method, was not recommended as it is measuring the total carbon increase but not considering the depth of penetration or gradient [31]. However, it was an interest to investigate how the resonant ultrasound spectroscopy test would response to the carburization with the mass gain since no research work has been conducted for this purpose using resonant ultrasound spectroscopy. This test is considered as supplemental analysis in support to the HK-40 alloy carburization test.

6.2 Test Setup and Procedure

As discussed earlier in Chapter 3, nine samples were cut from an as cast extra material of HK-40 alloy provided by the manufacturer into three groups labeled 1, 2 and 3. Each group consists of three samples with different dimensions consistent on each group. Weight and dimensions of each sample were measured three times to reduce human readings errors. The average density and dimensions were summarized in Table 6.1.

The three samples of group 1, namely 1A, 1B and 1C, were contained in a high alumina oxide (99.8 percent) combustion boat and connected with a thermocouple (Heavy duty type K, Inconel sheath from OMEGA Corporation) for temperature measurement. Similarly, the three samples of group 2 (i.e. 2A, 2B and 2C) and group C (i.e. 3A, 3B and 3C) were contained in two combustion boats as shown in Figure 3.8. Each combustion boat was located at different location inside the furnace tube to be exposed to different temperature. Figures 6.1 and 6.2 show the
sample positioning between two transducers connected to oscilloscope, signal generator and lock in amplifier.

Table 6.1: Summary of average weight and dimension of each sample.

<table>
<thead>
<tr>
<th>Sample Tag</th>
<th>Average Dimension (cm)</th>
<th>Average Density mg/cm^3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L</td>
<td>W</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
<td>1.5020</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.5052</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.5055</td>
</tr>
<tr>
<td></td>
<td>Std Div</td>
<td>0.0019</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>1.5043</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.5039</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.5015</td>
</tr>
<tr>
<td></td>
<td>Std Div</td>
<td>0.0015</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>1.7497</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.7460</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.7610</td>
</tr>
<tr>
<td></td>
<td>Std Div</td>
<td>0.007799</td>
</tr>
</tbody>
</table>

Figure 6.1: Sample positioning for resonant ultrasound spectroscopy and test setup [37].
Figure 6.2: Photo of the oscilloscope, function generator and lock-in amplifier used in the resonant ultrasound spectroscopy test.

Due to the limited size of the extra material provided by the manufacture, the samples were cut from different locations to optimize cutting nine samples. Some samples were cut from an area close to the inner diameter where the grains are equiaxed in shape. Some samples were cut from an area close to the outer diameter of the grains are columnar in shape with different orientation. Other samples consist of mixed grain shape.

6.3 Results and Discussion

Resonant ultrasound spectroscopy test was performed on each sample before and after carburization three times to reduce human errors. The frequency results then transferred to shear modulus and young modulus of the material using Python programming.

Tables 6.2, 6.3, and 6.4 listed the changes for the dimension, weight and density measurements before and after the carburization test.
Table 6.2: Dimensional comparison of each sample before and after the carburization test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length Before</th>
<th>Length After</th>
<th>% increase</th>
<th>Width Before</th>
<th>Width After</th>
<th>% increase</th>
<th>Depth Before</th>
<th>Depth After</th>
<th>% increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>1.501966</td>
<td>1.50876</td>
<td>0.45</td>
<td>1.252157</td>
<td>1.25349</td>
<td>0.11</td>
<td>0.753491</td>
<td>0.762</td>
<td>1.13</td>
</tr>
<tr>
<td>1B</td>
<td>1.505204</td>
<td>1.51638</td>
<td>0.74</td>
<td>1.254443</td>
<td>1.25476</td>
<td>0.03</td>
<td>0.752856</td>
<td>0.75946</td>
<td>0.88</td>
</tr>
<tr>
<td>1C</td>
<td>1.495425</td>
<td>1.51384</td>
<td>1.23</td>
<td>1.251331</td>
<td>1.27381</td>
<td>1.80</td>
<td>0.751078</td>
<td>0.76454</td>
<td>1.79</td>
</tr>
<tr>
<td>2A</td>
<td>1.504315</td>
<td>1.51003</td>
<td>0.38</td>
<td>1.254697</td>
<td>1.26111</td>
<td>0.51</td>
<td>1.00184</td>
<td>1.01092</td>
<td>0.91</td>
</tr>
<tr>
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<td>1.17</td>
<td>1.250315</td>
<td>1.26238</td>
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<td>1.003237</td>
<td>1.00965</td>
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</tr>
<tr>
<td>2C</td>
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<td>1.51638</td>
<td>0.99</td>
<td>1.256983</td>
<td>1.27419</td>
<td>1.04</td>
<td>1.001014</td>
<td>1.02235</td>
<td>2.13</td>
</tr>
<tr>
<td>3A</td>
<td>1.749743</td>
<td>1.75768</td>
<td>0.45</td>
<td>1.504061</td>
<td>1.51003</td>
<td>0.40</td>
<td>1.256284</td>
<td>1.26365</td>
<td>0.59</td>
</tr>
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<td>1.7653</td>
<td>1.11</td>
<td>1.50114</td>
<td>1.51892</td>
<td>1.18</td>
<td>1.2533</td>
<td>1.26873</td>
<td>1.23</td>
</tr>
<tr>
<td>3C</td>
<td>1.760982</td>
<td>1.77419</td>
<td>0.75</td>
<td>1.504252</td>
<td>1.51765</td>
<td>0.89</td>
<td>1.247966</td>
<td>1.27254</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Table 6.3: Weight comparison of each sample before and after the carburization test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (avg), mg</th>
<th>Gain %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carburization</td>
<td></td>
</tr>
<tr>
<td>1A</td>
<td>Before 10898.3</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>After 10927</td>
<td></td>
</tr>
<tr>
<td>1B</td>
<td>Before 10974.7</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>After 10984.6</td>
<td></td>
</tr>
<tr>
<td>1C</td>
<td>Before 10907.9</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>After 10946.9</td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td>Before 14628.1</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>After 14656.6</td>
<td></td>
</tr>
<tr>
<td>2B</td>
<td>Before 14611.9</td>
<td>0.21</td>
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<tr>
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<td>After 14642.5</td>
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</tr>
<tr>
<td>2C</td>
<td>Before 14646.7</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>After 14687.8</td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>Before 25622.2</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>After 25673.8</td>
<td></td>
</tr>
<tr>
<td>3B</td>
<td>Before 25488.6</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>After 25553.5</td>
<td></td>
</tr>
<tr>
<td>3C</td>
<td>Before 25600</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>After 25648</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.4: Density comparison of each sample before and after the carburization test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>1A</td>
<td>7690.634</td>
<td>7582.369</td>
</tr>
<tr>
<td>1B</td>
<td>7720.308</td>
<td>7601.698</td>
</tr>
<tr>
<td>1C</td>
<td>7761.028</td>
<td>7425.191</td>
</tr>
<tr>
<td>2A</td>
<td>7735.899</td>
<td>7613.404</td>
</tr>
<tr>
<td>2B</td>
<td>7745.902</td>
<td>7550.796</td>
</tr>
<tr>
<td>2C</td>
<td>7752.424</td>
<td>7460.129</td>
</tr>
<tr>
<td>3A</td>
<td>7749.758</td>
<td>7654.883</td>
</tr>
<tr>
<td>3B</td>
<td>7759.359</td>
<td>7511.509</td>
</tr>
<tr>
<td>3C</td>
<td>7743.926</td>
<td>7485.329</td>
</tr>
</tbody>
</table>

Figures 6.3, 6.4, and 6.5 show the variation in density, volume and weight, respectively. The red bars represent the original shear and Young’s modules of the samples in the as cast condition. The blue bars represent the samples of group A measured at different temperature 810 °C. The blue bars represent the samples of group B measured at different temperature 860 °C. The yellow bars represent the samples of group C measured at different temperature 890 °C. There is no consistency observed between any of the three parameters under consideration with temperature.

Figure 6.6, Figure 6.7 and Table 6.5 show the result of the analysis for the Shear modulus (C44) and Young’s modulus (C11). The red bars represent the original shear and Young’s modules of the samples as cast. Unfortunately, there is no solid relation between the temperature changing on one side and shear modulus and young modulus from the other side.
Figure 6.3: Percentage of density reduction for each sample after the carburization test.

Figure 6.4: Percentage of volume increase for each sample after the carburization test.
Figure 6.5: Percentage of weight increase for each sample after the carburization test.
Figure 6.6: Shear modulus of tested samples. The red bar represents the as cast condition measurements. The blue bars represent samples tested at 810 °C. The green bars represent samples tested at 860 °C. The yellow bars represent samples tested at 890 °C.

Figure 6.7: Young’s modulus of tested samples. The red bar represents the as cast condition measurements. The blue bars represent samples tested at 810 °C. The green bars represent samples tested at 860 °C. The yellow bars represent samples tested at 890 °C.
Table 6.5: Percentage of change of C11 and C44 measured as cast and after carburization test.

<table>
<thead>
<tr>
<th>Sample tag</th>
<th>% change of C11</th>
<th>% change of C44</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>-17.67</td>
<td>12.28</td>
</tr>
<tr>
<td>1B</td>
<td>-0.42</td>
<td>5.31</td>
</tr>
<tr>
<td>1C</td>
<td>7.31</td>
<td>9.60</td>
</tr>
<tr>
<td>2A</td>
<td>6.66</td>
<td>7.55</td>
</tr>
<tr>
<td>2B</td>
<td>9.08</td>
<td>5.99</td>
</tr>
<tr>
<td>2C</td>
<td>5.21</td>
<td>9.28</td>
</tr>
<tr>
<td>3A</td>
<td>4.12</td>
<td>8.71</td>
</tr>
<tr>
<td>3B</td>
<td>7.39</td>
<td>8.85</td>
</tr>
<tr>
<td>3C</td>
<td>13.22</td>
<td>7.24</td>
</tr>
<tr>
<td>Average</td>
<td>7.57</td>
<td>8.17</td>
</tr>
</tbody>
</table>

The results yield a high dependency of crystallographic structure, orientation and size of grains. No direct relation could be achieved between carbon pick up percentage and temperature. However, it could be observed very clearly that there was an increase in volume, weight and reduction of density. In addition, carbon uptakes decreased the compressional and shear strength. These observations reflect the complexity of carburization mechanism in a matter of initiation and propagation.
CHAPTER 7:  FINITE ELEMENT ANALYSIS (FEA)

7.1 Introduction

Guided wave testing has received a great deal of attention among nondestructive testing tools because of their capability of traveling long distance with minimal substantial attenuation compared to other wave forms [38]. Guided waves have several modes of propagation generating a specific amount of energy (specific modes) which strangely depends on certain factors such as: source transducer system, excited frequency and frequency bandwidth [39].

A two dimensional (2-D) COMSOL based finite element analysis model has been developed to investigate ultrasonic methods to detect and evaluate different stages of high temperature corrosion. Two mechanisms were considered in the simulation: 1) Carburization: where the indications are limited to much more subtle changes in material lattice conditions and 2) Metal dusting: where disintegration of metal surface causing metal loss in the form of pitting. These subtle defects do not include any cracking or pitting but, rather, are characterized by a relatively slight change in material density and elasticity. Theoretical mathematical expressions and results from the simulation were compared in terms of accuracy to reveal the base line approach for real testing development [40].

7.2 Modeling and Boundary Conditions

A simple axisymmetric 2-D model was used to represent a rectangular cross section of the tube and the carburized section. For the purpose of these simulations, it is assumed that the excitation and response is circumferentially symmetric. The length of the rectangle, which represents a longitudinal cross section of the tube, is 39.37 feet (i.e.12 meters) with a thickness of 0.25 in (i.e. 0.00635 m). These dimensions were chosen because they are similar to tubes used for pyrolysis furnace. The desire to simplify the simulation to 2-D instead of 3-D is driven by the file size and solving time. Each 2-D simulation’s file is about 50 GB and requires about five hours to run in a 3.8 GHz processor desktop.

The numerically simulated testing scheme uses a pulse-echo arrangement from a single location on the tube using waves which are guided along the tube wall length. The waves are excited and received using a ring transducer made up of elements distributed around the
circumference. By exciting all of the elements equally and concurrently, an axially symmetric mode is launched. The presence and axial location of defects in the tube wall are determined by any reflections and their arrival times [41].

Two different sizes of both carburization defect and pitting, due to metal dusting, were used in the simulations, namely 75 percent and 25 percent of the tube thickness with a half circle shape. The defect (carburization or pitting) is located 1.5 m to the right side from the center of the rectangle (i.e. cross section of the tube while the measuring point is at one meter from both sides. Both ends of the rectangle were fixed in x and y direction representing welds.

The purpose of having a defect at the right side and non on the left side is to compare the free passing wave on the left side with the reflection from defect on the right side (Figure 7.1).

![Figure 7.1: Schematic of the boundary conditions, transducer location, defect located at 1.5 meter right side from transducer and measuring point at one meter from transducer on both sides.](image)

Several preliminary simulations were performed to choose the appropriate wave function and frequency. The frequency has been chosen by sweeping the simulation from 50 to 500 kHz with an increment of 50 kHz. It was noticed that that the 500 kHz generated a surface waves on both sides of the tube (ID and OD). The excited wave W(t) has been chosen to be a Gaussian function with wave amplitude of 100 Pa excited over a small region at the center of the grid. Excitation with a 100 kHz Gaussian tone burst (Figure 7.2) was found to be non-dispersive and maintain waveform shape over long distances when no defects are present and has a delay time of 25x10^{-6} seconds [7].

\[
W(t) = 100 * e^{-f^2 * (t - (2.5/f))^2} * \cos(\omega * (t - 2.5/f))
\]  

(7.1)
In these simulations, the number of meshing elements is a function of the frequency and the speed of sound of the material for accurate results (see COMSOL documentation). Time dependent wave analysis requires very small size elements to achieve satisfactory convergence. The element size is a function of shear wave speed ($C_S$), frequency ($f$) and number of mesh elements per wave length ($N$), which was suggested to be 8 as an optimum fit number for solution convergence (COMSOL documentation):

$$\text{Maximum element size} = \frac{C_S}{2 \times N \times f}.$$  \hspace{1cm} (7.2)

Figure 7.2: 100 kHz Gaussian tone burst excited at the center of the tube $x = 0$.

The proposed function is a multiplication of a cosine wave, green color, by exponential wave, blue color (Figure 7.3).  

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Figure 7.3: Formation of Gaussian wave (red) by multiplying a cosine wave (green) with an exponential wave (blue).
7.3 HK-40 Alloy Speed of Sound

The speed of sound of the material depends mainly on the following properties; density of the material ($\rho$), Poisson’s ratio ($\nu$) and Modulus of Elasticity ($E$) (a.k.a Young’s Modulus) [42]. For HK-40 alloy these values are: $E = 186.16$ GPa, $\rho = 8,027.2$ kg/m$^3$, and $\nu = 0.3$.

The shear wave speed of sound ($C_S$) [43]:

$$C_S = \sqrt{\frac{G}{\rho}} \quad (7.3)$$

The shear modulus of elasticity ($G$) is a function of the Young’s Modulus and Poisson’s ratio [43]:

$$G = \frac{E}{2 \ast (1 + \nu)} \quad (7.4)$$

Substituting Equation (7.4) into Equation (7.3) yield to:

$$C_S = \sqrt{\frac{E}{2 \ast \rho \ast (1 + \nu)}} \approx 2,987 \frac{m}{s} \quad (7.5)$$

In addition to material properties, the longitudinal guided wave speed is characterized by the shape of the material propagating through (i.e, bulk, thick and thin beam/plate). The thin plate theory implies that the longitudinal wave length ($\lambda_L$) should be at least six times greater than the plate thickness ($t$)[44].

$$\lambda_L > 6 \ast t \quad (7.6)$$

The wave length is simply the speed of sound divided by the frequency

$$\lambda_L = \frac{C_L}{f} \quad (7.7)$$

While the longitudinal speed of sound for thin plate ($C_L$)[42] is:

$$C_L (\text{thin plate}) = \sqrt{\frac{E}{\rho(1 - \nu^2)}} \approx 5,048 \frac{m}{s} \quad (7.8)$$
Rearranging equations (7.6) and (7.7) reveal that the plate theory can be accurately applied when:

$$ t < \frac{C_L}{6 \cdot f} = \frac{5.048}{600,000} = 0.00841 \text{ m}. \quad (7.9) $$

### 7.4 Reflection from weld

As a starting point, it is desirable to simulate known conditions where reflected waves do not experience any mode conversion. Hence, a weld located 1.5 meter from the cylindrically symmetric transducer excitation was simulated (Figure 7.4) to investigate the reflection from incident wave and calculate its speed of sound at one meter from the transducer (Figure 7.5).

The following equation was used to calculate the speed of sound of the incident and the reflected waves

$$ C = \frac{\text{Wave traveled distance}}{\text{Time reading} - \text{Time delay}} \quad (7.10) $$

![Figure 7.4: Weld located at 1.5 meter from transducer (Right side).](image)

Based on (Figure 7.5), the first arrival of the incident thin plate longitudinal speed of sound of $C_L = \frac{1}{(22.83-2.5)x10^{-5}} = 4.919 \text{ m/s}$ while the first arrival of the incident shear speed of sound of $C_S = \frac{1}{(37.167-2.5)x10^{-5}} = 2.885 \text{ m/s}$.

The percentage of error of the calculated speed of sound (7.5) and (7.8) compared to the results from the simulation are very small. The percentage of err of $(C_S) = \frac{2.987-2.885}{2.987} \times 100 = 3.4 \text{ percent}$ while the percentage of error of $(C_L) = \frac{5.048-4.919}{5.048} \times 100 = 2.6 \text{ percent}.$
Figure 7.5: Travel time of incident and reflected waves from the weld.
In the case of reflection from weld, the wave travel distance is two meter minus two times half thickness of the weld (i.e. 0.00476*2). The thin plate longitudinal speed of sound reflection \( C_{L,R1} = \frac{2 - 0.00476^2}{(4.3 - 2.5) \times 10^{-5}} \approx 4.919 \text{ m/s} \) while the shear speed of sound reflection \( C_{S,R1} = \frac{2 - 0.00476^2}{(71.5 - 2.5) \times 10^{-5}} = 2.885 \text{ m/s} \).

The blue line which represents the left side of the tube with no weld shows the incident wave only. On the other hand, the green line which represents the right side with a weld at 1.5 meter shows some reflections from the weld.

Both incident and reflection waves were matching in speed, no mode conversions were observed and there is slight reduction in the peaks (i.e. signal strength).

### 7.5 Metal Dusting Simulation

This Section focuses on wave reflections due to shape changing in the form of pitting. Two different scenarios were considered: 25 percent and 75 percent depth of the pitting relative of the thickness of the tube.

#### 7.5.1 Depth of Pitting (25 Percent Relative to Tube Thickness)

A schematic drawing of the pitting morphology illustrated in Figure 7.6. The pitting depth is 25 percent in radius relative to the tube thickness. Figure 7.7 shows the incident wave and the reflected wave from the pitting.

![Figure 7.6: Schematic drawing of boundary conditions and defect location.](image-url)
Figure 7.7: Comparison of wave reflection measured at one meter from excitation, with a pitting defect (green) and without a pitting defect (blue) [40].
A higher magnification of the reflected wave is illustrated in (Figure 7.8). The peaks are weak compared to the peaks reflections from the bigger pitting (Figure 7.10) discussed in the previous section. However, they are still recognizable in terms of shape. The amplitude of \( C_{S,R2} \) was about five Pa while the amplitude of \( C_{S,R1} \) was about five Pa.

![Figure 7.8: Higher magnification of the reflected wave.](image)

### 7.5.2 Depth of Pitting (75 Percent Relative to Tube Thickness)

A schematic drawing of the pitting morphology is illustrated in Figure 7.9. The pitting depth is 75 percent in radius relative to the tube thickness. Figure 7.10 shows the incident wave and the reflected wave from the pitting.

It is noticed that there are new wave reflections appeared, namely \( C_{L,R2} \) and \( C_{S,R2} \) from the pitting model (Figure 7.10) compared to reflections from the weld model (Figure 7.5). The only explanation of the appearance of these new waves is that they are higher mode conversion due to the concaved shape of the pitting. Another confirmation is that the speed of sound of these two new reflections did not match with either of the excited wave speed of sound. From now on, \( C_L \) with its reflection will be ignored as their signal strength are very week compared to \( C_S \).
Figure 7.9: Schematic drawing of boundary conditions and defect location.

Figure 7.10: Comparison of wave reflection measured at one meter from excitation, with a pitting defect (green) and without a pitting defect (blue).
Figure 7.11 is a higher magnification of the reflected waves for further comparison in terms of shape and amplitude with the following Sections. The amplitude of \( C_{S,R1} \) was about 35 Pa while the amplitude of \( C_{S,R2} \) was about five Pa.

![Graph showing reflected waves](image)

**Figure 7.11:** Higher magnification of the reflected wave.

### 7.6 Carburization Simulation

This Section focuses on wave reflections due to elastic material properties changing due to carbon ingress within the material matrix. Two different scenarios were considered: 75 percent and 25 percent depth of the carburized zone relative of the thickness of the tube. One each situation, 5 percent and 15 percent increase in density will be investigated. The power of guided wave testing in this case in that wave will be reflected due to facing different materials properties, regardless if the density is increasing or decreasing (i.e. two boundary condition problem).

Even though the resonant ultrasound spectroscopy analysis discussed in earlier Section did not reveal a direct relation between the carbon absorption percentage and the different...
carburization temperature, it gave a baseline to assume the density for an early stage of carburization.

### 7.6.1 Depth of Carburization (25 Percent Relative to Tube Thickness)

A schematic drawing of the pitting morphology illustrated in Figure 7.12. The carburization depth is 25 percent in radius relative to the tube thickness. This schematic arrangement represents an early stage of carburization where the destiny is increased with 5 percent due to carbon ingress in the localized area.

![Schematic drawing of the pitting morphology](image)

Figure 7.12: Schematic drawing of boundary conditions and defect location.

#### 7.6.1.1 Change in Density (5 Percent Less Compared to HK-40 Alloy)

This Section represent the worst case scenario were the density decrease and the carburized zone is minimal. Figure 7.13 shows the incident wave and the reflected wave from the carburization defect and Figure 7.14 is a higher magnification of the reflected waves. The amplitude reading of $C_{S,R1}$ was about 2 Pa while the amplitude of $C_{S,R2}$ was about 1 Pa.

#### 7.6.1.2 Change in Density (15 Percent Less Compared to HK-40 Alloy)

In this Section, the reflected wave is from a carburization defect with a density 15 percent less than the tube base metal (Figure 7.15 and Figure 7.23). The amplitude reading of $C_{S,R1}$ was about three Pa while the amplitude of $C_{S,R2}$ was about one Pa.
Figure 7.13: Comparison of wave reflection measured at one meter from excitation, with a carburization defect (green) and without a carburization defect (blue).
Figure 7.14: Higher magnification of the reflected wave.
Figure 7.15: Comparison of wave reflection measured at one meter from excitation, with a carburization defect (green) and without a carburization defect (blue).
7.6.2 Depth of Carburization (75 Percent Relative to Tube Thickness)

A schematic drawing of the pitting morphology illustrated in Figure 7.17. The carburization depth is 75 percent in radius relative to the tube thickness. The carburized zone is less in density compared to the base metal of the tube due to carbon ingress in the localized area. Carbide formation cause an increase in the volume and hence a decrease in the density. An early stage of carburization where the density is assumed to be five percent less than the base metal and an advanced stage where the density is assumed to be 15 percent less than the tube base metal.

Figure 7.17: Schematic drawing of boundary conditions and defect location.
7.6.2.1 Change in Density (5 Percent Less Compared to HK-40 Alloy)

Figure 7.18 shows the incident wave and the reflected waves from the carburized zone. It is noticed that the reflection of the longitudinal waves are diminishing with localized material properties changing (i.e. carburization) compared to shape changing discussed in the previous Section. Figure 7.19, a higher magnification of the reflected waves, shows the amplitude and shape of $C_{S,R2}$ and $C_{S,R1}$.

![Wave Reflection Graph](image)

Figure 7.18: Comparison of wave reflection measured at one meter from excitation, with a carburization defect (green) and without a carburization defect (blue).

7.6.2.2 Change in Density (15 percent Less Compared to HK-40 Alloy cent)

In this Section, the density of the carburized zone was decreased to 15 percent to study the reflection amplitude strength compared with the five percent. Figure 7.20 shows the incident wave and the reflected waves from the carburized zone. Figure 7.21 is a higher magnification of the reflected wave. The amplitude reading of $C_{S,R1}$ was about 15 Pa while the amplitude of $C_{S,R2}$ was about two Pa.
Figure 7.19: Higher magnification of the reflected wave.
Figure 7.20: Comparison of wave reflection measured at one meter from excitation, with a carburization defect (green) and without a carburization defect (blue).
Figure 7.21: Higher magnification of the reflected wave.
7.7 Phased Array Transducers

This Section of the study investigates the use of multiple transducers (in a row with a wavelength a part from each other) to amplify the desired wave mode and its reflection to overcome the weak amplitude of the reflected wave (phased array). The worse-case scenario for measurement (early stage of carburization), which was a 25 percent depth of carburization compared to the tube thickness with five percent decrease in density, was remodeled using two and three transducers. A schematic drawing of the carburization morphology with two transducers is illustrated in Figure 7.22.

![Figure 7.22: Two transducers (a wavelength distance between them).](image)

Figures 7.23 and 7.24 show a higher magnification of the reflected waves shape and amplitude using two and three transducers, respectively, to be compared with Figure 7.14. Applying two transducers, the amplitude reading of \(C_{S,R1} \) was about four Pa while the amplitude of \(C_{S,R2} \) was about two Pa. Applying three transducers, the amplitude reading of \(C_{S,R1} \) was about six Pa while the amplitude of \(C_{S,R2} \) was about three Pa.

7.8 Results and Discussion

Issues of importance were the selection of the optimum guided wave modes and the establishment of relationships between the defect shape, size and the strength of wave reflection. The proper wave shape (function) and frequency was chosen based on multiple trials.

Initially, the analysis was performed considering a weld (rectangular shape) instead of a defect (concaved shape) at the same location to examine the type of wave reflection. The analysis showed that higher order mode reflection \(C_{S,R2} \) was due to the concaved shape of the defect. In the metal dusting case, \(C_{S,R2} \) has a constant amplitude of 5 Pa regardless of changing
the depth of the pitting. It could be explained that it is considered as a one boundary condition since the pitting has no material properties. On the other hand, \(C_{S,R2}\) was somehow related to the depth of carburization zone and its density. Its amplitude was varying on either changing the concaved shape depth or its density. This situation could be considered as a two boundary conditions.

The higher order mode reflection \(C_{S,R2}\) is due to concave shape of the defect. Its amplitude of five did not change with altering the size of the pitting from 25 percent to 75 percent (Figure 7.11 and Figure 7.8). This observation is a strong indication that this conversion is due to the angle concaved shape of the pitting regardless of its size.

The shear wave reflection has a great advantage over the longitudinal wave reflection in terms of amplitude strength. In detecting metal dusting (pitting), the amplitude of the reflected wave \(C_{S,R1}\) was very strong with high pitting depth to thickness ratio. It was measured at about 35 Pa compared to the excited wave amplitude of 60 Pa which is almost 60 percent. On the other hand, it dramatically weakened when reaching a 25 percent depth to thickness ratio. The reading was five Pa compared to the 60 Pa of the excited wave which is about 8 percent of the exited wave amplitude. On the carburization analysis, the amplitude of \(C_{S,R1}\) increase as the depth to thickness ratio increase. Similarly, the amplitude of \(C_{S,R1}\) increases as the density of the carburized zone decrease. However, the amplitude percentage of \(C_{S,R1}\) to the excited wave is very low ranging between 3 to 25 percent.

To overcome the very low amplitude of the reflected wave, the use of phase array was examined. The phase array is a technique used to amplify the desired shear wave mode while reducing competing wave modes (the longitudinal modes). Two and three transducers showed that it is doubling and tripling, respectively, the amplitude of reflected wave \(C_{S,R1}\). The reflection using two transducers doubled the amplitude of the \(C_{S,R1}\) from 2 to 4 Pa (Figure 7.14 and Figure 7.23), respectively. The three transducers tripled the amplitude reflection from 2 to 6 Pa (Figure 7.14 and Figure 7.24), respectively.
Figure 7.23: Higher magnification of wave reflections based on two transducers.

Figure 7.24: Higher magnification of wave reflections based on three transducers (a wave length distance between them).
CHAPTER 8: SUMMARY OF RESULTS AND DISCUSSION

The metallographic examination showed that not only can the degree of carburization vary dramatically around the circumference of tubes but also over very short distances along the length of the tube. Thus, temperature alone is not a determining factor. Surface condition was also identified as a major factor.

Impulse testing of the HK-40 alloy tube and resonant ultrasound spectroscopy (RUS) testing of the samples revealed a decrease in density of HK-40 tube as a whole due to high temperature thermal expansion. In addition a localized decreases in density in the carburized zones due to the intense diffusion of carbon leading to the formation of Cr$_{23}$C$_6$ which is larger in molar volume than the base metal.

The natural frequency of the bottom side of the HK-40 alloy tube compared to the as cast condition was shifted by about 2.11 percent (Table 5.1). This observation indicates that the speed of sound of the HK-40 alloy tube after carburization test is slower by 2.11 percent.

The resonant ultrasound spectroscopy (RUS) revealed a reduction of the shear wave due to carburization to on average of 8.17 percent (Table 6.5) while the average reduction in density for the samples at high temperature (Group C) is about 3.8 percent (Table 6.4). The following Equation (8.1) is used to find out the percentage of reduction of the shear speed of sound based on the resonant ultrasound spectroscopy, is used:

\[
\frac{C_s(\text{after carburization})}{C_s(\text{base metal})} = \sqrt{\frac{0.918 \times G}{0.962 \times \rho}} = \frac{0.918}{0.962} \approx 0.977
\]

That means the reduction of shear speed of sound due to carburization of the whole HK-40 alloy tube was about 2.3 percent (i.e., 1-0.977).

The result from the resonant ultrasound spectroscopy is in agreement with the impulse testing. It could be possible to utilize the impulse testing as a quantitative analysis by measuring the impulse response of the tubes and comparing the natural frequencies to estimate the extent of carburization and the overall integrity of the tube.

Use of a pulsed-echo method with a phased array transducer for example could provide a qualitative analysis that identifies the exact location of carburization and metal defects. For
example, centering the phased array at the center of the tube under investigation will cut the time of inspection to half by allowing for readings of both sides of the tube.
CHAPTER 9: CONCLUSION

1. The space and time of the initiation and growth of carburization is random and non-uniform in nature. Metallographic examination revealed inconsistency of carburization formation in morphology and location during isothermal anneals resulting in variation on depth and length. The energy dispersive X-ray (EDX) elemental mapping characteristic suggested that the primary carbide initially existing in the base metal Cr$_{23}$C$_6$ transformed to Cr$_7$C$_3$ confirming the literatures. As seen by the resonant ultrasonic spectroscopy (RUS) analysis, the internal carbide formation due to carbon uptake causes a weight and volume increase of the samples and hence a decrease in density. This expansion results in increasing the local strain and reduction in shear wave speed. This observation leads to deterioration of mechanical properties of the materials such as loss of ductility as determined by macro hardness measurements. Metal dusting, which is a severe form of carburization, resulting in detrimental microstructure features exhibiting a well-defined pattern (pitting) but their location of initiation is random. Their metal loss feature is the main reason of reducing the tube life. It would suggest that the service life prediction could be best determined from the greatest depth of these pitting and carburization.

2. Fundamental elastic wave studies (RUS and impulse testing) were conducted to understand the nature of the correlation of ultrasonic waves in assessing of the prediction of carbon uptake related to carburization level and the size, shape and depth of carburization and metal dusting damages. Impulse testing showed that it is possible to detect the overall material or structural changes of the tube due to carburization or metal dusting but lacks the ability to precisely locate and measure the specific carburization or metal dusting damage. In addition, the evidence of this test revealed that it was not able to measure any changes due to heat treatment in terms of grain growth and primary carbides reformation. The resonant ultrasonic spectroscopy (RUS) showed that there are changes in elastic moduli due to carburization and metal dusting but could not relate the carbon uptake with carburization level.

3. COMSOL simulation theoretically demonstrates the ability to detect and predict subtle carburization defects in materials over an extensive inspection area using guided wave testing methods. Multiple scenarios of carburization and metal dusting morphology and material properties were simulated based on the previous RUS and metallographic observations.
These simulations showed the ability of detecting late stages of carburization and metal dusting. It requires an application of more sensors arranged in a specific way (phase array) to predict early stage of carburization and metal dusting damages. The resulting theoretical predictions will be of use in designing and analyzing a laboratory experiment with the goal of detecting realistic carburization defects in materials of interest including furnace tubes.

4. The present practice tools range from hand held magnet to the more technologically sophisticated such as multi-frequency eddy current instruments. Unfortunately, all of the existing tools are point to point inspection which is time consuming. The modeling is used to allow for better experimental design to achieve NDE data of mechanistic interpretation of the microstructure and mechanical behavior of reactor/furnace material during service. These investigations allow the use of advanced ultrasonic techniques (phased array transducers) to assess qualitatively and the possibility with further application of more sensors and more integrating analytical programming can achieve quantitative determination of degradation of the tube working surface condition. The result will be a significant advancement of the present practice nondestructive examination (NDE). In addition, it will set the base for establishing a criteria to predict service life of the tube.
CHAPTER 10: FUTURE WORK

The present investigation provides evidence through modeling that the use of phased array tool can detect the location and size of carburization and metal dusting defects in the pyrolysis tubes. These conclusions open the door for future work to examine the pyrolysis tubes with the more complicated inner surface design such as the finned tube (Figure 2.4) and the mixing element radiant coil (Figure 2.5).
REFERENCES


