PROCESS CONTROL SYSTEM FOR DELUBRICATION OF PM STEELS

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Abstract

Lubricants are important additive in powder metallurgy (PM) steels as they are needed to improve powder compressibility and reduce tool wear. Removal of the lubricant results in production of number of gas species that can have harmful effect on the base material. Current paper describes process gas monitoring system for delubrication control that is built on industrially available gas sensors. Experimental results indicate that accurate delubrication process control can be performed by utilizing only CO_2 and O_2 sensors. It is recommended to perform delubrication below 500°C in dry inert atmospheres in the case of modern ethylene bis stearamide based lubricants.

1 Introduction

Powder metallurgy (PM) is a "net shape" components producing technology where near-net shape component is manufactured from metal powders by compaction with following sintering processes. When it comes to the PM structural steels, used mostly in automotive industry and household appliances, water atomised steel powder is the staring material. Water atomized powders are less costly and are characterized by highly-irregular shape that result in good green strength of powder compact after compaction. Presence of residual porosity results in lower mechanical properties of PM steels in comparison with the same parts produced by machining of wrought material or precision casting. Therefore in order to improve performance of PM parts, high-strength alloy steels are alloyed with a number of alloying elements. Introduction of such effective and environmentally friendly alloying elements like Cr, Mn and Si represents the modern trend in conventional PM manufacturing [1-7]. However, exist two important drawbacks with utilization of these alloying elements in conventional PM: a) all these alloying elements increase ferrite hardness that results in decreasing in powder compressibility; b) high affinity to oxygen of these alloying elements lead to their selective oxidation on the powder surface during powder manufacturing and further powder consolidation. This currently puts obstacles to wide introduction of Cr, Mn and Si in PM steels and is the topic of numerous researches in the area.

In conventional press and sinter PM technology, when water-atomized powder is used, lubricant is added in order to reduce inter-particle friction and friction between the PM compact and compaction tool. Typically between 0.4 to 1 wt. % of lubricant is added. Increasing demands on

mechanical properties of structural parts in combination with increasing complexity of parts geometries force PM manufacturers to re-consider lubricant itself (type, amount, method of lubrication, etc) as well as further delubrication process. Except good lubrication properties lubricant also has to ensure safe delubrication meaning minimal process temperatures/times, minimize oxidation risk of PM component and absence of delubrication defects (external and internal sooting in the parts as well as in the furnace, blistering, pop-corning, etc.). Historically lubricants used were based on metal-stearates (lithium and zinc-stearates) and their mixture with ethylene bis stearamide (EBS). As the metal-stearates have higher temperatures of evaporation/decomposition and they produce larger amount of residue and are environmentally harmful, purely organic lubricants based on EBS have become dominant on the market.

Initial stage of sintering is the lubricant removal and heating of compacts. In the case of iron-carbon PM steels typically lubricant is burned-off by using methane gas that allows efficient lubricant removal and at the same time fast heating of the components. However, due to the high oxygen affinity of the alloying elements used in modern PM this technique can't be used due to the risk of extensive oxidation of the components. Therefore lubricant has to be removed by controlled decomposition in inert atmosphere.

EBS-based lubricants are complex organic compounds [8], decomposition of which leads to production of water vapour and carbon oxides [9-12]. This lowers significantly the atmosphere purity and if process control is inadequate this can lead to oxidation of the material in the case of utilization of prealloyed powder [13]. Due to this fact fast removal of products of lubricant decomposition at low temperatures is an important issue during sintering of prealloyed with sensitive elements like Cr and Mn powder grades [13].

Previous studies point out carbon dioxide as one of the principal reaction products of the delubrication process, the emission of which was reported to be in tandem with large-molecular hydrocarbons [10]. In spite of the presence of number of published research concerning delubrication of PM steels, results are inconsistent and no feasible system to control delubrication process is established until now.

2   Experimental Procedure
2.1 Design of processing atmosphere monitoring system
The main focus of this study was to design the system for reliable and representative control of the delubrication process in the laboratory scale that can be transferred to the industrial scale. Therefore lubricant removal control system has to be built using available on the market industrial sensors. As the most of the gas sensors of interest are working only at room temperature (except oxygen probe) this mean that gas has to be sampled from the furnace, cleaned from particulates/dust/heavy volatile products and cooled down as fast as possible to prevent any gas composition changes.
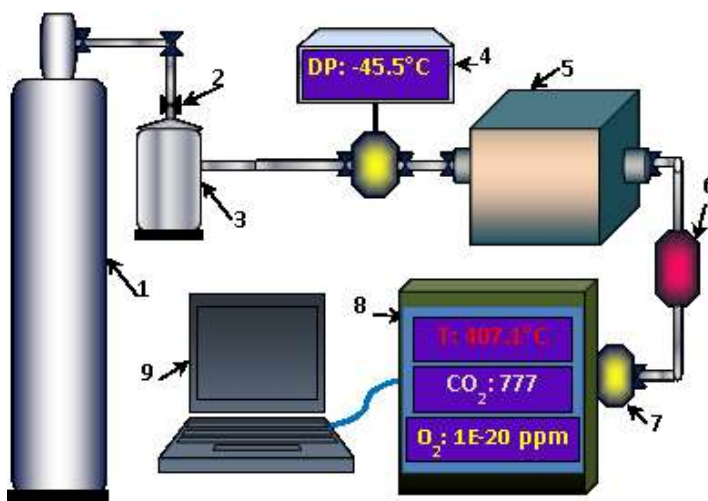
Processing atmosphere monitoring setup, see **Fig. 1**, was installed on the base of laboratory tube furnace *Entech* with the quartz tube. Two most critical issues were taken into account during design of such system: 1) proper sampling of the processing atmosphere that will give representative probe of the gas; 2) sensors' contamination. During the delubrication large amount of the heavy hydrocarbons is produced that are harmful for the sensors as these compounds will condense on the sensors and destroy the system. Therefore reliable filtration system has to be developed that at the same time will not affect fast sample transfer, gas composition and results of the analysis.

After a number of tests it was realized that only atmosphere probe from the close proximity to the specimen was suitable as the gas composition at the other points inside furnace and

especially furnace outlet are very dependent on the gas flow and furnace load. This leads to dilution of the exhaust gases and do not represent real microclimate around compact [14].

In order to avoid risk of sensors contamination, two-stage filtering system was developed, see **Fig.1**. First stage consists of stainless-steel pre-filter element (removal of particles >1 μm) for coarse filtration and large-molecule hydrocarbons condensation. Such filters are widely available on the market today, have been proved in the industry for about decade, are reliable, gas-tight, can be used for filtering of hot gases and under high pressures. Additionally filter design allow filter change in a couple of seconds without need to open the system. Additionally these filters are easy to clean in organic solvents (like acetone). Second stage consists of microfiber filter element (removal of 0.1 μm particles), similar to the one installed on most of the sensors just having larger capacity and adapted to fast exchange as well.

Measuring principle proposed is based on continuous on-line analysis of oxygen content (zirconia ceramic sensor) and carbon dioxide (sensor based on infra-red cell technology). There are number of analysers on the market that combine both of the sensors. During the laboratory experiments *Rapidox 3100A* (Cambridge Sensotec Ltd) dual O_2/CO_2 analyser was used. Purity of the inlet atmosphere was controlled by ceramic dew-point sensor (Michel Cermet II sensor). The same type of dew-point sensor was also connected together with the O_2/CO_2 analyser however analytical information obtained didn't give some additional information so it was ommited. Temperature was measured by thermocouple (K-type) installed inside the specimen.

Fig.1 Scheme of sintering atmosphere monitoring setup: **1**- gas cylinder (N_2, N_2/H_2 or N_2/CO - mixtures); **2**- valves; **3**- water source; **4**- hygrolog (inlet dew-point); **5**- furnace; **6**- coarse filter; **7**- fine filter; **8**- O_2/CO_2/temperature sensors; **9**- computer

3 Material and experiment

Designed experimental setup was tested first in dry nitrogen atmosphere of purity 5.0. Water-atomized prealloyed with chromium steel powder *Astaloy CrM* (Fe-3Cr-0.5Mo) was used as the test material as this is one of the most oxygen-sensitive powders on the market today (due to the high content of chromium). Powder was admixed with 0.6 wt pct of *EBS_L* as a lubricant. Charpy impact test bars (10×10×55 mm) were uniaxially compacted at 600 MPa to a green density of ~7 g·cm⁻³. Delubrication trials were performed at two different temperatures – 450

and 900°C for 30 min, heated at about 10°C·min^{-1}. Commonly used in industry flow rate of around 4 l·min^{-1} (~0.05 m·s^{-1}) was applied.

In order to show influence of processing conditions on powder oxidation, fresh fracture surface of delubricated compacts was carefully studied by means of high-resolution scanning electron microscopy combined with energy-dispersive X-ray analysis (HR SEM+EDX) utilizing *LEO Gemini 1550* SEM equipped with *INCA Energy* EDX analyser. Additionally analysis of surface oxide state after delubrication was performed by means of X-ray photoelectron spectroscopy (XPS) using a PHI 5500 instrument. The analyzed area during XPS analysis was about 0.8 mm in diameter and thus a large number of particles (~100 particles) was analyzed at the same time giving statistically reliable average result that represent the general surface of the powder compact. Photoelectrons were excited by monochromatic Al Kα source (1486.6 eV).

4 Results and discussion

Ethylene bis stearamide has a theoretical melting point around 145°C and boiling temperature around 260°C. Therefore vapour of EBS (evaporated lubricant) and some decomposition products (preferably heavy hydrocarbons) can be observed after this temperature. During both experiments beginning of de-lubrication process – evaporation and/or decomposition of lubricant into heavy hydrocarbons – was <u>visually</u> observed by appearance of dense smoke at around ~270°C, that is in agreement with boiling temperature of EBS. No any changes in CO_2 signal were observed at this stage, see **Figs. 2** and **3**, confirming evaporation and/or decomposition mechanism at this stage and lack of oxygen does not allow its oxidation in dry atmospheres. However, even when processing in air CO_2 signal was not registered when the lubricant evaporation started [15, 16]. Therefore monitoring of the CO_2 signal didn't allow detection of beginning and/or continuation of the first stages of delubrication connected with lubricant evaporation. At the same time it has to be emphasized that monitoring of neither dew-point nor CO content allows reliable detection of the lubricant evaporation process. This was shown during monitoring of the sintering process where similar setup was built and used where instead of oxygen probe CO sensor was used [14, 17, 18]. Nevertheless, this de-lubrication stage
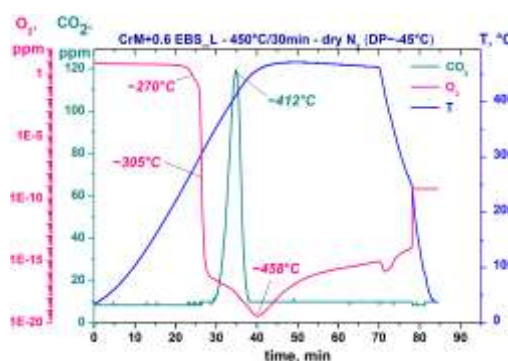
Fig.2 Temperature profile, O_2 and CO_2 content during delubrication of ***AstCrM+0.6EBS_L*** at 450°C for 30 min in dry nitrogen
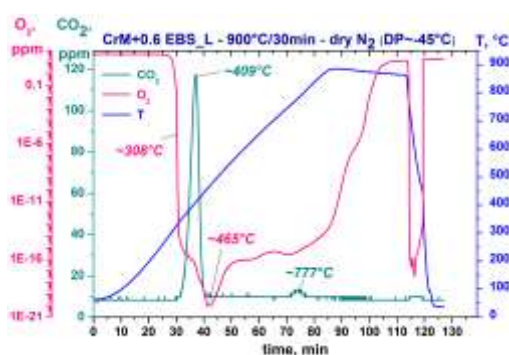
Fig.3 Temperature profile, O_2 and CO_2 content of ***AstCrM+0.6EBS_L*** during delubrication at 900°C for 30 min in dry nitrogen

can be easily registered by analysis of oxygen content profile – considerable drop of oxygen partial pressure was observed at this temperature range, see Figs.2 and 3. Oxygen content profile

shows first steep inclination at 270°C that coincides with the smoke appearance and lubricant boiling temperature. Second and steeper drop in the oxygen content was observed at ~300°C, see Figs. 2 and 3. First inflection point on oxygen profile gives a very important information concerning starting of intensive evaporation of lubricant. Zirconia oxygen sensor has unique characteristic to detect and control delubrication process that cannot be provided by any other solitary sensor.

This unique property of zirconia sensor is connected to the sensor design, see Fig. 4 – sensor is built on zirconia ceramic tube (sensor head) that is heated between 650 and 700°C in order to provide required oxygen ions conductivity inside ZrO_2 ceramic. Evaporated lubricant and heavy hydrocarbons produced during the first stage of lubricant decomposition are oxidized on hot oxygen sensor head, resulting in steep decrease in oxygen value on the sensor surface and therefore result in drop in measured value, see **Fig. 4**. Therefore oxygen sensor provides valuable information concerning starting of lubricant evaporation/decomposition that no other available on the market sensor can provide.
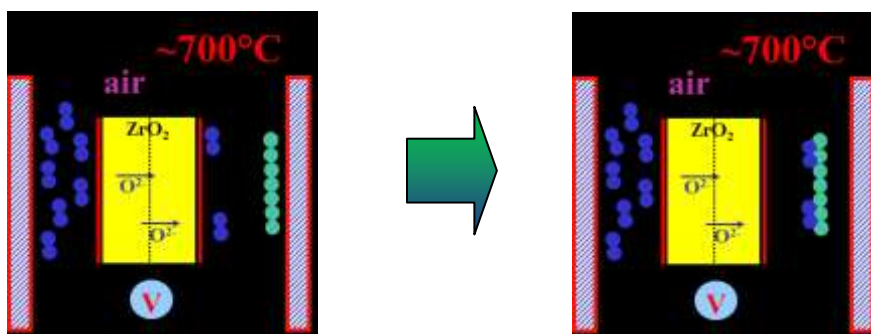
Fig.4 Design of the oxygen zirconia sensor. Detected oxygen on the sensor head (left) after starting of lubricant evaporation reacts with lubricant/heavy hydrocarbon in the sensor chamber (right) due to the high temperature that results in sharp decreasing in oxygen content on the sensor head detected

As it was emphasized in [10, 11] there are number of possible scenarios of decomposition of ethylene bis stearamide depending on base powder and processing parameters leading to production of number of light (methane, ethylene, etc) and heavy (hexadecane, heptadecane, etc.) hydrocarbons as well as other complex organic compounds (ketones, ketenes, amides etc.). Therefore such a variety of possible reaction products will require complex analytical equipment in order to be able to properly control delubrication process that is industrially not feasible. Hence indirect analysis of presence of hydrocarbons by use of oxygen sensor is very accurate, robust and reliable tool for monitoring furnace atmosphere.

Further oxygen decrease was observed with temperature increasing indicating intensive lubricant decomposition and its peak nearly coincides with the CO_2 peak temperature. Increase in oxygen signal with dwelling time at delubrication temperature was observed, see **Fig. 2**, however it doesn't reach the value of the oxygen content, characteristic to the processing gas. This is connected to the slow removal of the lubricant/hydrocarbons that condense on the stainless tubing of the sampling system. But as it is evident from the delubrication at higher temperature, see **Fig. 3**, oxygen content reaches its typical value with further heating due to much faster

tubing purification by hot gas. It is also important to note that in the case of industrial furnaces oxygen probe is placed directly into the furnace, therefore response time will be considerably improved.

Nevertheless there is one significant drawback with using zirconia oxygen probe for the delubrication monitoring in the commonly used reducing atmospheres. Active reducing agent (H_2 or CO) reacts with oxygen atoms on the hot surface of the sensor head in the same way as hydrocarbons, as is shown in **Fig. 4**, producing water vapor and carbon dioxide. Hence oxygen content is considerably lowered as it is was shown in [14, 15]. Therefore zirconia-based oxygen sensors do not provide any valuable information during delubrication in reducing atmospheres of high purity. If the processing atmosphere is not too dry (dew-point above -20°C) oxygen sensor can still be useful.

The main sharp CO$_2$-peak was observed at ~410°C independent on processing temperature, see **Figs. 2 and 3**. This peak is connected to the second stage of delubrication – decomposition of the EBS as well as other organic additives [14, 15]. During heating up to 900°C, see **Fig. 3**, additional weak CO_2 -peak was at around ~780°C in nitrogen atmosphere that is connected to the direct carbothermal reduction of surface iron oxides by carbon from lubricant residue.

Careful analysis of the processing atmosphere monitoring profiles during heating indicates that no pronounced processes are observed at temperatures higher then ~450°C. Oxygen content starts to increase indicating absence of the traces of hydrocarbons in the processing atmosphere and the main peak of carbon dioxide is observed at around 410°C. Further analyses of the delubrication of the same system in different atmospheres, chemical and thermogravimetry analyses, presented in [14, 15], confirms full lubricant removal during delubrication at 450°C. Almost all the lubricant was removed during heating stage; minor mass-loss was observed during holding at 450°C. This indicates that additionally delubrication time can be considerably shortened. However, it has to be taken into account that in the case of massive and complex-shaped compacts, high load of the furnace, etc., some holding at delubrication temperature is needed to assure full lubricant removal.

In authors previous work [13] it was shown that delubrication of prealloyed with Cr and Mn powder grades at higher temperatures can lead to considerable enrichment of surface oxides in Cr and Mn that leads to deterioration in mechanical properties after sintering. This is connected with the second stage of lubricant decomposition when high amount of CO_2 is produced, see **Figs. 2 and 3**. If this stage of lubricant decomposition is shifted to higher temperatures it can lead to oxidation. HR SEM observation of fracture surface and oxide particulates on the powder surface for the specimen delubricated at 450°C (process as in **Fig. 2**) indicate, see **Fig. 5**, that surface oxide is comparable with the base powder [13]. However, careful look on the fracture surface of the specimen, delubricated at the same atmosphere purity but at 900°C, see **Fig. 6**, clearly indicate higher amount of the particulate oxides on the powder surface, **Fig. 7**.

XPS analysis of the fresh fracture surface of the same compacts, see **Fig.8**, indicate considerable enrichment of the powder surface in Mn and Cr cations and further confirms significant oxidation of the powder surface of the delubricated at 900°C compact. Carbon signal is nearly the same in both cases, indicating nearly the same extent of the lubricant removal in both cases. In the compact, delubricated at 450°C, additionally zinc signal was detected, see **Fig. 8**, that was not detectable on the fracture surface of delubricated at higher temperature compact. This Zn signal is connected to the presence of Zn-stearate in tested lubricant that is removed at higher temperatures – around 600°C. Even if Zn-stearate was not removed during delubrication at lower temperatures, its content in the modern lubricant is on the level of couple weight percent

and therefore it is removed very fast during further heating stage. Therefore it is important to remove major part of lubricant at lower temperatures to avoid significant oxide formation when performing delubrication at high temperatures.
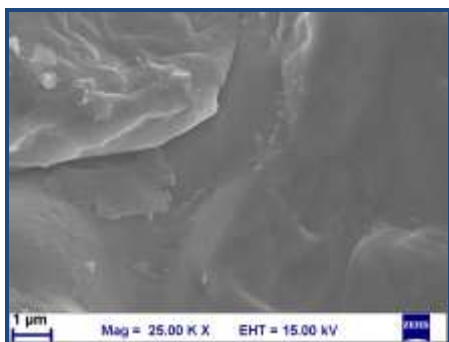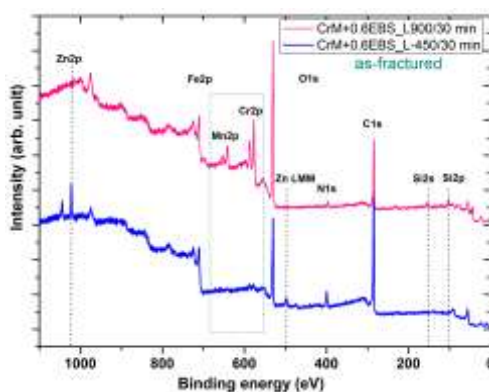

Fig.5 Fracture surface of the compact, delubricated at 450°C for 30 min in nitrogen
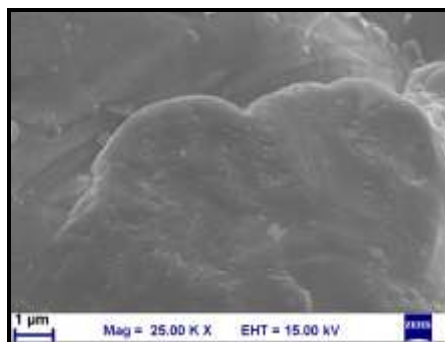
Fig.6 Fracture surface of the compact, delubricated at 900°C for 30 min in nitrogen
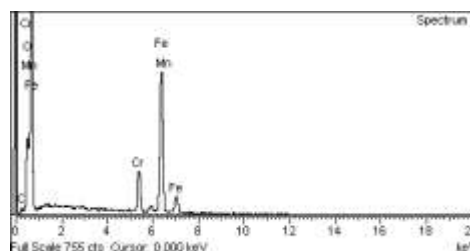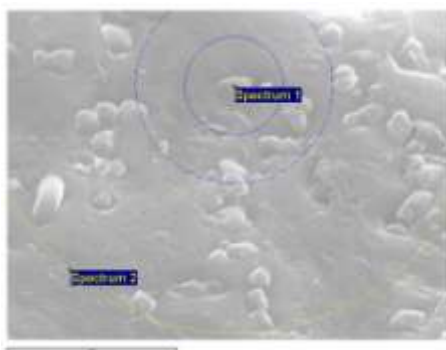
Fig.7 HR SEM+EDX analysis of the particulates on the fracture surface of the compact, delubricated at 900°C for 30 min in nitrogen

Fig.8 XPS survey spectra of the as-fractured compacts, delubricated at 450 and 900°C for 30 min in nitrogen

Based on the presented results it is advised to perform delubrication of compacts admixed with modern EBS-based lubricants at low temperatures around 450°C. It is important to note that higher heating rates shift peak temperatures (intensity of lubricant decomposition processes) to higher temperatures which have to be taken into account when choosing delubrication temperature and time.

5   Conclusions

Monitoring of processing atmosphere in the furnace during delubrication process of PM compacts clearly indicates that combination of the zirconia oxygen probe and CO_2 sensor allows careful monitoring of the different stages of the de-lubrication process. This unique property of zirconia sensor for the fast and reliable monitoring of delubrication process is connected to the sensor design. Evaporated lubricant and heavy hydrocarbons are oxidized by oxygen on the hot oxygen sensor head resulting in steep decrease in oxygen content on the sensor surface and therefore measured oxygen value. This allows indirect monitoring of the organic compounds content in processing zone. In this way zirconia oxygen sensor provides valuable information concerning starting of lubricant evaporation/decomposition that no other available on the market sensor can provide. Oxygen sensor indicates starting of lubricant evaporation and decomposition into hydrocarbons and CO_2 sensors allow monitoring further lubricant decomposition process. When applying low heating rates the largest part of the lubricant is removed by evaporation and/or decomposition into heavy hydrocarbons starting after ~270°C with a maximum at ~410°C, independent on processing atmosphere composition/purity and processing temperature. High risk of oxidation of the powder surface was registered when applying higher delubrication temperatures. Based on these results it is recommended to perform de-lubrication with low heating rate at temperature around 450°C in dry nitrogen atmosphere.

References
[1] E. Dudrová, M. Kabátová, R. Bidulský, A.S. Wronski: Powder Metallurgy, Vol. 47, 2004, No. 2, p. 181-190.
[2] E. Dudrová, M. Kabátová, S.C. Mitchell, R. Bidulský, A.S. Wronski: Powder Metallurgy, Vol. 53, 2010, No. 3, p. 244-250.
[3] R. Bidulský, M. Actis Grande, M. Kabátová, J. Bidulská: Journal of Materials Sciences & Technology, Vol. 25, 2009, No. 5, p. 607-610.
[4] J. Bidulská, R. Bidulský, M. Actis Grande: Acta Metallurgica Slovaca, Vol. 16, 2010, No. 3, p. 146-150.
[5] E. Hryha, C. Gierl, L. Nyborg, H. Danninger, E. Dudrova: Applied Surface Science, Vol. 256, 2010, No. 12, p. 3946-3961.
[6] R. Bidulský, M. Actis Grande, J. Bidulská, M. Vlado, T. Kvačkaj: High Temperature Materials and Processes, Vol. 28, 2009, No. 3, p. 175-180.
[7] R. Bidulský, M. Actis Grande, J. Bidulská, T. Kvačkaj: Materiali in Tehnologije, Vol. 43, 2009, No. 6, p. 303-307.
[8] L. Wimbert, K. Dollmeier, V. Kruzhanov, R. Lindenau: *Advanced Lubricants – A Complex Challenge for Powder Metallurgy: Density, Lubricity, Environment,* In: World PM 2010, Florence, EPMA/Shrewsbury, Vol. 1, 2010, p. 549-556.
[9] S.L Feldbauer: Metal Powder Report, Vol. 62, 2007, p. 14-19.

[10] M.M. Baum, R.M. Becker: Metallurgical and Materials Transaction B, Vol. 35B, 2004, p. 381-392.

[11] G.A. Poskrebyshev, M.M. Baum, J.A. Moss, D. Apelian: Applied Catalysis A, Vol. 327, 2007, p. 52-65.

[12] P. Quadbeck, B. Schreyer, A. Strauß, T. Weißgärber, B. Kieback: *In-Situ Monitoring of Gas Atmospheres During Debinding and Sintering of PM Steel Components*, In: World PM 2010, Florence, EPMA/Shrewsbury, Vol.2, 2010, p. 239-245.

[13] E. Hryha, L. Nyborg: *Oxide Transformation During Sintering of Prealloyed Water Atomized Steel Powder*, In: World PM 2010, Florence, EPMA/Shrewsbury, Vol. 2, 2010, p. 268-275.

[14] E. Hryha, E. Dudrova: Materials Science Forum, Vol. 534-536, 2007, p. 761-764.

[15] E. Hryha, S. Karamchedu, L. Nyborg: *Delubrication of PM Components Based on Cr-Prealloyed Steel Powder – Chances and Risks,* In: Euro PM 2011, Barcelona, EPMA/Shrewsbury, Vol. 3, 2010, p.105-110.

[16] S. Karamchedu, E. Hryha, L. Nyborg: Powder Metallurgy Progress, Vol. 11, 2011, No.1-2, p. 90-96.

[17] E. Hryha, L. Čajková, E. Dudrová: Powder Metallurgy Progress, Vol.7, 2007, No.4, p. 181-197.

[18] E. Hryha, E. Dudrová, L. Nyborg: Journal of Materials Processing Technology, Vol. 212, 2012, No. 4, p. 977-987.