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DEVELOPMENT OF A SENSOR SYSTEM FOR GAS CARBONITRIDING – FIRST RESULTS[1]

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Abstract

Carbonitriding is a thermo chemical heat treatment. It is applied increasingly to steel components to improve the mechanical properties and to adjust them to the expected load while reducing the weight. The aim of the project is to develop a system consisting of a set of sensors, a process model, and a closed loop for controlling the carbonitriding atmosphere composition that facilitates reproducible results according carbon and nitrogen depth profiles independent of furnace type, furnace condition or furnace load. The different depth profiles should be obtained by gas atmospheres with constant carbon and nitrogen potential. For this purpose, the carbon potential is controlled by an oxygen sensor with respect to decreased carbon monoxide content during ammonia addition. The nitrogen potential can either be controlled internally by measuring the resistance of an iron wire before and after ammonia addition or externally by measuring the residual ammonia content in the exhaust gas. Results of foil samples and exhaust analyses of ammonia will be presented.

Keywords: Gas carbonitriding; Carbon content sensor; Oxygen probe; Residual ammonia.

DESENVOLVIMENTO DE UM SENSOR PARA A CARBONITRETAÇÃO A GÁS – PRIMEIROS RESULTADOS

Resumo

A carbonitretação é um tratamento termoquímico cada vez mais aplicado em componentes de aço com o intuito de promover a melhoria das propriedades mecânicas a fim de ajustá-las às solicitações desejadas e consequente redução do peso. O projeto visa desenvolver um sistema de sensores e um modelo do processo capaz de controlar precisamente a composição da atmosfera e, assim, possibilitar que se atinjam resultados reprodutíveis da profundidade de penetração de carbono e nitrogênio indenpendentemente do tipo, das condições e da carga do forno. Os diferentes perfis de profundidade devem ser obtidos com atmosferas gasosas com potencial de carbono e nitrogênio constante. Para tanto, o potencial de carbono é controlado por um sensor de oxigênio que determina o decréscimo de monóxido de carbono durante a adição de amônia. O potencial de carbono também pode ser controlado internamente através da medição da resistência de um fio de aço antes e após a adição de amônia ou externamente pela medição do teor de amônia residual no gás de exaustão. Serão apresentados resultados das amostras de lâminas de aço e a análise da amônia do gás de exaustão.

Palavras-chave: Carbonitretação a gás; Sensor por resistência; Sensor de oxigênio; Amônia residual.

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1 INTRODUCTION

Carbonitriding is a special type of case hardening. It is defined as "the thermochemical treatment of a workpiece above Ac_1 to enrich the surface with carbon and nitrogen".[1] This leads to an improvement in the performance of components of low or unalloyed steels. The austenite is stabilized and the tempering resistance, wear resistance and especially the hardenability of the steel increase.

In general, gas carbonitriding uses a carrier gas, for example nitrogen-methanol mixtures or methane and propane based endo gas. The addition of ammonia, to achieve significant levels of nitrogen, is often given as percentages of the carrier gas. The higher the temperature, the faster the rate of diffusion, but also the greater the decomposition of ammonia into hydrogen and nitrogen gas.

The problem here is that the nitrogen content appearing in the surface region is not only dependent on ammonia addition. It also depends on the furnace type, the furnace condition, the carbon potential, the amount of gas, and the load size. As a consequence, highly variable nitrogen depth curves are observed. How big the impact of the furnace type, despite same furnace material, can be, is revealed by results with a bell-furnace-arrangement (Figure 1). The bell-furnace-arrangement is equipped with two furnaces of equal size. Both are made of the furnace material 1.4841. In furnace 1, a new furnace material was installed, so until the start of the project, only carburizing experiments without ammonia addition were carried out there. The older furnace 2 has been used for almost 2 years in carbonitriding operations. The pure iron foils were carbonitrided in each of the furnaces at 850 °C for at least 20 minutes, so that a chemical balance between the foil and the atmosphere was achieved. The standard deviation of the glow discharge optical emission spectroscopy (GDOES) measurement of nitrogen content is symbolized by error bars. It was + / - 0.02 % N.

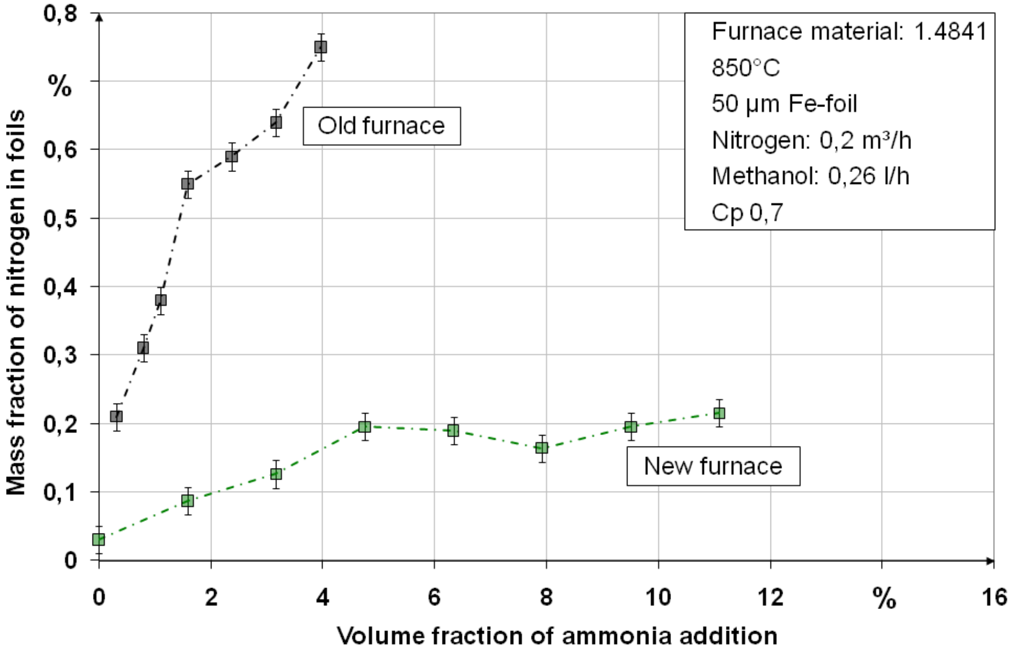


Figure 1. Different nitrogen contents in iron foils after heat treatment in two different furnaces in spite of the same ammonia addition and temperature (850°C).

The comparison of the achieved nitrogen contents shown in Figure 1 reveals large differences between the furnaces, in spite of the same temperature and amount of gassing. The major objective is therefore a furnace independent carbonitriding sensor system. Generally, there are two ways to approach the aim of furnace independent regulation: Firstly, based on internal measurements inside the furnace and secondly, using external measurements in the exhaust gas. A particular characteristic of the current project is that both possibilities can be exploited and combined.

2 FURNACE INTERNAL SENSOR SYSTEM FOR GAS CARBONITRIDING

2.1 Application of the Oxygen Probe During Carbonitriding

The oxygen sensor responds specifically to very small amounts of oxygen. The relationship to the carbon potential or the carbon activity results from the decomposition of carbon monoxide into carbon and oxygen. The determination is made using the Nernst equation. It is dependent on the carbon monoxide volume fraction. With the addition of ammonia, the carbon monoxide volume fraction is lowered. An incorrectly adjusted CO fraction of + / - 0.5 % results in a change in the carbon level of + / -0.03 %.[2] The lowering of the carbon monoxide volume fraction through the addition of ammonia can be calculated, controlled with exhaust gas measurements and taken into account for the closed loop for the carbon potential (Figure 2).[3]

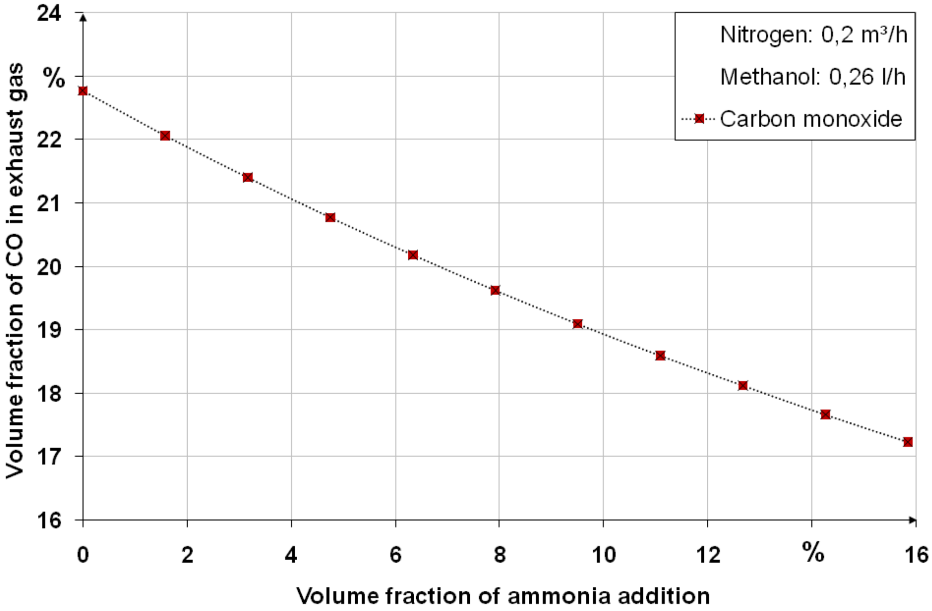


Figure 2. Decreased carbon monoxide volume fraction through entirely dissociated ammonia derived from a carrier gas from 0.2 m³ / h nitrogen and 0.26 l/h methanol.

2.2 Application of the Carbon Content Sensor in Carbonitriding Atmospheres

The carbon content sensor is structured as a carbon-flux sensor and can also be operated as such. It is able to determine the carbon content (CC) during carburizing. The determination of carbon content runs via the conductivity measurement of a thin iron wire (Figure 3). There is a linear relationship between the resistance of the wire and the carbon content (Figure 4).[4]

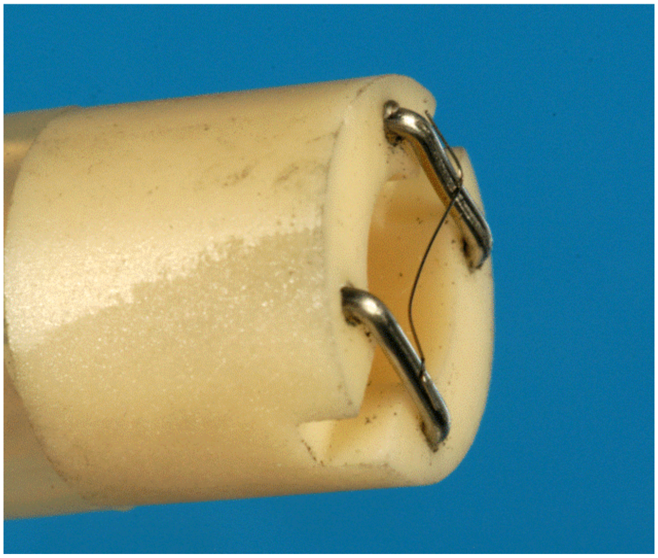
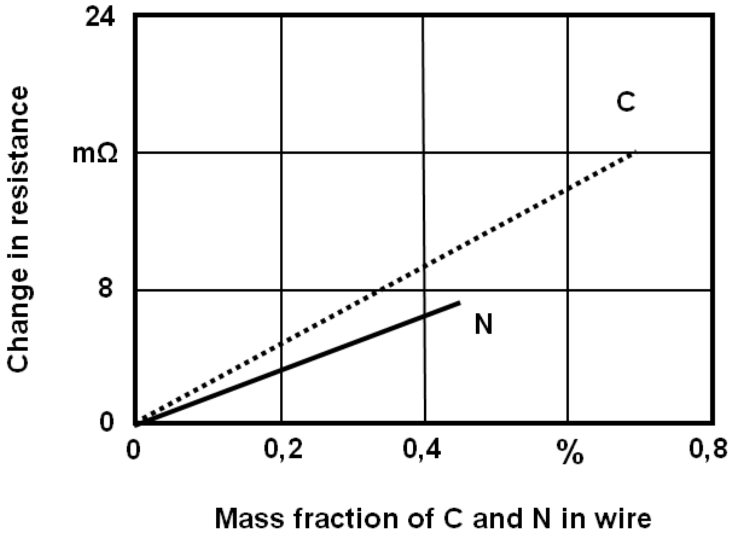


Figure 3. Sensor head of the carbon content sensor.



According to Chatterjee-Fischer 1969

Figure 4. Resistance change as a function of the carbon and nitrogen content of a wire.

The change of electrical resistance due to a change in the carbon content does not depend on the temperature within the range of 750°C - 1000°C. The calibration is done with a decarburization by hydrogen or by comparison with the carbon level of the oxygen probe. In contrast to the carbon flux mode, there is no continuous decarburization of the wire. A particular advantage of the wire sensor is the carbon monoxide independent measurement of the carbon content. If the wire is protected against precipitation and oxidation, the sensor will maintain its function for more than 5000 hours of operation.[5] However, there is a linear relationship between the mass fraction and the resistance not only for carbon but also for nitrogen (Figure 4). If the carbon content sensor is used in the carbonitriding atmosphere, it responds to both factors C + N in a sum as a resistance change. To indicate the dependency of the nitrogen content, an N is prefixed to the name of the value. Because the resistance change is calculated as carbon mass fractions due to his original conception for carburizing, the N is set in brackets: (N)CC.

2.3 Calculating Nitrogen Contents from Values of the Carbon Content Sensor

If the carbon content in the wire is kept constant, the difference in the nitrogen mass fraction w(N) can be calculated from the difference of two (N)CC values:

$$w(N,t_2) - w(N,t_1) = \left[(N)CC(t_2) - (N)CC(t_1)\right] \cdot \frac{3}{2}$$

The calculation is carried out by subtracting a (N)CC value at a particular time (t_1) without ammonia addition from another (N)CC value during ammonia addition (t_2). Then the value calculated as carbon mass fraction will be converted into nitrogen mass fraction by a factor of $\frac{3}{2}$. The factor $\frac{3}{2}$ arises from the different sensitivity of the sensor for carbon and nitrogen (Figure 4).[4]

The average nitrogen mass fraction of the foils treated in the furnace at -t_1- was 0.03 %. For the calculation of the nitrogen content during the experiments, the (N)CC value without ammonia addition has been aligned with the carbon potential of the oxygen probe and an assumed nitrogen content w(N, t_1) of 0.03 %.

To regulate the nitrogen potential by (N)CC values, the most important condition is a constant amount of carbon in the sensor wire before and after ammonia addition. Since the carbon and nitrogen atoms occupy the same places in austenite lattice, the carbon and nitrogen activity are affecting each other. To avoid this effect, the nitrogen levels must be set as small as possible. This can be achieved by a high furnace temperature, as shown in the following examples.

The nitrogen contents in the foils of the new furnace are low (Figure 5). In this case an influence of the carbon activity of the nitrogen content can therefore be neglected.

The carbon potential is controlled by an oxygen probe and the lowering of the carbon monoxide content is taken into account. For a better comparability of the carbon content, a line was drawn in the diagram of Figure 5. This is equivalent to the carbon content without the addition of ammonia. The standard deviation for the analytical investigation of the carbon mass fraction is + / -0.03. If we consider the scattering of the carbon content in Figure 5, the carbon content under ammonia addition lies within the margin of the uncertainty of the value without ammonia addition. In studies for various carbon potentials it has been established that the carbon content without ammonia addition could be held constant with a standard deviation of 0.02, respectively. An important precondition for calculating the nitrogen content was thus well fulfilled.

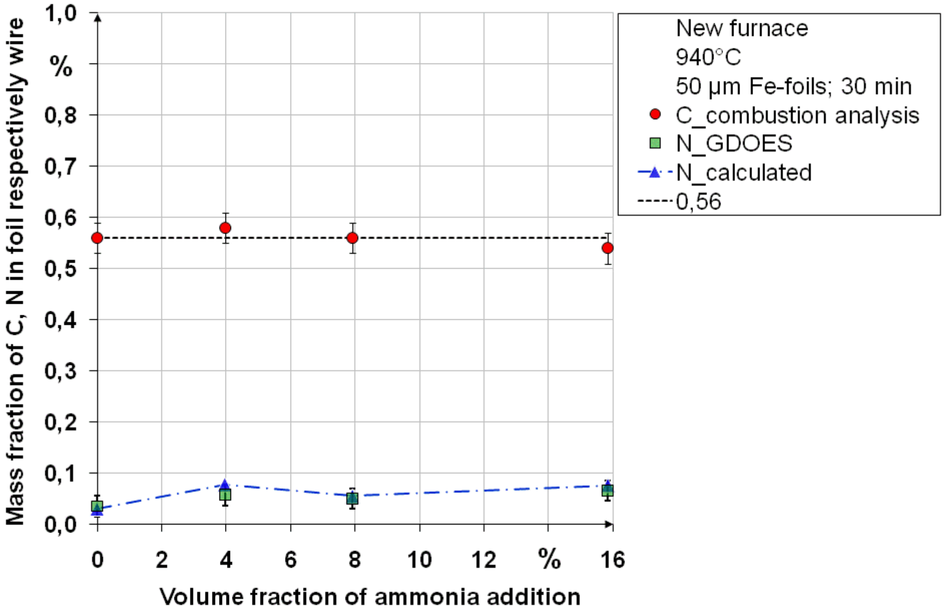


Figure 5. Very good correspondence of calculated and measured nitrogen contents during ammonia addition and constant carbon content. Measurement by means of glow discharge optical emission spectroscopy (GDOES).

The nitrogen contents calculated from the (N)CC values correspond very well to the nitrogen contents in the iron foils, which can be seen in Figure 5. In a series of experiments with a carbon potential of 0.8, a deviation from the calculated nitrogen content was observed at an ammonia addition of 16 % (Figure 6). This value can be explained not only by the influence of the measured nitrogen contents, but can also be attributed to a drift of the sensor, as there are more than 22 hours between the measurement at 16 % ammonia addition and the last alignment with the C-potential. The drifts in comparison with the oxygen probe determined over several weeks were under normal conditions within a range of + 0.03 and - 0.02 %C per day. Slow changes in the nitrogen content over a period of several days without alignment are therefore difficult to detect with the carbon content sensor.

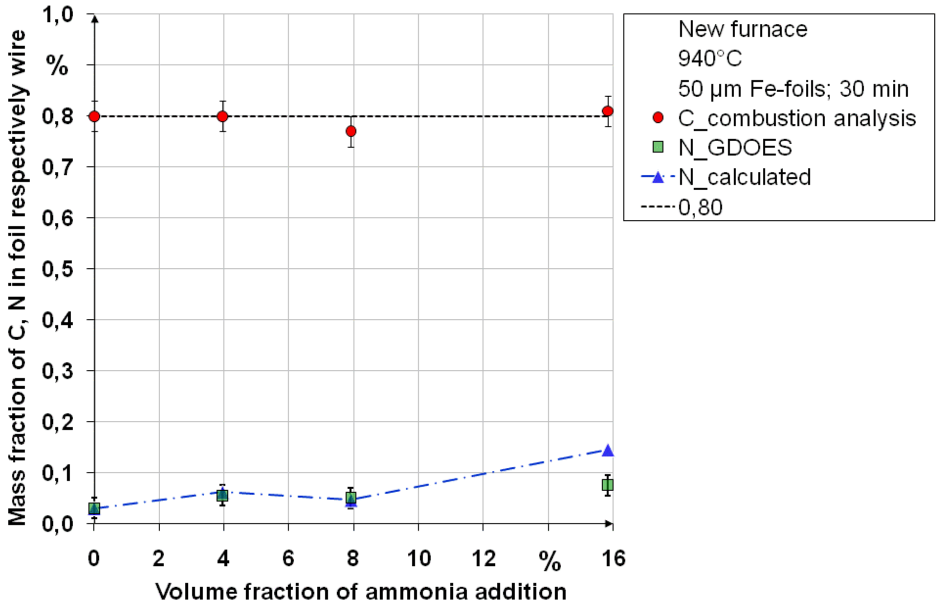


Figure 6. Too high calculated nitrogen content w(N, t_2) after a long time without alignment.

2.4 Decreasing Nitrogen Contents with Increasing Temperature

With increasing temperature, the rate of ammonia decomposition increases. As shown in Figures 5 and 6 the nitrogen contents in the new furnace at 940°C are very low. This raised the question of how rapidly the nitrogen content decreases when the temperature is increased and whether the nitrogen content could be well determined by (N)CC values. To clarify this, the temperature was gradually increased and the corresponding (N)CC values were determined at constant ammonia addition and constant carbon potential. All iron foils were carbonitrided for 30 minutes.

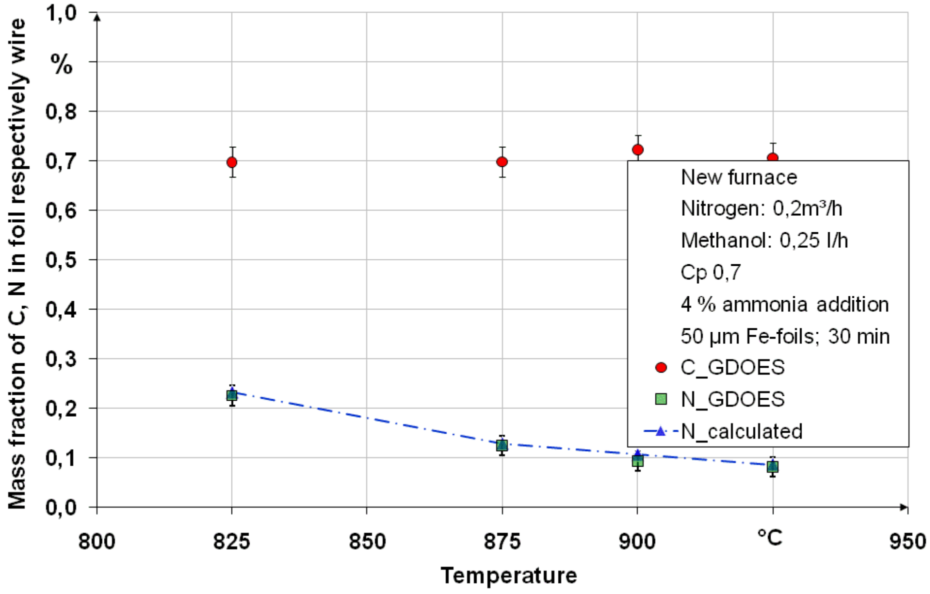


Figure 7. Decrease of the nitrogen mass fraction in the wire and in the iron foil through increasing temperature.

The nitrogen content of the iron foils decreased from 0.2 % at 825°C to 0.1 % at 900°C. Despite different temperatures, the nitrogen contents calculated from the measured (N)CC values agree very well with the GDOES measurements of the nitrogen contents of the iron foils. Therefore, the change in the resistance of the sensor wire is independent from the temperature within the range from 825°C to 940°C.

2.5 Increase and Decrease of the Nitrogen Mass Fraction in the Sensor Wire

In the experiments shown so far, the focus was on the nitriding of the sensor wire and the iron foils. If we want to use the sensor for regulating the nitrogen potential, the decrease of the nitrogen content is also of crucial importance. To clarify the decrease of the nitrogen content of the sensor wire, iron sheets were heat treated in the furnace during a phase with and without nitriding. The carbon potential and the (N)CC value were recorded continuously over time (Figure 8).

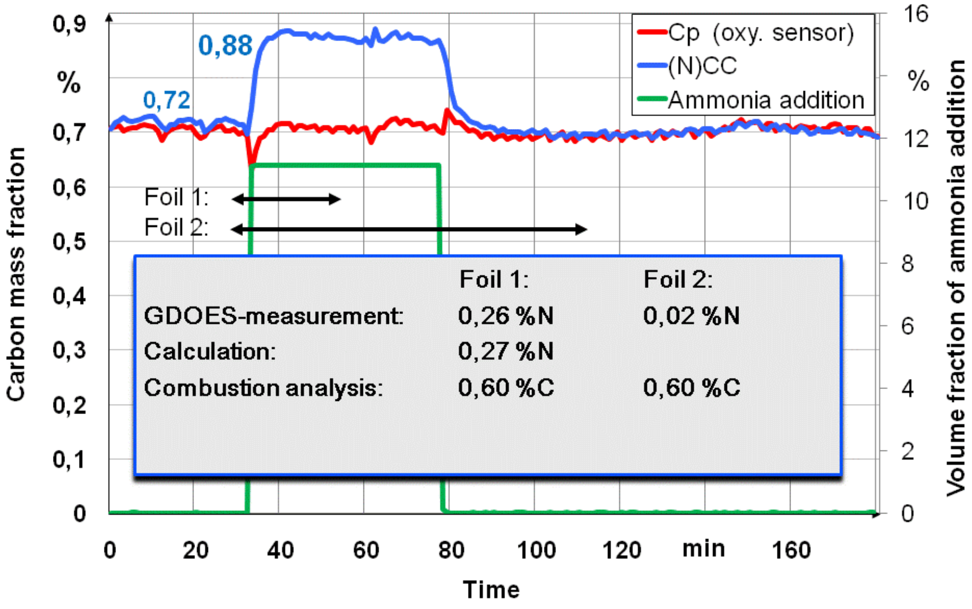


Figure 8. Increase and decrease of the nitrogen mass fraction in the wire and the iron foil.

After some minutes with a constant carbon potential, two foils were introduced into the furnace. Then ammonia was added with a volume fraction of 11 %. The regulation takes the reduction of the carbon monoxide content into account. After 30 minutes the first foil was removed from the furnace. The second foil remained in the furnace for 1 hour after the deactivation of the ammonia addition.

The time course of the (N)CC values in Figure 8 shows a rapid increase and decrease of nitrogen content in the wire within a few minutes. The calculated nitrogen mass fraction out of the (N)CC values for the first foil is at 0.27 %. The match with the GDOES measurement of the nitrogen content of 0.26 % is very good. The analysis of the second foil, which remained in the furnace after the deactivation of the ammonia addition, showed a nitrogen mass fraction of 0.02 %. This documents the effective decrease of the nitrogen content in the iron foil and the sensor wire.

3 FURNACE EXTERNAL SENSOR IN THE EXHAUST GAS

3.1 Thermodynamic Stability of the Carbonitriding Gases

The first sub goal of the exhaust gas analysis was to record all relevant gases that contain carbon, nitrogen, and oxygen. For this purpose the most stable gases in carbonitriding atmospheres were calculated using the commercially available software THERMO-CALC. These are hydrogen (H_2), carbon monoxide (CO), nitrogen (N_2), water (H_2O), carbon dioxide (CO_2), methane (CH_4), ammonia (NH_3), and hydrogen cyanide (HCN). For all these gases, with the exception of nitrogen, calibrations were made or reviewed.

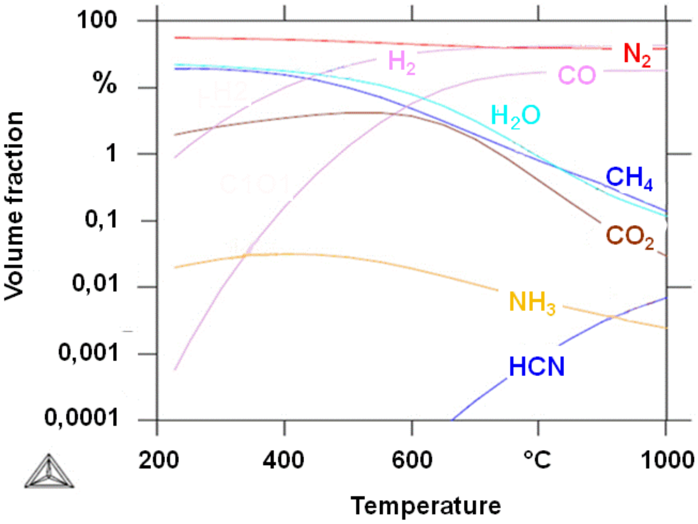


Figure 9. Calculation of the temperature dependent equilibrium volume fractions for carbonitriding on the basis of their thermodynamic stability. The calculations are made for a gas consumption derived from a carrier gas with 20 % CO, 40 % H_2 and 40 % N_2 with an ammonia addition of 5 %.

3.2 Furnace Comparison at 900°C and Correlation of Residual Ammonia with the Nitrogen Content in Iron Foils

The high number of participating gases and the reactions shown in Figure 10 indicate the complexity of the carbonitriding reactions that take place during carbonitriding. Each of the gases influences the carbonitriding because of its reactivity and concentration. A high concentration of carbon monoxide and methane leads to an accumulation of carbon in the surface layer. On the other hand, high concentrations of hydrogen, water gas and carbon dioxide cause low carbon contents.

The enrichment of the surface layer with nitrogen can be achieved by ammonia, hydrogen cyanide and to a lesser extent by gaseous nitrogen.

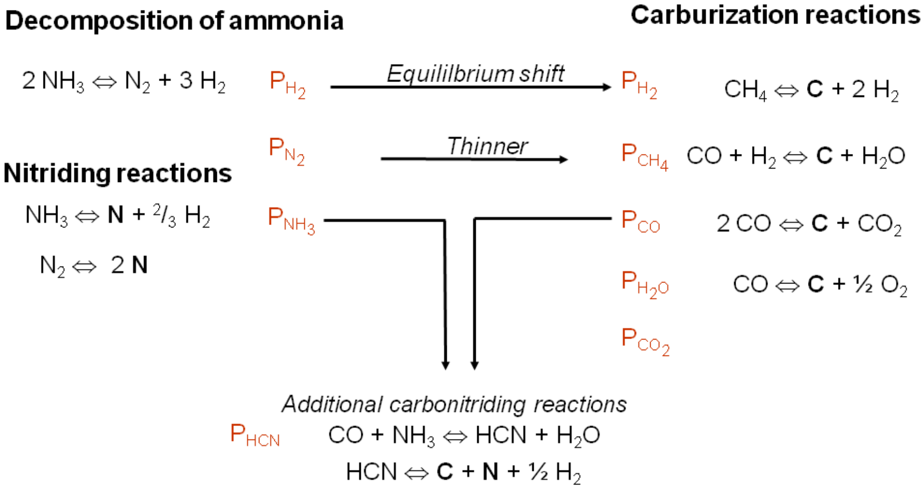


Figure 10. Carbonitriding reactions.

Exhaust gas measurements and kinetic considerations[6] showed that the retention of the gases in the furnace is not sufficient to ensure that all gases are present in thermodynamic equilibrium. The measured ammonia levels shown in Figure 11 reveal major differences between the two furnaces with new and old furnace material, despite the same temperature and gassing. The residual ammonia levels at an ammonia addition of 5 % are in both cases well above those of the thermodynamic equilibrium shown in Figure 9. The residence time in the furnace is therefore not sufficient for the ammonia level to decay to the value of the thermodynamic equilibrium. However, the ammonia content in the exhaust gas is characteristic of the observed nitrogen content in iron foils as shown in Figure11 and offers a much better furnace independent correlation than in the case of the ammonia additions shown in Figure12 and Figure 13.

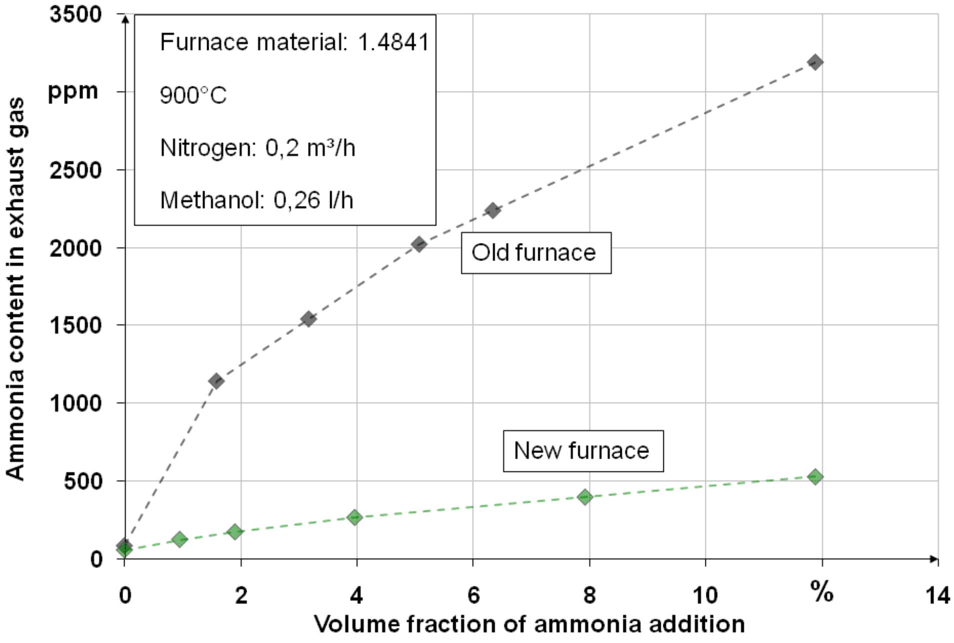


Figure 11. Comparison of the amount of residual ammonia for the old and new furnace material.

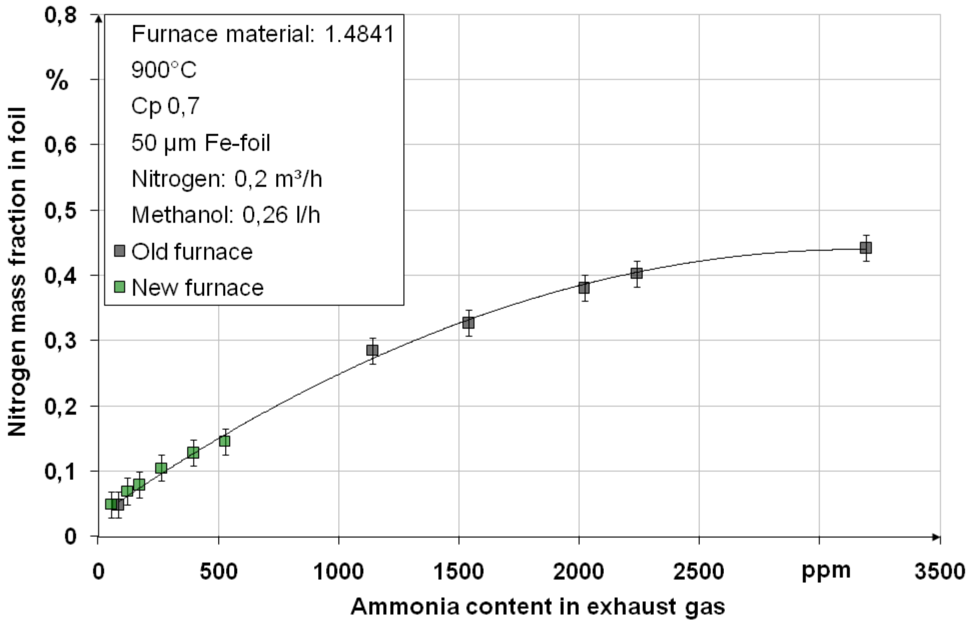


Figure 12. Correlation between the nitrogen mass fraction in iron foils and the residual ammonia for the old and new furnace material.

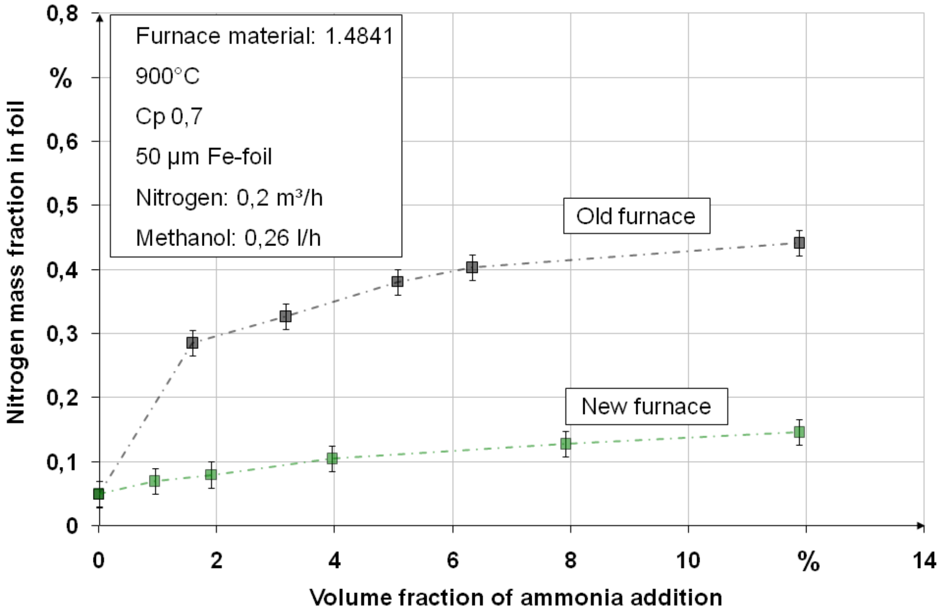


Figure 13. Different nitrogen mass fractions in iron foils in spite of the same ammonia addition and temperature (900°C).

4 CONCLUSION

The ammonia concentration measured in the exhaust gas offers a better correlation with the adjusted nitrogen content than the amount of added ammonia, both for the new and the old furnace.

With the application of the carbon content sensor during carbonitriding there is a second possibility to control the nitrogen potential. It was shown that the differences in the nitrogen content of iron foils are very predictable with the (N)CC values within the temperature range of 825°C to 940°C, if both foils have the same carbon content and if the period between the corresponding (N)CC values is small (<12h). The carbon content in the iron foils can be kept constant during ammonia addition, if the influence of the nitrogen activity on the carbon activity is negligible.

The sensor can be used under appropriate safeguards for a long period of time. The nitrogen content of the sensor wire decreases within minutes and if there is no ammonia addition the average value for the nitrogen mass fraction in the iron foils amounts to 0.03.

Acknowledgements

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