THE EFFECTS OF CONTAMINATION AND CLEANING ON
AISI 9310 VACUUM CARBURIZED STEEL

by

Jodi Lowell

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APPROVED:

Richard D. Sisson, Jr.

George F. Fuller Professor

Director of Manufacturing and Materials Engineering
Abstract

A serious concern in the practice of heat treatment is the effect of surface contamination and the effectiveness of subsequent cleaning on the performance and appearance of the finished products. This study examined the effects of contamination on the appearance, hardness, carbon concentration, and retained austenite percentages in vacuum carburized AISI 9310 steel. The effectiveness of commonly-used cleaning methods was also determined. Seven categories of typical contamination were selected for testing: rust preventative oil, hot and cold cutting fluid, and four levels of oxidation. Samples of AISI 9310 steel were contaminated and then half from each category were cleaned and the other half remained contaminated. All samples were vacuum carburized to a case depth of 0.35wt% carbon at 0.9mm. The properties were experimentally determined post-heat treatment.

It was determined that there was no significant difference in the contaminated, cleaned, and non-contaminated samples for any of the hardness, carbon concentration, and percentage of retained austenite measurements. However, most contaminated samples had undesirable appearances after heat treatment. Therefore, when a high quality surface appearance is not necessary or if further surface processing is done on these parts, this study determined that cleaning of AISI 9310 steel is not necessary before vacuum carburization. This implies a potential cost and time savings for heat treatment companies. However, when the customer specifies a clean, lustrous surface, effective cleaning is required before vacuum carburizing.

Keywords Contamination, cleaning, vacuum carburization, oxidation, cutting fluids, rust preventative oil, AISI 9310
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Nomenclature

c    Cleaned

CCF  Cold cutting fluid

CHTE Center for Heat Treating Excellence

EDS  Energy-dispersive X-ray spectroscopy

HCF  Hot cutting fluid

HRC  Rockwell-C hardness

nc   Not cleaned

OES  Optical emissions spectrometry

RA   Retained austenite

RPO  Rust preventative oil

SEM  Scanning electron microscope

XRD  X-ray Diffraction
1 Introduction

Vacuum carburizing is a useful method for surface hardening of steel. In the practice of this process, however, heat treaters have found that the finished, post-processing products do not always meet the desired mechanical properties and appearance. It was speculated that this could be a result of contamination on the parts pre-processing. Therefore, the Center for Heat Treating Excellence (CHTE) sponsored an investigation of the effects of contamination on vacuum carburized steel. The objectives of this investigation were as follows:

- **Objective 1**: To determine the effects of contamination on the appearance, hardness, carbon profile, and microstructure of vacuum carburized AISI 9310 steel.
- **Objective 2**: To determine the effectiveness of typical cleaning methods on the appearance, hardness, carbon profile, and microstructure of vacuum carburized AISI 9310 steel.

To accomplish these objectives, an experimental investigation was conducted and samples that were contaminated, contaminated and cleaned, and as normalized were vacuum carburized. For objective 1, post-vacuum carburized contaminated and non-contaminated samples were compared. For objective 2, post-vacuum carburized contaminated and cleaned samples were compared. The following sections of this paper will detail the introductory knowledge needed to understand the background of this investigation, the methodology that was followed, the results of the various tests conducted, the analysis of those results, and finally the conclusions of this study.
2 Background

2.1 Steel
Steel is an iron and carbon based alloy with the phase diagram shown in Figure 1. This experiment involves AISI 9310 steel which is in the nickel-chromium-molybdenum steel family with 0.10% carbon. The composition of the steel and the principle functions of the alloying elements are shown in Table 1 and Table 2 respectively. The typical applications of AISI 9310 include gears especially in the automotive and aerospace industries, components for small arms, and track rod pins (CES EduPack, 2009).

Table 1: AISI 9310 composition

<table>
<thead>
<tr>
<th>C</th>
<th>Ni</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>3.0-3.50</td>
<td>0.45-0.65</td>
<td>1.00-1.40</td>
<td>0.08-0.15</td>
<td>0.15-0.30</td>
<td>0.025 max</td>
<td>0.025 max</td>
</tr>
</tbody>
</table>

Table 2: Alloying elements' principle functions
(from: (Heat Treating Data Book, 2006))

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Principle function</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>To control strength level</td>
</tr>
<tr>
<td>Ni</td>
<td>Hardenability &amp; improve notch toughness at low temperatures</td>
</tr>
<tr>
<td>Mn</td>
<td>Hardenability</td>
</tr>
<tr>
<td>Cr</td>
<td>Hardenability &amp; oxidation resistance</td>
</tr>
<tr>
<td>Mo</td>
<td>Hardenability &amp; improve creep strength</td>
</tr>
<tr>
<td>Si</td>
<td>Deoxidizer</td>
</tr>
<tr>
<td>P</td>
<td>Ferrite strengthening &amp; corrosion protection</td>
</tr>
<tr>
<td>S</td>
<td>Improve machinability</td>
</tr>
</tbody>
</table>
Carburization is a surface hardening heat treatment process. First, the material should be pretreated if necessary. For example, AISI 9310 should be normalized and tempered before carburization (Heat Treating Data Book, 2006). Then carburizing is done by introducing a carbon-rich gas into a furnace containing the parts to be heat treated at about 1600-1700°F. The introduction of the carbon-rich gas to
the furnace is called the boost step and the release of this gas from the furnace is called the diffuse step. Gas carburized samples typically have 1 boost and diffuse step. In the boost step, the carbon diffuses into the lattice of the part to be heat treated. This causes the surface to be harder due to carbides and an increase in the covalent bonding in the steel (Sverdlin & Ness, 1997). However, a more significant mechanism for the carbon’s strength hardening property is the increase in dislocation density in the martensite BCC lattice. Also, carbon increases the stability of the austenite phase, which means that an increase in the amount of carbon introduced to the steel, increases the amount of retained austenite present post-carburization. However, as the carbon super-saturates the austenite lattice, the diffusionless transformation from austenite to martensite occurs, which is the second major mechanism for hardening by the carburization process. For significant hardening in the steel, it is necessary for an increase in both carbon concentration and martensite (Tensi, Stich, & Totten, 2007).

Carburization produces many desirable materials properties. Some of those properties include high compressive-residual stresses within the effective case depth, high toughness, high wear resistance and durability, and high power-to-weight ratio. The high power-to-weight ratio makes this an ideal process in the manufacturing of transportation, in particular aerospace and helicopter, applications.

2.3 Vacuum Carburization
Vacuum carburizing is based on the same principles as gas carburizing. However, there are some differences in the process parameters. The carbon-rich gas is pulsed into the vacuum furnace, leading to many boost and diffuse cycles, as shown in Figure 3. When the gas is pumped into the vacuum chamber (the boost step), the concentration of carbon in the atmosphere is high (as seen in Figure 4) and the activity is almost infinite. This high activity leads to a higher affinity for diffusion and thus, when the carbon-rich gas contacts the parts’ surfaces, the gas decomposes into carbon and nascent hydrogen molecules. During the diffuse stage, the carbon is driven further into the lattice, causing a lower concentration of carbon on the surface. This larger concentration gradient draws more carbon into the lattice during the next boost cycle. If the amount of carbon at the surface is too high, there will be too much austenite retained in the sample corners since the corners have a reduction in access to the sample core (Davis & al., 1991). If the carbon activity is too high, massive carbides can form within the carburizing target parts and the carbon will have a high thermodynamic stability in the form of graphite, which will precipitate out of the gaseous solution and foul the insides of the furnace. This phenomenon is called sooting. The result of sooting is expensive in the cost of cleaning materials and operation down-time needed to clean the furnace. Therefore, the carbon-rich gas is diffused shortly after boosted
to reduce the possibility of sooting. The length of time of the boost and diffuse cycles is controlled to produce a desired case depth, which is typically defined to an effective hardness like Rockwell-C 50.

![Figure 3: Pulsed vacuum carburizing process](#)

There are many advantages to using vacuum carburizing instead of gas carburizing. A vacuum atmosphere allows for a more uniform distribution of the carbon-rich gas rather than an enriched endo-gas atmosphere. The high circulation of carbon-rich gas and absence of other gases in the furnace leads to lower partial pressures of the gas needed to achieve the same carburizing conditions. This, therefore,
reduces the amount of gas consumed in the overall process. Since the vacuum environment and uniform gas conditions are more easily controlled, there is better reproducibility and standardization in vacuum carburized parts (Davis & al., 1991). It enables carburization within small diameter openings and leads to thicker case depths. However, due to energy costs, it is more cost effective to use gas carburization on thicker (>0.6mm) case depths than it is to use the vacuum variation. It also goes much faster than the gas method since there is a higher activity of carbon in the atmosphere and is usually done at higher temperatures, which means a faster carbon into iron lattice diffusion rate (Heat Treating Data Book, 2006). There is also a significant reduction in oxygen present in the furnace compared to gas carburizing. This lower oxygen partial pressure leads to far less surface oxidation and more importantly, less intergranular oxidation (IGO). IGO has been shown to reduce performance and significantly reduce the life of a part (Bykowski, Speer, Krauss, Johnson, & Burnett, 2008). Figure 5 shows the difference in lifetime (L10 and L50) between 4120 and 4320 steels carburized at varying temperatures (low, medium, and high), reheated, and under low pressures (vacuum). Another important advantage of vacuum carburization especially in heat treating gears is that much closer final dimensions are achieved, which reduces the amount of machining needed to the post-carburized parts (Davis & al., 1991). This reduces the amount of labor, machine maintenance, and possibility for deformation. The distribution of internal stresses can cause extreme deformation during machining, so reducing the amount of machining needed to the gears could reduce the number of rejected gears. Lastly, another advantage of vacuum versus gas carburizing is that the vacuum technique is much “greener” than the gas since it does not have high concentrations of CO and CO₂ (greenhouse gases), which is a concept of growing importance to industrial companies and consumers (Heat Treating Data Book, 2006).
2.4 Cleaning
All manufactured parts have the possibility to acquire surface contamination at some point throughout their processing. The contaminants can find the surface of a part in an upstream process or transportation between locations or machines. Contaminants can affect downstream processes in the form of equipment contamination or damage and process inefficiencies. As mentioned previously, equipment contamination or damage can require operation delays as the equipment is cleaned or replaced. The efficiency can be lowered due to a thin film barrier for heat and mass transfer. This leads
to inconsistent and non-uniform mechanical and physical properties, such as diffusion, and varying grain
development. Surface contamination can also lead to poor surface finish or quality, resulting in an
unhappy customer (Mark Fretz, personal correspondence, Oct. 29, 2008). Therefore, these parts must
undergo surface finishing procedures which reduces the overall process efficiency. Typical contaminants
for gears, the main application of this experiment, include cutting fluid from previous machining,
quenching oil, rust, and rust preventative oil.

While it would be ideal to have clean parts, it is not always necessary. For example, some light oils are
evaporated in a furnace and have little impact on the equipment and part so their removal is not
necessary. Therefore, the first step in the approach of contamination removal is determining if it is
necessary to clean the part. The two variables that factor into this decision the most are the cleanliness
requirements and cost effectiveness of cleaning the part. If it is deemed necessary to clean the part,
there are even more variables to consider when selecting a method of contaminant removal. These
variables include the contaminant and part material compatibility, part size and geometry,
environmental friendliness of cleaning agent or method, the facility capabilities, and downstream
operations that could be affected by cleaning technique (Sisson & al, 2008). CHTE has developed a
software program in which a user can input these parameters and the program will report on the
cleaning method that should be used. Figure 6 details the typical selection choices for the most
common contaminates.
There are multiple methods and pieces of equipment to measure sample cleanliness and identify contaminants. The quantitative cleanliness measurements can be completed using x-ray fluorescence spectrometry (XRF), laser-induced breakdown spectroscopy (LIBS), laser assisted microwave plasma spectroscopy (LAMPS), Fourier-transform infrared spectroscopy (FTIR), desorption electrospray ionization (DESI), desorption atmospheric pressure chemical ionization (DAPCI), and most commonly, common mass spectrometry (Sisson & al, Characterization, Evaluation, and Removal of Surface Contamination from Pre and Post Heat Treated Parts: 2008-01, 2008). CHTE suggests the simple methodology in Figure 7 for the qualitative identification of the contaminant category (i.e., particle or oil contamination) which will dictate which required cleaning method.
Figure 7: Methodology for contaminant identification

from: (Sisson & al, Characterization, Evaluation, and Removal of Surface Contamination from Pre and Post Heat Treated Parts: 2008-02, 2008)
3 Methodology

The purpose of this experiment was to determine the effect of contamination and cleaning on vacuum carburized AISI 9310 steel. The evaluation of the effect of contamination was done by comparing the as normalized and the contaminated samples. The determination of the effect of cleaning was done by comparing the contaminated and the cleaned samples. Figure 8 details the experimental procedure and Table 3 contains the test matrix used for this project.

![Figure 8: Experimental flowchart](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>Contamination</th>
<th>Carburizing condition</th>
<th>No. of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 9310</td>
<td>Hot cutting fluid</td>
<td>Cleaned</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not cleaned</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Cold cutting fluid</td>
<td>Cleaned</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not cleaned</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Rust preventative oil</td>
<td>Cleaned</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not cleaned</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Rust – 2 days</td>
<td>Cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Rust – 4 days</td>
<td>Cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Rust – 7 days</td>
<td>Cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Rust – 19 days</td>
<td>Cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not cleaned</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>None</td>
<td>Normalized</td>
<td>8</td>
</tr>
</tbody>
</table>
The samples were contaminated with oxidation, hot and cold cutting fluid, and rust preventative oil, and the cleaning techniques that were used were acid and alkaline cleaning. The vacuum carburization was done at ECM USA, Inc. at 930°C using C2H2 gas for about 9.5 hours in a confidential boost and diffuse recipe, and then quenched using high pressure nitrogen gas. This was immediately followed by the cryotreatment done at -100°C for 8 hours and then tempering at 166°C for 3 hours. The cryotreatment was done since the alloying elements in AISI 9310 as well as the carbon diffused in during the carburization lowered the martensite start temperature. The alloying elements affected the martensite start and finish temperatures by either stabilizing the austenite or martensite phases (Sverdlin & Ness, 1997). The effect of carbon and the other alloying elements can be seen in Figure 9. The tempering was done to relieve the localized stresses caused by the carbon super-saturation and lattice distortion, as well as the stresses caused by quenching (Tensi, Stich, & Totten, 2007). The samples were analyzed using mass flux (change in weight), surface hardness (Rockwell-C), microhardness (Vickers), optical emission spectroscopy (OES) for carbon concentrations, and x-ray diffraction (XRD) measurements. The samples were also examined in an optical microscope and a scanning electron microscope (SEM).

![Figure 9: Effect of carbon concentration (a) and other alloying elements (b) on the martensite start temperature. From: (Sverdlin & Ness, 1997)](image)

### 3.1 Sample preparation

A 63-inch in length, 1.25-inch in diameter bar of AISI 9310 steel was purchased in cold-finished condition. Since carburizing of this alloy is done in the austenitic phase and on non-stressed pieces, the bar was then cut into 3 smaller pieces in order for the bar to fit into the furnace for normalization. The samples were normalized in a furnace at 1650°F for 4 hours and then were cooled in the chamber. This
was done to get a microstructure of fine ferrite and pearlite (Vander Voort G., 2003). Once normalized, the bar was sliced into approximately 8mm in length pieces, a hole drilled for use of hanging the parts in the carburizing furnace, and sequential numbers were etched onto the face of each sample using a CNC lathe. Since Olga Karabelchtchikova showed in her research that the surface roughness affects the overall carburization (Karabelchtchikova, 2007), the pieces were manually loaded into a mini-mill in which they were trimmed to have the same surface roughness as the other side of each coupon. Following machining procedures, rust preventative oil was applied to each coupon to temporarily protect the surface until the proper contamination and cleaning could be administered.

Once all of the samples were completed, the preparation for contamination began. The samples were rinsed in acetone and then submerged in acetone and ultrasonically cleaned. This was to remove any of the rust preventative oil and machining chips that remained on the sample surfaces. The samples were then weighed on a high-precision scale out to the hundred-thousandths position, or 5 significant figures past the decimal point. This was considered the initial sample mass. The coupons were then ready for the contamination stage in the sample preparation.

3.2 Contamination
There were 3 contamination sources that were investigated: rust, cutting fluid, and rust preventative oil. There were 2 testing conditions for the cutting fluid which included samples at room temperature exposed to the cutting fluid and then samples that were heated and then exposed to cutting fluid. There were also 4 testing conditions for rust in which the discriminating factor was the length in time that the samples experienced a high-humidity environment. The mass of all samples was measured both before and directly after the contamination. The following section details the method of contamination.

3.2.1 Rust
There were 4 sets of 8 samples each that were oxidized in a closed tank containing close to 100% humidity. The 4 sets were distinguished by the length of time that they hung in the tank: 2 days, 4 days, 8 days, and 19 days. It was arranged so that the samples would not make contact with each other and that more samples could be added in such a way that the samples already in the rusting process would not be disturbed. The arrangement can be seen in Figure 10.
3.2.2 Cutting fluid
The cutting fluid that was used for this experiment was an emulsion of 5 percent Castrol Clearedge 6519 concentrate and 95 percent tap water with a pH value of 9 sampled from one of the machines in the WPI machine shop. This is a typical cutting fluid that is used in machining in places that include WPI machine shop’s CNC machines (Sisson & al, Characterization, Evaluation, and Removal of Surface Contamination from Pre and Post Heat Treated Parts: 2008-02, 2008).

Two separate cases of cutting fluid contamination were examined. For the first, 8 coupons at room temperature were dipped into cutting fluid also at room temperature. The second set of 8 coupons was heated to 300°C for 5 minutes and then dipped into cutting fluid that was at room temperature. This was to simulate the heating of the metal in the cutting or grinding process. It was taken into consideration that the coupon would heat the cutting fluid; therefore, there was a large enough volume of cutting fluid that the fluid temperature did not raise considerably, which would alter the parameter for the latter coupons dipped into the cutting fluid. In both cases, after the coupons were taken out of the fluid, they were laid out to dry on aluminum foil.
3.2.3 Rust preventative oil
Rust preventative oil is a common contaminate on sample surfaces. This contaminant was even applied to all of the coupons after the final machining stage before the study began. For this study, however, the rust preventative oil was cleaned off before any weight measurements were taken. The intentional contamination of 8 coupons was done by individually dipping the samples into a container of unused Houghton Rust Veto 4225 rust preventative oil. They were then allowed to hang dry.

3.3 Cleaning
Two cleaning methods were used to remove the contaminants from the coupons. These methods were selected based on their prevalence and common practice in the industry, as well as for the compatibility with the AISI 9310 steel and the contaminants. After the cleaned coupons were dry, they were weighed and their masses recorded. Then a cleanliness test was performed on one sample from each category: as normalized, rusted 2, 4, 7, and 19 days (cleaned and not), cold cutting fluid (cleaned and not), hot cutting fluid (cleaned and not), and rust preventative oil (cleaned and not). Details about the cleaning process and the cleanliness test are described in this section.

3.3.1 Acid cleaning
Acid cleaning was used to remove the light rust on the samples that were oxidized for 2, 4, 7, and 19 days. The acid solution was 400mL of 50 vol% HCl and 50 vol% deionized (DI) water at room temperature. The coupons were submerged in the solution for 1 minute and then submerged in 3 separate 400mL DI water containers for 1 minute for each container. The samples were then rinsed a final time with DI water and then hung to dry. The acid solution was replaced with another 400mL of 50 vol% HCl and 50 vol% DI water bath part way through the experiment when bubbles were no longer forming on the oxidized layers of the coupons after the initial submersion.

3.3.2 Alkaline cleaning
An emulsion of 5 vol% Cerfa-Kleen 5378 in 95 vol% DI water at 76°C was used to remove the cutting fluid and rust preventative oil. These conditions mimic the cleaning practices of one unnamed CHTE-associated company. However, the CHTE-associated company usually submerged the samples for 15 minutes in the cleaning solution. For this experiment, the sample were submerged in the cleaning emulsion for 10 minutes and then, similar to the acid cleaning procedure, the coupons were submerged in 3 separate DI water containers for 1 minute per container. The samples were then rinsed with fresh DI water and then hung to dry. Samples were slightly agitated in the cleaning solution by rocking the samples or the beaker. This was done to dislodge the bubbles on the coupons’ surfaces in order to allow for more even contact with the cleaning agent.

3.3.3 Cleanliness Test
The cleanliness test was based off of the suggested evaluation process from the CHTE 08-02 report, which has been reproduced in Figure 11. This test was performed after the coupons were all contaminated and cleaned (if applicable).
3.3.3.1 **Black light**
The room was darkened as much as possible for this test. A box was also placed over the samples but lifted enough to shine the black light on the samples and to see the illuminated coupons. A visual inspection was done to find any traces of oils or fluorescent particles.

3.3.3.2 **White towel test**
White paper towel found in the laboratory was used for this test. For the purposes of this experiment, strips of paper towel were cut and used to wipe the surface of the sample. White cloth could also be used in place of the paper towel, especially in applications where the surface finish is delicate or must be impeccable (i.e., no scratches).

3.3.3.3 **Scotch tape**
Strips of regular, commercial scotch tape were used. The strips were pressed against the opposite side of the samples that were tested with the white towel. This was done to evaluate the efficacy of these two tests individually and ensuring neither test influenced the other.

3.3.3.4 **Water break test**
This test was not performed since there was not enough oil on the surface of even the non-cleaned samples contaminated with the rust preventative oil.
3.4 Analysis
In order to analyze the effects of contaminants on the carburized samples as well as the effects of cleaning those contaminants from the samples, quantifiable data is needed. This is done through different techniques such as weight gains measurements, hardness tests, micrographs, and retained austenite values. These techniques are described in this section.

3.4.1 Weight gain measurements and calculations
Weight gain measurements were critical for this experiment and were, therefore, taken several times through the course of the experiment. The mass of each sample was determined after the samples were normalized and cleaned in the acetone and ionic cleaner. The samples were then weighed again after they were contaminated. The samples that were cleaned were weighed after this was done. Then a final pre-carburization mass value was taken for 1 sample from each condition that went through the cleanliness test as previously described. The mass of each sample after the carburization process was also determined. All mass measurements were done with the samples being completely dry (including the oil and cutting fluid contaminants). It was from these measurements that the overall weight gain from carburization was determined.

3.4.1.1 Mass flux
The weight measurements enabled the calculation of the mass flux, \( J_C [g/cm^2*s] \), of each sample and an average carburization weight gain and flux for each condition. For each sample contaminated with cutting fluid, rust preventative oil, and the as normalized samples, the flux was calculated as the post-carburization mass minus the mass of the last pre-carburization measurement [g] divided by each sample’s surface area, \( A_s [cm^2] \) and boost time [s], as seen in Equation 1.

\[
J_C = \frac{\delta}{\delta t} \left( \frac{\Delta M}{A_s} \right) = \frac{\delta}{\delta t} \left( \frac{M_{after
carburization} - M_{after
carburization/condition/cleaning/cleanestest}}{A_s} \right)
\]

Equation 1: Flux of rust preventative oil- and cutting fluid-contaminated samples as well as the as normalized samples

For the rusted samples, however, there was a problem with the rust falling off of the samples in transit or in the furnace. Therefore, the flux was calculated by integrating the area under the empirical carbon profile curve and then dividing by the time in the boost stage of carburizing, as seen in Equation 2.

\[
J_C = \frac{\int_{C_{initial}}^{C_{surface}} f(distance)}{t_{boost}}
\]

Equation 2: Flux of rusted samples

For both methods of flux calculations, the surface area was determined for each sample using the following formula:
\[ A_{\text{surface}} = 2\pi r^2 + 2\pi rt = 2\pi(r+t) = 2\pi(15.587mm) \cdot (15.587mm + t) \]

Equation 3: Sample surface area

Where \( t \) [mm] is the sample thickness. Due to tolerances in the manufacturing process, the thicknesses varied slightly among the samples. The time used for both methods was the boost time, 1445 seconds.

3.4.2 Hardness measurements and profiles

Two hardness measurements were taken for each of the samples – macrohardness as well as microhardness. The first was the macrohardness, or surface hardness, which was done using the Rockwell-C equipment. The second was the microhardness profile that was done using sample cross-sections and the Vickers hardness equipment. The microhardness profiles were also used to determine the case depth of the samples, based on Rockwell-C values equal to 50, or the equivalent Vickers hardness measurement of 513. Both macro and microhardness measurements were taken for all vacuum carburized samples.

3.4.3 Surface carbon and carbon profile measurements

The remaining sections of the samples that were cut for cross-section analysis were used for further analysis, which included surface carbon and carbon profile measurements. The weight percent of carbon at the surface of the vacuum carburized samples as well as the carbon profiles throughout the samples were determined using optical emissions spectrometry (OES). For the surface measurement, the samples were untreated and the OES burns happened on the top layer of the samples. For the carbon profile, the samples were hand-ground on a belt sander until a clean, flat surface was formed. Then this layer’s burns were done with the OES. This process of grinding and OES burning was repeated in order to form the profile. For the HCF, CCF, and RPO-contaminated samples as well as the as normalized samples, the profile formed was compared to that generated by CarbTool, a carbon profile predicting software (Wang & Sisson, 2009), using the calculated fluxes from Equation 1. For the oxidized samples, the area under the carbon profile curve made using the OES was calculated and then divided by the boost time, as seen in Equation 2, and this flux was input in CarbTool to produce a graph to compare to that from the OES measurements.

3.4.4 Photomicrographs

Photomicrographs were obtained by cutting at least one sample from each condition as well as others that had unusual hardness or weight gain measurements. The cross sections were then mounted, polished, and etched in order to view the grain boundaries. The etchant was the commonly used 2% nital, consisting of 2% nitric acid. The samples were viewed and images captured using an optical microscope as well as a scanning electron microscope (SEM).

3.4.5 Retained austenite measurements

The other face of the samples used for carbon measurements were utilized for x-ray analysis and retained austenite calculations. The allowable amount of RA is typically specified because of the changes in properties of the \( \gamma \)- and \( \alpha \)-phases. It is desirable for a gear to have a high surface hardness and therefore a high resistance to surface contact fatigue, which means that the surface should contain more of the harder \( \alpha \)-phase. The core of the gear, however, should remain more ductile so that it can
better absorb impact and fatigue stresses. Though the RA can be transformed to martensite by mechanical work (i.e., typical tooth-tooth contact with gears being used) (Abudaia, Evans, & Shaw, 2003), it is usually desirable to install the gears with the transformation already taken place. The mechanical transformation can lead to grinding cracks and more importantly, dimensional instability which is a huge problem for the aerospace and helicopter industrial who work in tolerances of thousandths of inches (Bensely, Prabhakaran, Mohan Lal, & Nagarajan, 2005).

Each application and many gears require different maximum amount of RA specifications depending on this balance between hardness and ductility. For example, heat treated parts done in Sikorsky must follow the United Technologies specification SS 8015 which sets the maximum amount of allowable RA to be 20% (Aircraft, 1996). Other gear customers require 15-20%. The aerospace industry has much higher standards with a maximum RA level set to 4% (Abudaia, Evans, & Shaw, 2003).

The high amount of RA results from a non-martensite finish in the quenching of the samples. This is because of the lowering of the martensite temperature caused by the alloying elements, in particular open γ-field elements like Ni and Mn. There is an opposing force to this phenomenon which supports the formation of martensite; the elements which do this are called closed γ-field elements and include Cr, P, Mo, and Si. Other alloying elements disrupt the Fe-C phase diagram and cooling curves by introducing a bi-product of carbides. The elements that most often result in carbides are Ti, Cr, and unavoidably, Fe (Bhadeshia & Honeycombe, 2006). In order to overcome the high amounts of RA caused by the lowering of the martensite temperature, the samples are cryotreated, thus allowing the samples to progress closer to the theoretical martensite finish temperature.

The retained austenite (RA) levels were measured using x-ray diffraction and the fraction of RA levels were calculated according to the ASTM standard of measurement E 975-84 (E 975-84: Standard Practice for X-Ray Determination of Retained Austenite in Steel With Near Random Crystallographic Orientation", 1989). An analytical program made in Excel, see Appendix 1: Retained austenite calculation program made in Microsoft Excel, was used in the calculations as well. The spectra from selected samples, at least one from each condition (cleaned and non-cleaned samples from each contamination category), were collected with the x-ray diffraction machine. From the spectra, the integrated intensity under the γ-200, α-200, γ-220, and α-211 peaks as well as the peak location were used in the retained austenite calculations. The FullProf Suite software package’s WinPlotr program was used to calculate the area under the peaks and determine the location of each peak.
4 Results and discussion

4.1 Cleanliness tests

4.1.1.1 Black light
This method was inconclusive since there was not a noticeable difference between any of the samples, except for the difference between the luminous steel and the non-luminous rust. This was an impractical test since there it was so difficult to achieve adequate darkness. Therefore, the evaluation process continued.

4.1.1.2 White towel and scotch tape
The results of these tests can be seen in Figure 12. These methods both detected the rust, but were not useful for the cutting fluid, rust preventative oils, or as normalized samples. The usefulness of this test was not great because the rust that is so visible in Figure 12 can easily be seen on the samples themselves, which makes this test seem redundant and unnecessary for heat treating operators.

![Figure 12: White towel and scotch tape tests: rusted samples (left) and cutting fluid, rust preventative oil, and as normalized samples (right)](image)

4.2 Visual appearance
An important qualitative not quantitative result was the visual appearance of the post-carburized parts, as seen in Appendix 2: Macro-scale pictures comparing pre- and post-carburization. All samples lost their luster and became dull in appearance after the carburization process. Other than the dull
appearance, the as normalized, i.e. non-contaminated, samples did not seem to have a significant difference in appearance after carburizing than before the process.

For all rusted samples when rust was apparent, the color of the oxidization changed before and after the carburizing process. Before the carburization, the rust was a burnt-orange to dark brown color. However, after the carburization, the rust was black. The rust also seemed well-adhered to the surface before the carburization and afterwards, it rubbed off slightly easier but still had good adhesion to the steel surface. The small amounts of rust that was present on the samples oxidized for 2 days before the carburization was not present afterwards. Also, the cleaned and non-cleaned samples had little difference between them visually. The samples oxidized for 4 days and then cleaned seemed to have no rust on the faces of the samples except for 1 sample, but they all had some rust on the sides of the samples. The samples rusted for 4 days and not cleaned before carburization had visual rust on the faces and sides of the samples. There started to be a difference in the cleaned and not cleaned samples with the samples oxidized for 8 days, with more the cleaned samples appearing to be a darker shade of dull gray color but with less black surface rust on the sample faces. The samples oxidized for 19 days had a similar pattern with the darker shade of gray color, however, the cleaned samples appeared to have more of the black surface rust on the faces than the not cleaned samples. This is the opposite result than the prediction since cleaning is done to improve the carburization and appearance. This could be due to the adherence of the rust before the carburization. If is possible that the cleaning removed the less-adhered oxides, leaving only the well-adhered rust. The not cleaned samples had the less-adhered rust rubbed off in transit, possibly removing some layers of better adhered rust with it. This is all speculation, however, since this observation is contradictory to historical heat treatment knowledge.

The cleaned and not cleaned HCF-contaminated samples were a similar shade of dull gray color after the carburization. However, the not cleaned samples had a splotchy residue appearance on the samples that made them look dirty and not aesthetically desirable. The cleaned samples had barely any of this discoloration. The cleaned and not cleaned CCF-contaminated samples had a similar result as the HCF-contaminated samples. There did not seem to be a difference in the appearance between the cleaned and not cleaned RPO-contaminated samples soon after the samples were carburized. The samples were stored individually in sealed bags in the same environmental conditions for all samples, however, after about 6 months after the samples were heat treated, the cleaned samples had significantly more dark-brown colored rust than the not cleaned samples. This was most likely the result of the cleaning procedure being too aggressive rather than the RPO contamination or an incorrect cleaner was chosen for the AISI 9310 steel chemistry. It is believed that the RPO will burn off of the samples in the furnace at the given carburizing conditions.

### 4.3 Mass measurements and flux calculations

It was determined that mass measurements for the oxidized samples could not be used in the flux calculations. This was because the calculated flux was too low and the change in mass for all of the rusted 19 days (R4 cleaned and not cleaned) samples lost weight after carburized. This contradicts the carbon and hardness profiles and the basic principles of thermodynamics; therefore, it was determined that the mass losses during transportation were not accounted for in the weight measurements. It was
not possible to assume that all of the rust fell or was rubbed off the sample during transportation because there was still visible discoloration in the form of oxidation on the surface on the R3 and R4 samples. Therefore, the mass measurements for the oxidized samples could not be used due to the unknown source of the weight loss.

For the HCF, CCF, RPO, and as normalized samples, the mass measurements and calculations for weight gains were all very similar, averaging between 0.13505g (HCF-c, average) to 0.14082g (as normalized, average) weight gain. Once the samples were compared using the flux measurements, which corrected for the minute differences in the sample surface areas, the difference between the representative HCF, CCF, RPO, and as normalized samples was also minimal: 3.877e 6 g/cm²s (CCF-nc) to 4.061e 6 g/cm²s (CCF-C). This showed that neither these contaminants nor the cleaning had a significant effect on the vacuum carburization of the samples.

Table 4: Calculated carbon fluxes for representative samples (black) and selected samples with hardness anomalies (red).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>$J_c$ (g/cm²s) *</th>
<th>Anomaly**</th>
</tr>
</thead>
<tbody>
<tr>
<td>64 R1-nc</td>
<td>4.394E-06</td>
<td>3.994E-06</td>
<td></td>
</tr>
<tr>
<td>18 R1-c</td>
<td>4.210E-06</td>
<td>4.243E-06</td>
<td></td>
</tr>
<tr>
<td>91 R2-nc</td>
<td>4.264E-06</td>
<td>3.789E-06</td>
<td></td>
</tr>
<tr>
<td>95 R2-c</td>
<td>4.254E-06</td>
<td>4.318E-06</td>
<td>High wt% C at surface</td>
</tr>
<tr>
<td>98 R4-nc</td>
<td>3.986E-06</td>
<td>3.985E-06</td>
<td>Low wt% C at surface</td>
</tr>
<tr>
<td>100 R4-c</td>
<td>3.877E-06</td>
<td>3.807E-06</td>
<td>Low average HRC</td>
</tr>
<tr>
<td>86 CCF-nc</td>
<td>3.899E-06</td>
<td>3.886E-06</td>
<td>Low average HRC</td>
</tr>
<tr>
<td>106 CCF-c</td>
<td>3.969E-06</td>
<td>3.861E-06</td>
<td>Low average HRC</td>
</tr>
<tr>
<td>103 as normalized</td>
<td>4.008E-06</td>
<td>4.019E-06</td>
<td></td>
</tr>
</tbody>
</table>

*fluxes for the oxidized samples were not found using mass measurements; rather, using the OES carbon profile

**HRC (Rockwell-C hardness) and wt% C at surface are discussed in the following sections
4.4 Hardness measurements

The average macrohardness measurements of the various testing conditions made with the Rockwell-C equipment were within a range of 61.4 to 62.3, or a 0.9 difference, seen in Table 5. This indicated that the contaminants had a limited effect on the surface hardness of the samples. Also interesting was that the as normalized samples had on average, higher hardnesses than contaminated and contaminated-then cleaned samples. This was to be expected, however, since there would have been no additional boundary layer which the carbon atoms would have had to penetrate in order to be absorbed into the steel. From these measurements, a few anomalies – either hard or soft measurements – were discovered, and those were the samples that were chosen for further analysis.

<table>
<thead>
<tr>
<th></th>
<th>Average Rockwell-C hardnesses by contamination category</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1-nc</td>
<td>61.9</td>
</tr>
<tr>
<td>R1-c</td>
<td>61.7</td>
</tr>
<tr>
<td>R2-nc</td>
<td>61.9</td>
</tr>
<tr>
<td>R2-c</td>
<td>61.7</td>
</tr>
<tr>
<td>R3-nc</td>
<td>61.9</td>
</tr>
<tr>
<td>R3-c</td>
<td>61.6</td>
</tr>
<tr>
<td>R4-nc</td>
<td>61.4</td>
</tr>
<tr>
<td>R4-c</td>
<td>61.5</td>
</tr>
<tr>
<td>HCF-nc</td>
<td>61.8</td>
</tr>
<tr>
<td>HCF-c</td>
<td>61.9</td>
</tr>
<tr>
<td>CCF-nc</td>
<td>62.0</td>
</tr>
<tr>
<td>CCF-c</td>
<td>61.7</td>
</tr>
<tr>
<td>RPO-nc</td>
<td>62.1</td>
</tr>
<tr>
<td>RPO-c</td>
<td>61.8</td>
</tr>
<tr>
<td>As normalized</td>
<td>62.3</td>
</tr>
</tbody>
</table>

Microhardness profiles, as seen in Appendix 3: Microhardness profiles, were created with the Vickers hardness equipment. The microhardness profiles of the samples that had the anomalies in the Rockwell-C hardness measurements, shown in red in the legend and green for the data points, confirmed their abnormal macrohardness measurements. Those profiles were consistently either higher or lower than the representative samples from each contamination category. However, there was not a significant difference in the profiles for the cleaned versus not cleaned samples or those compared to the as normalized samples. This suggested that there was not a significant difference in the internal hardness due to the cleanliness of the samples.

4.5 Surface carbon & carbon profile measurements

The surface carbon and the carbon profile were measured with OES and can be seen in Appendix 4: Empirical OES carbon profiles. It was noticed that the weight percent of carbon was much higher on the surface of the oxidized and not cleaned samples of HCF, CCF, and RPO than on the cleaned and as normalized samples. This could be due to the oxidized samples’ greater surface roughness, especially
those oxidized for 7 and 19 days with thicker layers of oxides. An increase in surface roughness could allow for the sooted carbon to adhere onto the surface. Regardless, for all of the samples, the weight percent carbon was high on the coupon surface.

Once below the surface layer, it was noticed that there was not a significant difference in the contaminated versus non-contaminated samples or the cleaned and not cleaned samples, as seen in Appendix 4: Empirical OES carbon profiles. Also, the weight percent of carbon began to align with the values predicted in CarbTool. Values were predicted using the flux calculations for each sample, which for the cutting fluids, rust preventative oil, and as normalized samples were based on the weight gain during carburizing, the length of carburizing time, and the surface area of each sample. For the oxidized samples, the flux came from the empirical OES carbon curves. The flux, the material properties, and the vacuum carburizing information, such as the recipe, were input into the CarbTool software. The software produced predictions on the carbon profile which were then compared to the profiles formed with the OES data. The result of these comparisons, found in Appendix 5: Combined HV, CarbTool, and empirical carbon profiles, was that the CarbTool accurately predicted the carbon profile.

4.6 Combined hardness and carbon profiles
The Vickers hardness and carbon profiles were plotted together as a function of depth into the sample, as seen in Appendix 5: Combined HV, CarbTool, and empirical carbon profiles. The two axis were matched so that the desired case depths of HV=513 and weight fraction of carbon=0.35 were aligned. The relationship between the microhardness and the carbon profile was compared for equivalent depths into the sample, as represented in Figure 13. This corresponds to data done by Shingo and Takehito determining that the hardness is proportionally related to the carbon concentration at levels below 0.6wt%; above that concentration, however, the hardness and weight percent carbon do not correlate (Shingo & Takehito, 2000). In this research, 0.6wt% carbon would be at a depth of approximately 0.65 to 0.8mm into the sample.

![Graph showing the relationship between microhardness (HV) and weight percent of carbon (wt % C).](image)
Linear interpolation of the raw data was used to determine the case depths of the selected samples, as seen in Table 6. Case depths were determined using three sources: Vickers hardness values, carbon concentration, and the CarbTool predicted carbon concentration. The desired case depth was defined as a value of 50 on the Rockwell-C scale, which converted to a Vickers hardness value of 513, or at a concentration of 35-weight percent carbon at 0.9 mm (0.035 inches). The case depth of 0.9mm was not achieved for any of the samples, but the case depth values determined using CarbTool and the empirical values were consistent with each other. The case depths found using the Vickers hardness values were significantly higher than those from the other two methods. This is due to the dependence of the martensite hardness on the carbon concentration, which at these case depths would be below the 0.6wt% carbon level.

### Table 6: Calculated case depths

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>Case depth - HV (mm)*</th>
<th>Case depth - CarbTool (mm)**</th>
<th>Case depth - measured wt% C (mm)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>R1-nc</td>
<td>1.44</td>
<td>1.25</td>
<td>1.28</td>
</tr>
<tr>
<td>18</td>
<td>R1-c</td>
<td>1.37</td>
<td>1.19</td>
<td>1.20</td>
</tr>
<tr>
<td>91</td>
<td>R2-nc</td>
<td>1.39</td>
<td>1.22</td>
<td>1.27</td>
</tr>
<tr>
<td>95</td>
<td>R2-c</td>
<td>1.45</td>
<td>1.23</td>
<td>1.24</td>
</tr>
<tr>
<td>53</td>
<td>R3-nc</td>
<td>1.49</td>
<td>1.23</td>
<td>1.25</td>
</tr>
<tr>
<td>21</td>
<td>R3-c</td>
<td>1.37</td>
<td>1.15</td>
<td>1.16</td>
</tr>
<tr>
<td>98</td>
<td>R4-nc</td>
<td>1.40</td>
<td>1.23</td>
<td>1.26</td>
</tr>
<tr>
<td>100</td>
<td>R4-c</td>
<td>1.37</td>
<td>1.25</td>
<td>1.24</td>
</tr>
<tr>
<td>99</td>
<td>R4-c</td>
<td>1.47</td>
<td>1.24</td>
<td>1.26</td>
</tr>
<tr>
<td>58</td>
<td>HCF-nc</td>
<td>1.43</td>
<td>1.27</td>
<td>1.28</td>
</tr>
<tr>
<td>62</td>
<td>HFC-c</td>
<td>1.31</td>
<td>1.27</td>
<td>1.31</td>
</tr>
<tr>
<td>103</td>
<td>HFC-c</td>
<td>1.18</td>
<td>1.17</td>
<td>1.09</td>
</tr>
<tr>
<td>86</td>
<td>CCF-nc</td>
<td>1.30</td>
<td>1.25</td>
<td>1.26</td>
</tr>
<tr>
<td>106</td>
<td>CCF-c</td>
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<td>1.29</td>
<td>1.20</td>
</tr>
<tr>
<td>82</td>
<td>CCF-c</td>
<td>1.34</td>
<td>1.24</td>
<td>1.25</td>
</tr>
<tr>
<td>15</td>
<td>RPO-nc</td>
<td>1.48</td>
<td>1.27</td>
<td>1.25</td>
</tr>
<tr>
<td>8</td>
<td>RPO-nc</td>
<td>1.44</td>
<td>1.26</td>
<td>1.23</td>
</tr>
<tr>
<td>43</td>
<td>RPO-c</td>
<td>1.30</td>
<td>1.27</td>
<td>1.23</td>
</tr>
<tr>
<td>101</td>
<td>RPO-c</td>
<td>1.27</td>
<td>1.25</td>
<td>1.20</td>
</tr>
<tr>
<td>10</td>
<td>as normalized</td>
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<td>1.22</td>
</tr>
<tr>
<td>61</td>
<td>as normalized</td>
<td>1.37</td>
<td>1.28</td>
<td>1.22</td>
</tr>
</tbody>
</table>

*Case depth assuming Rockwell-C=50 or HV=513

**Case depth assuming 35wt%C
4.7 Metallography

Selected samples were etched with nital, a common etchant for ferrous metals, and examined with an optical microscope. The photo-micrographs of the samples can be seen in Appendix 6: Metallography. There did not appear to be a visual difference between the contaminated and non-contaminated samples or the cleaned and not cleaned samples. The samples’ edges consisted of tempered martensite with little retained austenite, which was expected to be seen, and the center of the samples looked like Figure 14.

![Figure 14: Sample 58 - Sample center at 50X (left) and 2700X (right)](image)

Since the features seen were similar for all of the cases, only two were selected for further examination using an SEM. The work done in the SEM provided high magnification pictures as well as the ability to use energy-dispersive X-ray spectroscopy (EDS) which uses the x-rays that are emitted from target atoms after they are struck by electrons from a SEM electron beam (Thomann, 2001). EDS was utilized to identify the elements in the suspected carbide features found during the examination with the optical microscope as well as the suspected sooted carbon deposits on the oxidized samples.

The large amount of precipitates, as seen in Figure 15, that were found at the sample corners and on some samples very close to the edges were investigated. Using EDS, these were confirmed to be chromium carbides, as seen in Figure 16. However, it was also suspected that there were iron carbides, most likely $\text{Fe}_3\text{C}$, present, which can be supported by examining the phase diagram as seen in Figure 1 and the concentration of carbon at the surface of the sample versus carburization time, as seen in CarbTool, or the concentration of carbon as a function of time and position. Examples of the figure seen in CarbTool can be seen in Figure 4 and the plot of concentration of carbon versus time and position can be seen in Figure 17. Through EDS, it was determined that iron carbides were also present in the samples, as seen in Figure 16. The precipitates formed especially at the corners of the samples because that was where the carbon was saturated during the preliminary carburizing stages and have less access to the core since that is where two carburizing surfaces come together (Davis & al., 1991). While a network of these precipitates can be unfavorable when considering bending fatigue and the fracture
performance of a material, they can be also be deemed beneficial since they increase the parts’ resistance to abrasive wear (Davis & al., 1991), which is important in the case of gears.

Figure 15: Carbide features at the corner of sample 58: 20X (top left), 1300X (top right), 5500X (bottom)
chromium carbide

steel matrix
Figure 16: EDS analysis of carbides on sample 58
Carbides are formed during the carburization process, but the size and distribution of these carbides can be modified during the post-carburizing processing, especially during quenching and cryotreatment. Cryotreatment in particular leads to a greater distribution of carbides (Bensely, Prabhakaran, Mohan Lal, & Nagarajan, 2005). It is also suggested that submicroscopic carbides form during this process which helps alleviate some of the internal stresses caused by the $\gamma \rightarrow \alpha$ phase transformation. It is suggested that this reduction in internal stress may be the mechanism through which the materials have better properties (Davis & al., 1991). Regardless, many of the carbides are removed in the post-carburization final machining step of the process.

EDS also confirmed that the black discoloration on the oxidized samples in place of the rust prior to carburization was indeed carbon sooted onto the rust’s rough surface area. This can be seen in Figure 18. This was predicted due to the high carbon concentration in the furnace and on the sample surface.
4.8 Retained austenite
The XRD spectra were consistent for all of the selected samples that were examined, as seen in Appendix 7: XRD spectra. The calculated retained austenite levels, as seen in Table 7, were between 11.0 and 14.3, and with the anomaly samples excluded, the range was much tighter – 12.2 to 14.3 with the exception of sample 95 R2-c with 11.7 percent RA. A correlation between percentage of retained austenite and the different contaminants or the cleaned and non-cleaned samples was not apparent. The only exception was that the anomaly samples constituted 5 of the 6 lowest values of retained austenite. This was not thought to be significantly relevant due to the small scale of difference between
all of the samples. Therefore, differences between contaminants and cleanliness levels did not seem to have a significant effect on the retained austenite levels of vacuum carburized AISI 9310 steel.

Table 7: Percentage of retained austenite by contamination category

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>R1-nc</td>
<td>13.2</td>
</tr>
<tr>
<td>18</td>
<td>R1-c</td>
<td>12.5</td>
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<tr>
<td>91</td>
<td>R2-nc</td>
<td>14.0</td>
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<tr>
<td>95</td>
<td>R2-c</td>
<td>11.7</td>
</tr>
<tr>
<td>53</td>
<td>R3-nc</td>
<td>12.2</td>
</tr>
<tr>
<td>21</td>
<td>R3-c</td>
<td>14.3</td>
</tr>
<tr>
<td>98</td>
<td>R4-nc</td>
<td>12.3</td>
</tr>
<tr>
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<td>58</td>
<td>HCF-nc</td>
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<td>12.9</td>
</tr>
<tr>
<td>103</td>
<td>HFC-c</td>
<td>11.9</td>
</tr>
<tr>
<td>86</td>
<td>CCF-nc</td>
<td>13.3</td>
</tr>
<tr>
<td>106</td>
<td>CCF-c</td>
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<tr>
<td>61</td>
<td>as normalized</td>
<td>13.2</td>
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</table>

4.9 Summary of results

After extensive testing and analysis, the following conclusions have been made about the effect of contamination on vacuum carburizing of AISI 9310 steel and the effectiveness of current cleaning methods:

- Cleanliness tests:
  - Black light: inconclusive and impractical for applications outside of the laboratory
  - White towel and Scotch tape: not viable except for already visible oxidation
- Visual appearance:
  - All samples lost their luster post-carburization – expected result
  - As normalized samples – no difference post-carburized versus pre-carburized
  - Rusted samples – all burnt-orange to brown colored rust changed to black rust after carburization. Post-carburization results:
    - Rusted 2 days – no visual rust
- Rusted 4 days and cleaned – no visual rust (except 1 sample) on the samples’ faces but some on the sides
- Rusted 4 days and not cleaned – visual rust on faces and sides
- Rusted 8 days and cleaned – darker shade of gray and less rust on faces than not cleaned samples
- Rusted 19 days and cleaned – darker shade of gray and more rust than not cleaned samples
  - HCF – cleaned and not cleaned same shade of dull gray. Not cleaned samples had a splotchy residue appearance
  - CCF – same as HCF-contaminated samples
  - RPO – no difference in cleaned versus not cleaned samples soon after carburization. After storage, however, the cleaned samples had significantly more dark-brown colored rust than the not cleaned samples
- Mass measurements and flux calculations: flux was difficult to accurately calculate for oxidized samples due to the unknown loss of rust during transport, but was calculated using the area under the carbon profile curve obtained by OES measurements. Flux for HCF, CCF, and RPO-contaminated samples can be considered accurate due to good agreement between the CarbTool, which used the flux calculation, and OES carbon profiles. No significant difference in carbon fluxes between cleaned and not cleaned samples, however, there was a greater flux in the rusted samples than the HCF, CCF, RPO, and as normalized samples which could be a result of a different method of flux calculation.
- Macrohardness (Rockwell-C): only varied between 61.4 and 62.3 – not significant
- Microhardness profiles (Vickers): no significant difference
- Metallography: no significant difference between contaminated and non-contaminated samples or cleaned and non-cleaned samples. Expected microstructures of tempered martensite with small amounts of retained austenite near the samples’ surfaces were seen. Extensive iron carbide networks were found at the corners of most samples and some samples had small individual carbides along the edges.
- Surface carbon: the weight percent of carbon was higher than expected on all sample surfaces, but was greater on oxidized samples and not cleaned HCF, CCF, and RPO samples. Varied between 0.78 and >1.68 with an average between 0.85-0.88 wt% C.
- Carbon profile: most samples except for the more heavily oxidized samples had good agreement between empirical results and those predicted using the flux inputted into CarbTool. Within the precision of the measuring equipment, there was no visible difference between the representative cleaned and not cleaned samples.
- Combined hardness and carbon profiles: case depths do not match the anticipated 0.9mm (0.035 inches), but rather 1.1-1.5mm. Case depths found using Vickers hardness measurements were consistently greater than the other measurements, but case depths found using the OES empirical profiles and the profiles predicted in CarbTool were comparable.
- Retained austenite: between 11 and 14% RA, no significant difference and no pattern regarding contaminant or cleanliness level
<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>$J_C$ (g/cm²*s)</th>
<th>Cs</th>
<th>HRC</th>
<th>RA (%)</th>
<th>Case depth - HV (mm)*</th>
<th>Case depth - CarbTool (mm)**</th>
<th>Case depth - measured wt% C (mm)**</th>
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</thead>
<tbody>
<tr>
<td>64</td>
<td>R1-nc</td>
<td>4.394E-06</td>
<td>0.92</td>
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<td>1.34</td>
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<td>1.22</td>
</tr>
</tbody>
</table>
5 Conclusions and recommendations

In the end, heat treaters are responsible for producing case-hardened pieces for a paying customer. From a financial prospective, it would be ideal if cleaning the parts was not necessary, saving the heat treating company cleaner purchasing and disposal costs, workers’ wages and for the extra time necessary to perform the cleaning, and time thus allowing for a higher throughput of parts. However, the quality is not purely based on the quantitative measurements, such as hardness and elemental analysis, but is also based on the end-product aesthetics. A splotchy discoloration due to a residual fluid on a final product making the new part appear used, for example, is undesirable to a customer. Therefore, this study concluded that the AISI 9310 steel parts do not need to be cleaned prior to vacuum heat treatment if further surface processing is necessary or if the surface finish is unimportant, thus saving the time and expense.

It is recommended that this work on the effects of contaminants and cleaning on vacuum carburized AISI 9310 steel be continued further. An investigation should be done about the extensive carbides, including work on the network mechanism for formation. Also, this project was unable to quantifiable identify the level of oxidation needed to deem cleaning the part necessary. This should be a point for further study, along with the mechanism for oxidation removal and the interface between the oxide layer and the diffusing carbon into the steel. It is also suggested that the procedure presented in this research be duplicated with the oxidized samples except include a mass measurement directly before and after the carburization process in order to eliminate the uncertainty of weight loss due in transit.
6 References


Thermocalc. (n.d).


Appendix 1: Retained austenite calculation program made in Microsoft Excel

<table>
<thead>
<tr>
<th>Sample 64</th>
<th>R1-nc</th>
</tr>
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<tbody>
<tr>
<td>Element:</td>
<td>α Martensite</td>
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<tr>
<td>Structure:</td>
<td>BCC</td>
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<tr>
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<td>a = 2.87 (averaged a &amp; c)</td>
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<tr>
<td>Radiation:</td>
<td>Cr</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>λ_0/λ_e</th>
<th>Fe λ_e</th>
<th>λ_0/λ_e *n_e</th>
<th>Δf</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.291</td>
<td>1.74346</td>
<td>1.314054</td>
<td>-21.1</td>
<td>23.6399</td>
</tr>
</tbody>
</table>

| h | k | l | h_v+b_v+½l_v | h_u+b_u+½l_u | 2B | Sin θ | Sin 2θ/A | t_p | f | θ | a | b | F^2 | e²⁰⁻²⁰ | L-P | p | R |
|---|---|---|---------------|---------------|----|-------|--------|------|----|----|----|----|----|--------|--------|-----|----|----|
| 0-200 | 2 | 0 | 0 | 0 | 1 | 105.63 | 0.79666817 | 0.347477 | 14.50182 | 12.40182 | 24.60354 | -35.15 | 615.2207 | 0.926 | 2.796012 | 6 | 17.10176 |
| 0-211 | 2 | 1 | 1 | 0 | 2 | 153.64 | 0.9774898 | 0.426005 | 12.84669 | 10.74069 | 21.491589 | -5.3813 | 401.90538 | 0.886 | 9.077101 | 24 | 159.535 |

| Element: | γ Austenite |
| Structure:| FCC   |
| Lattice parameters: | a = 3.6 |
| Radiation: | Cr |

<table>
<thead>
<tr>
<th>λ_0/λ_e</th>
<th>Fe λ_e</th>
<th>λ_0/λ_e *n_e</th>
<th>Δf</th>
<th>V</th>
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</table>

| h | k | l | h_v+b_v+½l_v | h_u+b_u+½l_u | 2B | Sin θ | Sin 2θ/A | t_p | f | θ | a | b | F^2 | e²⁰⁻²⁰ | L-P | p | R |
|---|---|---|---------------|---------------|----|-------|--------|------|----|----|----|----|----|--------|--------|-----|----|----|
| γ-200 | 2 | 0 | 0 | 0 | 1 | 11 | 78.12 | 0.638886 | 0.277955 | 14.10612 | 14.06012 | 56.02649 | -8.68383E-15 | 3138.783 | 0.955 | 3.011689 | 6 | 27.35182 |
| γ-220 | 2 | 2 | 0 | 0 | 2 | 1 | 11 | 128.96 | 0.902435 | 0.393904 | 11.4402 | 11.9402 | 45.3608 | -1.11147E-14 | 2037.402 | 0.9 | 3.976975 | 12 | 40.59971 |

Continued on next page.
<table>
<thead>
<tr>
<th>Retained Austenite:</th>
<th>Peak I</th>
<th>Peak III</th>
<th>Peak II</th>
<th>Peak IV</th>
</tr>
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<td>989.94</td>
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<td>I(211)α</td>
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<tr>
<td>R(200)α</td>
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<tr>
<td>R(211)α</td>
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</table>

\[
\frac{I(200)_{\gamma}}{I(200)_{\alpha}} = \frac{R(200)_{\gamma} C_{\gamma}}{R(200)_{\alpha} C_{\alpha}} 0.234378
\]

\[
\frac{I(200)_{\gamma}}{I(211)_{\alpha}} = \frac{R(200)_{\gamma} C_{\gamma}}{R(211)_{\alpha} C_{\alpha}} 0.226671
\]

\[
\frac{I(220)_{\gamma}}{I(200)_{\alpha}} = \frac{R(220)_{\gamma} C_{\gamma}}{R(200)_{\alpha} C_{\alpha}} 0.075253
\]

\[
\frac{I(220)_{\gamma}}{I(211)_{\alpha}} = \frac{R(220)_{\gamma} C_{\gamma}}{R(211)_{\alpha} C_{\alpha}} 0.072778
\]

\[
(C_{\gamma}/C_{\alpha})_{\text{ave}} 0.15227
\]

\[
C_{\gamma} 0.132148 \text{ Percentage of retained austenite}
\]
Appendix 2: Macro-scale pictures comparing pre- and post-carburization
Pre-carburized samples

Post-carburized samples
Pre-carburized samples

Post-carburized samples
Pre-carburized samples

Post-carburized samples

As normalized
Appendix 3: Microhardness profiles

**Rust 2 days**

- Distance from surface (μm)
- Vickers hardness
- R1-nc
- R1-c

**Rust 4 days**

- Distance from surface (μm)
- Vickers hardness
- 18 R1-c
- 91 R2-nc

**Rust 7 days**

- Distance from surface (μm)
- Vickers hardness
- 95 R2-c
- 53 R3-nc

**Rust 19 days**

- Distance from surface (μm)
- Vickers hardness
- 98 R4-nc
- 99 R4-c
- 100 R4-c
**Hot Cutting Fluid**

- 58 HCF-nc
- 62 HCF-c
- 103 HCF-c
- 61 As annealed

**Cold Cutting Fluid**

- 86 CCF-nc
- 82 CCF-c
- 106 CCF-c
- 61 As annealed

**Rust Preventative Oil**

- 8 RPO-nc
- 15 RPO-nc
- 43 RPO-c
- 101 RPO-c
- 61 As annealed
Appendix 4: Empirical OES carbon profiles

Rust 2 days

Rust 4 days

Rust 7 days

Rust 19 days
Contaminant: HCF

Contaminant: CCF

Contaminant: RPO

Contaminant: Oxidation
Appendix 5: Combined HV, CarbTool, and empirical carbon profiles

Note: “X” = Case depth of 0.35 weight fraction carbon and “-” = Case depth of 513 HV
Appendix 6: Metallography

Sample 98 (R4-nc)

Sample 99 (R4-c)
Sample 100 (R4-c)

Sample 58 (HCF-nc)
Sample 82 (CCF-c)

Sample 10 (as norm)

No corner photo available.
Appendix 7: XRD spectra

![XRD spectra graph]

- Sample 64
- Sample 18
- Sample 91
- Sample 95
- Sample 53
- Sample 21
- Sample 98
- Sample 99
- Sample 100
- Sample 58
- Sample 103
- Sample 62
- Sample 86
- Sample 82
- Sample 106
- Sample 15
- Sample 8
- Sample 43
- Sample 101
- Sample 10
- Sample 61