THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Delubrication of Chromium Prealloyed Powder Metallurgy Steels

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Abstract

Consolidation of steel components produced by means of powder metallurgy (PM) is achieved typically through compaction and sintering. During consolidation, final dimensions of the part are already achieved after compaction, while sintering imparts strength to the components. Prior to the compaction stage, lubricants are added to the metal powder to reduce the inter-particle and die-wall friction during pressing and hence improve powder compressibility and ejection of the component from the compaction tool. These lubricants have to be safely removed after compaction since they are source of oxygen and carbon that can negatively affect further sintering process as well as final performance of the sintered components. Lubricants commonly used for PM steels are based on ethylene bis-stearamide (EBS) and their removal is achieved through thermolysis in the initial zone of the sintering furnace. With increasing demands on the achievable densities and performance of PM components, lubricants and possible risks of improper delubrication have received interest. Among the problems encountered during sintering, those concerning delubrication are frequent but difficult to detect. Hence previous studies have aimed at improving the efficiency of lubricant removal and predicting the same. Delubrication being a complex process still poses problems in practice and its proper control requires a system which monitors the delubrication sequence and can be incorporated into a closed loop control.

In the present work, a reliable approach for in-situ monitoring of delubrication of PM steel compacts is presented. The method is based on continuous monitoring of the processing atmosphere using sensors commonly used in the industry (CO_2 and O_2). It was demonstrated that the initial stages of lubricant removal can be monitored using the oxygen sensor based on zirconia ceramics and the later stages can be detected utilizing CO_2 sensor based on infrared cell technology. Based on the established methodology, a systematic study on the effect of various process parameters on lubricant removal in the processing of chromium prealloyed PM steels has been conducted. Effect of temperature, holding time, heating rate, process gas composition (inert, reducing and oxygen containing atmospheres) and purity (wet and dry gases), flow rate and graphite addition was evaluated. Additionally, change in surface chemistry of the base powder occurring during delubrication and its effect on sintering have been studied using X-ray photoelectron spectroscopy and scanning electron microscopy combined with the energy dispersive X-ray analysis.

Based on the experimental results it is recommended to perform delubrication at ~ 450 °C applying low heating rates in dry-nitrogen atmosphere with flow sufficient enough to provide dynamic gas conditions around the component surface. This is especially important in the case of powder prealloyed with oxygen sensitive elements like chromium.

Key words: lubricant, delubrication, processing atmosphere control, surface oxide, sintering atmosphere, alloyed sintered steels

Preface

This Licentiate thesis is based on the work performed at the Department of Materials and Manufacturing Technology, Chalmers University of Technology, between November 2010 and April 2013. The project work has been carried out under the supervision of Associate Professor Eduard Hryha and Professor Lars Nyborg.

This thesis consists of an introductory part followed by the appended papers:

I. Delubrication of PM components based on Cr-prealloyed steel powder-chances and risks

   E. Hryha, S. Karamchedu, L. Nyborg

   Proceedings of Euro PM 2011, 2011, Vol.3, pp.105-110

II. Influence of process parameters on the delubrication of PM steels

   S. Karamchedu, E. Hryha, L. Nyborg

   Powder Metallurgy Progress, 2011, Vol. 11, pp.90-96

III. Control of delubrication process for PM components based on prealloyed steel powders

   E. Hryha, S. Karamchedu, L. Nyborg

   Proceedings of the 2012 Powder Metallurgy World Congress & Exhibition, Japan Powder Metallurgy Association and Japan Society of Powder and Powder Metallurgy (2013)

IV. Surface chemical reactions on powder surface during delubrication of chromium prealloyed PM steels and their effect on further sintering process

   S. Karamchedu, E. Hryha, L. Nyborg

   In Manuscript

Contribution to the appended papers

I. Part of the experimental work was performed by the author.

II. The author planned and executed the experimental as well as the analytical work concerning the monitoring process atmosphere, wrote the paper.

III. Some parts of the experimental work were performed by the author, sintering atmosphere monitoring and video recording of delubrication process together with co-authors.

IV. The author performed the delubrication and sintering experiments for the samples along with SEM and EDX analysis of the fracture surfaces, participated in XPS characterization of the components and performed evaluation of XPS results. The manuscript was written mainly by the author in cooperation with the co-authors

Green compacts and bulk chemical analyses for carbon and oxygen contents for all the papers were provided by Höganäs AB.

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1 INTRODUCTION

Powder metallurgy (PM) steels are typically produced from water-atomized powder that is consolidated through uniaxial compaction and sintering. In such a process, the final shape of the part is already achieved after the compaction stage and subsequent sintering operation imparts the necessary strength [1]. Lubricants are admixed to metal powder prior to the compaction stage since they reduce the friction between the metal particles and the die-wall, and inter-particle friction during pressing. After compaction, the ‘green’ compacts are subjected to sintering. Sintering is usually performed in continuous furnaces at elevated temperatures under controlled processing gas conditions where neck formation between the powder particles takes place. After compaction, lubricants have to be removed since they pose problems during the subsequent sintering stage. Complex organic compounds based on ethylene bis-stearamide (EBS) are commonly used as lubricants for PM steels and their removal is achieved through the thermolysis in the initial zone of the sintering furnaces before the actual sintering begins.

For the structural components produced through PM route, it is recognized that improving mechanical performance of the parts is necessary to ensure market growth and maintain competitiveness with other production techniques. Among other approaches, this has been addressed through: a) improving the density of the components since mechanical properties of PM parts significantly dependent upon density [2] and b) development of cost-effective alloy systems suitable for high performance applications [3]. Since lubricants play a decisive role in the compaction process which controls the density of the parts, increasing demands on achievable density levels has led to an increased interest in lubricants and related issues. In the present thesis, an attempt to address the issues concerning lubricant removal has been made. A carefully controlled lubricant removal process is vital and challenging since many problems encountered during sintering are related to improper delubrication [4–8]. Such problems include sooting, micro-cracking and degradation of the properties of components in terms of chemistry and mechanical performance. Also, improper delubrication can result in deposition of decomposition products on the furnace parts and components. These problems lead to lower productivity and increase in maintenance costs.

Previous studies concerning delubrication have attempted to optimize the parameters for efficient lubricant removal and based on these investigations, process control strategies are established. However, different opinions exist regarding the choice of time, temperature and especially processing atmosphere composition and purity for delubrication. Although complete lubricant removal can be easily obtained in small lab-scale, due to the complexity of the process, it would be ideal if lubricant removal can be accurately determined in real-time in an industrial process. It has been suggested that monitoring of the processing gas composition during delubrication would provide robust monitoring of the delubrication process [8–10]. From the point of view of alloy development, alloying systems based on chromium have been developed for high performance applications to replace traditional alloying elements such as nickel and copper due to economic and recyclability reasons. Introducing alloying elements such as chromium imposes concerns regarding processing the components due to the high oxygen affinity of chromium and hence, it requires that each stage of processing has to be redefined to execute strict control. Recent investigations concerning sintering of chromium alloyed PM steels concentrate on various aspects but have not paid their attention towards the effect of delubrication.

The focus of this thesis is hence to develop a methodology for monitoring of the delubrication process and to optimize the process conditions for efficient and cost-effective delubrication for chromium alloyed PM steels with minimal effect on the compact properties. It is important to note that the same delubrication process can be applied with the same efficiency to any other PM steels with the alloy composition having lower or similar affinity to oxygen as prealloyed with chromium PM steels studied.

2 POWDER METALLURGY

A brief overview of the powder metallurgy process is presented in this chapter. The objective is to depict the correlations between various stages involved in the processing of powder metallurgy steels, which enables a better understanding of the issues concerning delubrication presented in chapter 3.

2.1 History and Outlook

PM involves production and consolidation of metal powders into useful engineering components. A typical consolidation process consists of a forming stage where the powder is converted into the required shape (typically around room temperatures) followed by a ‘temperature assisted sintering process’ which facilitates the formation of metallurgical bonds between the powder particles. The emergence and development of PM can be looked upon in connection with three principle characteristics of the process.

The first characteristic is that the process does not involve melting of the major constituent, which can be connected to the emergence of the technology itself. Making objects without melting is traced back to early civilizations where products including iron implements were produced as early as 3000 BC [1], [11], since the technology for obtaining high enough temperatures for melting these metals was not available. After the emergence of melting technologies, PM was largely ignored. The PM technology was revived for production of tungsten filaments for the same reason that tungsten cannot be processed through the melting route. The second characteristic of PM is connected to the usage of powder as the starting material. This is advantageous in terms of upholding chemical homogeneity in the parts, as the segregation of the elements is restricted to the size of the powder. This also permits for freedom in alloy design since strict compositional control and otherwise unachievable compositions can be realized by keeping the alloying elements in the solid solution due to rapid solidification during powder production. Based on this principle, products like tool steels and super alloys are developed. The third characteristic which is more relevant to PM steels and the context of this thesis is the capability of the process to produce complex net-shaped quality precision components while being suitable for high volume production. This enables PM to compete with other manufacturing methods like casting, machining and forging while being cost efficient. The cost effectiveness of PM is because the process avoids or minimizes machining, allows maximum utilization of the raw materials (>95%), requires the lowest amount of energy per kilogram to produce a finished part and has a short overall production time [1], [12]. These factors contribute to the recognition of PM as ‘green technology’ for sustainable manufacturing [13]. Sintered steel components have evolved on the basis of net-shaped high volume production and since then developments have taken place more than for any other reason on the basis of cost effectiveness of the process. The highest consumer for PM structural parts is the automotive industry. In a recent review it has been estimated that the average weight of PM parts per car is 10 kg for those manufactured in Europe and 19.8 kg for those manufactured in North America [14], [15].

2.2 Powder Metallurgy Steels

PM steels have become the most significant products of PM technology today and account for more than 80% of the total volume of all materials produced. Improvement in the quality of powder, development of new alloy systems and sophistication in the processing techniques have extended the range of applications for sintered ferrous and alloy ferrous parts.

The PM process begins with the production of powder. To suit various applications, powder with a wide range of chemistry, size, shape and other attributes is produced using different manufacturing techniques. Several methods exist for the production of metal powder and can be broadly classified into (i) methods based on mechanical dispersion of solids and melts such as mechanical milling and atomization, and (ii) methods based on chemical processes such as solid-state reduction and electrolytic reduction. Among these, the production techniques employed for high volume and low cost production are water atomization and oxide reduction.

Iron or steel powder is generally mixed with lubricants, graphite powder and optionally other alloying elements (also in powder form) prior to the consolidation stage. The mixing process may also involve special treatments of the powder mix where organic binders are used to glue the additives to the iron/steel powder to improve the consistency and minimize segregation and dusting.

Processing methods for PM steels can be categorized under pressure based densification, sintering based densification and hybrid densification methods [1]. In pressure based densification, the powder is compacted in a die where the final dimensions are set and minimum densification occurs during sintering [12]. For this case, the powders are large, compaction pressures are high and the sintering temperature is rather low. In contrast, for sintering-based densification the processing starts with loose powder, which is just shaped during the forming stage and then sintered to full or near full density at high temperatures. For such a process, powder size is small and sintering temperatures are high. Between these extremes are other processes which rely on hybrid densification where the compaction and sintering stages are combined, like hot pressing and hot isostatic pressing. On a relative tonnage basis, press and sinter technology (pressure based densification) contributes to about 85-90% of the ferrous powder sales.

In the context of this thesis, powder production through atomization and pressure based consolidation through uniaxial pressing and sintering are relevant and are discussed in the following sections.

2.2.1 Production of Iron and Steel Powders – Water Atomization

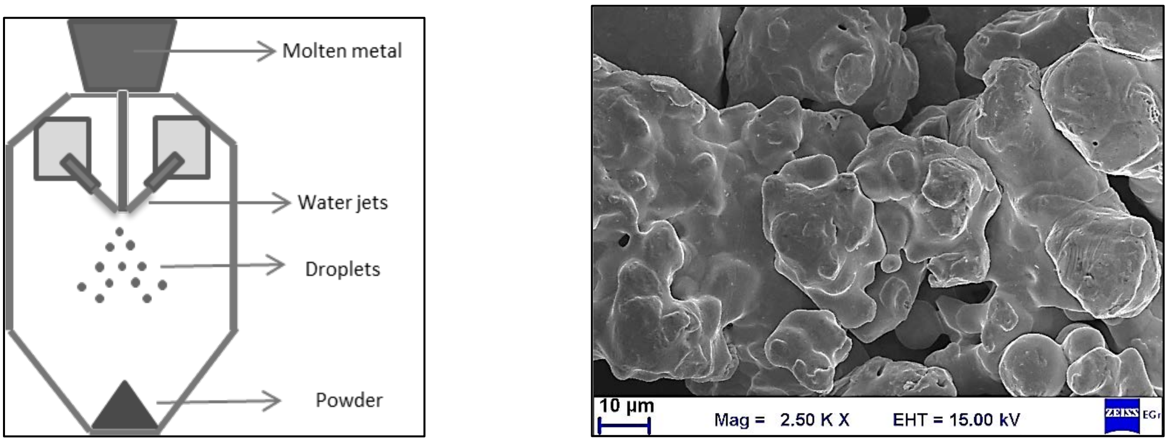

Figure 1 Schematic of the Water Atomization process (Left), SEM image of water atomized steel powder (Right)

Water atomization is the predominant mode for production of elemental and alloy ferrous powder. In this process, molten metal is poured either directly or by means of a ladle into a tundish. The melt from the tundish runs down through a nozzle as a molten metal stream. High pressure water jets are directed onto the molten metal stream forcing it to disintegrate into droplets that solidify into powder (see Figure 1). Water atomization results in irregular shape for the powder which makes the powder suitable for compaction since this shape allows the metal particles to interlock during pressing. However, because of rapid cooling, the metal particles are hard (martensitic) and covered by oxide layers on the surface. The powder is hence subjected to drying, followed by a reduction annealing treatment to soften it and reduce the surface oxides. Thin surface oxide products are observed on the powder particle surfaces even after reduction annealing due to their re-formation during cooling and handling [16–18]. The production rate by water atomization is very high which makes it suitable for high volume production at rather low cost. The primary variable in this process is the pressure and geometry of the water jets and employing higher pressure results in finer powder size. The mean particle size used in practice is around 70-80 µm with 10-30% of the powder below 45 µm and less than 10% of the particles being above 150 µm [19]. Chemistry of the powder is another important variable. Alloying additions are usually added to the melt to atomize alloy powder. For water atomization, oxygen content of the powders is a good measure of the production skills and quality. In general, high purity powder exhibits highest compressibility.

2.2.2 Alloying

Ferrous powders are used mostly for structural applications and they have to be alloyed suitably to achieve the desired properties. In general, alloying elements decrease the compressibility of the powder and increase the cost. Steel powders can be classified into three different categories based on the method of alloying – *prealloyed*, *admixed* and *diffusion bonded* powders.

In prealloying, the alloying elements are added to the melt before water atomization which results in homogeneously alloyed powder. Another important advantage is that prealloying allows addition of oxidation sensitive alloying elements such as chromium and manganese which are difficult to be introduced in other forms. The disadvantage with prealloying is that the compressibility of the powder is lowered as a possible consequence of the solid solution hardening effect of the alloying elements. Molybdenum is commonly used in prealloyed form due to its lower effect on compressibility. Molybdenum prealloyed grades are used as base powders for diffusion bonding and admixing.

In admixing, iron powder is mixed with alloying elements in the form of powder prior to the compaction stage. Alloying in this case is achieved during sintering through diffusion. The primary advantage of admixing is that the compressibility of the powder mix is high. While the disadvantage is that it can result in inhomogeneous distribution of alloying elements due to slow diffusion and segregation. Typically carbon is added to ferrous powders in the admixed form as graphite since carbon has a highly detrimental effect on compressibility if prealloyed.

Diffusion bonding is a method where fine alloying element particles typically of the size of a few tens of microns or lower are bonded onto the surfaces of the iron powder through a diffusion-based annealing process. This again avoids segregation while retaining compressibility. However, inhomogeneity in distribution of alloying elements is still observed for the case of diffusion bonded powders. Nickel and copper are usually alloyed by diffusion bonding to ferrous powders.

Water-atomized steel powder, pre-alloyed with chromium and molybdenum, has been used in the present work.

2.2.3 Compaction - Uniaxial pressing

In uniaxial pressing, the powder is placed inside a compaction tool and compressive stress of 400-800 MPa is applied simultaneously from top and bottom. Upon compaction, the metal particles interlock at the surface irregularities and with increasing densification they plastically deform increasing the area of the particle contacts along with some degree of cold welding. The final mechanical properties of sintered parts are strongly dependent on the density values. Since the final shape of the part is already achieved after the compaction, it is an important stage which dictates the density of the parts. Tensile strength and fatigue strength increase roughly linearly with increase in density [2] and as a result the average density of the sintered parts has hence increased over the last few decades to meet these demands. Achieving high density at relatively low cost by single press and single sintering is of prime importance for PM industry. Methods such as *warm compaction* - where the powder and the die are heated to around 150 °C, *warm die compaction* - where only the die is heated but not the powder and *high velocity compaction* - where the speed of compaction is increased up to 500 times, have been developed to improve the achievable density levels upwards by 0.2-0.3 g/cc [3], [20], [21]. Each of these methods has its own set of advantages and disadvantages. Since there is an increasing production cost associated with these processes, compaction at room temperature is still the most used method for high volume industrial production.

2.2.4 Lubricants

Friction between the powder and die wall is a fundamental issue in traditional powder metallurgy involving die compaction. During pressing it has a major impact on the density gradients within the pressed part and during ejection it influences the surface quality of the parts and causes tool wear. Lubricants are hence used to decrease the ejection forces and minimize the tool wear. Lubrication can be achieved either through admixed lubricants or die-wall lubrication. Typically, lubricants are admixed as fine particles to metal powder in concentrations between 0.3 and 1.0 wt.% prior to compaction. Lubricants aid compaction a) by reducing inter-particle friction which decreases the required compaction pressure and improves homogeneity of density distribution and b) by reducing the friction between the powder and the die-wall which lowers the tool wear and heat buildup at the die-wall and improves the tool life. Hence, lubricants play an important role in integrated approaches for achieving high densities [3].

Lubricants used for cold compaction can be divided into three groups: metal soaps, amides and composite lubricants. Metal soaps are the oldest group of solid lubricants used for compaction of metal powders. Zinc stearate is a popular lubricant which falls under this category. The advantage with zinc stearate is that it provides good lubricity and flow properties for the powder mix. Its major disadvantages are environmental and health issues concerned with zinc sublimation during delubrication process and residues after delubrication observed on the surface of the compacts and on the furnace parts after lubricant removal [22]. The Amides consist of di-amide with two fatty acid chains with stearic acid being the most common fatty acid chain used. Commercial amide waxes have a melting interval between 130- 150 ^{o}C and can be efficiently delubricated [23] since they are purely organic. Common lubricant stearates contain 12 to 22 carbon atoms with a typical length of 18 carbon atoms and ethylene bis-steramide (EBS, industrial name '*Acrawax*') which is widely used for PM steels belongs to this family of lubricants. The disadvantage with amide waxes is their poor flow properties compared to zinc stearate. Composite lubricants are complex organic compounds combining different chemical substances which provide possibilities to compose lubricants with properties tailored for specific applications [24]. Composite lubricants based on modified EBS are widely used as they provide superior or equivalent green and sintered properties as compared to pure EBS, especially with respect to the ejection forces [25]. It is a complicated process to select lubricants since their chemistry, powder size and shape all have conflicting implications. For example, finer lubricant particles are preferred for achieving higher densities while coarser particles are more effective in reducing the ejection forces. For warm compaction and warm die compaction, powder mixes are specifically designed as the lubricants have to withstand the increased temperatures keeping lubricity [26].

Though lubricants aid compaction, several disadvantages are associated with them such as reduction of powder flow rate, limitations on the compact green density and those associated with improper delubrication. Though indispensable for the reduction of die-wall friction and lowering of the ejection forces, lubricants have the most lowering effect on the achievable theoretical density levels for the powder mixes. During compaction, some part of the lubricant is squeezed towards the die-wall and only lubricant particles between the first powder layer and the tool wall participate in lubrication [27]. Rest of the lubricant gets entrapped inside the closed pores where it develops a hydraulic pressure opposing the densification process. In practice the amount of lubricant is optimized by striking a balance between the interparticle friction, green strength, green density and ejection force. Problems associated with lubricant removal are discussed in chapter 3.

2.2.5 Sintering

Compacts only possess modest strength (green strength) required for the handling and have to be sintered to impart the required mechanical performance for their application. During sintering, compacts are heated to high temperatures (2/3 to 4/5 of the melting temperature of the main component of the powder mix) to facilitate the formation of ‘necks’ between the particles. These necks are formed at the particle contacts established during compaction and this neck formation is driven by the minimization of surface energy which progresses through atomic diffusion processes and evaporation/condensation mechanisms. A prerequisite for the sinter neck formation is sufficient reduction of the surface oxides on the powder particle surfaces [28–30]. Typical sintering process consists of a heating phase, followed by a sintering phase where the compacts are held at a constant temperature for enough time to achieve sufficient bonding between the particles and finally a cooling phase during which the microstructure is decided by the cooling rate as illustrated in

Figure 2. Before the beginning of sintering, the lubricant in the compact has to be removed so that it does not inhibit the neck formation between the particles. This is achieved through thermolysis during the initial stages of heating. For this purpose, a part of the furnace is kept at a controlled temperature which is referred to as the delubrication/dewaxing/preheat zone.

Two features which are essential for performing sintering are furnaces and protective gas atmospheres. Two kinds of sintering furnaces are most commonly used industrially: batch and continuous. The advantage with batch furnaces is that individual processes such as delubrication and sintering can be optimized without interference between the processing atmospheres. But their productivity is lower when compared to continuous furnaces. Continuous furnaces on the other hand have high productivity and hence are used extensively for PM parts production. In continuous furnaces atmosphere optimization is difficult due to openings between the different zones.

Continuous furnaces are equipped with zones (chambers) for delubrication and pre-heating, sintering (high temperature) and cooling. Modern furnaces are equipped with fans in the cooling zone to perform accelerated cooling to harden the steel components directly after sintering thereby avoiding further heat treatment which is referred to as sinter-hardening. Typical sintering temperatures for industrial production using continuous furnaces are in the 1120-1150 °C range and the holding time at this temperature is between 15-30 minutes. Ceramic mesh belt, pusher or walking beam furnaces are used when sintering is to be performed at high temperatures up to 1250 °C. The maximum temperature limit is set by the strength of the mesh belt in relation to the stress caused by the load on the belt. High temperature sintering is beneficial in terms of more efficient sinter-neck formation and pore rounding due to accelerated diffusion processes and better reduction of oxides. Its disadvantage is that dimensional control becomes more difficult which is not desirable.

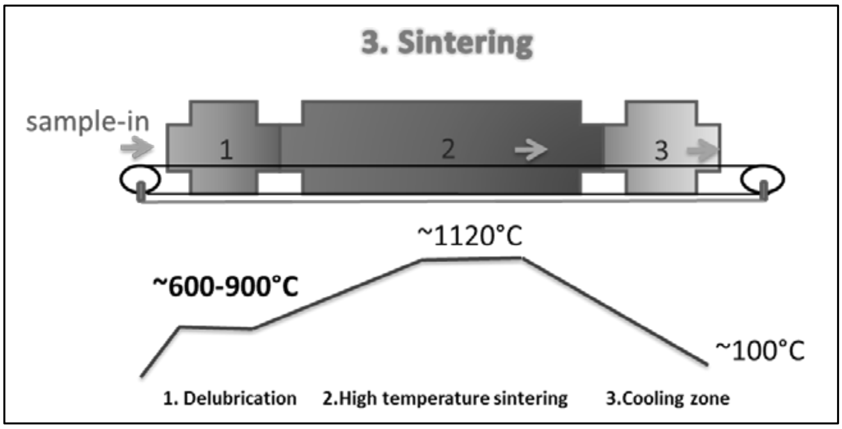

Figure 2 Schematic of a continuous sintering furnace

The second important feature for sintering is the protective atmospheres (term interchangeably used with sintering atmospheres/processing atmospheres/atmospheres), the primary purpose of which is to control the reactions between the compacts and surroundings. Main functions that the sintering atmospheres have to ensure are: a) efficient delubrication during preheating, b) reduction of surface oxides on the powder particles for enabling metal to metal contact, c) prevention of oxidation during sintering and cooling, and d) controlling the carbon content (carburization and decarburization reactions) of the ferrous parts. A secondary purpose of the atmospheres is to flush out the lubricant decomposition and oxide reduction products out of the furnace. The flow of the sintering atmosphere is hence from the sintering zone to the delubrication zone in order to prevent these products from entering the high temperature sintering zone. *Endogas* atmospheres produced through combustion of hydrocarbons are commonly used for sintering of ferrous components. However, for the case of steels containing oxidation sensitive alloying elements like chromium which is the case in the present work, high purity N_2 atmospheres containing up to 10 vol.% H_2 are used. Sometimes CH_4 or CO is added to the atmosphere to provide the possibility for carbon control during sintering.

2.3 Chromium prealloyed PM steels

Due to the high surface area present for the case of PM steels, they are subject to significant risk of oxidation compared to wrought steels. For this reason, traditionally, alloying elements such as Cu, Mo and Ni have been used as they are easily reducible compared to Fe. However, utilizing Cr as a substitute for these alloying elements provides several advantages. The first advantage is the economic benefit since Cu and Ni are significantly more expensive than Cr. Also, Ni is associated with health issues and Cu with recyclability problems. Furthermore, Cr has higher hardenability which makes it suitable for high performance applications [31] and sinterhardening [32]. The major challenge concerning usage of Cr as an alloying element is its high oxygen affinity, which poses strict demands on processing. By prealloying, the activity of chromium can be reduced roughly down to its content and it has been shown that for the low levels of chromium, prealloying does not significantly degrade compressibility of the powders [33]. Though usage of chromium-alloyed powder has been demonstrated already in the eighties, such powder has not found extensive usage due to the expensive production methods [34–36]. Hence only about decade ago Höganäs AB, Sweden, introduced a cost-effective prealloyed steel powder grade Astaloy CrM containing 3% Cr and 0.5% Mo produced through water atomization and subsequent reduction annealing [37]. This powder grade is now well-established and used in production of PM steel parts for high performance applications. Delubrication studies in the present work have been conducted on compacts of this powder grade.

2.3.1 Surface characteristics

Previous investigations on the surface characteristics of water atomized chromium-prealloyed steel powder have shown that such powder is predominantly covered by a ~6nm thick Fe oxide layer with some minor presence of fine particulate oxides rich in Cr, Mn and Si of the size of a few hundred nanometers [16], [38], [39]. The coverage by easily reducible iron oxide layer on the powder has been estimated to be around ~94% [18], implying that most of the particle contacts after compaction are at Fe-oxide rather than the stable oxide particulates, hence implying good sinterability. The onset of formation of inter-particle necks is thus dependent on the efficient reduction of the Fe-oxide layer. There have been several investigations concerning these materials: thermodynamic and experimental assessment of sintering atmospheres, processes occurring during sintering with respect to reduction of surface oxides, changes in size, shape and morphology of the surface products, development of interparticle sintering necks during the heating and sintering and final properties obtained after sintering [17], [19], [39–47]. Regarding the surface chemical characteristics of these materials, it has been shown that the composition of the surface products changes during the heating stage and the temperature range between 800 and 1000 °C is critical for processing. In this temperature regime, formation of inter-particle connections takes place and as a consequence there is a risk of surface oxide enclosure inside the necks. Further, at the expense of the Fe-oxide, thermodynamically stable Cr-Mn spinel oxide particulates are formed. These studies also demonstrate that N_2-H_2 mixes are good candidates for sintering these materials owing to the positive effect of hydrogen in terms of reducing the surface oxides during the heating stage.

Since delubrication precedes the actual sintering stage, changes induced during delubrication in terms of surface products are carried over to the next stages and have a direct impact on the final sintered properties. As the effect is more pronounced when strong oxide forming elements like chromium are present, it has been one of the reasons for choosing Astaloy CrM for performing delubrication studies. Though there has been extensive research concerning the sintering of Cr prealloyed PM steels, detailed studies related to surface chemical changes occurring during delubrication have not been reported.

3 DELUBRICATION

In this chapter, some critical aspects concerning delubrication are discussed with focus on EBS lubricants. Previous studies concerning delubrication have been directed at improving the efficiency of lubricant removal, being able to accurately determine the completion of the same. Thermogravimetry (TG) has been used extensively to determine the critical temperatures during lubricant removal. Some researchers have used spectroscopic techniques combined with TG analysis to study the products evolved during delubrication, by which process control strategies can be devised.

3.1 Delubrication defects

In practice, several composite lubricants are used in the industry in accordance with varying requirements, which makes delubrication of wide range of products in the same furnace challenging. While designing new lubricant mixes, the ease with which they can be removed hence plays an important role [48]. Sooting, decrease in strength, variation in compositional levels (particularly carbon), micro-cracking and variation in dimensions of the part are defects resulting due to improper delubrication [4], [7], [49]. However, the biggest risk, that has been the focus of this work, is the oxidation by the products of the lubricant decomposition, which in the case of powder alloyed with oxygen sensitive elements as chromium can be detrimental. It is also claimed that EBS is prone to sooting since it has a carbon to hydrogen atomic ratio of 2 while lubricants that decompose cleanly have a ratio of 4 [8], [50]. Sooting is associated with one or a combination of the following factors: too low dew- point (i.e. water vapor content) in the preheat zone, too short holding times, too high belt speed, lower holding times at delubrication temperature, too high belt load, too high heating rates, cracking of hydrocarbons from the lubricant vapors or additions in the sintering atmosphere. Some authors report that sooting is not directly connected to the organic part of the lubricant [2] while others claim that sooting via lubricant vapors is plausible [8]. Sooting is observed in the form of stains, black spots, granular soot, internal sooting or blistering (which is the worst form of sooting) [4], [51]. Low strength and variation in carbon levels are related to the ingress of lubricant vapors into the sintering zone. They can also be a result of lubricant remaining in the compacts (resulting from incomplete delubrication) entering the high temperature sintering zone, where it decomposes, deteriorating the purity of the sintering atmosphere (too high CO_2 or CO levels). Improper delubrication can also lead to deposition of delubrication products on the compacts and furnace parts, even in the cooling zone [52], leading to maintenance problems and increase in costs.

3.2 Sequence of events during delubrication

Delubrication consists of two stages: melting and decomposition. Upon reaching the softening/melting point, lubricants melt and further decompose into a number of molecules including CO_2, CO, CH_4, C_2H_4, H_2O and heavy hydrocarbons [9], [10]. For EBS, the melting range is reported to be between 135 and 150 °C [8], [23], [53]. Decomposition depends on the chemical structure of the lubricant and for EBS it begins at temperatures as low as 150 °C with a maximum occurring around 450 °C [9]. The sequence of events identified through visual observation of the delubrication process is: melting of the lubricant, followed by oozing out of the lubricant melt (as droplets) to the surface of the compact where they coalesce into larger droplets (see Figure 3), lubricant evaporation and full disappearance of droplets along with the formation of a semi-transparent dense gas [22], [54]. Also, bubbling of the lubricant was observed at some places on the compact surface prior to evaporation but was less prominent for EBS when compared to zinc stearate [22]. Oozing out of the molten lubricant is believed to be due to free pore volume being insufficient to accommodate the molten lubricant since this was only observed in the case of samples with higher densities [54]. It is possible that the molten lubricant drips down from the bottom of the compact depending upon the density and geometry of the part [22], [55]. Bubbling of the molten lubricant is connected to the escaping of the gases from inside the compact [54]. However, the visual observations reported in the studies mentioned in this section were from delubrication experiments performed at high heating rates and the temperatures corresponding to different would change with a change in heating rate.

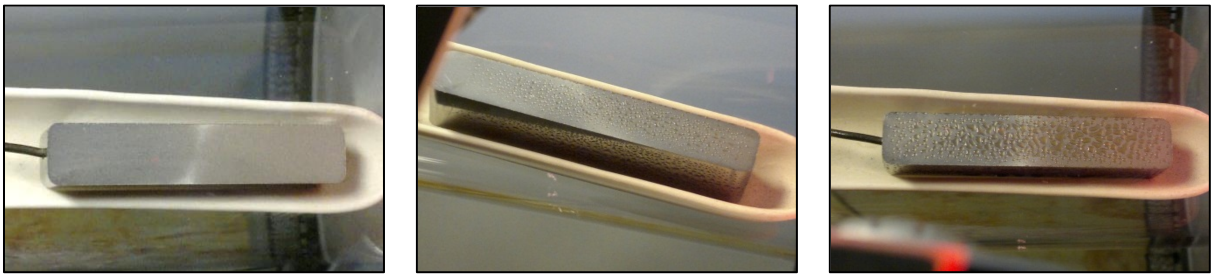

Figure 3 Images of the compact at different times during the delubrication process: visual observations from the present work

3.3 Chemistry of delubrication

The chemical structure of the EBS molecules is shown in Figure 4. Within the molecule, bond strength varies between ~326 to ~544 kJ, indicating that the decomposition is continual. In the ascending order of bond strengths within the molecule, C-N bonds have the lowest value, followed by the C-C bonds at the center of the molecule, then C-C bonds at the extremes, followed by C-H bonds, and C=O (double bonds) being the strongest [8], [56]. Using DTA, thermal decomposition profile for EBS was obtained which showed four endothermic peaks, three of which were below 200 °C indicating melting, and a fourth endothermic peak related to decomposition around 400 °C (heating rate was 10 °C/min). Additionally, an exothermic peak was observed following the endothermic peak at 400 °C, which was suggested to be due to the breaking down of the strong bonds in the molecule resulting in the formation of CO_2 or CO from the oxygen molecules in the lubricant [8], [56].

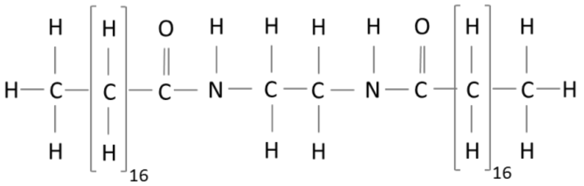

Figure 4 Chemical structure of the EBS molecule

Determining the completion of delubrication requires a good understanding of how and in which form the lubricant is removed and what products are formed during this process. This information is valuable for devising suitable sensors for monitoring the process. Also, this information is crucial for development of new lubricants. Detailed investigation of the gas-phase products produced during thermolysis of EBS revealed that CO_2 and aliphatic hydrocarbons with absorption band between 3000 and 2700 cm^{-1} were the major emission products [9]. Their emissions were in tandem with a maximum around 450 °C and CO, CH_4, C_2H_4 and NH_3 were reported as the minor products. Also, the chemical structures of condensable large molecular hydrocarbons formed during EBS decomposition were identified. Based on these results, a reaction mechanism for lubricant pyrolysis was proposed. Similar results concerning major delubrication products were observed from other studies on evolution of gas-phase products [57], [58].

3.4 Effect of Process Parameters on Delubrication

There are conflicting opinions regarding the choice of optimum processing parameters for efficient delubrication and claims supporting both sides of the argument exist which are discussed in this section. Industrial best practice to ensure complete lubricant removal is to heat slowly below 600 °C before the compacts enter the high temperature zone [1]. However, temperatures up to 900 °C are used sometimes in practice [5].

3.4.1 Heating Rate

Heating rate has the most significant effect on delubrication according to a statistical study, suggesting that it is essentially a thermal process [59], [60]. Temperature corresponding to lubricant removal shifts towards higher values with increase in heating rate [54], [59–61]. Some authors attribute this to the sluggish mass transfer rate compared to high heat transfer rate, since mass transfer out of the compact involves processes such as melting, vaporization and decomposition which are slow [54].

Some authors opine that slow heating rates are to be employed to ensure complete lubricant removal [7], [56], [62]. The basis for this view is that, though the melting of lubricant takes place around 150 °C, evaporation and progressive elimination only begins at higher temperatures and most of the lubricant is removed in a narrow temperature interval between ~300 to less than 500 °C. Employing high heating rates during this temperature interval might hence result in rapid decomposition and the associated volumetric changes might induce defects in the parts such as micro-cracking. This narrow temperature range for lubricant removal is because of the relatively short carbon chain in EBS compared to that of binders used for example in metal injection mounding such as polypropylene [50], [56], [62]. Another reason is related to the argument that the presence of carbon containing vapors above 600 °C can lead to undesired reactions such as sooting which affects the final sintered properties. Since higher heating rates shift delubrication to higher temperatures, to minimize effect of corresponding to these undesired reactions a slow heating rate is recommended. Contrary to these arguments, since the rate of sooting due to the decomposition of carbon monoxide and hydrocarbons in the atmospheres is high between 500-600 °C and is catalyzed by the presence of metallic iron, nickel and cobalt, higher heating rates would avoid sooting as the compact passes through this regime quickly [54], [55], [63–65]. It is also claimed that higher heating rates might aid in breaking down the lubricant into smaller hydrocarbon species which can be easily flushed out [61].

3.4.2 Effect of Density and Sample Geometry

Density can be expected to play a significant impact on delubrication since the mass transport of the molten lubricant and the lubricant vapors occurs through the pore channels of the compacts. However, delubrication temperatures were found to be independent of density for compacts with relative densities between 85 to 94% [22], [61], [66]. Contrary to these studies, for compacts with densities below 90% relative density, an increase in the decomposition temperatures with increase in density is reported [50], [67] and this increase was attributed to a dramatic decrease in the number of pores on the surface with increase in density.

When densities exceed 7.0 g/cc, pores get almost filled with lubricant and rapid heating under such circumstances brings significant risk of defects in the compacts. Also, lubricant residues are believed to be high in high density compacts due to the hindered transport of the lubricant [48]. For high density compacts, delubrication hence becomes much more critical. Generally, carbon deposition is expected to be higher for more porous compacts as internal deposition would occur while for high density compacts the deposition is supposed to be external [64].

Beginning and ending of delubrication occurred at lower temperatures for warm compacted parts than that for the cold compacted parts and this was attributed to the better metal lubricant contact for the warm compacted parts aiding heat transfer [66]. Also, for compacts subjected to warm compaction, the temperatures for the beginning and ending of delubrication decreased with increase in density. The mass loss curve for lubricants used for warm compaction is different from that of the lubricants used for cold compaction due to their complex chemistry. However, the delubrication rate was found to be an intrinsic property of the lubricant since for both room temperature and warm compaction, it was found to be independent of density [66].

Surface to volume ratio is considered to play a significant role on delubrication. However, observations from another study have shown that there is little influence of the surface to volume ratio on delubrication kinetics indicating that the rate determining step for delubrication is the lubricant evaporation and decomposition step [61]. This claim concedes with the visual observations of delubrication in another study [22]. In another investigation, for compacts with densities above 85% relative density, it is claimed that lower surface to volume ratio aids delubrication while the opposite is true for the case of compacts with densities below the mentioned value [67].

3.4.3 Gas Flow Rates

The gas flow in furnaces is from the sintering zone to the delubrication zone in order to prevent lubricant decomposition products from contaminating the processing atmosphere in the high temperature zone. Lubricant vapors thus drawn off with furnace gas and removed at regular intervals or electrostatic separators are used for this purpose [12]. When gas flow in the furnace is insufficient, it can lead to condensation/deposition of the delubrication products on the furnace walls and the other compacts. Also, when the amount of reactive gases in the atmosphere is low, meaning poor buffering capacity, imbalances caused due to lubricant decomposition products ingress into the sintering zone is not taken care of, resulting in defective parts. Moreover, insufficient gas flows can lead to soot deposition on the parts [7]. In a study related to decomposition of Zn-stearate at high temperatures, it was observed that gas phase transfer plays a significant role [68]. When the gas flow was insufficient, it resulted in the formation of a stagnant lubricant vapor layer on the compact surface, increasing the local C to H concentration ratio above 1, leading to soot formation [68]. This principle is valid even for the pre-heat zone in the furnace where carbon-containing lubricant vapors are present. Though usually continuous furnaces are used for sintering, in some cases, to prevent ingress of lubricant decomposition products into the high temperature sintering zone, furnaces with separated delubrication chambers which are connected at right angles or furnaces with U-shaped construction are used [12].

3.4.4 Catalytic Effect

Based on the observations concerning the evolution of gas-phase products during the decomposition of EBS, it is proposed that lubricant removal is aided by the catalytic effect due to iron/carbon matrix [69]. While in another investigation, it has been reported that the catalytic effect due to iron/carbon is minimum but the alloying elements exercise this effect [57]. Furthermore, TG studies indicated that the effect of base powder on delubrication is minimum [61], [66]. To what extent catalytic effects are active still needs to be clarified.

3.4.5 Processing Atmosphere

The presence and concentration of various gaseous species in the processing atmosphere can alter the effectiveness of the delubrication process. Apart from flushing out the delubrication products, processing atmosphere can play a role in the lubricant removal by providing reaction species which aid decomposition of the organic molecules. The primary factor to be considered for selection of processing atmosphere for delubrication is the sensitivity of different materials with respect to it. For example, nitrogen based atmospheres when used for stainless steels at high temperatures can result in nitrogen pickup. There are differing opinions regarding the choice of atmospheres for efficient delubrication if they should be oxidizing, reducing, wet (high dew-point/moisture content) or dry (low dew-point). Studies supporting and opposing each view exist which are presented in the following sub-sections.

Neutral (dry): Delubrication performed in neutral dry atmospheres is advantageous in the sense that it has little effect on the surface chemistry of the powder [1], [62], [70]. However, a popular notion is that deficiency of hydrogen and oxygen in the lubricant leads to improper delubrication associated with the formation of soot when subjected to thermolysis in neutral-dry atmospheres. Development of lubricant mixes with additives consisting of oxidizing agents that oxidize the residues upon lubricant decomposition to ensure clean removal support this notion [48]. Regarding neutral atmospheres, one view is that usage of argon is effective in flushing out the heavy long chained delubrication compounds preventing their condensation on the cold parts of the furnace since argon is heavy [71].

Oxygen/Air: *S*ince lubricants do not possess enough oxygen molecules to decompose into CO and CO_2 which can be flushed out easily, it is argued that supplying sufficient oxygen improves breaking down of the hydrocarbons. For pure EBS, it was seen that the delubrication finish temperature (corresponding to 95% weight loss) decreased with addition of 1% O_2 to the nitrogen gas [23]. However, with further increase in oxygen content it increased and a maximum was reported for the case of delubrication in air. While delubrication of stainless steel compacts was performed, it was seen that it is effective to use air up to 400 °C, but above this temperature, a weight gain associated with oxidation of the powder was observed [70].

Burn-off units: are developed supporting the view of oxidizing atmospheres improving the delubrication efficiency. These units function based on injecting the off-gases produced upon igniting air and fuel mixtures of a given ratio using special burners to generate an oxidizing atmosphere. This ignition also generates heat. During burn-off, lubricant vapors along with the reducing atmosphere components such as carbon monoxide and hydrogen will be oxidized [72]. Lubricant burn-off is considered to be more effective than addition of oxygen to the processing atmosphere [6], [71] and it is claimed that sooting can be avoided using the burn-off process [54], [64]. The biggest drawback with burn-off is the oxidation of the compacts and high heating rates but at the same time it is the most cost-effective way of heating up compacts. However, there are claims suggesting that burn-off gives variable and less repeatable properties of the compacts, especially in terms of oxidation of the powders [1], [72].

Moisture: Among the oxidizing agents oxygen, moisture and CO_2, some authors are of the opinion that addition of moisture to the processing atmospheres is the most effective for efficient lubricant removal since oxygen injected into the sintering atmosphere would nonetheless react to form water [5], [53], [60]. Also, higher dew-point is considered to decrease the sooting tendency. Based on this, auxiliary systems such as bubblers and humidifiers for sintering furnaces have been introduced into the market [7]. A decrease in activation energy for lubricant decomposition in the presence of moisture is reported based on a kinetic model suggesting that moisture plays a major role in the chemistry of decomposition [60]. It has been reported that moisture additions to argon improved the efficiency of delubrication while keeping lower levels of contamination in the material than when lubricant removal was performed in pure argon or argon mixed with air [71]. Although an improved efficiency in delubrication is observed due to moisture addition, a weight gain during holding at the delubrication temperature corresponding to possible oxidation is reported [8]. There are also studies indicating that humidity has a decreasing effect on the efficiency of delubrication [23], [70]. Further, in another investigation where the pyrolysis products of EBS decomposition were studied, the effect of moisture was observed to be minimum, except that the magnitude of CO peak observed above 800 °C was doubled and shifted to higher temperatures in the presence of moisture [9]. This peak is attributed to the reaction of water vapor with the reaction products of delubrication.

The most common problem with devices used to introduce oxidizing species into the processing atmosphere is related to the control of the amount of oxidant that is being introduced [7].

Hydrogen: From the experience of lubricant removal on steel strip coils, it is known that pure hydrogen gives the best results [73]. Thermogravimetric studies on delubrication of steel and stainless steel compacts support this argument [1], [8], [22], [70]. Since pure hydrogen is very expensive and unsafe, it is a common practice to use nitrogen-hydrogen mixes. It was shown that higher hydrogen content provides greater weight loss of the lubricant [1]. Delubrication in N_2-H_2 yielded different pyrolysis gas-phase product profiles compared pure N_2 [9]. In the presence of H_2, the CO peak observed at 725 °C for pure N_2 shifted to 850 °C along with a decrease in intensity. This can be due to the reduction reactions of the surface oxides [41], [47], [74], [75].

There are approaches suggesting usage of a combination of the species mentioned above within the delubrication zone. For example, there are studies indicating that a combination of H_2 and H_2O with a high H_2/H_2O ratio gives the best delubrication results [1], [8], [23]. However, as discussed in the section 2.2.5, most of the industrial production for PM steel components takes place utilizing continuous sintering furnaces where sintering atmosphere control in the different sintering zones is rather tricky and in such cases usually nitrogen-based atmospheres are used throughout the furnace.

3.5 Delubrication Monitoring Attempts

Most of the studies concerning delubrication have been performed based on utilizing thermogravimetric analysis for measuring the lubricant weight-loss under given time, temperature and atmosphere conditions. Based on these investigations, critical temperatures for lubricant removal are determined and optimum parameters for delubrication are proposed. Mathematical models have been developed which can predict the completion of delubrication based on this approach [60], [76]. But due to the complex nature of the process, in-situ monitoring methods to determine and control lubricant removal by adjusting the parameters accordingly are sought for. Monitoring systems for sintering furnaces equipped with sensors for oxygen, hydrogen, dew-point, carbon monoxide, carbon dioxide and methane exist [51], [77]. Using these sensors closed-loop control systems have been implemented for sintering which take readings from the furnace and make adjustments to the composition and atmosphere flow rate to improve the sintering performance [78]. However, usage of sensors for atmosphere analysis in the preheat zone is limited due to the volatile lubricants, high dew-points and sample line plugging [8]. Indirect observation of improper delubrication is achieved through the CO/CH_4 sensors used in the hot zone detecting the presence of lubricant decomposition products that are not completely removed in the preheat zone and enters the high temperature zone.

Previous studies have indicated that monitoring gas-phase products is a reliable approach for monitoring the delubrication process [8], [9], [56], [57], [60]. Using this approach, an in-situ delubrication monitoring system based on measuring the concentration of short chained hydrocarbon products during lubricant removal has been demonstrated [8], [56]. The level of these hydrocarbons is claimed to be indicative of the delubrication process as seen from the combination of TG measurements and Raman scattering analysis during the progress of delubrication [10]. Since lubricant is the only possible source for their origin, a drop in their concentration to a predetermined level is considered to be indicative of the completion of the process. This method is supported by a recent investigation where gas-phase products from delubrication were measured [69]. Practical application of this technique at an industrial scale for monitoring delubrication of EBS resulted in difficulties mainly due to the condensation of large molecular hydrocarbons blocking the sampling lines to the analyzer. The difficulties were lesser for monitoring the removal of polypropylene since it breaks easily into smaller hydrocarbons [8], [56]. However, results from another study where pyrolysis products of EBS were studied suggest that monitoring small molecular hydrocarbons would not be representative for monitoring delubrication since their emission maxima occur at temperatures well below that of the emission maxima for the major decomposition products identified [9]. It has been suggested that delubrication monitoring sensors would instead require detection of CO_2 or aliphatic hydrocarbons with the absorption range between 3000 and 2700 cm^{-1} based on the maximum concentration of various gases identified during EBS decomposition. It is argued that CO and CO_2 formed during delubrication might be affected by catalysis effects due to Fe/C base material in which case they might not serve as good indicators [69].

4 RESEARCH OBJECTIVES

The main focus of this work has been:

1) To establish a method for the assessment and control of delubrication process through process atmosphere monitoring by means of sensors commonly used in the industry. This includes correlation and validation of the observations from the established method with those from complementary methods − thermogravimetric analysis, in-situ visual (video) experiments and chemical analysis.
2) To perform a systematic study on the influence of various process parameters on delubrication using the established method and to propose optimal processing conditions for delubrication.
3) To investigate the effect of delubrication process parameters on the surface chemical characteristics of chromium prealloyed PM steels and the sintering process from the point of view of the inter-particle neck formation and their strength, microstructure formation and final mechanical performance of sintered PM components.

5 EXPERIMENTAL DETAILS

The main focus of this thesis has been to develop a methodology based on process atmosphere monitoring for the study and optimization of delubrication process. Also, surface chemical analysis has been performed to study the changes occurring during delubrication on the powder particle surfaces that affect further sintering.

5.1 Materials

Water-atomized commercial powders grades Astaloy CrM (Fe-3Cr-0.5Mo) and Astaloy CrA (Fe-1.8Cr), produced by Höganäs AB, Sweden, were used as the basic material for this study. Delubrication experiments were performed on Charpy impact test bars (ISO 5754: 10×10×55 mm) uniaxially compacted to a green density of ~7 $g \cdot cm^{-3}$ for Astaloy CrM and ~7.3 $g \cdot cm^{-3}$ for Astaloy CrA, respectively. The powder was admixed with 0.6 wt.% of the ethylene bis-stearamide based lubricant (EBS_L) for the case of low density, and 0.5 wt.% of EBS_L for the case of high density samples. Some samples were additionally admixed with 0.5 wt.% of graphite (UF4 grade) for experimental studies concerning the influence of graphite addition and Fe/C interface on delubrication. Samples with carbon addition were also used for establishing the influence of delubrication on sintering.

5.2 Processing Atmosphere Monitoring

Delubrication experiments were performed in a laboratory tube (quartz) furnace *Entech* upon which a process atmosphere monitoring system was installed.

A schematic of the experimental setup is shown in Figure 5. The process gas inlet tube was connected to a dew-point meter through a water bath which was placed on a heater for injecting moisture into the processing atmosphere. This was used for performing experimental trials with wet atmospheres. Humidity of the inlet atmosphere was controlled by the ceramic dew-point sensor (Michel Cermet II). The process gas from the dew-point meter passes through a flow meter where the flow of the gas into the furnace was regulated.

The monitoring principle is based on continuous on-line analysis of oxygen (zirconia ceramic sensor) and carbon dioxide (sensor based on infra-red cell technology) concentrations in the process atmosphere. Dew-point was monitored in some experiments in parallel to O_2 and CO_2 utilizing the same ceramic dew-point sensor. The process gas flowing through the furnace is collected by a sampling tube placed in close proximity to the sample undergoing delubrication by continuous sampling using *Rapidox 3100A* dual O_2/CO_2 analyzer (Cambridge Sensotec Ltd). The gas temperature entering the sensor should not exceed 55 °C. Hence a stainless steel sampling tube was used, passing through which the temperature of the gas reduces to acceptable limits before reaching the sensors. The sampled gas then passes through a two-stage filtering system which was installed to avoid sensor contamination. First coarse filtration stage consisted of a stainless-steel pre-filter element for removal of particles >1 μm and for the condensation of heavy-hydrocarbons. The second stage consisted of microfiber filter element for the removal of particles of the size order of 0.1 μm. The dew-point meter was also used as a sensor for some process atmosphere monitoring experiments. Temperature measurement was simultaneously made by a thermocouple (K-type) installed inside the specimen. The readings from the sensors and the thermocouple were then continuously logged during the process using a computer program and were processed.

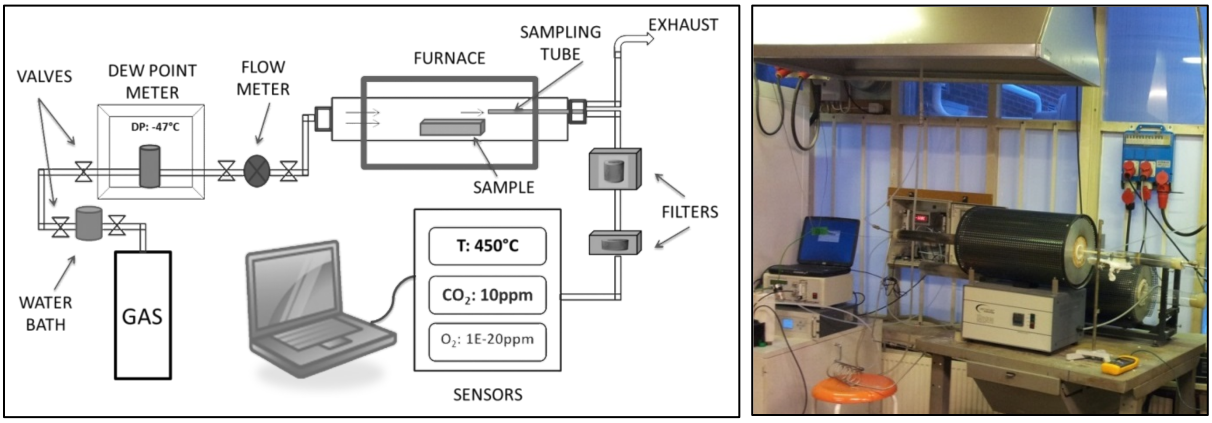

Figure 5 Schematic (Left) and Laboratory set-up (Right) of the Processing Atmosphere Monitoring System

5.2.1 Description of the sensors

Oxygen sensor

Solid ceramic electrolyte and acid/base electrolytic sensors are two popular oxygen monitoring devices used in the processing industry [77]. The oxygen sensor used in the experimental set-up for the present work is a solid ceramic electrolyte sensor. This sensor operates on a zirconia (ZrO_2) ceramic tube which is heated to temperatures around ~700 °C in the analyzer which becomes an oxygen ion conductor at this conditions. The working principle is based on the difference in oxygen partial pressure between the sample gas and a reference gas, generally air, generating an electromotive force between the electrodes which is measured. This is correlated to the oxygen content of the sample gas through the calibration of the sensor. The oxygen sensor used in this research provides analysis over the full range of oxygen partial pressures ($10e^{-20}$ ppm to 100% O_2). The advantage with ZrO_2 is their quick response time, easy maintenance and relatively low costs. For the sensor used in the present work, the response time was 5 seconds for a 90% response to a step change. Another important implication for using ZrO_2 sensors instead of oxygen sensors based on galvanic cells for monitoring delubrication is explained in detail in section 6.1.

Carbon dioxide (CO_2) sensor

Infrared (IR) sensors for CO_2 detection are spectroscopic devices used for gas detection which work based on the principle that each species absorbs IR radiation of a particular wavelength range. IR light is directed through a chamber containing the sampling gas to the detector. CO_2 sensor provides high accuracy and stability in measurements with a response time of 30 seconds.

Additionally, a video camera was installed for performing in-situ visual (video) delubrication experiments to track changes occurring through direct observation. The intention is to be able to correlate and validate the observations made using the process atmosphere monitoring (see Figure 6).

Figure 6 Setup and screen-shots from in-situ video of delubrication

Employing the process atmosphere monitoring setup (see Figure 5) a systematic study of the effect of individual process parameters on delubrication has been performed. Influence of process atmosphere composition and purity, delubrication temperature, graphite addition, heating rate, flow rate, holding time and density were studied.

summarizes the processing conditions employed for the delubrication experiments.

Table 1 Processing conditions employed for the delubrication experiments

Variable	**T, °C**	**Atmosphere**	**Heating Rate (°C/min)**	**Flow (Litres/min)**	**Dwell time (min)**
Atmosphere	450	**N_2(dry), N_2 (wet), N_2+10H_2, N_2+0.3CO, N_2+H_2O, Air(dry)**	~10	4	30
Temperature	**900**	N_2(dry), N_2+10H_2, N_2+0.3CO	~10	4	30
	500, 400,300	N_2(dry)			
Graphite addition **(0 and 0.5 wt.%)**	450	N_2(dry), N_2+10H_2, N_2+0.3CO	~10	4	30
	900	N_2(dry), N_2+0.3CO			
Heating rate	450	N_2(dry), N_2+10H_2, N_2+0.3CO	**~10, ~20, ~30, ~50**	4	30
	500,400, 300	N_2(dry), N_2+0.3CO			
Flow rate	500	N_2(dry), N_2+0.3CO	~50	**6,4,2,1,0.75, 0.5,0.25,No flow**	30
	450	N_2(dry)	~10	**7.5 L/min**	30
Holding time	450	N_2(dry)	~10	4	**0,10,20**
Density **(7.0-7.3 g/cc)**	450	N_2(dry), N_2+10H_2, N_2+0.3CO, Air(dry)	10	4	30
	900	N_2(dry), Air(dry)			

5.3 Analytical Techniques

5.3.1 Thermogravimetry

Thermogravimetric (TG) analysis involves determination of amount and rate of weight change for a material in relation to change in temperature in a controlled atmosphere. During the analysis, the temperature is increased slowly so that one of the components decomposes or evaporates. The weight of the sample is determined before the analysis and then the weight change with increase in temperature is measured and a weight loss curve is generated which is usually represented in terms of a relative mass change. The basic components of the analyzer hence consist of a sample holder, a high resolution balance system and a furnace, all placed inside a chamber. The chamber is vacuum-tight and ensures very pure and well defined atmosphere control during the test.

The equipment used in the present work is a simultaneous *TG/DTA/DSC thermal analyzer STA 449 F1 Jupiter* equipped with a high sensitivity balance system with high resolution in terms of weight and temperature measurement. The equipment has a top loading design with an ultra-nano balance with a resolution of 25 ng. A W/Re thermocouple was used for monitoring the temperature. The TG sample carrier system was used since it allows for analysis of large samples, in our case ~5 g. After loading the sample, before performing the experiment, the measuring system was evacuated three times before each test to ensure required gas purity and composition for each experiment. Analysis was performed on both small pieces crushed from the compacts and pieces cut from the green compacts to study the lubricant removal by varying the process parameters.

5.3.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a surface sensitive technique which is based on the principle that a surface irradiated by X-rays creates photoelectrons. In XPS, a low-energy X-ray beam is directed towards the sample which ejects electrons due to the photoelectric effect [79]. Soft X-rays with specific energies are used in order to excite the atoms of the material, placed in an Ultra High Vacuum (UHV) environment, which emits characteristic photoelectrons. In an event where an electron from one of the core levels is ejected by the incident X-ray, the photon will have a kinetic energy (KE) given by the expression

$$KE = h\vartheta - BE - \varphi$$

where hv is the energy of the exciting radiation, BE is the binding energy of the emitted electron in the solid and φ is the spectrometer work function. The kinetic energy of the emitted electron is measured by means of a hemispherical analyzer and thus the binding energy (BE) is calculated which is unique for each electron level for each element (see Figure 7). An electron energy analyzer directly resolves the elements in the sample. One of the most important capabilities of XPS is its ability to measure shifts in binding energy of the core electrons resulting from changes in chemical environment which can be due to change in the nearest neighbor, oxidation state or compound characteristics. The emitted photoelectrons of interest have relatively low kinetic energies and hence have a higher probability of undergoing inelastic collisions with the atoms if they travel very far before leaving the surface. Thus only electrons originating from a few atomic layers below the surface will contribute to the XPS peaks making it a surface sensitive technique. This also describes the need for a good vacuum environment −UHV ($<10^{-7}$ Pa). Typical analysis depth is approximately between 3 to 10 nm, depending on the material. Since not only the energy but also the number of electrons for each energy interval is detected, proportionality between the surface elements present is created. Detection limit for the elements is typically in the parts per thousand ranges [80].

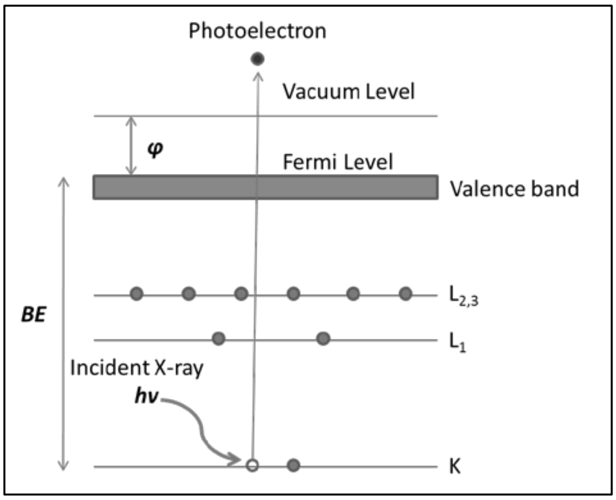

Figure 7 Schematic of the principle of XPS

In this study, XPS has been used for the determination of surface oxide layer composition and thickness as well as for identifying the chemical states of the elements present in the surface layer. The XPS analyses in this study were carried out by means of PHI 5500 spectrometer operated using monochromated Al Kα source ($h\nu$=1486.6 eV). For the settings employed, the produced X-rays irradiate approximately an area of 0.8 mm^2 of the sample. The instrument is equipped with an ion gun providing the possibility to perform depth profiling by means of which the oxide thickness and compositional profiles at different etch depths of the samples were obtained. In the present work, depth profiling is performed by Argon etching (Ar^+) over an area of 4×5 mm^2 with an etch rate of 2.85 $nm \cdot min^{-1}$, calibrated on a Ta_2O_5 foil.

5.3.3 Scanning Electron Microscopy

In the present work, surface chemical analyses performed using XPS have been complemented with high resolution scanning electron microscopy (HR-SEM) combined with energy dispersive X-ray spectroscopy (EDS).

SEM is widely used primarily because it provides high resolution imaging combined with good depth of field imaging. In an SEM, a beam of electrons is deflected to raster over a rectangular area on the sample. The electron beam is formed in an electron gun and the beam is focused by a lens system down to a nanometer width. Information is then collected by detectors located around the electron gun. A typical SEM setup can detect emitted electrons, scattered electrons and photons, all which are products of the interaction of the electron beam with the sample in the interaction volume [81]. The energy of the electron beam typically ranges from 1-40 kV. By studying the photons emitted due to atomic excitation by the electron beam in the X-ray region, information about the elements can be obtained since X-rays are characteristic and uniquely indicative of the elements of their origin. This is referred to as energy dispersive X-ray spectroscopy (EDX or EDS).

For the purpose of the present work, LEO 1150 Gemini equipped with a Field Emission Gun (FEG-SEM) and INCA Energy EDX analyzer is used. Since the analysis was to be performed on the surface of the powder and the features of interest were sizing to the order of a few hundred nanometers on the powder surface, the parameters used for imaging and EDX analysis were: acceleration voltage of 15 kV and an aperture size of 20 μm with a working distance of 9 mm. The imaging was performed using an in-lens secondary electron detector as it provides high resolution and improved topological contrast at low beam voltages.

5.3.4 Chemical Analysis

The bulk chemical analysis for determining the carbon and oxygen content was conducted using instruments equipped with infrared detectors. For determining the oxygen content, the sample placed in a graphite crucible is melted in an induction furnace under flowing helium. The oxygen in the sample reacting with the crucible forms CO and CO_2, the presence and amount of which are detected by IR sensors. For the determination of carbon, the sample is combusted in an induction furnace under the flow of oxygen. From the CO and CO_2 evolved due to the carbon in the sample reacting with the oxygen, the amount of carbon is determined. These analyses were provided by Höganäs AB.

6 SUMMARY OF RESULTS AND DISCUSSION

This thesis is based on the results from four appended papers. The focus of the work has been to establish an industrially feasible method for monitoring and controlling the delubrication process. Paper I focuses on the description of the established methodology which is based on using sensors commonly used in the industry for studying the delubrication process. In this study, the process atmosphere gas has been monitored during delubrication and the obtained in-situ curves from the sensors have been correlated with the phenomena occurring during individual stages in the lubricant removal process. Paper II focuses on optimizing the delubrication process parameters. Through a systematic study, by varying the process parameters during delubrication, the effect of individual parameters on the delubrication process has been reported and optimum parameters for the process are arrived at. Paper III and IV focus on the effect of delubrication process parameters on the surface characteristics of the powder particles and on further sintering. XPS combined with SEM and EDX analysis of the fracture surfaces has been performed to study the surface chemical changes occurring during delubrication and their impact on sintering.

6.1 Processing Atmosphere Monitoring

Experimental set-up for processing atmosphere monitoring was installed based on industrial O_2, CO_2 and dew-point sensors. The inlet process gas purity was controlled using the dew-point sensor and a thermocouple was placed inside the sample to record the temperature. In-situ measurements of the signals from the sensors were recorded into a process atmosphere monitoring profile during the delubrication process as shown in the Figure 8. Compacts based on water atomized chromium pre-alloyed steel powder Astaloy CrM admixed with lubricant EBS_L were used for the study. Graphite was additionally admixed for some samples. From the process atmosphere monitoring profiles, it was seen that the oxygen sensor indicated the initial stages of delubrication. An inflection point on the O_2 signal observed around ~270°C indicates the beginning of lubricant evaporation. This was in good agreement with the direct observation of evaporation of the lubricant as seen from the in-situ video/visual observation of the sample (visually smoke was observed in the setup at this temperature) and also from the inflection point on the weight-loss curve obtained through TG. Significant drop in the oxygen partial pressure is noticed after this temperature, which is connected to the working principle of the sensor-ZrO_2 ceramic placed at ~700 °C to aid oxygen ion transport as described in section 5.2.1. Delubrication products reaching the sensor burn on the hot surface of the sensor resulting in an oxygen partial pressure drop (see Figure 9). A drop in the partial pressure hence indicates the presence of delubrication products and the beginning of the process. The oxygen sensor however proved ineffective while using reducing atmospheres. The active reducing agent (in this case H_2/CO) reacts with the oxygen present on the surface of the sensor and results in lowering the partial pressure from the start. No changes in CO_2 signal were observed during the initial stages of delubrication represented by the oxygen sensor. This is because initial stages of decomposition at lower temperatures involves lubricant evaporation and decomposition forming heavy hydrocarbons which are not converted to CO_2 due to the lack of oxygen in the dry atmospheres.

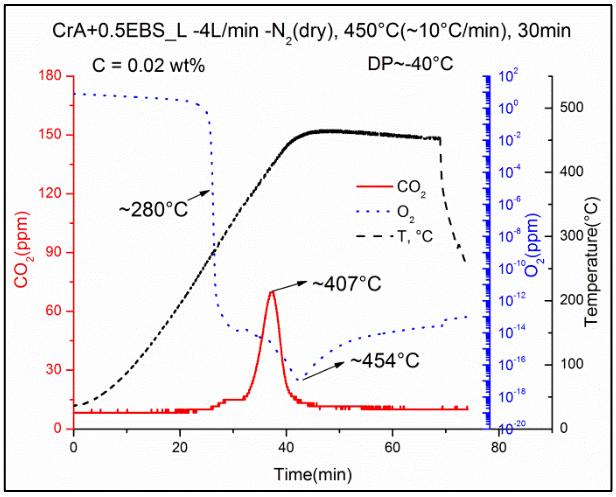

Figure 8 Processing Atmosphere Monitoring Profile

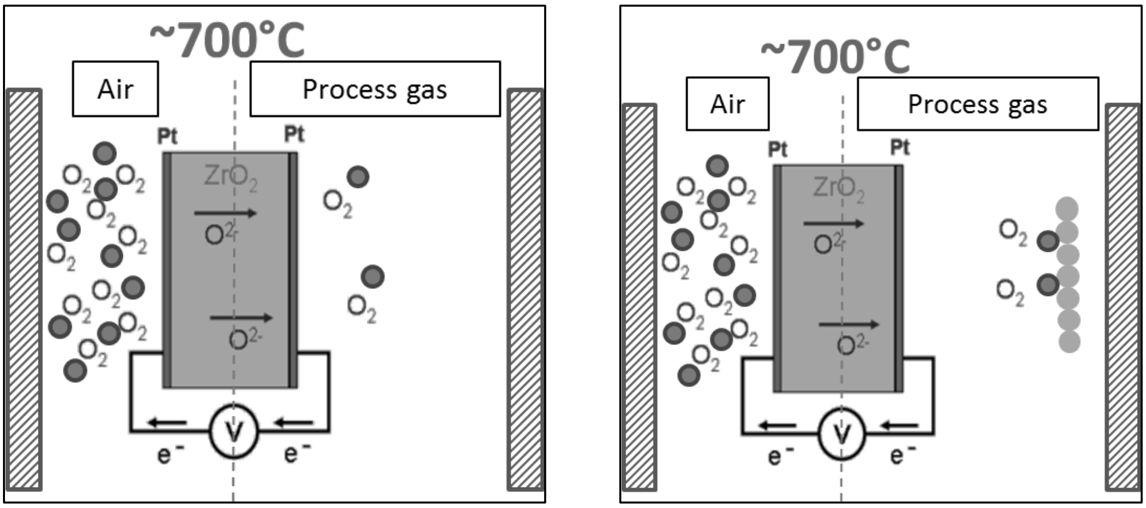

Figure 9 Schematic illustration of the indication of beginning of lubricant removal by the oxygen sensor

The oxygen level further decreases with increase in temperature and has a maximum slope at ~300 °C representing intense decomposition and reaches a minimum value around the temperature where it coincides with the peak on the CO_2 signal. CO_2 signal with a peak observed at ~410 °C indicates second stage (decomposition) of delubrication. An increase in the oxygen content was observed during dwelling at the delubrication temperature but it does not reach to the oxygen level characteristic for the nitrogen gas purity used. This increase in oxygen content can be connected to the slow removal of the hydrocarbons which condense on the walls of the sampling system. Additional weak CO_2 peaks were observed during heating for delubrication at 900 °C − around ~600 °C and 800 °C − connected to the carbothermal reduction of the surface oxides by the residues of carbon from the lubricant. For the samples admixed with graphite, these peaks were more intense. However, increasing the temperature to 900 °C did not change the character of the first CO_2 peak at ~410 °C.

Visual observation of the delubrication process indicating different stages of lubricant removal is shown in Figure 10.

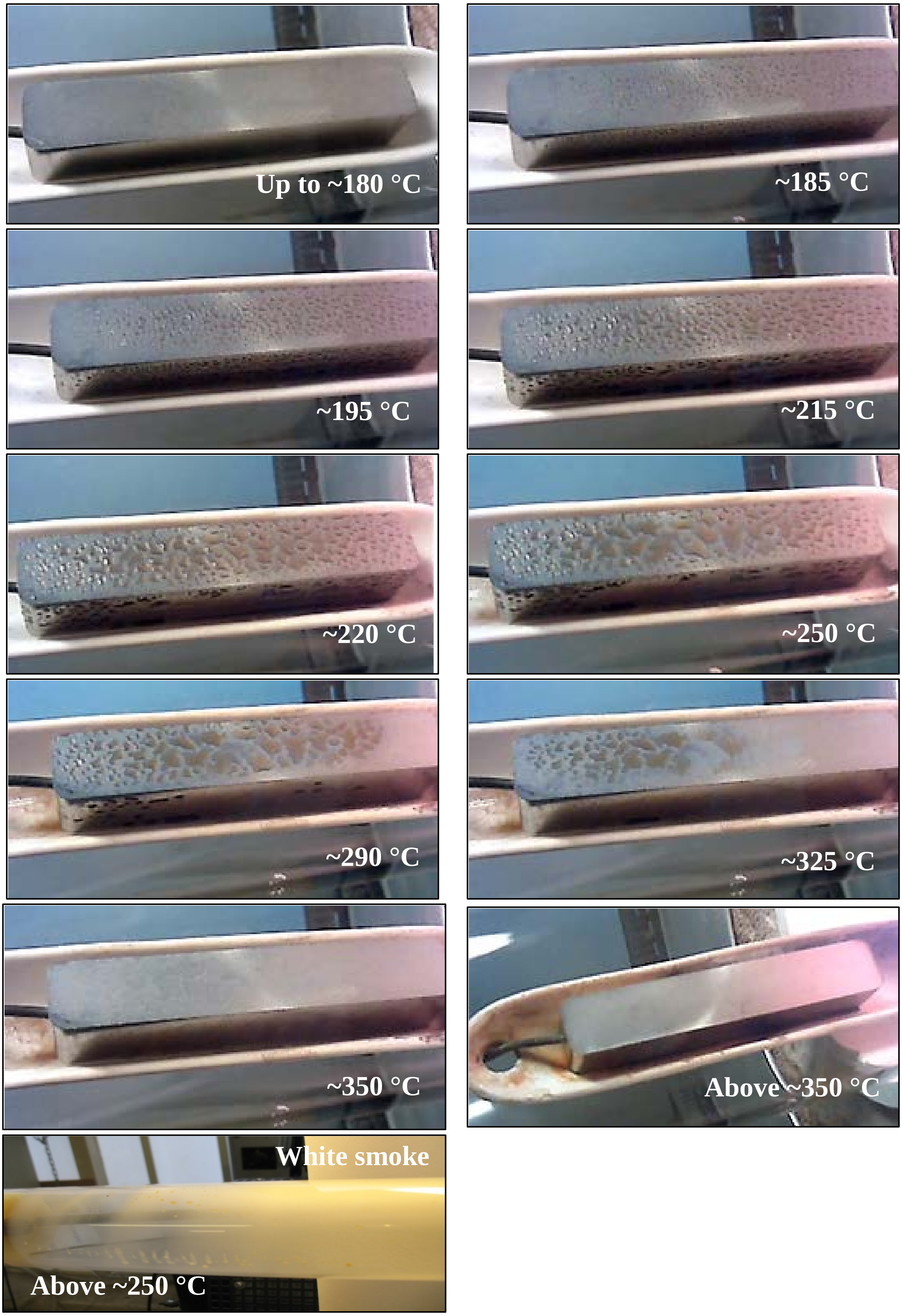

Figure 10 Screen-shots from the video taken during different stages of delubrication of the sample

During visual observation of the delubrication process, no changes were observed until the sample temperature reached ~180 °C. When the sample temperature was around ~180 °C, transparent droplets were observed on the compact surfaces. With increase in temperature, these droplets grew in number and slowly changed from being transparent to brown. These changes were observed between 200-220 °C. Around 250 °C, size of the droplets increased and coalescence of these droplets was observed. Some deposits and white smoke observed in the tube starting around the same temperature. Evaporation of droplets was observed around 280 °C starting from at the right end of the sample which is at a slightly higher temperature compared to the rest of the sample. Droplets evaporation continues until 350 °C after which all the droplets are seen to disappear. Above 350 °C, no visual changes were observed.

The observations from process atmosphere monitoring were in good correlation with the results obtained from in-situ visual observation (video of the whole process), thermogravimetric analysis and bulk carbon and oxygen analysis of the compacts.

6.2 Effect of Processing Parameters on Delubrication

Using the process atmosphere monitoring set-up the effect of individual process parameters on the delubrication process has been evaluated.

6.2.1 Effect of Processing Atmosphere

It was shown that the effect of processing atmosphere on the delubrication process in case of inert and reducing atmospheres was minimal. The CO_2 peak was observed around ~410 °C independent of the processing atmosphere composition and purity, except for the case of processing in air where it shifted to higher temperatures with a multifold increase in intensity. This shift is attributed to the burning of the delubrication products condensed in the stainless-tube sampling system. The influence of moisture was observed to be minimal. A shoulder on the CO_2 peak was observed for the case of processing in air and for the case of wet atmosphere which coincides with the intense evaporation peak on the oxygen signal.

6.2.2 Effect of Processing Temperature

Increasing the processing temperature to 900 °C did not alter either the position of the CO_2 peak nor inflection points on O_2 signal. This was confirmed by results from the chemical analysis on the samples which showed that the content of carbon and oxygen obtained was similar to that for the case of delubrication at 450 °C.

6.2.3 Effect of Graphite Addition

Addition of graphite did not influence the peak positions on the processing atmosphere monitoring profiles indicating that the influence is minimal on the process. For the samples heated to 900 °C, addition of graphite resulted in more intense additional peaks at higher temperatures indicating intensive carbothermal reduction reactions.

6.2.4 Effect of Heating Rate

The samples were subjected to high heating rates (up to ~50 °C/min) by introducing them into the furnace preheated to a set (delubrication) temperature to simulate the situation for processing in a batch furnace. A clear shift in CO_2 peak towards a higher temperature with increasing heating rate was registered, indicating that the delubrication process has to be performed at higher temperatures (~500 °C) in such cases. Also, from the O_2 signal it was seen that the melting/evaporation process is accelerated bringing risk of green-cracks formation.

6.2.5 Effect of Processing Atmosphere Flow

When the flow was increased from a nominal 4 L/min (~0.04 m/s) to higher values (~0.08 m/s) it was seen that the CO_2 peak intensity was diluted but the position remained the same indicating that the increase in flow does not influence delubrication. When the flow was decreased below nominal to insufficient (nearly static) flow conditions, the sample surface still remained clean after delubrication at 500 °C. However, when the temperature was decreased further to 400 °C deposition of delubrication products was observed on the sample surfaces and the situation worsened on decreasing the temperature further to 300 °C. Process monitoring results showed that the process is not complete for 400 °C and especially not for 300 °C. Furthermore, at 300 °C carbon dioxide peak is absent indicating that the decomposition reaction does not start at this temperature. This is also confirmed by the residual carbon content indicating that almost all the carbon (lubricant and its decomposition products) remains in the sample.

6.2.6 Effect of Holding Time

Chemical analysis and thermogravimetry indicate that almost the entire lubricant removal occurs during the heating stage. Holding time at 450 °C does not significantly influence the residual carbon content in the specimen and was on the level from 0.02 to 0.04 wt.% independent of the holding time (0, 10, 20 and 30 min). However, holding time is recommended to account for the case when massive parts with complex geometry are processed. Also industrial furnaces have considerably higher load, meaning that additional holding time is required to assure lubricant/decomposition products purge off.

6.2.7 Effect of Density

Independent of the atmosphere composition and temperature it was observed that increasing the density from 7.0 to 7.3 g/cc did not affect the delubrication process. The only difference observed was in the intensity of the CO_2 signal which was lower than that for the case of lower density samples. This is related to lower amount of lubricant added in the case of high density samples which is 0.5 wt.% instead of 0.6 wt.% for samples with a density of 7 g/cc.

6.2.8 Thermogravimetry Studies

Thermogravimetry results confirm that during delubrication at 450 °C with heating rate of 10 °C/min all the mass loss occurs during heating stage. This once again indicates that the holding time can be significantly shortened. It was noticed that the inflection points on the mass loss curve from thermogravimetry correspond well to inflection points on the oxygen profile from process atmosphere monitoring.

6.3 Surface chemical changes

The XPS was performed on samples delubricated in dry nitrogen atmosphere at 450 and 900 °C, and in air at 450°C, respectively. Delubrication in N_2 at 450 °C gave a surface condition similar to that of the base powder. Increasing the delubrication temperature to 900 °C resulted in considerable increase in the concentration of Cr and Mn oxides on the surface. This was confirmed from the SEM and EDX analysis which revealed the presence of particulate oxides rich in the aforementioned elements. Presence of these elements on the surface is related to the growth of undesirable thermodynamically stable oxides at the expense of pre-existing Fe-oxide layer. Delubrication in air at 450 °C results in a six fold increase in the oxide layer thickness around the edges of the sample. High resolution SEM imaging on this sample showed presence of regions with the oxide thickness exceeding 100 nm.

6.3.1 Influence of Delubrication on Sintering

The samples delubricated at 450 °C and 900 °C in dry nitrogen and 450 °C in air were subjected to sintering at 1120 °C in $90Ar/10H_2$ atmosphere in a dilatometer to obtain controlled sintering conditions. Along with these samples, another sample that was delubricated at 300 °C in N_2 under static flow conditions at higher heating rate was also sintered. The samples sintered after delubrication at 450 °C showed high values of impact energy and high hardness along with low carbon loss and low final oxygen content since the surface state of the powder is retained after delubrication. After sintering, the samples delubricated at 450 °C in air showed the lowest impact energy and hardness values. This is due to the high carbon loss which is “spent” for the reduction of the thick iron oxide layer formed during delubrication. After sintering, the samples delubricated at 900 °C showed the highest impact energy values but lower hardness values. This was also associated with the highest oxygen content and high carbon loss. These were related to the growth of thermodynamically stable oxides, and the impact energy is related to the neck formation occurring already during the holding stage of delubrication at 900 °C for 30 min. Delubrication at 300 °C resulted in incomplete delubrication and sintering of the sample resulted in inferior mechanical properties.

7 CONCLUSIONS

- A methodology for studying the delubrication process has been successfully demonstrated based on process atmosphere monitoring using industrial CO_2 and O_2 sensors.
- The initial stages of delubrication (melting and evaporation) are indicated by the O_2 sensor with evaporation starting at ~270 °C and the later stages (decomposition) are detected by the CO_2 sensor with a maximum peak at ~410 °C using which the process can be monitored and controlled.
- The effect of various process parameters on delubrication has been studied and it was shown that the process atmosphere composition, purity (presence of moisture), presence of admixed graphite, effect of holding time at 450 °C, increase in the flow rate above the nominal level (4 L/min) and increase in processing temperature above 450 °C had a minimal effect (technologically) on the delubrication process.
- An increase in the heating rate shifts the delubrication process towards higher temperatures in which case a higher delubrication temperature (~500 °C) is necessary for complete lubricant removal.
- At higher temperatures and higher heating rates, decreasing the flow rate below nominal resulted in slight oxidation indicated by discoloration of the specimen. But when the flow rates were significantly reduced to static conditions and the processing temperatures were reduced to 400 °C and below, deposition of decomposition products on the sample surfaces was observed.
- Surface chemical states of the powder after delubrication at 450 °C in dry N_2 was similar to that of the as-received powder and upon further sintering resulted in the optimum properties in terms of mechanical behavior and chemistry.
- Delubrication in air resulted in an increase of the thickness of the surface iron oxide layer especially near the edges (6 fold) of the sample and subsequent sintering of the sample resulted in a higher carbon loss and lowest impact energy and hardness values.
- Increasing the delubrication temperature to 900 °C results in the transformation of the Fe-oxide layer into more thermodynamically stable Cr-Mn-Si oxides. Hence sintering of the samples resulted in higher carbon loss and oxygen content with lower hardness values.
- Sintering the samples delubricated at 300 °C under static conditions with a high heating rate resulted in inferior mechanical behavior.
- Based on the results, it is recommended to perform delubrication with a low heating rate (~10 °C) in an inert atmosphere at the temperature of around 450 °C with flow rates enough to provide even weak dynamic gas flow conditions around the component surfaces.

8 SUGGESTIONS FOR FUTURE WORK

- Transfer of the established methodology to an industrial process for implementing delubrication process control
- Effect of furnace load in industrial conditions on delubrication needs to be evaluated
- Effect of the part geometry on delubrication
- Delubrication of the lubricants used in warm compaction
- Possibility of using additives for improved lubricant removal

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