The influence and control of gases and their blends during sintering of carbon steel parts

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Abstract:

Producers of sintered parts face higher challenges in their production due to higher demands on variation in mechanical properties of the parts going along with the pressure on reduced operating costs due to a competitive market. The composition and quality of the sintering atmosphere as well as the full understanding of the best way to use atmosphere compositions thereby plays an important role in both, the influence on the final properties of the sintered parts as well as on the specific operating and maintenance costs, such as the belt life. This paper provides an overview about the influence of the atmosphere on the quality of the sintered carbon steel parts and also provides ideas to improve the performance of the furnace equipment such as the belt life to reduce maintenance costs.

1. Introduction

Heat treatment atmospheres were discussed in several papers in the past and are treated as "technical standards" in the sintering process of carbon steel parts. However, the operator of sintering furnaces always faces challenges in material properties in the day-to-day business due to atmosphere issues. Typically these challenges are related to carburizing or decarburizing of the steel parts, resulting in undesired variations of mechanical parameters of the sintered parts as well as to maintenance problems of the furnace due to surface reactions of the transport belt with the sintering atmosphere or sintered parts.

This paper will describe on a practical level the impact of atmosphere components like Carbon monoxide, Carbon dioxide, Methane, Hydrogen and Moisture and their gradients inside the furnace on the part quality as well as on the lifetime of the transport belt.

As a protective atmosphere for the sintering process of carbon steel, some companies use an endothermic generated atmosphere. This atmosphere, produced by an under stoichiometric partial burning process of natural gas or propane with air, can be generated by 1) external endothermic generators supplying several furnaces, 2) in-situ generators installed inside the furnace or 3) by an endothermic reactor installed on top or inside of the furnace. Compared with atmospheres composed of technical gases, such as nitrogen (N2) and hydrogen (H2), these endo generated gases have variations in produced gas composition. Operating the endogenerator to hard on the hydrocarbon side to avoid decarburization of the parts will result in high maintenance efforts and sooting problems with an impact on the reliability on the atmosphere supply. Using a higher concentration of air (oxygen) to reduce the danger of sooting creates a lower carbon potential and will decarburize the part surfaces. For this reason, most sintering companies now use atmospheres based on a nitrogen blend, mostly with hydrogen-levels up to 5%. However, Nitrogen/Endo-blends also deliver significant advantages on the product quality compared to pure Endo.

2. Impact of the Atmosphere Composition on the Sinterparts

2.1. Thermodynamic Background

In general, sintering atmospheres are used to prevent oxidation on the compact surface and to provide a bright surface finish. Air, therefore, has to be purged from the furnace and the remaining traces of oxygen have to be reduced by a reactive component in the atmosphere blend. However, the reducing reaction should not produce too many oxidising and decarburising components such as moisture (H_2O) (1) or carbon dioxide (CO_2) (2), so it is important to provide a sufficient flow rate of a protective atmosphere to prevent air ingress. It can be seen that heat treatment atmospheres always have residual amounts or traces of oxidising components. The following reactions can represent the oxidation of metal (Me):

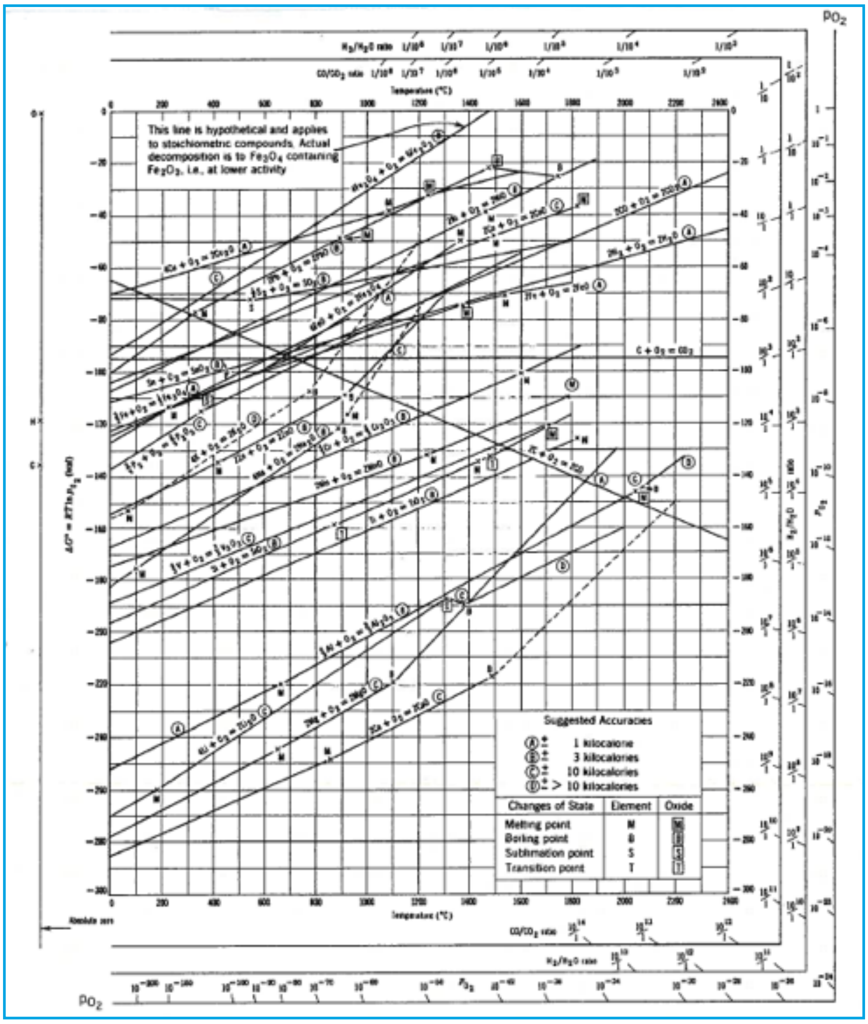


Figure 1: The Ellingham-Richardson- Diagram [1]

$2 H_2 + O_2 \Leftrightarrow 2 H_2O$ (1)	2 Me + O2 ó 2 MeO		(3)
$2 CO + O_2 \Leftrightarrow 2 CO_2$ (2)	$Me + H_2O \Leftrightarrow MeO + H_2$	$K = pH_2/pH_2O$	(4)
	$Me + CO_2 \Leftrightarrow MeO + CO$	$K = pCO/ pCO_2$	(5)

Reactions (4) and (5) show that the oxidising or reducing potential always depends on the equilibrium of pH_2/pH_2O or pCO/pCO_2 and not only on the amount of oxidising components in general. In atmospheres without reducing components or used at low furnace temperatures, the amount of residual oxygen is critical. The Ellingham-Richardson Diagram [1] (Figure 1) therefore shows the reaction equilibria for different types of metals. It can be seen, that alloying elements like Chromium, Silicon, Vanadium, Manganese require a much higher ratio of H_2/H_2O for oxide free sintering than Iron.

Especially in the sintering process of carbon steel, surface decarburisation has to be avoided. By producing water vapour or carbon dioxide in the furnace atmosphere, the operator has to ensure that the amount of these decarburising components are not leading to decarburisation of the steel surface according to the following reactions (CS: carbon in steel surface):

$CS + H_2O \Leftrightarrow CO + H_2$	(6)
$CS + CO_2 \Leftrightarrow 2 CO$	(7)
$CO + H_2O \Leftrightarrow CO_2 + H_2$	(8)

Furthermore, it is important to consider, that all gases stay in an equilibrium (water-gas equilibrium) (8)

Due to the high temperature in the sintering zone, the amounts of CO_2 and H_2O in the endothermic generated atmosphere have to be very low to achieve the required carbon potential for a neutral atmosphere to the steel surface. This has to be realised by providing a sufficient amount of CO and by reducing the decarburising components with additional introduction of hydrocarbons into the furnace (Reaction 9 and 10). However, to make sure most of the moisture will be converted into CO and H_2 an overstoechiometric amount of hydrocarbons is used, resulting in unreacted CH4 and as well in sooting.

$$CO_2 + CH_4 \Leftrightarrow 2\,CO + 2\,H_2 \qquad (9)$$
$$H_2O + CH_4 \Leftrightarrow CO + 3\,H_2 \qquad (10)$$

Because the same atmosphere composition is also used in the cooler sections of the sintering furnace, this very often results in sooting inside the furnace, depositing soot on the belt or the parts. Figure 2 provides an overview about the variation of the carbon potential by using endothermic generated atmospheres at different temperatures and compositions.

This thermodynamic process can be simplified by using a dry nitrogen/hydrogen atmosphere. In Nitrogen/Hydrogen-atmospheres the driving force for decarburisation is mainly related to moisture created by air ingress or vaporisation of water containing residuals. Practically in most cases for sintering of carbon steel, due to the low dew point of technical gases the flammable

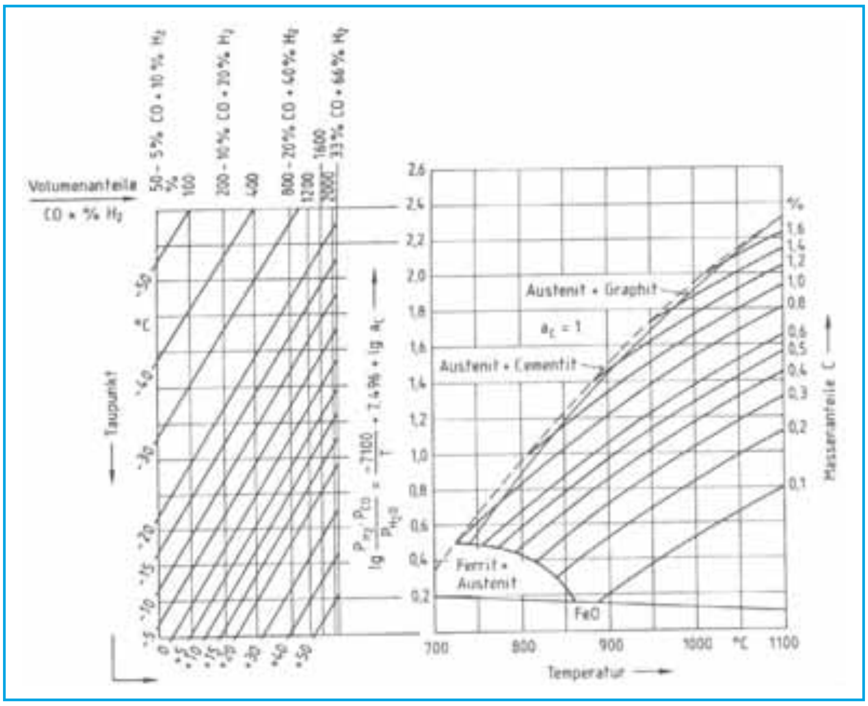


Figure 2: Equilibrium relations between dew point and temperature for gas carburising of γ-iron [2]

components in the blend can be reduced down to less than 5% (which is below the explosion point).

2.2. Sintering Tests

Tests were done with different Endogas compositions and the effect on the microstructure of carbon steel containing 0.74 weight % carbon was evaluated:

catalyst is already in worse condition, but the residual CH4 might help in the furnace atmosphere to balance the carbon losses out of the material and to help reducing the moisture inside the high temperature zone of the furnace.

Looking at the equilibrium carbon potential calculations of the atmosphere composition of

Table 1: Sintering atmospheres used in the tests

	Generator 1	Generator 2	N_2/ Endo	N_2/H_2
CO/%	19	20	6	0
CO_2/%	1,2	0,3	0,3	0
CH_4/%	1,2	0,04	1,1	0
H_2/%	40	40	13	5
Dp/°C	21	1	-16	<-65°C

The produced gas composition in the generator 2 is based on the optimal setting to avoid sooting, but also run on a reasonable low dew point and CO2 level, resulting in an optimal Carbon potential in an equilibrium atmosphere condition in the retort of the generator. Generator 1 operates on a high dew point, but has high residual CH4. This means the

generator 1 and 2 (Figure 2) the expected Carbon Potential in the atmosphere composition in the high temperature zone of the furnace is far below the C-level of the steel powder (0,74%C).

To compensate the decarburising effect in the high temperature zone, some operators introduce additional hydrocarbons in the hot

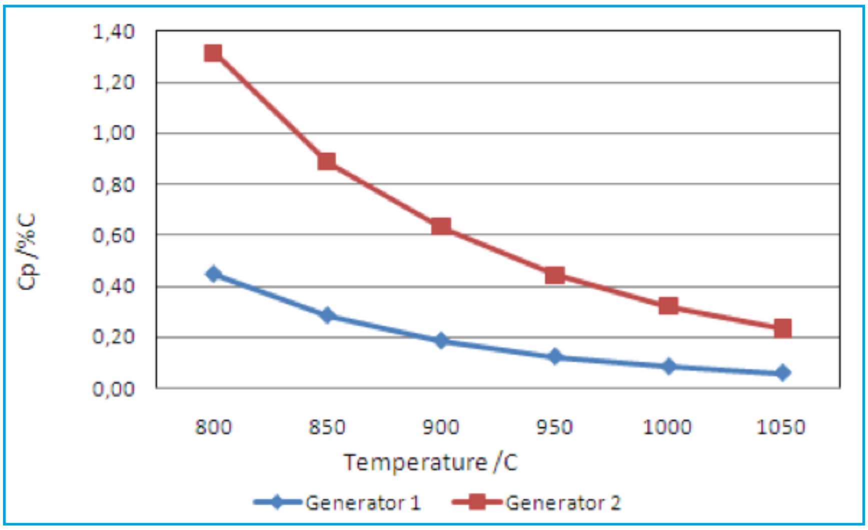


Figure 2: Calculated carbon potential for generator 1 and 2 in the furnace related to furnace temperature

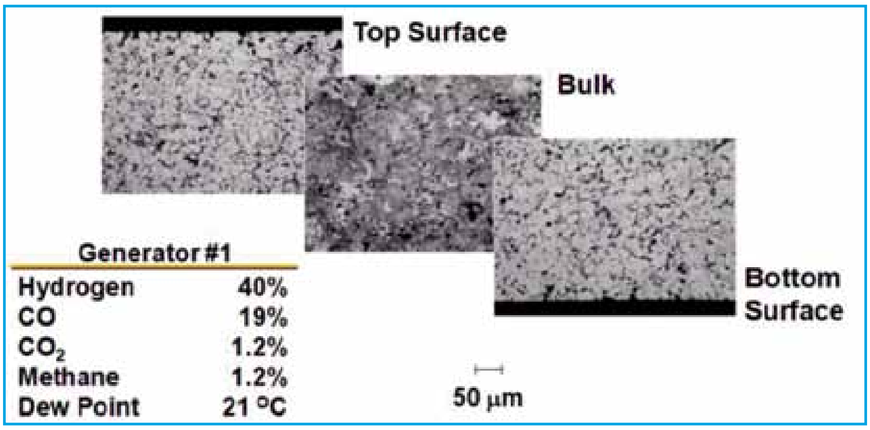


Figure 3: Microstructure of sintered parts in endothermic generated atmosphere

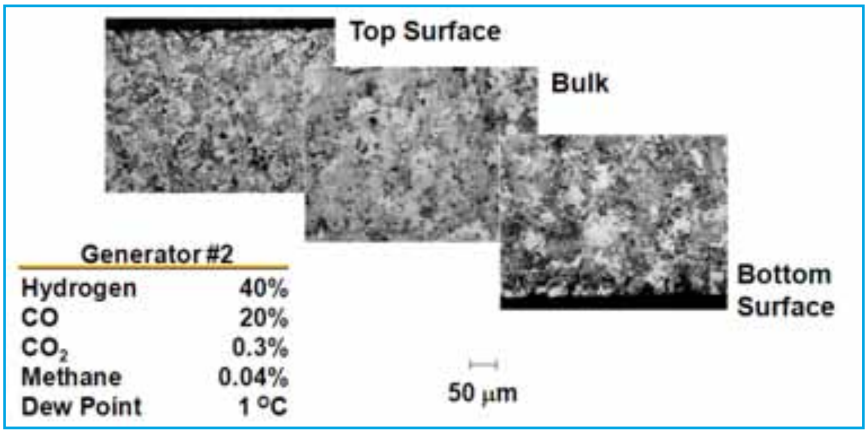


Figure 4: Microstructure of sintered parts in endothermic generated atmosphere

zone. This helps to balance the carbon losses of the steel in endothermic atmospheres at the high temperature level, but results in carburising and sooting in the low temperature areas. Apart from reactions with the parts, that might also effect furnace equipment like transport belts (Chapter 3). This means in endothermic generated atmospheres a well balanced atmosphere composition and distribution is key for homogeneous material properties.

In N_2-Endo diluted atmospheres, this effect does not appear so much, because of the far lower dew point and thereby lower decarburising tendency. The carbon potential in the atmosphere thereby is not such important anymore, since there is no carbon balance required to compensate the effect of decarburisation due to the higher dew point.

In Nitrogen-Hydrogen Atmospheres the whole effect of decarburisation is just based on residual moisture. In atmospheres below -30°C the decarburising effect inside the sintering zone is typically too slow to effect the surface composition during the sintering time.

2.3. Sintering of carbon steel, test results

Sintering trials of carbon steel compacts were carried out with endothermic generated atmosphere, endothermic generated atmosphere diluted with dry nitrogen and nitrogen/5% hydrogen atmospheres. Figure 3 and 4 show the microstructures of parts, sintered in endothermic generated atmospheres. The bulk carbon content of the sintered bars was 0,74%. The microstructure of the parts in Figure 4 shows a very severe or total surface decarburisation. This results in parts with lower surface hardness than desired and dimensional changes outside the desired range. As described in section 2.1., the reason for the surface decarburisation is an unacceptable high presence of moisture and carbon dioxide, which results in a carbon pick-up out of the steel surface. The atmosphere composition, produced by an ideal endo generated atmosphere, contains less moisture and carbon

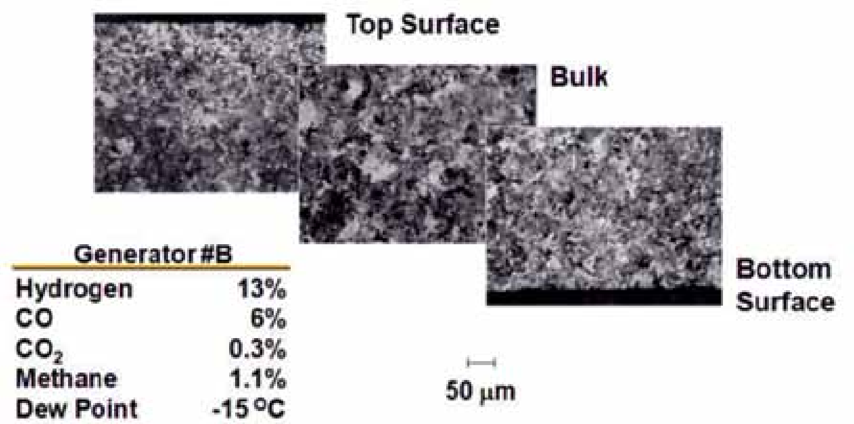


Figure 5: Microstructure of sintered parts in nitrogen diluted endo atmosphere

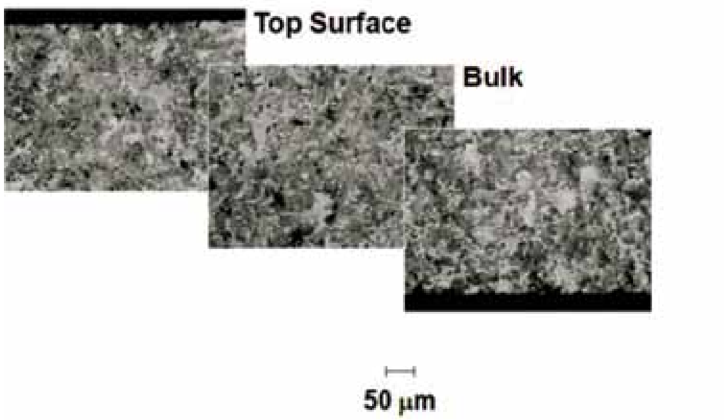


Figure 6: Microstructure of dry nitrogen- 5%hydrogen atmosphere

dioxide, which results in less pronounced partial surface decarburisation (Figure 4).

This partial decarburisation can be minimized by further reducing the moisture and carbon dioxide level in the atmosphere. Figure 5 shows a microstructure of a part sintered in endothermic atmosphere diluted with dry nitrogen and hence having a significantly reduced moisture level. The decarburisation problem is nearly avoided. There is only a slight surface decarburisation visible, which can be explained by the relatively high carbon dioxide level. However, the parts have shown improvements in hardness and fulfilled the customer requirements. A further increase of quality can be realized using a dry nitrogen/5% hydrogen atmosphere having no carbon monoxide and carbon dioxide and a dew point of <-65°C. Figure 6 shows the microstructure of a sintered part in nitrogen/5% hydrogen-atmosphere. It can be seen that surface decarburisation was totally avoided.

2.4. Summary of the atmosphere comparison

In principle all used atmospheres can deliver acceptable sintering qualities. However, using purely endothermic produced atmospheres require a very sensitive atmosphere setup in the generator and control in the furnace. Dilution with N2 can make endothermic generated atmospheres more reliable. Significant improvements have been achieved in part quality by dilution of Endogas with Nitrogen resulting in:

- Reduces Variations and Spread in Physical Properties (Dimensional Changes and surface hardness, transfers rupture strength)
- Improved microstructural homogeneity and less surface decarburisation
- Producing Components with Stringent Specifications

Another improvement can be achieved by Sintering in Nitrogen-Hydrogen Atmosphere, whereas the H2-level in sintering of carbon steel can be reduced below 5%. Parts treated in this atmosphere have shown

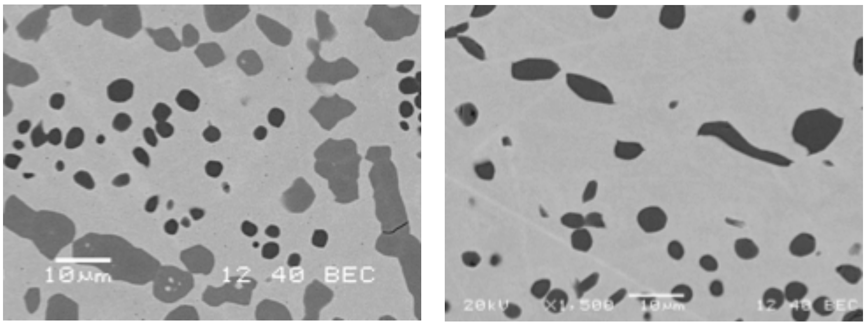
- A tight spread inside the desired physical properties range
- a uniform Microstructure

3. Effect of the Atmosphere Composition on the Service Life of Conveyor Belts

3.1. Material Degradation of a Stainless Steel Belt in a Sintering Furnace

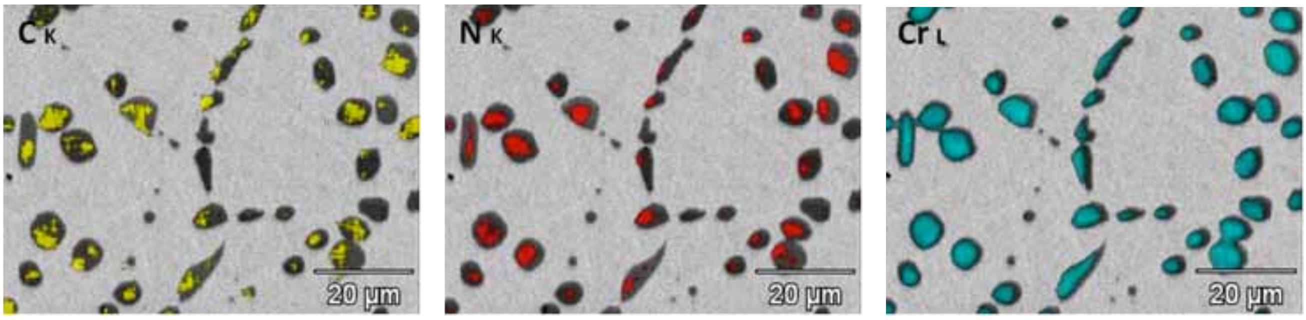
Wire mesh belts, used to convey powder metal parts through continuous sintering furnaces, are commonly made of austenitic stainless steel (AISI type 314 or 1.0314). Mechanical properties of the belt deteriorate during service because of high temperature material degradation, related to creep, oxidation, carburization and nitridation [4-6]. Conveyor belts are usually removed from service due to excessive deformation or cracking of the wire spirals or cross-rods.

Carburization and nitridation of austenitic stainless steel belts occurs in all sintering atmospheres. Even though nitrogen-hydrogen atmospheres do not consist of carbon-bearing compounds, contrary to endothermic atmospheres, the belt



(a) (b)

Figure 7: Microstructures of the belt spiral wire, backscattered electron images (BEC): (a) from the endo atmosphere; (b) from nitrogen-hydrogen atmosphere



(a) (b) (c)

Figure 8: Distribution of carbon (yellow, a), nitrogen (red, b) and chromium (cyan, c) on the cross-section of the belt spiral wire after 9 months of service in nitrogen-hydrogen atmosphere.

is always exposed to carbon-bearing compounds that form during delubrication of powder metal parts. Carbide and nitride precipitation, resulting from nitridation and carburization, leads to material embrittlement [4-6]. An example of an extensively brittle belt after service in the endothermic atmosphere is shown in Figure 7a. Examinations conducted by scanning electron microscopy (SEM), combined with energy dispersive x-ray microanalysis (EDX), indicate that the precipitated particles are chromium-rich carbides (light gray) and chromium-rich carbonitrides (dark gray).

An example of a belt after about 9 months of service in the nitrogen-6%hydrogen atmosphere is shown in Figure 7b. SEM/EDX examinations indicate that the particles that precipitated on grain boundaries and within grains are chromium-rich carbonitrides, Figure 8.

A surface layer of chromium oxide can considerably protect stainless steels from carburization and nitridation [6, 4]. However, the oxides scales are destroyed in the reducing environment of the high heat zone of a sintering furnace operating with a standard nitrogen-hydrogen atmosphere. The belt material experiences cyclic oxidation and reduction within the furnace, as it is reduced in the high heat zone and re-oxidized in the lower temperature, more oxidizing cooling zone. However, the oxide reduction in high heat zone of the furnace can be eliminated by controlled increase of moisture content of a nitrogen-hydrogen sintering atmosphere, which will result in increased service life of a conveyor belt [3].

3.2. Protective Effects of the Dew Point Controlled Hydrogen-nitrogen Atmosphere

3.2.1. Belt Trials

Two long-term belt trials were conducted in an industrial furnace to compare the effects of two nitrogen-hydrogen atmospheres on service-related belt degradation. The high heat zone temperature of the furnace was 1129 °C. The first trial was carried out using standard nitrogen-6 % hydrogen atmosphere. The dew point of this atmosphere in the high heat zone of the furnace was -51 °C. The second trial was conducted using a newly developed humidification system. In this test, the dew point of the nitrogen-6 % hydrogen atmosphere in the high heat zone of the furnace was maintained in the range of -40 to -37 °C. This dew point range was selected based on the oxidation-reduction diagram for the Fe-23Cr-19Ni system and pure iron, which was calculated using FactSage™ software [7]. The diagram in Figure 9 shows that the dew point of -40 to -37 °C, which was maintained throughout the second trial, was oxidizing to the stainless steel belt at the sintering temperature of 1129 °C and at the same time was reducing to the sintered metal powder materials (point B in Figure 9). The position of point A in Figure 9 corresponds to the dew point and temperature of the standard furnace atmosphere in the high heat zone. The conditions indicated by point A are reducing to the austenitic stainless steel belt.

The two belts that were used in the trials were made of the same type steel (AISI type 314). Both belts had the same designation BEF-36-10-8-10, which stands for balanced extra flat weave with 36 spiral loops per foot of width and 10 cross-rods per foot of length, 8 gauge rod and 10 gauge spiral.

Service-related belt degradation was evaluated based on material examinations of the samples taken at 4, 7, 8 and 11 months of service.

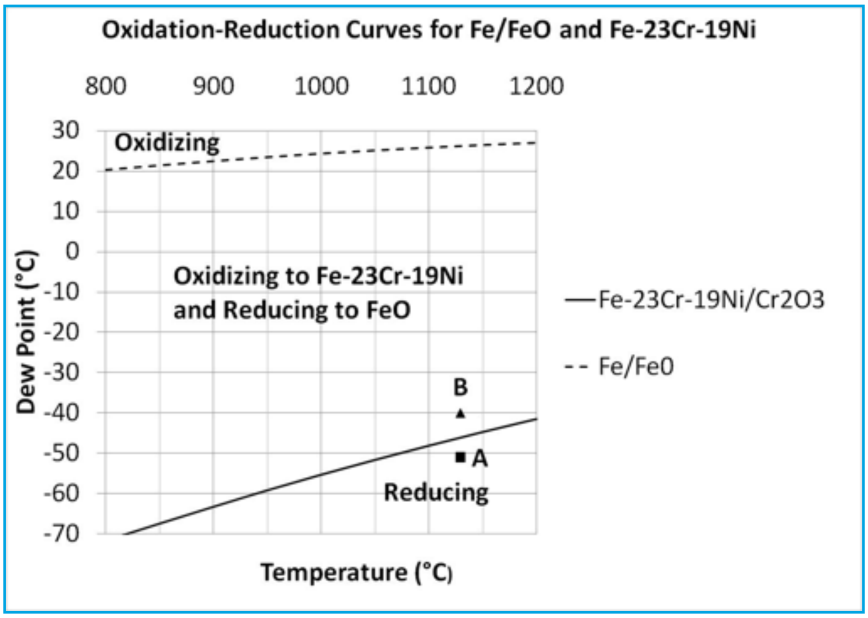


Figure 9: Oxidation-reduction diagram for Fe-23Cr-19Ni system and pure iron under partial pressure of hydrogen equal to 6079.5 Pa (0.06 atm).

The material examinations included microstructure analysis, tensile tests, microhardness tests and analysis of nitrogen and carbon concentrations.

Routine quality control procedures for sintered compacts did not reveal any nonconformance related to the increased moisture content of the sintering atmosphere. Statistical analysis of the data for two part types made of nickel steel containing 0.5 weight % carbon did not detect any significant difference in the apparent hardness and dimensions after sintering in the modified atmosphere, as compared to the standard nitrogen-hydrogen atmosphere.

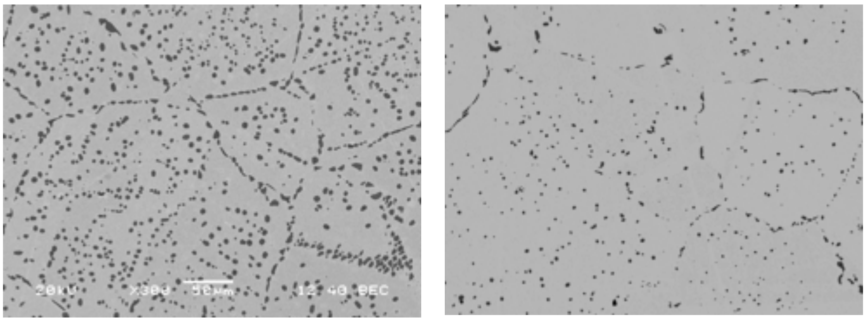
3.2.2. *Material Examination Results*

The material examinations of samples taken from the two belts that were tested in the standard and humidified atmospheres revealed the following. Chromium or chromium-rich carbonitrides have been detected in the microstructures of the both belts. The concentration and size of particles as well as length of continuous chains of particles increased with time. The concentration of particles and the length of continuous chains of particles are higher in the specimens from the standard atmosphere after the same time of service, Figure 10. So, the deterioration of the belt from the standard atmosphere is more advanced than the deterioration of the belt from the humidified atmosphere.

The phenomena causing degradation of both belts included internal oxidation of chromium, manganese and silicon. An example of surface and subsurface zone of the wire, containing internal oxidation of chromium, manganese and silicon is shown in Figure 11. Overall, the depth of internal oxidation for the belt from the modified atmosphere was about half that for the belt from the standard atmosphere, Figure 12.

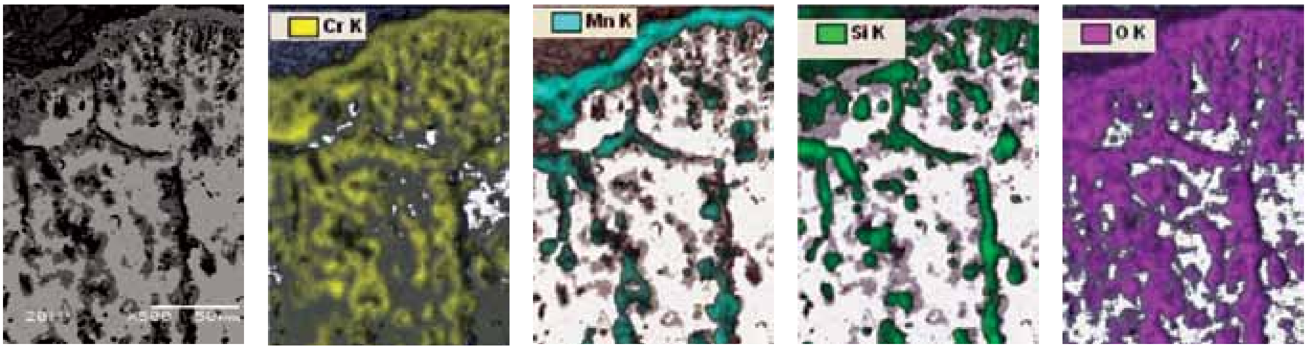
Surface oxide scales of both belts consisted of chromium and manganese oxides. However, a less protective iron-rich outer oxide layer was observed on the belt from the standard atmosphere. No iron-rich outer oxide layer was observed on the belt from the humidified atmosphere. This is an indication of a more protective oxide scale on the belt from the modified atmosphere [8].

The depth of chromium-depleted zones in the subsurface was deeper in the belt from the standard atmosphere. The average combined carbon and nitrogen concentrations and the rate of concentration increase with time were higher for the belt from the standard atmosphere [8].



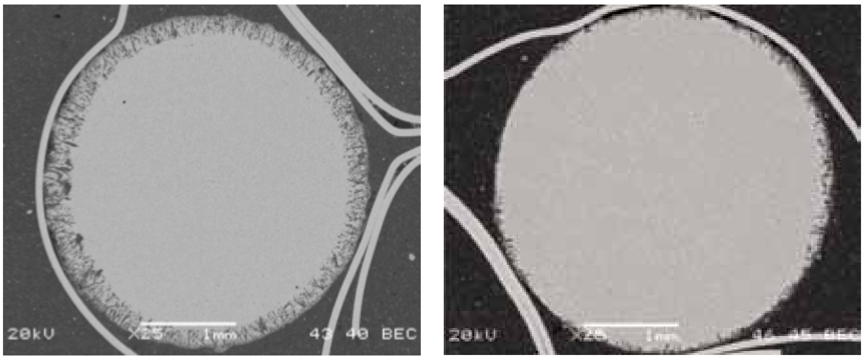
(a) (b)

Figure 10: Central areas of belt wires after 8 months of service, axial cross-sections, BEC: (a) belt from standard atmosphere; (b) belt from humidified atmosphere.



(a) (b) (c) (d) (e)

Figure 11: Surface and subsurface region of the wire from the belt after 11 months of service in the humidified atmosphere: (a) BEC; (b) overlay of chromium on BEC; (c) overlay of manganese on BEC; (d) overlay of silicon on BEC; (e) overlay of oxygen on BEC.



(a) (b)

Figure 12: Internal oxidation in the subsurface region of belt spiral wire after 11 months of service, transverse cross-section, BEC: (a) standard atmosphere; (b) humidified atmosphere.

The strength of the belt material decreased with time of service and was significantly higher for the belt from the modified atmosphere. Assuming that the tensile strength is the main factor in determining service life, the modified atmosphere increased the service life by about 30 % [8].

3.2.3. Benefits of Modified Nitrogen-Hydrogen Atmosphere versus Standard Nitrogen-Hydrogen Atmosphere

- Lower concentration of particles; shorter chains on grain boundaries
- Lower nitrogen pickup
- Lower depth of internal oxidation
- Lower depth of chromium-depleted zone
- More protective surface oxide scales
- No reduction of the protective surface oxide scales
- Higher tensile strength and elongation; lower rate of tensile strength reduction
- The effects listed above result in extended service life of conveyor belts used in humidified nitrogen-hydrogen atmospheres

4. Conclusions

The evaluation of sintered parts under several types of standard sintering atmospheres has shown that the highest quality results were produced in a dry nitrogen/ <5%H2- atmosphere. This is related to a very low dew point, resulting in a limited driving force for decarburization as well as the elimination of carbon species like carbon monoxide and hydrocarbons, resulting in sooting. However, the strongly reducing atmosphere destroys the protective surface oxide scales on the transport belt of the furnace. Although high surface quality parts are produced in this atmosphere, the service life of the transport belt is not optimal.

The results of belt tests in an industrial furnace using nitrogen-hydrogen atmospheres showed that the service life of a belt could be extended by increasing the moisture content of the sintering atmosphere. The belt used in the humidified atmosphere was better protected from high temperature oxidation, nitridation and carburization, which delayed the material degradation leading to the belt failure. A 30 % increase in belt life was attributed to the protective oxide scales that were maintained on the belt surface in the nitrogen-hydrogen atmosphere modified using our newly developed humidification system.

The described work shows that the set-up and control of the sintering furnace atmosphere is the key to producing parts with stringent high quality properties and can also be used to lower operating costs by reducing the maintenance efforts as achieved by extending the service life of a conveyor belt.

Acknowledgement

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