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In-Situ Monitoring of Gas Atmospheres During Debinding and Sintering of PM Steel Components

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Abstract

Processing of powder metallurgical components is related to high specific surfaces, in particular in the first stages of the process. Thus, high specific surfaces give rise to carbonization and oxidation during debinding and sintering due to reactions with degradation products of binders and additives. Since measurements in the furnace exhaust system may lead to ambiguous results, the objective of the present work is to observe reactions of PM components with the process atmosphere directly in the furnace. Therefore, in-situ FTIR gas phase measurements of the debinding and sintering of PM steel components were performed in reducing atmospheres. The results show the composition of the degradation products in the low temperature region <450 °C as well as carbothermic reactions and methane formation at temperatures >500 °C. With such informations, temperature and dwell time schedules may be optimized. As a conclusion, it is shown that in-situ monitoring of the gas phase composition in sintering furnaces is a strong instrument for the improvement of PM processes.

Introduction

PM steel components are widely used in automotive industry, e.g. for the production of gear wheels. These applications need for the proper comply with the definition of chemical composition in order to ensure the required material properties. In particular the presence of oxygen and carbon may harm the mechanical and corrosive strength. Such impurities can be a result of incomplete debinding or reduction processes. Most commonly, debinding is carried out by thermolysis. The fundamentals of thermal decomposition of polymers were investigated in earlier studies [1, 2]. Polymers undergo a variety of intrinsic degradation processes during thermolysis, including depolymerization, random scission, and side group elimination, that produce volatile degradation products, and side reactions such as cyclization and cross-linking that lead to the formation of residual carbon [3].

A typical binder that is used in powder metallurgy is ethylenbisstearamide (EBS, C₃₈H₇₆N₂O₂). Basically, the polymer basically consists out of a dimer with two long-chain aliphatic hydrocarbons and two functional carboxylic groups, which are connected by an ethyl group. The decomposition of such a binder has been studied mixed with a Fe/C system in vacuum, where the main decomposition products have been identified as CO, CH₄, CO₂ and C₂H₄. Two competing decomposition pathways have been described: decomposition of the primary EBS products, which form CO or CO₂, and catalytic decomposition of EBS on iron/carbon surfaces has been observed. This effect was attributed mainly to the catalytic decomposition of low volatility products formed during self-decomposition of EBS [4].

The debinding process typically is attributed to the decomposition of the molecular chains. But even at higher temperatures, essential reduction and decarburization proceeds. E.g., the reduction of surface oxides is required for the formation of sintering contacts. PM steels are reduced by carbothermic reactions (that means using the Boudouard equilibrium between formation of CO and CO₂) or by hydrogenation. Such reductions of the surface oxides characteristically occur in unalloyed steels at ~700 °C, whereas the main reducing step occurs at T>1000 °C [5]. Even in inert atmosphere, carbothermic reductions are attended with decarburization processes. Furthermore, decarburization occurs in hydrogen atmos-

phere by formation of methane at temperatures $>550\text{ }^{\circ}\text{C}$ [6]. Such decarburization processes can disturb the well balanced carbon induced properties and need to be controlled in-situ. In-situ monitoring of the sintering process has been carried out by using optical kinetic field methods [7]. The reduction and decarburizing processes as well as the thermal decomposition of metal powder/binder compositions and its interaction with the debinding atmosphere has been studied in combined thermogravimetric measurement with infrared analysis [8], but nevertheless, in-situ monitoring of gas phases directly in the debinding furnace has not studied yet. Thus, the objective of the present work was to study the gas composition during debinding of prealloyed steels by in-situ FTIR analysis.

Experimental

The samples used in the experiment were prepared by various prealloyed powders with varying carbon content and chromium content. As a reference unalloyed steel was chosen. The chemical compositions of the powders are listed in table 1. The binder was a commercial available ethylenbisstearamide binder (1.5 weight-%). The powders and binder were mixed and than pressed in cylindrical geometry.

Tab. 1: Chemical composition of the studied PM steels.

| | C | Cr | Mn | Cu | Si | P | Mo |
|----------|------|------|------|-----|-----|------|------|
| sample 1 | 0.2 | | 0.3 | 0.5 | | 0.45 | |
| sample 2 | 0.8 | 1.5 | | | | | |
| sample 3 | 0.8 | 3 | | | 0.5 | | |
| sample 4 | 0.4 | 1.24 | 1.36 | | | | |
| sample 5 | 0.4 | 1.24 | 1.36 | | | | 0.85 |
| sample 6 | 0.15 | | | | | | |

The green parts were subjected to debinding and sintering at RT-1200 $^{\circ}\text{C}$ in a tube furnace in $\text{N}_2\text{-H}_2$ (20 % H_2) as well as in pure H_2 -atmosphere. The gas flow was 6 l/min. The samples firstly were heated to 450 $^{\circ}\text{C}$ with a dwell time of 10 min, and subsequently heated to 1250 $^{\circ}\text{C}$ with a dwell time of 30 min. The heating rate was 3 K/min. In order to observe the process gas composition, in-situ gas phase observation was carried out by Fourier-Transform-Infrared spectroscopy (FTIR), using a ThermoFisher Scientific Antaris IGS. The infrared beam from the broadband IR source (1000 – 4000 cm^{-1}) first passed through a mirror system and entered the tube furnace via KBr windows. In order to identify single species, reference spectres (CO , CO_2 , CH_4 , C_2H_4), were taken with the help of gas filled reference cells. Spectres were taken in temperature steps of 5 K. Each spectrum was analyzed in respect of the detected species. Furthermore, the relative absorption of the main components (CH groups, CO , CO_2 , CH_4 , H_2O) was evaluated as a function of temperature.

Results

In order to refine the debinding temperature range of the system, the weight loss of the binder during thermal treatment was measured by thermogravimetric analysis in Ar-H_2 atmosphere. The results are shown in Figure 1. The onset of mass loss is at 250 $^{\circ}\text{C}$. Mass loss appears in a single step, where the organic material decomposes in the temperature range of 336 - 408 $^{\circ}\text{C}$. At higher temperatures, only small changes of mass are visible. In total, the mass loss amounts 96.9 %.

The absorbance spectra during debinding of sample 1 in the temperature range of 365-660 $^{\circ}\text{C}$ under H_2N_2 is shown in Fig. 2. At low temperatures $<300\text{ }^{\circ}\text{C}$, only H_2O is detected. Higher temperatures lead to a broad peak in the range of 2700-3000 cm^{-1} , indicating the presence of CH groups. At such temperatures also CO_2 and CO is detected. Furthermore C-C valence bonds are observed at temperatures of $\sim 400\text{ }^{\circ}\text{C}$. The characteristic fingerprint

range at 1300-1800 cm^{-1} is covered by H_2O bands so that further analysis of species is inhibited.

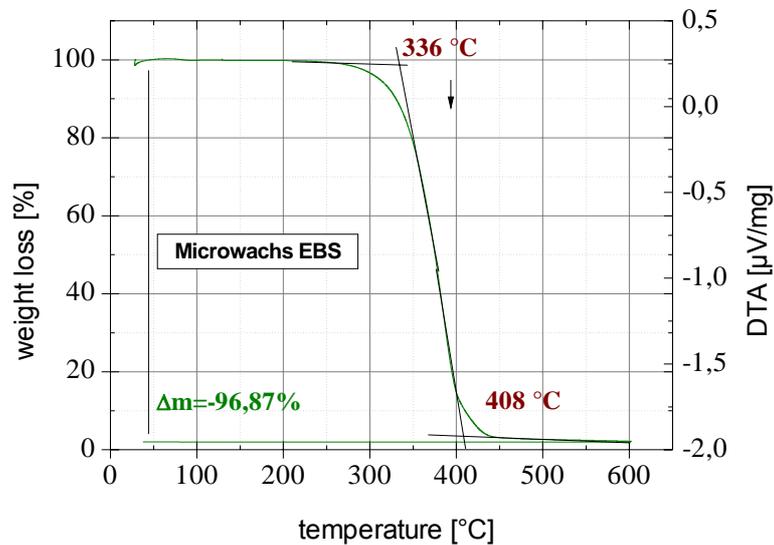


Fig. 1: Thermogravimetry of debinding of the ethylenbisstearamid binder under Ar- H_2 atmosphere. The main debinding step occurs between 336 – 408 °C.

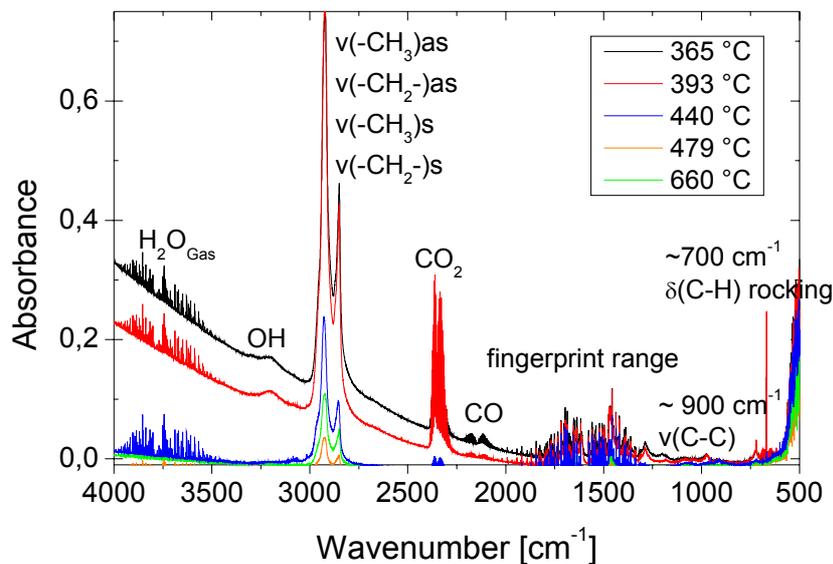


Fig. 2: Absorbance spectra of PM steel (sample 1) at temperatures from 365 – 660 °C. At the typical wavenumbers of H_2O -, OH-, CO_2 - and CO-absorption peaks are observed. Furthermore, a distinct characteristic CH-group absorption peak is measured at temperatures >350 °C.

The relative absorption due to the presence of the main cracking products H_2O , CO_2 , CO, CH_4 and the CH groups of sample 1 is displayed in Figure 3. In the figure, the decomposition of the binder is indicated by a combined maximum of the detected species. However, the main decomposition product is given by CH groups, which is a main group within the ethylenbisstearamide molecule. The absorbance of the above mentioned species increases at 325 °C with a coincident double peak at 355 and 384 °C. At higher temperatures the absorbance of all relevant species increases constantly with a uniform slope. However, since the main transmission decreases at $T > 500$ °C, the decrease of the absorbances may not

attributed to an increase of the gas concentrations. Focussing on the CO absorbance, a further increase occurs at temperatures of 670 – 820 °C. Maxima of the H₂O formation are visible at 820 and 947 °C.

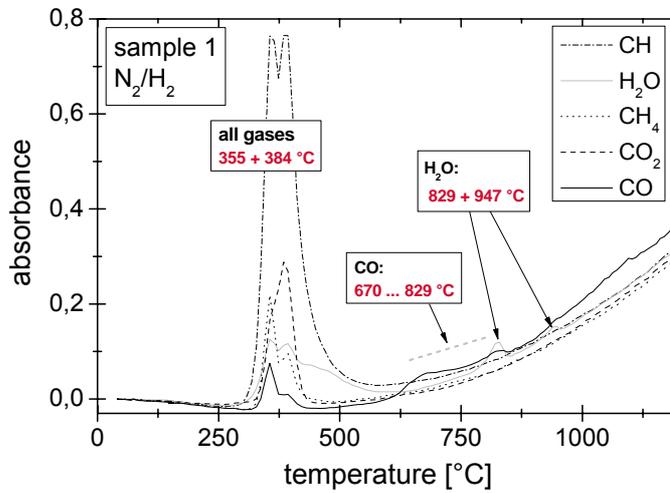


Fig. 3: Absorbance of the main detected species during debinding of sample 1 as a function of temperature under H₂N₂ atmosphere. The main debinding step occurs within the temperature range of 325 °C – 500 °C and is indicated by the CH-absorption peak.

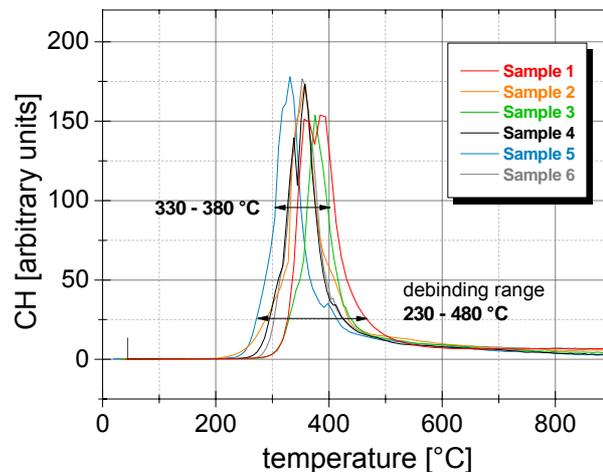


Fig. 4: CH-group absorbance of various PM steels as a function of temperature under H₂ atmosphere. The release of CH indicates the main debinding step and occurs between 230 – 480 °C.

In the next step, the absorbance of the CH groups was observed, using various alloying elements. The results of the heat treatment under H₂ atmosphere are shown in figure 4. In general, CH groups occur at 230-480 °C, with considerable differences of the occurring peak temperature range between the alloys. E.g., the peak temperature of the Cr and Mo containing sample 5 shows a maximum at 330 °C, whereas the absorbance of the CH band of sample 1 (low carbon, Cu, P) is maximal at 393 °C. The maximum absorbance of all samples is nearly the same. The full width at half maximum ranges between 47 K (sample 5) and 72 K (sample 1). The characteristic double peak as seen in Fig. 3 is only visible for sample 1.

The absorbance of the CO band is displayed in Figure 5. In accordance to the absorbance due to the presence of CH groups a maximum absorbance is observed between 324 °C (sample 5) and 381 °C (sample 3). In contrast to Fig. 4 the maximum absorbances is slightly dependent on the alloying element. At higher temperatures, the absorbance of the CO band during heating of sample1 shows further saddle with maxima at temperatures of 615 and 845 °C, whereas the Cr-containing and steels with low carbon content do not show such features. A further release of CO of sample 1 is detected at temperatures >900 °C. A comparable increase of the CO release can be attributed to sample 2 and sample 3. Here, the onset of the CO release is shifted to higher temperatures.

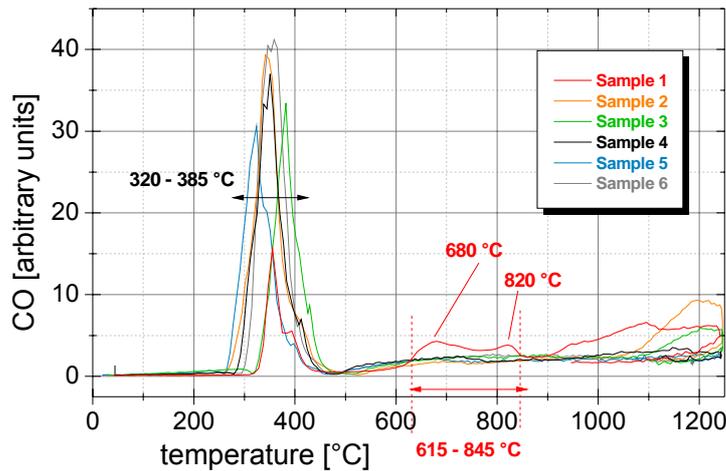


Fig. 5: CO absorbance of various PM steels as a function of temperature under H₂ atmosphere. At low temperatures, CO indicates the progression of the binder decomposition. At temperatures of 600-800 °C only Cr-free alloys show CO in accordance to [5].

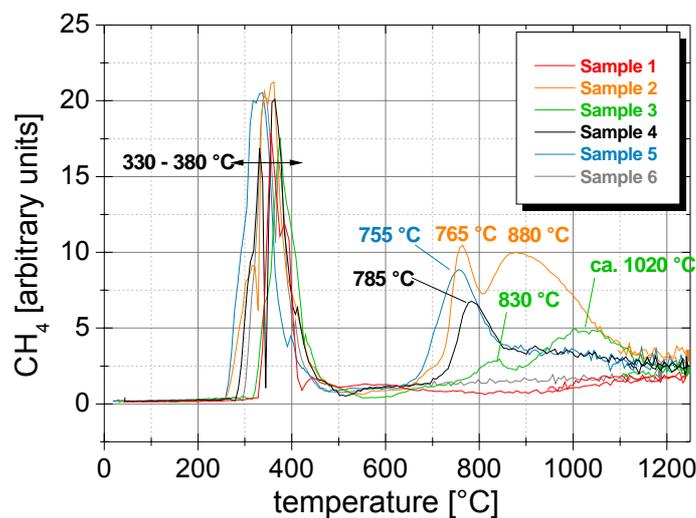


Fig. 6: CH₄ absorbance of various PM steels as a function of temperature under H₂ atmosphere. The release of CH₄ at higher temperatures is dependent on the carbon content of the alloy. Low carbon steels show nearly no CH₄ at T>700 °C.

Absorption due to the presence of methane during heating of the samples with varying alloying elements is shown in Figure 6. The low temperature range <500 °C is comparable to

the absorbance of the CO- and CH bands. At higher temperatures a significant influence of alloying elements becomes visible. Here, sample 1 and sample 6 with low carbon content show no absorbance. Sample 4 and 5 with medium carbon content of 0.4 wt.-% exhibit a single maximum at 755 and 785 °C, respectively. Two maxima are displayed by sample 2 and 3. These samples feature higher carbon contents of 0.8 wt.-%.

DISCUSSION

The decomposition of ethylenbisstearamide containing PM steels during debinding and sintering is a complex process that occurs within several temperature steps. At temperatures 330 – 410 °C the backbone of the binder decomposes as demonstrated by the thermogravimetric measurement and the parallel detection of all relevant decomposition products (CH-groups, CO, CO₂, H₂O, CH₄). Ethene (C₂H₄) as identified in [4] has not been observed in the recent work. Both the thermogravimetric measurement and the gas analysis show a single step decomposition of the EBS binder. The major decomposition products are CH valence groups, as expected due to the presence of aliphatic hydrocarbons as one main element in the molecular structure of the EBS chain structure. Here, the hydrogen fractions of the process gas atmosphere are the hydrogen-source for the molecular chain fragments. Poskrebyshev et al. declare the decomposition of EBS in presence of Fe/C to be triggered by catalytic effects [4]. In contrast, in the present work the decomposition of pure EBS does not start at significantly higher temperatures, but rather small amounts of alloying elements may have a significant influence on the decomposition temperature. E.g., the lowest decomposition temperature is shown by molybdenum containing alloys. Molybdenum is a carbide forming element. In the form of Mo₂C it is used as catalyst for the shift-reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. Interestingly, the CO fraction of the molybdenum containing sample 5 is slightly reduced (in contrast to the CH and CH₄ bands, which are nearly equal for the various alloys).

At higher temperatures, in Cr-free steels further CO maxima are detected. Such CO formation is commonly attributed to the carbothermic reduction of iron oxides ($\text{Fe}_2\text{O}_3 (\text{s}) + 3\cdot\text{C} \leftrightarrow 2\text{Fe} + 3\cdot\text{CO}$) in the presence of carbon. The source of the carbon may be dissolved carbon of the prealloyed powders or char as residue of the EBS decomposition. The Gibbs free energy of the reduction is negative at temperatures >680 °C giving rise to the start of the reactions at the mentioned temperature. In the same way both processes show CO formation maxima at 600 - 650 °C. The peaks at 680 and 820 °C are both due to carbothermic reduction of oxides. Even in inert atmosphere such reactions lead to decarburization of PM steels during sintering. As shown by studies with different Fe powder fractions and preoxidized powders [9], the first peak indicates reduction of the surface oxides and the high temperature peak that of the internal oxides within the powder particles. The detection of a water peak of sample 1 at 829 and 847 °C indicates further reduction processes via $\text{Fe}_2\text{O}_3 (\text{s}) + 3\cdot\text{H}_2 \leftrightarrow 2\cdot\text{Fe} + 3\cdot\text{H}_2\text{O}$ with negative Gibbs free energy at $T > 635$ °C.

Prealloyed steels containing chromium do not show any further CO or H₂O formation at temperatures >500 °C. Danninger et al. attribute the absence of such CO peaks to the transformation of iron oxides to chromium oxides, which are much more stable at 700 °C [5]. The main reduction occurs at temperatures >1000 °C. Here, higher temperatures of the CO peaks are related to higher chromium content of the studied samples. Other reports on debinding of unalloyed steels in inert atmosphere also describe a decarburization maximum at 700 °C [10].

During debinding and sintering of PM steels in hydrogen atmosphere at temperatures >700 °C the formation methane can be detected in some cases. The appearance of a characteristic double methane peak also has been reported in earlier paper [5], where debinding of an unalloyed PM steel in H₂ leads to complete decarburization. In the Fig. 6 it is shown, that the formation of methane is dependent on the carbon content as well on the alloying elements. No methane formation detected for low carbon steels (sample 1 and 6). High carbon contents lead to formation of a double peak with a pronounced first peak in the case of lower chromium content. The second peak at higher temperatures is not detected, when samples with medium carbon content (0.4 wt.-%) are heated. The formation of two maxima in the absorption vs. temperature plots indicates two different formation mechanisms. In general, methane may be formed via the reactions



Thermodynamically, the first reaction is more likely at lower temperatures. Obviously, the first methane formation at lower temperatures is restrained by the presence of chromium, which is a strong carbide forming element and therefore carbon is bonded. Reaction (2) is thermodynamically possible even at higher temperatures. Furthermore, the formation of CO needs for higher temperatures (see above). Here, high carbon contents are the requirement for the formation of methane at higher temperatures. In general, at equal concentrations infrared absorption of CO is ~ 10 times higher than that of the methane species. Since the data reveals that the relative absorption maximum of CH₄ is 4 times higher than the absorption due to CO, one may estimate that the absolute concentration of methane is up to 40 times increased compared to that one of CO. Thus, formation of CH₄ is the main mechanism for decarburization of steels at high temperatures.

Conclusion

In the present paper the decomposition of ethylenbisstearamide (EBS) as binder in PM steel components has been studied in situ via FTIR. It has been shown, that EBS in steel components decomposes mainly in CH-groups, CO, CO₂, H₂O and CH₄. Due to their central position in the molecular chain of EBS, the CH-groups are the dominating species in the spectra of the process gas. Decomposition is detected within the temperature range 230-480 °C, where the debinding temperature is significantly dependent on the presence of alloying elements. The lowest decomposition temperature is featured by molybdenum containing alloys, which is attributed to catalytic effects. A change of the decomposition pathways due to the presence of alloying elements has not been shown.

At higher temperatures, CO and H₂O have been detected attributed to oxidation reduction effects in chromium free alloys. In hydrogen atmosphere, at temperatures >700 °C decarburization occurs due to the formation of methane. The presence of carbon and chromium plays a major role for such reactions. High carbon fractions involve the formation of massive methane fractions, whereas chromium inhibits the decarburization process due to bonding of carbon by formation of chromium carbides.

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