Specifying Nitriding Process Requirements

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Abstract

Discovering microstructural features of white layer in a nitrided part has appealed to many scientists and researchers. A slight change in microscopic properties can bring a huge difference in their macro-scale behavior. A thorough knowledge of the compound (the white layer) and of the diffusion zone will enable materials scientists to monitor the grain size (the phases within the material), which alter the macro-scale toughness and strength and finally the amount of porosity.

Unlike carburizing, which is a more matured technology, nitriding specifications are genetically stated as surface hardness and hardness at depths. No constituents or type and percent of compounds are mentioned.

This paper will attempt to address methodologies used to identify different constituents of both the compound and the diffusion layers of a nitrided part. Three different materials have been heat treated for this study. Three different methods of investigation were used: optical microscopy, electron dispersive spectroscopy (EDS) and electron probe microanalysis (EPMA).

This is the beginning of a series of investigations which are underway. In this article, information already known will be the starting point. In future articles, more in depth investigation of the white layer and of the diffusion zone will be shown.

Introduction

Investigation of microstructural features of white layer in a nitrided part has appealed to many metallurgists and researchers for quite some time. It was noticed that a slight change in microscopic properties could bring a significant difference in their macro-scale behavior. A thorough knowledge of compound layer and diffusion zone could enable materials scientists to monitor the grain size, the phases within the material, which alter the macro-scale toughness and strength and finally the amount of porosity. A sketch designating the areas of interest and investigation is shown below (Figure 1).

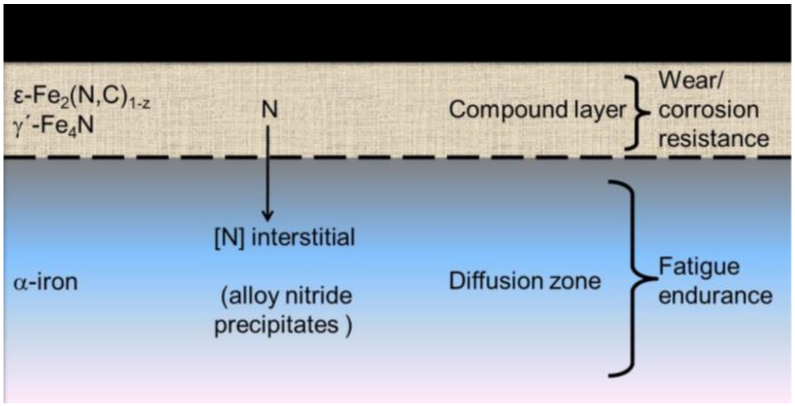


Figure 1. Schematic of the compound layer and diffusion zone structure of nitrided iron/steel [1].

In carburizing, requirements such as percent retained austenite, the amount of desired martensite in critical areas and depths, or allowable bainite, and other similar requirements, are often times specified. These specifications are based on tests, validations and experience or lessons learned.

Unlike carburizing, which is a more matured technology, nitriding specifications are mostly generically stated with a given surface hardness requirement and specified hardness at depths (effective case depth) only. No constituents or type and percent of compounds are mentioned, although, as shown in Figure 1, the compound layer is a mixture of two phases, epsilon phase ε-$Fe_2(N,C)_{1-z}$ and gamma prime phase γ'-Fe_4N. For example, the ε percent, which is harder and has a different expansion coefficients ratio than γ', is not mentioned in any specification; this is unfortunate, since the ε to γ' ratio is a factor for low distortion of the nitrided case. Neither is the depth to which these layers would diffuse. The main hurdle is the ability to identify the different constituents in compound layer or the diffusion layer.

This paper will address the use of several methodologies to identify different micro constituents of both the compound and of the diffusion zone of a nitrided part. Three different materials were heat treated for this study but the main focus has been a nitrided 4140 gear. Once the process has proved viable it will be applicable to other heat treated nitrided parts.

Background on Nitriding

A brief background of nitriding process evolution is shared with the readers. In the early 20th century, Adolph Machlet, of American Gas in New Jersey patented the nitriding process. But it is only in recent years we have seen advancement of this process in the USA. It is Adolph Fry, a German scientist that has made this process more acceptable in the industry. The difference between the US and German processes is that the US process used hydrogen as a diluting gas to control the nitriding potential (ability to nitride), while the German method relied more on alloying elements, core hardness and tensile strength.
Nitriding can be a single step process or a two-step process (Floe process).

A surface exposed to a nitriding medium will generally form two distinct layers. The outside layer is called the compound layer (or white layer) and its thickness generally falls between zero and 0.001" (25 μm). Underneath the white layer a diffusion case or diffusion zone exists. Both the white layer and diffusion zone together comprise what is generally referred to as the case. The photomicrograph in Figure 2 shows the diffusion zone as dark color, and the white compound layer with a dark oxide coat on top. The nitrided case can be etched with other reagents, producing identifiable colors on the microstructure (Fig 2, ref 2).

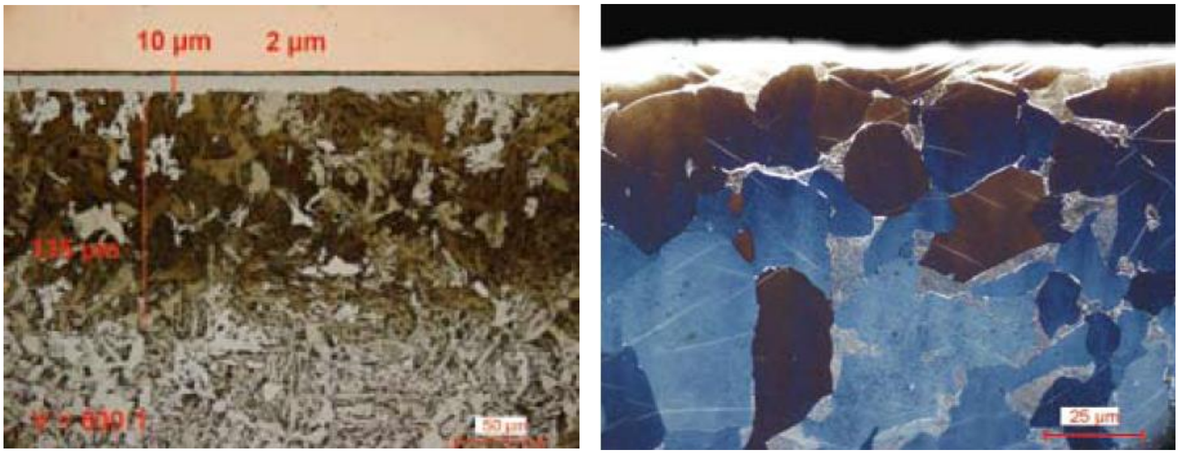


Figure 2. Illustration of a nitrided case. Left: Alloyed steel, nitro carburized, etched with 1% Nital [2]. Right: Nitrided steel, color etched with Beraha's reagent [2].

In recent years, the nitriding process control has moved from controlling the ammonia dissociation to controlling the nitriding potential, since the equilibrium concentration of nitrogen in the alloy and the existence of particular phases in the nitride layer is related to the nitriding potential and temperature. This has greatly improved the prediction of the results and ensured the reliability of the nitriding process. But what is missing is a definition of the process parameters based on the performance specifications. There has not been a defined micro-constituent requirement based on performance review. The standard practice is to specify surface hardness and effective case depth only; however, the heat treating community needs an effective tool to predict the nitriding performance for a wide variety of steels, similar to what is done for carburizing specification. In this paper, the nitrogen concentration profile has been chosen as the standard measurement criteria to determine the effectiveness of the nitriding process.

Experimental Work and Results

The purpose of this investigation was to choose the best reliable method to determine the variation of the nitrogen content in the white layer and the diffusion zone produced by nitriding, and to study the morphology of the white layer. Later investigation will be focused on carbon distribution within the two layers. Once the investigation reveals the best measurement process and equipment, further tests will be conducted accordingly.

Three materials: *Ductile Iron 100-70-30*, *AISI 4140 Alloy Steel* and *AISI M2 High Speed Tool Steel* (see Table 1) were chosen because they are often found in applications that require good strength and tribological characteristics and are therefore subjected to nitriding. Also they cover a large range of microstructures and constituents and, as a result, the effect of nitrogen diffusion on the morphology and chemistry of the material is expected to become more readily apparent.

Table 1. Chemical Composition of the Investigated Materials, Wt. %

Specimen	C	Si	Mn	S	P	Cr	Ni	Cu	W	Mo	V
Ductile Iron 100-70-30	3.50-3.90.	2.25-3.00	0.15-0.35	0.025 max	0.05 max						
AISI 4140 Carbon Steel	0.38-0.43	0.15-0.30	0.75-1	0.04	0.035	0.8-1.10				0.15-0.25	
AISI M2 High Speed Tool Steel	0.78-1.05	0.20-0.45	0.15-0.40	0.03	0.03	3.75-4.50	0.3	0.25	5.50-6.75	4.50-5.50	1.75-2.20

The investigation consisted of metallographic analysis of the specimens using optical microscopy and scanning electron microscopy (SEM) to observe the morphology of the nitrided layer. Energy Dispersive Spectroscopy (EDS) and Electron Probe Microanalysis (EPMA) were used to semi-quantitatively (EDS method) and quantitatively (EPMA method) determine the elemental percentage of nitrogen and its distribution in certain fields of view within the nitrided layer. EDS was utilized for all specimens, while EPMA only for the *AISI 4140 Alloy Steel* (gear material). The results are shown as *EDS Site Analysis*, which quantifies the X-Ray spectra generated from an entire chosen site; as *EDS Line Analysis* and *EPMA Line Analysis,* which quantifies the X-Ray spectra generated from individual positions along an arbitrary line; and as *EDS Elemental Mapping* and *EPMA Elemental Mapping*, which shows the elemental distribution of elements (their position).

All the samples were examined after being cut in cross-section, prepared metallographically and either unetched or etched with nital 3%. Different instruments were utilized: a) the initial study used the metallograph Axiovert 200MAT Zeiss and the SEM Zeiss EVO MA25 equipped with X-Max Silicon Drift Detector (SDD) for EDS analysis; b) the second study used the Scanning Electron Microscope, HITACHI, model S4800 also for EDS analysis; and c) the third study used the Electron Probe Microanalysis CAMECA, model SX 100 for EPMA analysis.

Initial Study – EDS Analysis

Specimen *Ductile Iron 100-70-30*

This material is basically a composite between pearlitic steel and nodular graphite particles. The cross-section microstructure of the nitrided *Ductile Iron 100-70-30* specimen is given in Figure 3. The thin white layer follows the contour of the free surface, engulfing the graphite particles but not interacting with them. The white layer has two different regions, or sub layers: the greyish/ white outer layer, rich in both nitrogen and oxygen and the white inner layer, deprived of oxygen (see Figure 4). Most likely the greyish/ white outer layer indicates slight superficial iron oxidation. From Figure 4 it is apparent that the white layer has an average nitrogen concentration of approximately 7.5wt%N, while the amount of nitrogen in the diffusion zone decreases to approximately 4wt%N. In Figure 5 the variation of nitrogen is again observed, however in more discrete manner. The nitrogen distribution in the white layer and diffusion zone is further shown in Figure 6.

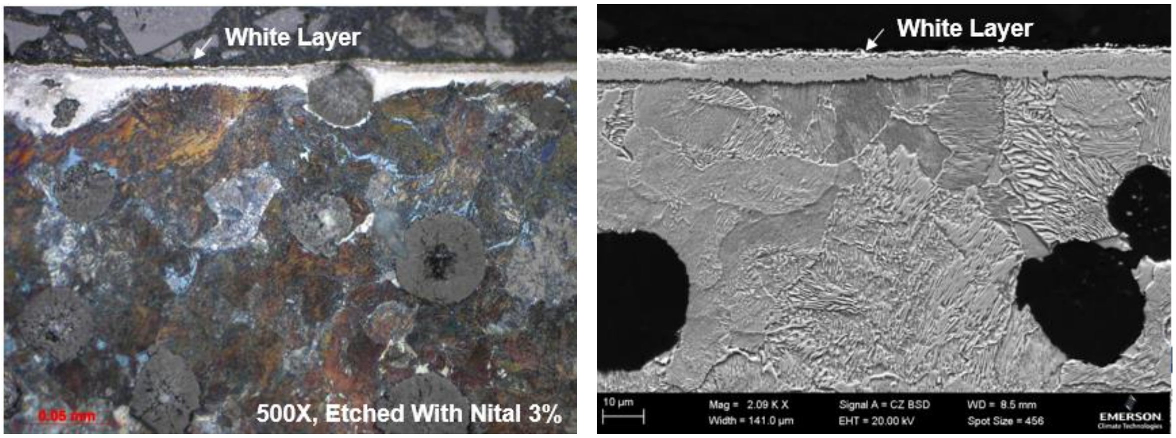


Figure 3. Cross-section microstructure of the nitrided Ductile Iron 100-70-30 specimen. Left: optical microscopy image. Right: electron microscopy image.

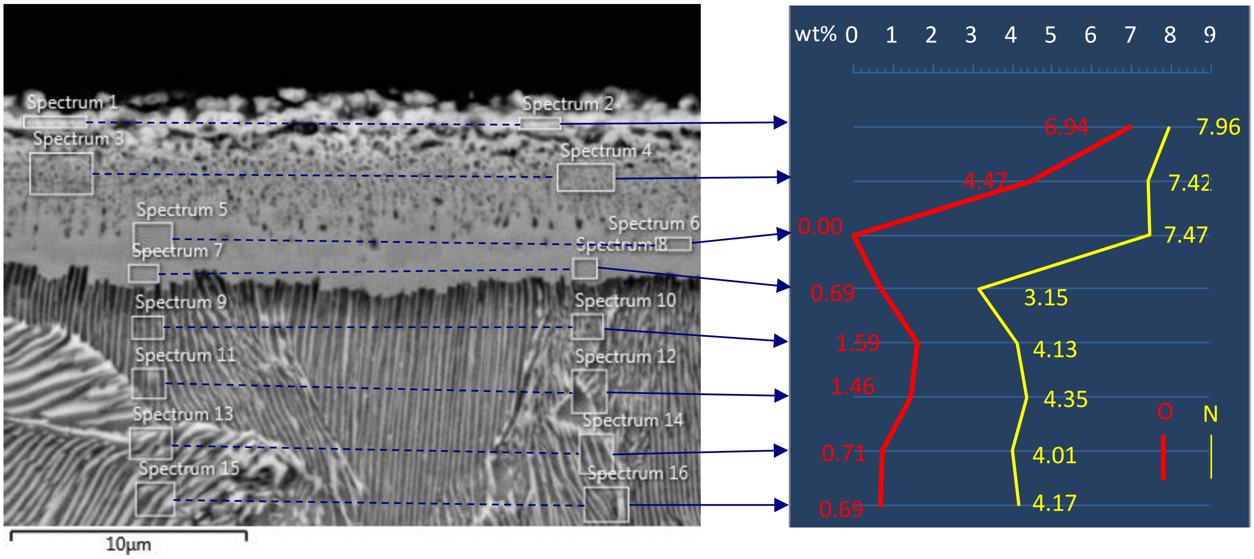


Figure 4. EDS Site Analysis of the cross-section microstructure of the nitrided Ductile Iron 100-70-30 specimen. Left: position of the sites. Right: nitrogen and oxygen percentage corresponding to various sites from left (each value is an average of two readings, see Table 2).

Table 2. Nitrogen and Oxygen Content in Sites 1 to 16 from Figure 2, Wt. %

Spectrum Average	N	O
Spectrum 1, 2	7.96	6.94
Spectrum 3, 4	7.42	4.47
Spectrum 5, 6	7.47	0.00
Spectrum 7, 8	3.15	0.69
Spectrum 9, 10	4.13	1.59
Spectrum 11, 12	4.35	1.46
Spectrum 13 , 14	4.01	0.71
Spectrum 15, 16	4.17	0.69

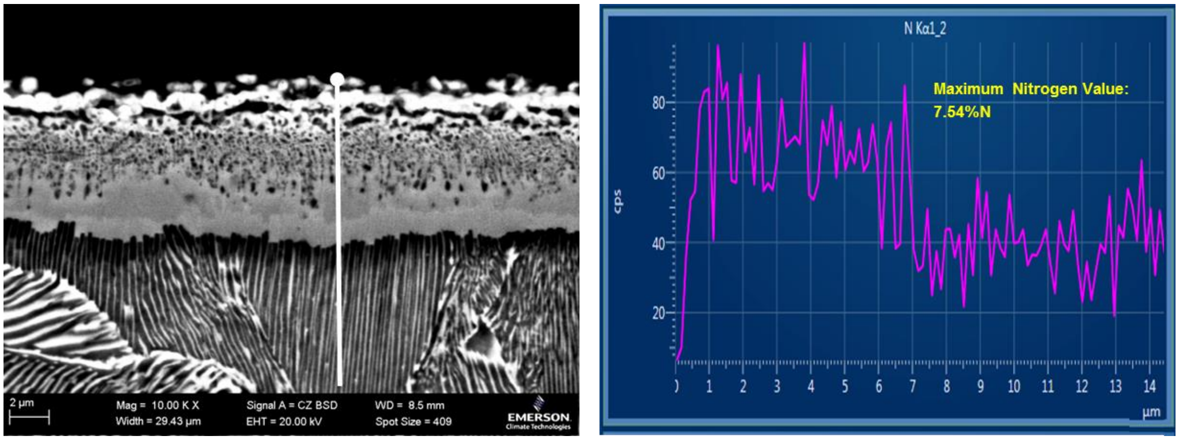


Figure 5. EDS Line Analysis of the cross-section microstructure of the nitrided Ductile Iron 100-70-30 specimen. Left: position of the line. Right: nitrogen variation along the line at left. Note that the end of line is still in the diffusion zone.

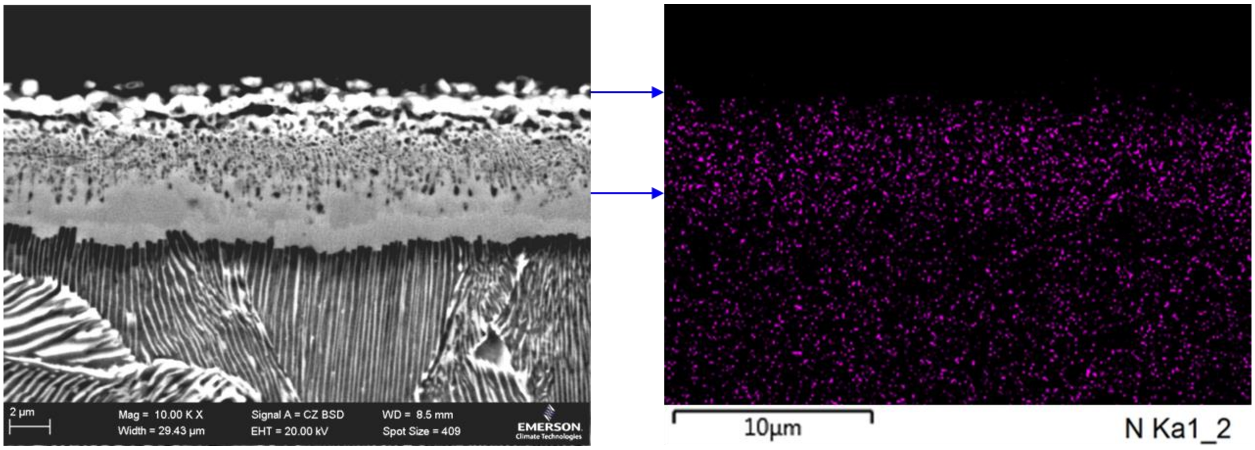


Figure 6. EDS Elemental Mapping of the cross-section microstructure of the nitrided Ductile Iron 100-70-30 specimen. Left: secondary electron image. Right: nitrogen dot map of the same field of view (magenta dots indicate presence of nitrogen).

After concluding the prior investigation, it was decided to limit the methods of investigation only to *EDS Site Analysis* and *EDS Line Analysis* for the *AISI 4140 Alloy Steel* and *AISI M2 High Speed Tool Steel* specimens. The *EDS Elemental Mapping* results were not included in this study, since they did not reveal more significant information than the one acquired using the other two methods.

Specimen *AISI 4140 Alloy Steel*

This common gear material with a tempered martensite core was gas nitrided. The cross-section microstructure of the nitrided *AISI 4140 Alloy Steel* specimen is given in Figure 7. After nitriding, the white layer is extended along the grain boundaries toward the core. This is even more apparent in Figure 8, where the *EDS Line Analysis* clearly shows the increase in nitrogen content along the grain boundary. Although optically the white layer may appear very uniform, more subtle feature can be distinguished at higher magnification. The layer has some areas that are harder and slightly richer in nitrogen content than others; they appear elevated and bright in Figure 9, as opposed to dark, recessed areas that are slightly softer (were polished at a deeper level) and contain less nitrogen. Most likely these are sub grains having slightly different orientation. It is apparent that the white layer and the diffusion zone have approximately the same average nitrogen concentration as the similar zones in the *Ductile Iron 100-70-30* specimen.

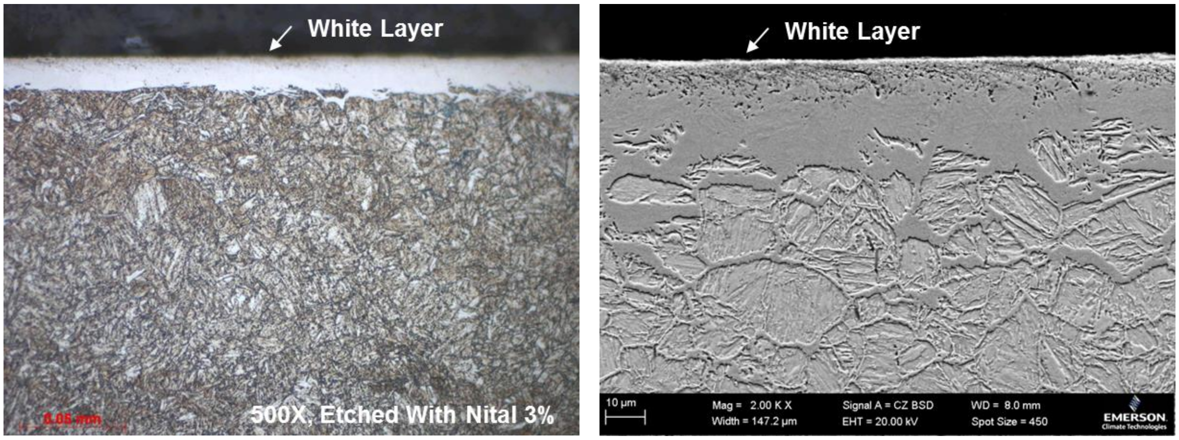


Figure 7. Cross-section microstructure of the nitrided AISI 4140 Alloy Steel specimen. Left: optical microscopy image. Right: electron microscopy image.

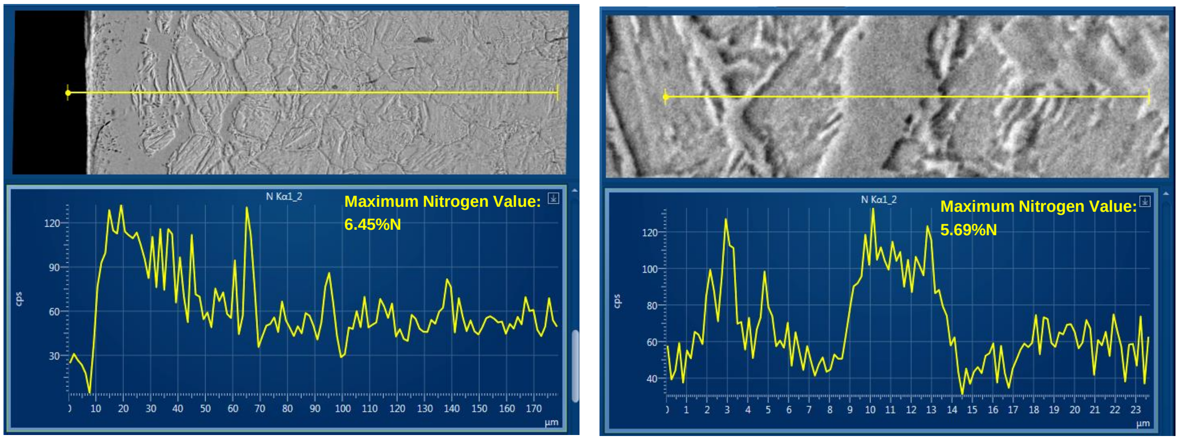


Figure 8. EDS Line Analysis of the cross-section microstructure of the nitrided AISI 4140 Alloy Steel specimen showing the grain boundary effect. Left: position of the line and nitrogen variation along the line at low magnification. Right: close-up from left, clearly showing the increase in nitrogen content along the grain boundary.

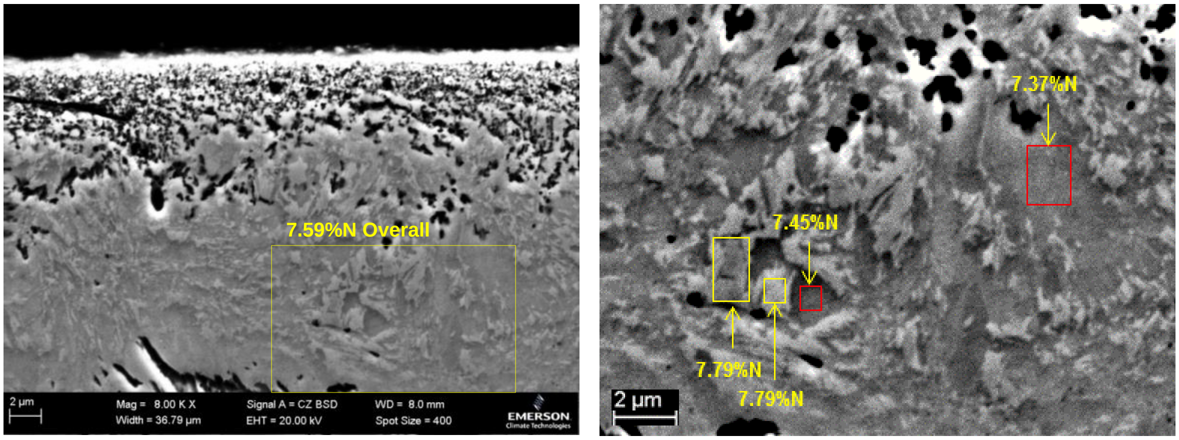


Figure 9. EDS Site Analysis of the cross-section microstructure of the nitrided AISI 4140 Alloy Steel specimen showing the variation in morphology and nitrogen content within the white layer. Left: area having 7.59%N overall. Right: close-up from left showing elevated, brighter areas having slightly higher nitrogen content than the dark recessed areas.

Specimen *AISI M2 High Speed Tool Steel*

This is a heavily alloyed steel, with a tempered martensite microstructure at the core and alloyed carbides uniformly distributed throughout the section. The cross-section microstructure of the nitrided *AISI M2 High Speed Tool Steel* specimen is given in Figure 10. The white layer is very thin or missing at the surface, most of it being observed as a subsurface network of white compound; by contrast, the diffusion zone appears to be well established, with the nitrogen profile having a slow slope from the surface towards the core (see the nitrided case in Figure 11 and Figure 12). The same conclusion can be reached by studying Figure 13: the nitrogen profile indicates a relatively small gradient of nitrogen between the white compound and the matrix. This may be caused by the presence of molybdenum, which is a carbide former. It is apparent that the white layer and the diffusion zone have approximately one percent lower average nitrogen concentration as the similar zones in the *Ductile Iron 100-70-30* and *AISI 4140 Alloy Steel* specimens, most likely also due to the presence of molybdenum in the composition.

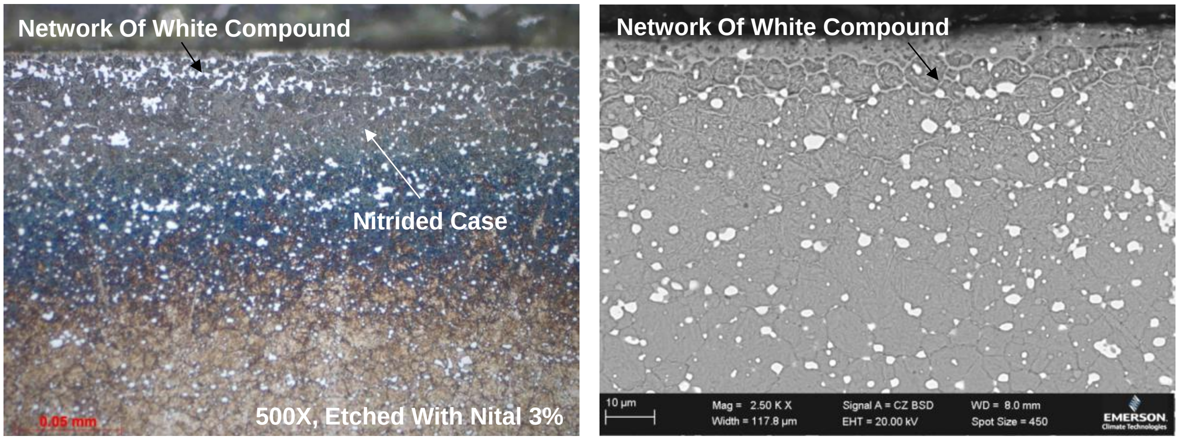


Figure 10. Cross-section microstructure of the nitrided AISI M2 High Speed Tool Steel specimen. Left: optical microscopy image. Right: electron microscopy image.

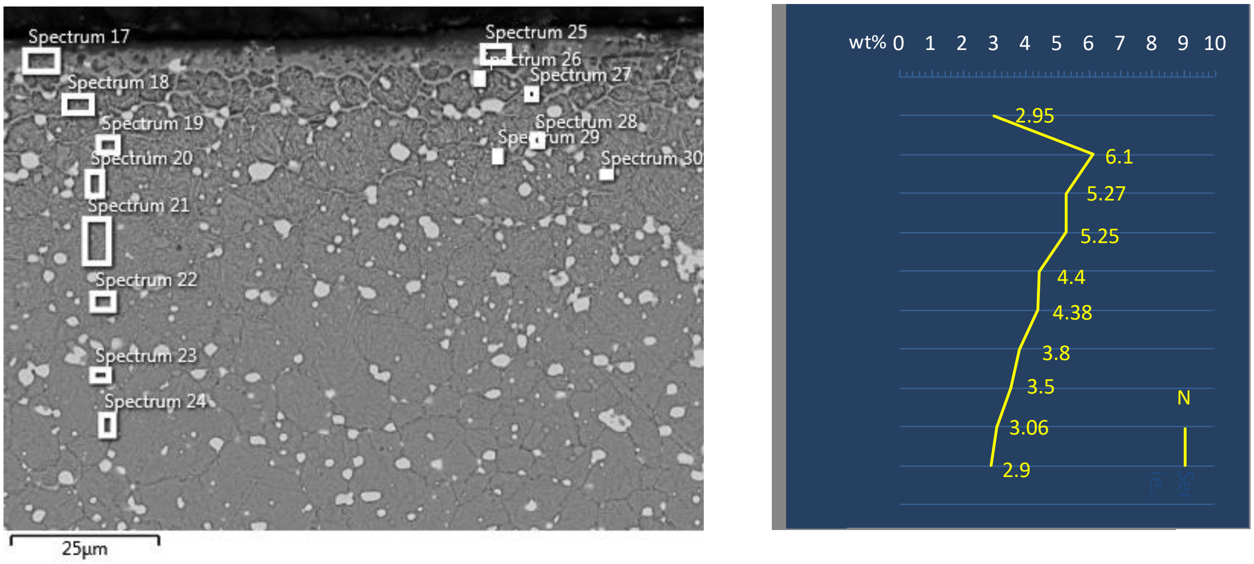


Figure 11. EDS Site Analysis of the cross-section microstructure of the nitrided AISI M2 High Speed Tool Steel specimen. Left: position of the sites. Right: nitrogen percentage corresponding to various sites from left (some values are an average of two or three readings, see Table 3).

Table 3. Nitrogen Content in Sites 17 to 29 from Figure 9, Wt. %

Spectrum Average	N
Spectrum 17	2.95
Spectrum 25, 26	6.10
Spectrum 27, 28, 29	5.27
Spectrum 18	5.25
Spectrum 19	4.40
Spectrum 20	4.38
Spectrum 21	3.80
Spectrum 22	3.50
Spectrum 23	3.06
Spectrum 24	2.90

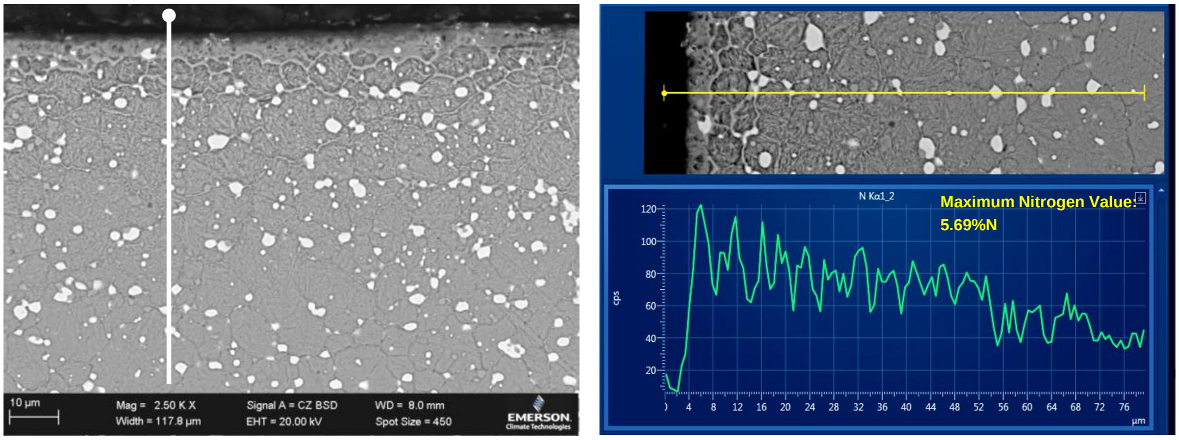


Figure 12. EDS Line Analysis of the cross-section microstructure of the nitrided AISI M2 High Speed Tool Steel specimen showing the slow decrease in nitrogen content throughout the diffusion zone. Left: position of the line. Right: nitrogen variation along the line at left.

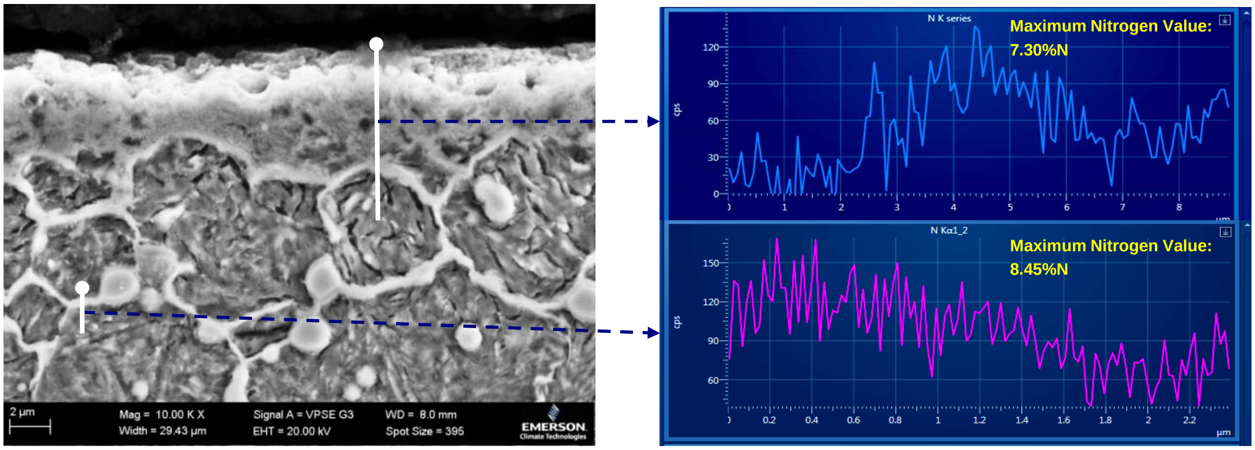


Figure 13. EDS Line Analysis of the cross-section microstructure of the nitrided AISI M2 High Speed Tool Steel specimen showing the relatively small gradient of nitrogen between the white compound and the matrix. Left: position of the lines at surface and at grain boundary. Right: nitrogen variation along the two lines.

Second Study – EDS Analysis

The Scanning Electron Microscope HITACHI model S4800 was used for a second investigation. The cross section shown in Figure 14, left, is from the same gear investigated in the initial study, except this is an adjacent location to verify the results from the first trial; ultimately the studies yielding more comprehensive results would be utilized for future investigation. Three regions in the gear were identified as critical areas, but only the *EDS Line Analysis* showing nitrogen variation at the nitrided gear flank are presented in Figure 14, right.

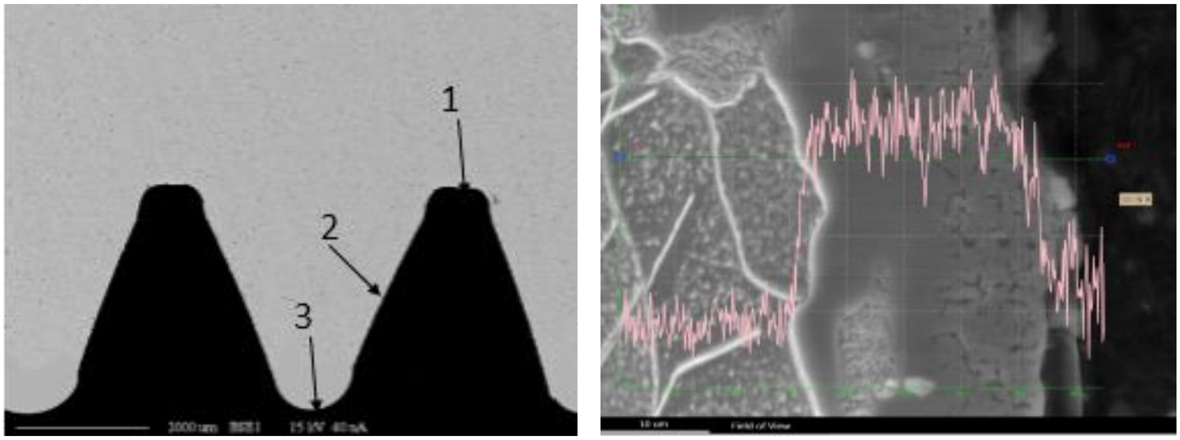


Figure 14. EDS Line Analysis of the cross-section microstructure of the AISI 4140 Alloy Steel nitrided gear specimen. Left: position of the line. Right: EDS Line Analysis showing nitrogen variation at the nitrided gear flank, Area 2 (the pink line). Notice the sharp drop in concentration at the grain boundary

Third Study – EPMA Analysis

Another method of measurement, Electron Probe Microanalysis (EPMA) was introduced to study the same nitrided gear investigated in the initial and second study. This is a much more precise analysis and delivers a quantitative measurement, not semi-quantitative as the EDS method. The EPMA measurements were conducted using the Electron Probe Microanalysis from the CAMECA, model SX 100.

EMPA was employed to assess the elemental distribution of nitrogen within the specimen by performing *EPMA Elemental Mapping* that also illustrates the large case depth variations (see Figure 15*)*. The nitrogen variation along the depth of the nitriding case and the thickness measurements of the nitrided layer was performed as *EPMA Line Analysis* for Area 6, where the corner effect is present (see Figure 16*)*.

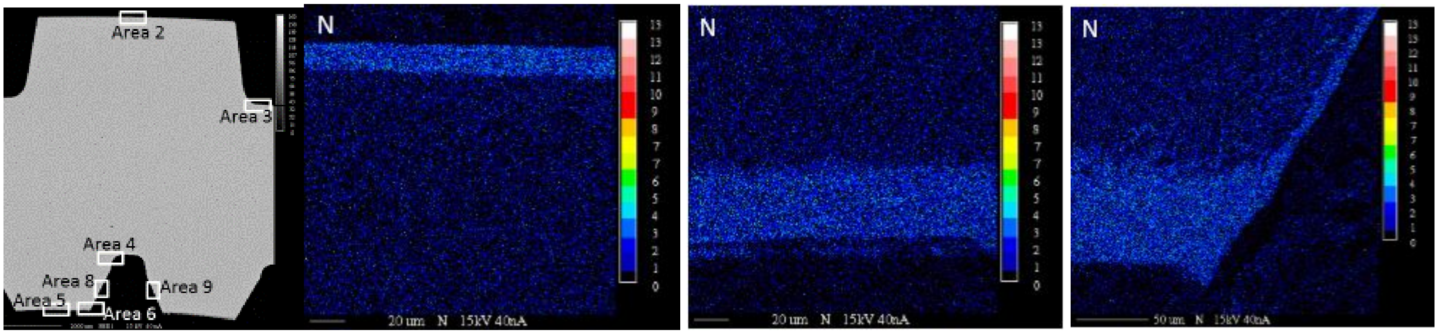
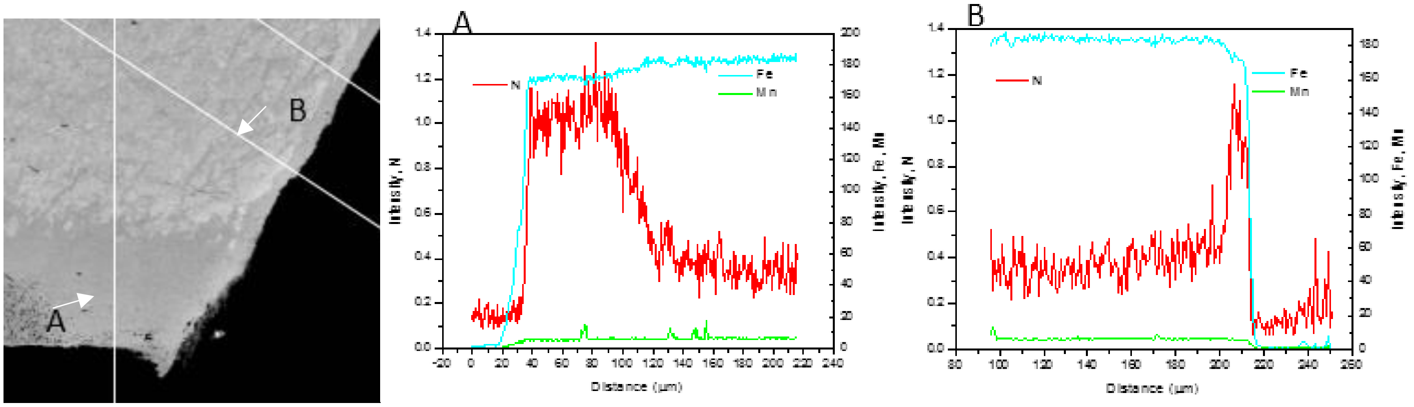


Figure 15. EPMA Elemental Mapping of the cross-section microstructure of the AISI 4140 Alloy Steel nitrided gear specimen. Left: position of the areas of measurements. Right: EPMA Elemental Mapping of Areas 2, 5 and 6 (from left to right), showing case depth variations. The right picture (Area 6) shows heavier nitrogen concentration at the corner of the gear.



Nitride layer thickness: 74 µm

Nitride layer thickness: 8 µm

Figure 16. EPMA Line Analysis of the cross-section microstructure of the AISI 4140 Alloy Steel nitrided gear specimen. Left: position of lines A and B. Center and Right: EDS Line Analysis showing large variation at the top (center graph) and flank (right graph) of the nitrided gear, both in terms of the nitrogen content and of the nitride layer thickness. The nitride layer thickness is 74 µm at the top and 8 µm at the flank of the gear.

Discussion

The goal of the paper was is to define the micro-constituents and nitrogen content of the white layer and of the diffusion zone of a nitrided part using the most appropriate methods of measurement. To this end, the investigation consisted on metallographic analysis of the specimens using optical microscopy and scanning electron microscopy (SEM) to observe the morphology of the nitrided layer, while the Energy Dispersive Spectroscopy (EDS) and Electron Probe Microanalysis (EPMA) methods were used to determine the elemental percentage of nitrogen and its distribution in certain fields of view within the nitrided layer.

The results were shown as *Site Analysis*, which quantifies the X-Ray spectra generated from an entire chosen site; as *Line Analysis*, which quantifies the X-Ray spectra generated from individual positions along an arbitrary line; and as *Elemental Mapping*, which shows the elemental distribution of elements (their position).

All employed methods showed that the percent nitrogen decreased from the surface to the core as shown in Figure 17. It is apparent from the investigation that that the white layer has an average nitrogen concentration of approximately 6-7wt%N, while the amount of nitrogen in the diffusion zone decreases to approximately 3-4wt%N. The amount of nitrogen incorporated into the case depends of the alloying elements of the matrix. Here carbon has a role and more explanation is given later in the section. But for now core hardness plays a part in the reaction. Typically core hardness in alloys for nitriding is maintained in the range of 28 to 32HRc. If the tempering temperature is increased to achieve lower core hardness for example to facilitate machining carbides are formed by combining carbon with Fe, Cr, W, Va and other alloys in solid solution essential to form good nitriding structure and hardness, thus lowering the nitrogen content of the nitrided case in these materials.

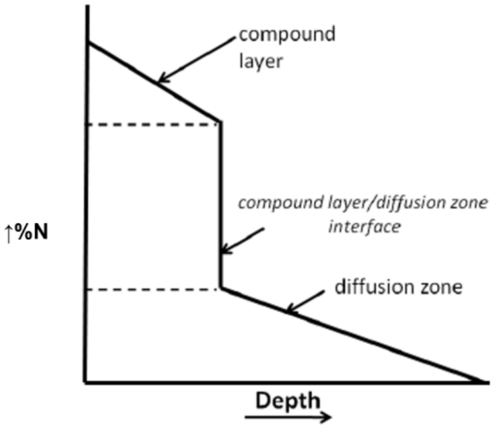


Figure 17. Illustration of the variation of nitrogen content with depth from the surface toward the core of the specimen.

The three materials that were chosen for investigation (pearlitic ductile iron, gear steel, tool steel) are often found in applications that require good strength and tribological characteristics and are therefore subjected to nitriding. Also they cover a large range of microstructures and constituents and, as a result, the effect of nitrogen diffusion on the morphology and chemistry of the material is expected to become more readily apparent.

Depending on material, the white layer may contain sub-layers with various nitrogen and oxygen content, or sub-grains having slightly different hardness, most likely due to their orientation. The white layer may be confined at the very free surface of the specimen, it may extended in filament form toward the core, or it may form a subsurface network of white compound, depending on the propensity of the microstructure to allow diffusion along the grain boundaries.

It appears that, for all practical purposes, all methods employed in this study were suitable to determine the nitrogen content within the nitrided case. Later investigation will be focused on carbon distribution within the two layers, since some amount of carbon present in solid solution (in austenite) participates in the formation of the epsilon phase ε-$Fe_2(N,C)_{1-z}$ during nitriding. The carbon content therefore determines the amount of ε formed: the higher the carbon content, the greater the amount of ε phase will be formed in the compound layer. Nitrogen, being an austenite stabilizer, facilitates this reaction. As stated earlier, the alloying elements present in solid solution also may contribute to the nitriding propensity of an alloy.

Conclusion

One of the big hurdles to specifying nitriding requirement, the subject of this paper, is to prove that nitriding is a viable option to traditionally carburizing process. Rather than comparing case depth (process time) and mechanical properties, such as bending strength and fatigue properties aligning nitriding to low distortion, corrosion resistance and impact would be a more acceptable method of introducing nitriding. Nitriding has a niche corner in heat treat industry and is application driven. Thus specification should be written for performance only and not as comparison.

Follow up steps will be to conduct experiments to achieve certain microstructural variations and measure the micro-constituents. Test parts will go through validation and a viable specification requirement for nitriding would be published.

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