

# In-situ sensors for nitrocarburizing applications

Emil Stålnacke<sup>1</sup>, Sven Haglund<sup>1</sup>, Magnus Dahlström<sup>2</sup> and Erik Spolander<sup>3</sup>

<sup>1</sup>Department of Production Technology, Swerim AB "Swedish Research Institute for Mining, Metallurgy and Materials", Stockholm, 164 07 Kista, Sweden

<sup>2</sup>Linde Gas AB, Stockholm, 169 68 Solna, Sweden

<sup>3</sup>Bodycote Värmebehandling AB, Göteborg, 424 23 Angered, Sweden

Nitrocarburizing is a thermochemical process used to enhance wear-, corrosion- and fatigue resistance in steels in wide variety of applications. Due to the complex atmosphere and relatively high temperature, 510 – 580°C, many challenges are presented when attempting to monitor it and control for a specific outcome. Monitoring ammonia (NH<sub>3</sub>) is of particular interest due to its strong correlation to the nitriding potential, which in turn can be related to the metallurgical outcome. Current methods to monitor NH<sub>3</sub> rely on two main methods: 1) extracting the furnace gas to a separate measuring station outside the furnace where NH<sub>3</sub> is measured, or 2) estimating NH<sub>3</sub> indirectly through measurements of N<sub>2</sub>, H<sub>2</sub> and CO/CO<sub>2</sub>. Risks associated with extractive methods pertains to the formation of salts that clog the extraction pipes, owing to water condensation. While estimating NH<sub>3</sub> from other gases avoid the risk of salt formation, there are concerns regarding the accuracy of these estimates. The present study evaluated an alternative measuring setup, using Tunable Diode Laser Absorption Spectroscopy (TDLAS), which allowed for direct measuring of NH<sub>3</sub> content without extractive analysis. The study was conducted in an industrial environment, and the results obtained from TDLAS were compared to measurements done by Fourier Transform Infrared technique (FTIR) and estimates based on the furnace's hydrogen sensor. Overall, TDLAS showed good agreement with FTIR measurements, indicating its accuracy in directly measuring NH<sub>3</sub> content. Additionally, it was found that directly measured NH<sub>3</sub> deviated significantly from estimated NH<sub>3</sub>. It is thus concluded that measured NH<sub>3</sub> should be preferred when controlling the furnace using nitriding potential. To this end, TDLAS can provide a cost-efficient method for measuring NH<sub>3</sub> directly in industrial environments.

**Keywords:** Steel, nitrocarburizing, sensors, tuneable diode laser, ammonia, hydrogen, in-situ, nitridation potential

## Introduction

Nitrocarburizing is a thermochemical heat treatment process that is used to enhance the performance of many demanding industrial steel components, for example gears. The resulting outer microstructure, the compound layer, is hard and offers improved resistance to wear and corrosion. [1 – 3]. The process involves exposing the steel to a reactive atmosphere consisting of ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) at 540 – 590°C, resulting in surface absorption and inward diffusion of nitrogen and carbon in the steel [4, 5].

In-situ monitoring of ammonia content is however very difficult. The upper limit of most commercial solid-state sensors for ammonia is only a few hundred ppm [6, 7], whereas 15-40% ammonia is expected in nitrocarburizing. Other common instrumentation options include Fourier transform infrared spectroscopy (FTIR) [8], but a such a setup cannot tolerate the high temperature inside the furnace. Extracting the gas is a possibility to circumvent the temperature exposure, but if condensation occurs during extraction, ammonium carbonate can form and clog the pipes in addition to alteration of the gas composition [9].

While in pure nitriding, hydrogen content can be used to estimate ammonia content, such estimations are questionable in nitrocarburizing since an unknown amount of hydrogen is consumed during carburization.

One alternative monitoring method of particular interest which has not seen wide adoption is tuneable diode laser spectroscopy (TDLAS). In this setup, a laser is passed through the analyte gas and a series of mirrors to a photon detector, from which the composition of the gas can be determined [6, 10]. The absorption spectrum of ammonia is 800 – 1400 nm [8], so by using an infrared laser, ammonia is detectable at a relatively a high detection range in relation to solid-state sensors [6, 8].

The goal of the present study is to investigate the usage of TDLAS method in measuring ammonia in-situ for typical industrial nitrocarburizing conditions. The measured data will be compared to conventional methods, including estimations of ammonia based on the furnace's hydrogen sensor, and extractive gas analysis measured in FTIR.

## 2. Experiments

The experiments were performed in a industrial furnace, in two stages. Throughout the trials, the ammonia content and nitridation potential,  $r_N$ , was analyzed using three parallel setups: 1) TDLAS, 2) Extractive analysis, and 3) Estimation based on furnace hydrogen sensor data.

In Trial 1 first approximate 50% NH<sub>3</sub> was added, while in Trial 2 90% was added followed by 50% NH<sub>3</sub> and 5% CO<sub>2</sub>. For Trial 2, no results TDLAS sensor were available. In Table 1 below the used process gas flows are summarized.

The TDLAS sensor used was a Mettler Toledo G-Pro 500, which was mounted close to the exhaust pipe of the furnace, where the approximate temperature 80–120°C was documented. Extractive gas analysis was done in-situ using a Bruker Matrix MG01 FTIR for measuring ammonia, and hydrogen using ABB Advanced Optima with Caldos25. The extraction pipes were heated to avoid formation salt precipitation. Estimations of ammonia based on the pre-installed hydrogen sensors was performed.

Table 1 Summary of trials performed in the project. There was a difference in NH<sub>3</sub> flow from the mass flow regulators (MFR) and flow measured by traditional flowmeters located directly after the MFR's. Measured NH<sub>3</sub> process flow from flowmeters is shown within brackets.

Time	N <sub>2</sub> [m3/h]	NH <sub>3</sub> [m3/h]	CO <sub>2</sub> [m3/h]	Tot.gas [m3/h]	Comments
07:55	20	0	0	20	Flush
10:55	6	5 (5.75)		11	Trial 1 A.
11:23	5	5 (5.75)		10	B.
11:53	4	6 (7)		10	C.
12:04	20	0	0	0	Trial 1 end
12:46	10	0	0	0	Flush
14:48	0	9 (10)		9	Trial 2.A
15:12	5	5 (6)		10	B
15:36	4	5 (6)	0.5	9.5	C
15:54	20	0	0	20	Trial 2 end

### 3. Results and discussion

From Figure 1, comparison of measured values from TDLAS during the first quarter of trial 1 corresponds well with FTIR extractive analysis. The fact the TDLAS value increases faster could very well be due to the measuring setup of the FTIR instrument. Extraction point for gas from furnace for FTIR instrument was not optimal. Gas circulation between gas extraction point and furnace chamber was questionable and can be the reason for difference between measured values in the early phase of trial 1.

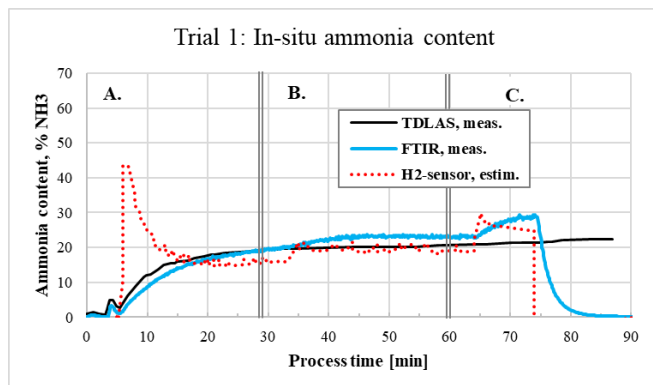


Figure 1: Comparison of analyzed ammonia values from FTIR and TDLAS together with calculated value from H<sub>2</sub>-sensor.

In the final part (C.) of Trial 1, TDLAS did not seem to capture the change in NH<sub>3</sub> content well. FTIR instrument

reacted to the change in NH<sub>3</sub> process flow from 50 % to 60 % but TDLAS only registered a slight increase in measured NH<sub>3</sub> content. This could however be an effect of contamination of the instrument.

In Trial 2, FTIR and the hydrogen sensor could be compared. As can be seen in Figure 2, the hydrogen measurements are identical.

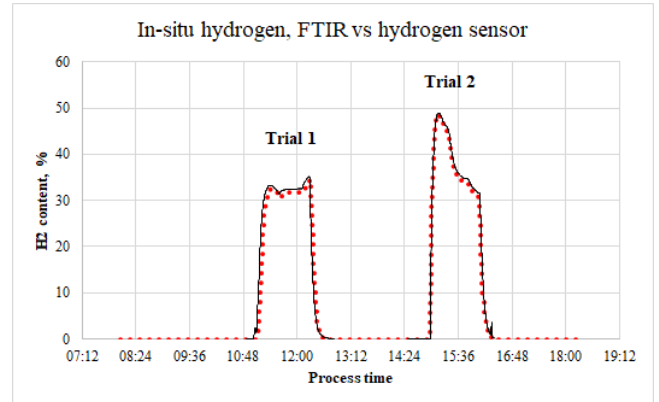


Figure 2: Measured hydrogen content from FTIR and H<sub>2</sub>-sensor.

Measured ammonia from FTIR and calculated ammonia from hydrogen sensor, from trial 1 & trial 2 is shown in Figure 3. As can be seen, the calculated ammonia value in most cases underestimates the ammonia content. The same can be said about  $r_N$  when comparing values based on H<sub>2</sub>-sensor and FTIR respectively in Figure 4. This discrepancy indicates the value of having actual, measured ammonia content and not only to rely on indirectly estimated values.

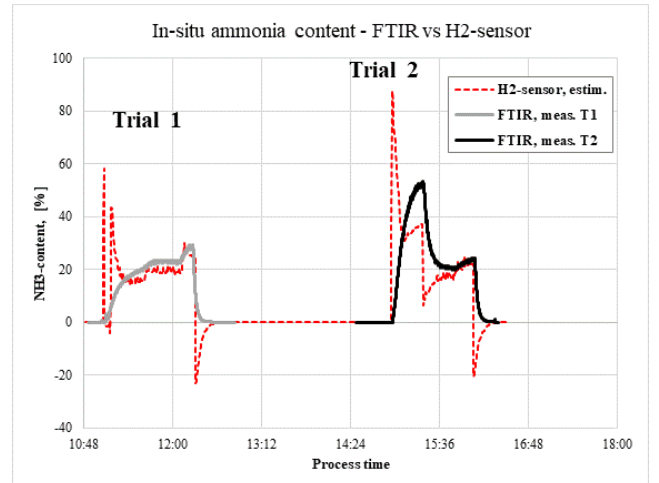
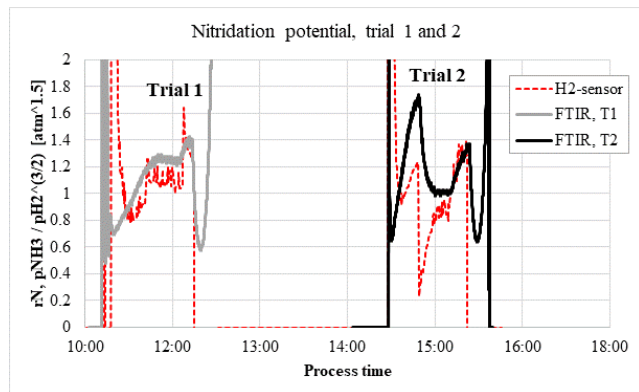


Figure 3: Comparison of NH<sub>3</sub> based on values from FTIR (measured) and H<sub>2</sub>-sensor (estimated) respectively.

Comparing the calculated ammonia and corresponding  $r_N$ -value it is highly dependent on process flow of N<sub>2</sub> and NH<sub>3</sub>, change in flow results in instant change in NH<sub>3</sub> and  $r_N$ . The furnace atmosphere will change gradually and strive for a state of equilibrium with furnace chamber, components, and load carrier. Another factor that influences calculated NH<sub>3</sub> content is the MFR. As noticed in the trials there was a difference in process flow of NH<sub>3</sub> from MFR and flowmeter. It is important to calibrate and verify flow

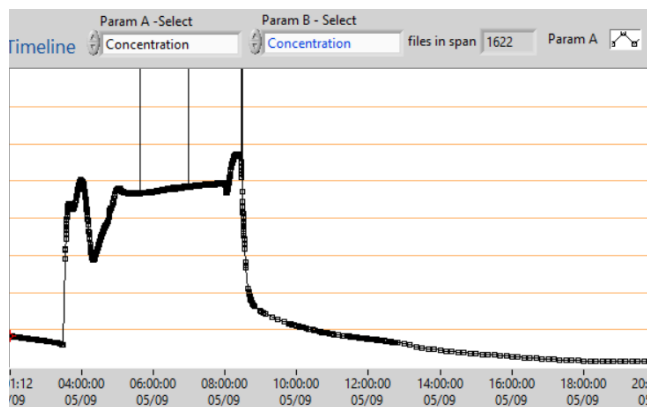
readings from MFR and make sure process pressure of  $\text{NH}_3$  and  $\text{N}_2$  is according to specification of both MFR and flowmeter.



**Figure 4:** Comparison of  $r_N$  based on values from FTIR and  $\text{H}_2$ -sensor respectively.

When a nitrocarburizing process has finished the furnace is cooled down in order to protect the threatened component from de-nitriding or oxidation. During this stage, about  $20 \text{ m}^3/\text{h}$  nitrogen is used which most likely should result in an ammonia content close to zero after only a few minutes.

However, according to Figure 5 below, the measured ammonia content decreased quickly in the beginning, but at about 5 %  $\text{NH}_3$  the decrease slow down dramatically. The time needed to go from 5%  $\text{NH}_3$  to 0.7 % was more than 10 hours. According to the manufacturer this is caused by residual  $\text{NH}_3$  in the measuring wafer and can likely be solved by performing a “blow back” with nitrogen after each heat treatment cycle.



**Figure 5:** Measured  $\text{NH}_3$ -content. When  $\text{NH}_3$  additions halts and the contains no  $\text{NH}_3$ , the measured  $\text{NH}_3$  content rapidly decreases to about 5%. A subsequent decrease to 0.7% took an additional 10 h.

### 3. Conclusions

Ammonia measurements performed by the TDLAS sensor showed good agreement with by FTIR, indicating it’s potential for in-situ monitoring. The experiments also shows that there is a large difference between actual, measured  $\text{NH}_3$  content, and  $\text{NH}_3$  estimated from measured  $\text{H}_2$  from pre-installed hydrogen sensor. In order to control the furnace by e.g nitridation potential, measured  $\text{NH}_3$  is preferred.

When  $\text{NH}_3$  flow was decreased drastically, the TDLAS

sensor was slow in reaching low values (below 8%  $\text{NH}_3$ ). This is believed to be possible mitigate by installing a  $\text{N}_2$  blow-back system that cleans the sensor. No ammonium carbamate was deposited in the measuring head. The sensor was placed in a position where the gas temperature was rather low witch is believed to be the major cause of the measurement problems during the experiments. Removing of the cooling fins reduced the problem significantly.

### Acknowledgments

This study was done and financed by the members of the Swedish center for heat treatment Värmebehandlingscentrum (VBC). Thanks is extended towards Metler Toledo for providing the TDLAS-sensor for the study.

### References

- [1] T Holm, P Olsson, E Troell: *Stål och värmebehandling: En Handbok*, (Swerea IVF, Mölndal, Sweden), pp 481-527
- [2] E. Mittemeijer and M. Somers: *Thermochemical Surface engineering of steels*, (Woodhead Publishing, Elsevier, Cambridge, UK, 2015), pp. 3-15.
- [3] A Sitzmann, S Hoja, S Schurer, T Tobie, K Stahl: “Deep nitriding—contact and bending strength of gears with increased nitriding hardening depth” *Forsch Ingenieurwes* (2022) 86, pp. 649–659
- [4] M. A. J. Somers: Nitriding and Nitrocarburizing: Status and Future Challenges, *Heat Treat & Surface Engineering Conference & Expo*, (2013), Chennai, India
- [5] B. Schwarz, H. Göhring, S. R. Meka, R. E. Schacherl, E.J. Mittemeijer: “Pore Formation Upon Nitriding Iron and Iron-Based Alloys: The Role of Alloying Elements and Grain Boundaries”, *The Minerals, Metals & Materials Society* (2014) 45, pp. 6173–6186
- [8] D. Popa and F. Udrea: “Towards Integrated Mid-Infrared Gas Sensors” *Sensors* (2019), 19, 2076
- [10] I. Burlacov, K. Börner, H.-J. Spies, H. Biermann, D. Lopatik, H. Zimmermann, J. Röpcke: ”In-situ monitoring of plasma enhanced nitriding processes using infrared absorption and mass spectroscopy” *Surface and Coatings Technology* (2012) pp. 3955–3960
- [6] D. Kwak, Y Lei, R. Maric: “Ammonia gas sensors: A comprehensive review” *Talanta* (2019) 204, pp. 713–730
- [7] B. Timmer\*, W. Olthuis, A. van den Berg: “Ammonia sensors and their applications—a review”, *Sensors and Actuators B* (2005), 107, 666–677
- [9] *Furnace atmospheres no. 3* (Linde Group, Pullach, Germany, 2015)