DTA, TGA and Mass Spectrometer Investigation of the Sintering Processes of Iron Powders Coated with Hydrocarbons and Iron Powders Premixed with Graphite

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Abstract. Sintered ferrous components produced by powder metallurgy method emerged as candidates for replacing these manufactured by casting and forging. The present paper studies a new method for introduction of carbon into the master alloy powder at sintering of metal powders and its influence on the microstructure, homogeneity and mechanical properties of the final product. Special attention is paid to the thermodynamics and the kinetics of the processes taking place at sintering, and how they influence the resulting microstructure and the mechanical properties.

Keywords: powders, hydrocarbon coating, Differential Scanning Analysis (DTA) and mass spectrometry, fracture strength, fracture surface.

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1. Introduction

The Powder Metallurgy (PM) method is nowadays widely used of producing machine parts which in the past have been manufactured by casting or forging. This is mainly due to the low cost of the PM technology and the method ability to process the parts to near-net shape. A serious problem at the application of PM, however, is the introduction of alloying additions into the inceptive powder [1–16]. Indeed, due to the difference between the specific weights of the alloying element and the metal powder, the direct introduction of the alloying additions into the powder mixture leads to segregation. As a result the produced parts have inhomogeneous microstructure and lower densities, hence, inferior mechanical properties. Aiming to solve the problems outlined, some alternative methods of introduction of the alloying elements into the master alloy powder were proposed and applied [6–15].

A method discussed here and described in detail elsewhere [6, 8, 12–15] was developed as an alternative of the classical methods of alloying and was aimed to circumvent some of the problems above. The method is based on coating of the master alloy powder particles with a thin layer of hydrocarbon plastic, thus facilitating the introduction of the alloying element, the carbon, into the sintered compact.

The aim of the present paper is to identify and study some of the processes taking place at sintering of compacts produced from coated with Polyvinyl Alcohol (PVA) powders, the thermodynamics and the kinetics of these processes, and how they influence the mechanical properties of the final product.

2. Experimental

The effect of the way of carbon introduction into the master alloy powder on the ensuing microstructure, homogeneity and fracture characteristics of the final product, the sintered compact, were studied on a commercially available iron powder ASC 100.29 produced by Höganäs AB. Two series of powder samples were prepared: from coated with PVA iron powder and from iron powder premixed with graphite. The coating procedure is described in detail elsewhere [6, 8, 12–14, 16]. Briefly the coating technique is as follows: The PVA is subjected to pyrolysis at 400 °C in an atmosphere of pure argon or
nitrogen, thus breaking the long PVA molecules into hydrocarbon radicals. The leftover, a black powder, is milled and dissolved in benzene or toluene producing a solution of hydrocarbon radicals described by the generalized chemical formula C_7H_7. After filtration the C_7H_7 solution is mixed with the metal powder in proportions ensuring the desired final concentration of the carbon in the sintered compact. The solvent remaining in the powder mixture is removed by heating of the powder-C_7H_7 solution mixture to approximately 70 °C until it is completely dry. To avoid clotting of the powder particles the mixture is vigorously stirred during the time of the solvent evaporation [15, 16]. The amount of carbon introduced into the sintered compact is determined empirically by specially developed empirical calibration graphs which allow estimation of the carbon weight introduced into the master alloy powder [14, 15].

Prior to the compaction the inceptive powder premixed with graphite were subjected to a mill and mix procedure in a rotating ball-mill for 30 min [14–16]. Two series of specimens were prepared: coated with PVA and admixed with graphite ASC 100.29 powder. The as prepared powders were compacted at 600 MPa in the form of cylinders measuring ø10 × 12 mm. The decomposition of the hydrocarbon coating and the formation of the highly reactive carbon layer on the particle surface took place during the sintering of the compact. From the as prepared compacts small sample specimens, ∼100–200 mg by weight, were taken for the studying of the sintering kinetics. The kinetic studies were carried out in an inert atmosphere between 400 °C and 1300 °C, with a heating rate of 10 °C/min, in a SETARAM LABSYS evo calorimeter coupled with a mass spectrometer. During the heating the released heat, the weight of the sample, and the partial atomic mass intensities of the released gases were measured. The results obtained with the Differential Scanning Analysis (DTA) and the Thermo Gravimetric Analysis (TGA), and the intensity of one of the monitored by the mass spectrometer atomic mass the a.m.u. 44 (CO_2) are shown in Figs 1–4. Here, a.m.u. stays for the atomic mass unit.

3. Results and discussion

Because of the complicated character of the sintering processes the DTA curves obtained from different experiments within the specimen series did not match closely each other. Usually, the DTA and the TGA data obtained is a result of
Fig. 1. Results from the DTA and TGA experiments obtained at sintering of compacts produced from premixed with graphite ASC 100.29 powder.

Fig. 2. Mass spectrogram of the CO$_2$ intensity in the exhaust gas obtained at sintering of compacts produced from premixed with graphite ASC 100.29 powder.

Fig. 3. Results from the DTA and TGA experiments obtained at sintering of compacts produced from coated with C$_7$H$_7$ASC 100.29 powder.

Fig. 4. Mass spectrogram of the CO$_2$ intensity in the exhaust gas obtained at sintering of compacts produced from coated with C$_7$H$_7$ASC 100.29 powder.

the overlapping of different processes occurring at sintering, which makes every experimental DTA- and TGA-curve unique and difficult for interpretation. However, from the experimental evidence and from the knowledge gathered up to now, some common features generally valid for all sintering processes.
could be distinguished [1, 12–21]. These are:

1. Diffusion of the alloying element, here the carbon, inside the sintered compact body. Obviously the carbon diffusion could take place in two ways namely, directly through the body of the powder particles, or along the particles surfaces. It should be noted that the latter is much faster, thus it could be assumed that this is probably the most common way of carbon transport inside the sintered compact;

2. Carbon reduction of the metal oxides formed during the processing and handling of the powders. A list of possible carbon reduction reactions of iron oxides that could take place during sintering is given in Table 1, together with the corresponding Gibbs free energies and the equilibrium constant $K_p$. The reduction process, however, depends on the carbon transport between the deposits of the carbon and the oxides. The position of the reduction agent, the carbon, differs for the two methods of alloying. In the method using coated powders, the carbon layer is firmly adhered to the particles surface and stays attached to it after the compaction. On the contrary, in the case of the premixed powders the graphite is loosely distributed throughout the powders mix. Thus, a considerable risk of carbon segregation into the pores formed during compaction exists. As a result the diffusion mechanisms of carbon to the oxide deposits may differ for the two methods of alloying studied, thus leading to different patterns of the reduction process;

3. Dissolution of the carbon inside the powder particles. Actually, this is the process of alloying of the sintered compact, which together with the processes of carbon reduction and densification is one of the goals pursued at sintering;

4. Removal of the gases produced by the reduction process from inside and out of the sintered compact body. The failing of this process would produce highly porous sintered compact, hence, bad mechanical properties;

5. Densification of the sintered compact, namely, reduction of the excess surface inside the sintered compact via the formation and growth of interconnecting bridges between the powder particles and diminishment of the porosity of the sintered compact.

The processes so outlined could be distinguished and traced on the obtained DTA and TGA data and on the mass spectrograms. Thus analyzing the data from these devices one could readily predict the quality of the final product.
Table 1. List of the possible carbon reduction reactions at sintering and their Gibbs energies $\Delta G(T)$ and equilibrium constants $K_p$ as a function of the temperature $T$

<table>
<thead>
<tr>
<th>Gr No.</th>
<th>Reduction reactions</th>
<th>The Gibbs free energies of the reactions, $\Delta G(T)$</th>
<th>$\lg (K_p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 1</td>
<td>FeO+C=Fe+CO</td>
<td>18180–359T+26T ln(T)</td>
<td>−949/T+19− ln(T)</td>
</tr>
<tr>
<td>I 2</td>
<td>Fe$_2$O$_3$+3C=2Fe+3CO</td>
<td>55533–932T+47T ln(T)</td>
<td>−2899/T+49−3 ln(T)</td>
</tr>
<tr>
<td>I 3</td>
<td>Fe$_3$O$_4$+4C=3Fe+4CO</td>
<td>77745–1376T+84T ln(T)</td>
<td>−4058/T+72−4.4 ln(T)</td>
</tr>
<tr>
<td>II 4</td>
<td>2FeO+C=2Fe+CO$_2$</td>
<td>17402–423T+36T ln(T)</td>
<td>−908/T+22−2 ln(T)</td>
</tr>
<tr>
<td>II 5</td>
<td>2Fe$_2$O$_3$+3C=4Fe+3CO$_2$</td>
<td>54190–976T+49T ln(T)</td>
<td>−2829/T+51−2.5 ln(T)</td>
</tr>
<tr>
<td>II 6</td>
<td>Fe$_3$O$_4$+2C=3Fe+2CO$_2$</td>
<td>39827–784T+53T ln(T)</td>
<td>−2079/T+41−2.8 ln(T)</td>
</tr>
<tr>
<td>III 7</td>
<td>FeO+CO=Fe+CO$_2$</td>
<td>−7787–63T+11T ln(T)</td>
<td>407/T+3−0.6 ln(T)</td>
</tr>
<tr>
<td>III 8</td>
<td>Fe$_2$O$_3$+3CO=2Fe+3CO$_2$</td>
<td>−13436–44T+T ln(T)</td>
<td>701/T+2−0.1 ln(T)</td>
</tr>
<tr>
<td>III 9</td>
<td>Fe$_3$O$_4$+4CO=3Fe+4CO$_2$</td>
<td>19090–192T+23T ln(T)</td>
<td>−997/T+10−1.2 ln(T)</td>
</tr>
</tbody>
</table>

3.1. Kinetic processes at sintering of coated powders. Analysis of the DTA and the TGA data

Although the composition of the powder and the carbon content are identical for both series, some substantial differences between the DTA data of the specimens prepared from powders premixed with graphite and these coated with C$_7$H$_7$ could be distinguished and analyzed. The results presented are selected in a way to show as much as possible of the common effects which could be encountered by the interpretation of the DTA data obtained. Analyzing the onset and the offset temperatures of the DTA peaks it is possible to deduce the following important features of the sintering process: the progress of the transport processes, i.e. the carbon diffusion inside the sintered compact, the degree of the carbon dissolution into the sintered compact matrix and the progress of the carbon reduction process. The results from the TGA are complimentary and allow studying the reduction kinetics, e.g., the rate of the reduction process via the change of the samples weight.

The DTA-curves of the specimens premixed with graphite (Fig. 1) show two easily distinguished endothermic peaks located at $\sim$ 750°C and at 910°C together with several small peaks in the temperature interval 950–1200°C. The presence of a pronounced peak at 910°C is due to the $\alpha \rightarrow \gamma$ transition of pure iron (see Fig. 5) and points out that the bulk amount of the iron is
Fig. 5. The iron side of the Fe-C phase diagram [17]

still unalloyed. The peak at 750 °C is due to the ferrite-austenite transition, see the PSK-line of the Fe-C phase diagram in Fig. 5. This result shows that the process of dissolution of the carbon into the iron is started, but because of the presence of the peak at 910 °C it means that the dissolution is still in its early stages. The results also show that the graphite powder particles are segregated into the pores formed after the compaction at the interstices between the iron powder particles, thus forming randomly distributed segregates throughout the compact. In this case, with the increasing of the temperature the graphite is dissolved into the adjacent iron particles forming a supersaturated solution of carbon into the Fe-matrix. This lowers significantly the melting point of the Fe-C alloy (see the ECF-line in Fig. 5), making possible the formation of semi-liquid zones around these particles. The small endothermic peaks seen on the DTA-curve above 1100–1170 °C are probably a result of the formation of semi-liquid zones around these undissolved carbon segregates. The diffusion rate of the carbon in the iron matrix could be deduced by the steepness of the DTA-curve in the temperature interval 500–900 °C. As seen in Figure 6 the carbon reduction processes in this temperature interval are not so active, thus the thermal effect observed in the DTA-curve could be prescribed entirely to the combined diffusion-dissolution process. Figure 7 shows a 3D graph
of the enthalpy $\Delta H (T)$ of dissolution of carbon into iron (the z-axis) vs the composition (0–0.15 atomic fractions) and the temperature 700 K and 1500 K, i.e., 427 °C and 1227 °C. As seen in Fig. 7 the dissolution is an endothermic process traceable in the DTA-curve as a downward sloping with the increase of the temperature line. Shortly, by the slopes of the DTA-curve in this temperature interval, one could easily deduce the fastness of the carbon diffusion. Obviously, the higher the diffusion rate, the steeper the slope of the DTA-curve. In Figure 2 it is seen that the diffusion is not fast which could be attributed to the limitations imposed on this transport process by the rate of the bridge formation between the powder particles. Indeed, if these bridges do not exist or are formed slowly, the transport of carbon from particle to particle is retarded, hence, the gentle slope of the DTA-curve observed. From this result, it could be concluded that because of the discontinuation of the carbon flux a certain compositional heterogeneity inside the final product could be expected.

The TGA-curves of the specimens produced from powders premixed with graphite (Fig. 1) show that up to 930 °C the mass of the sintered compact is
Fig. 7. 3D plot of the enthalpy \( \Delta H \sim 0.1 \text{ kJ/mole (z-axis)} \) of the carbon dissolution in an Fe\(_{1-x}\)C\(_x\) alloy. Here XC denotes the mole fractions of the carbon in the iron almost constant. Beyond that temperature a change of the sintered compact weight is observed due to the reduction of the oxides present. According to the thermodynamic calculations, however, (Fig. 6 and Table 1) the reduction reactions should start much earlier. The only plausible explanation of this experimental fact is that the observed retarding has a transport origin, i.e., it is due to the combined effects of carbon transport toward the oxide deposits and the kinetics of densification.

Concluding the analysis of the DTA and the TGA data for the pre mixed with graphite powders it could be noted that the transport and the densification processes are closely intertwined. The formation of bridges between the particles in this particular case requires higher temperatures and longer times, which explains the delayed transport of the carbon inside the sintered compact. The sintering time is limited by the production costs involved, therefore, the details prepared from powders premixed with graphite will always possess inherent compositional heterogeneity, because the time required for complete homogenization usually exceeds the production time.

As seen from the DTA-data, Fig. 3, the coated specimens exhibit a sequence of small endothermic peaks within the temperature interval 600–900°C. One also notes the absence of pronounced peaks, so typical for the
specimens prepared from powders premixed with graphite, and the considerable steepness of the DTA-curve compared to the DTA-curve in Fig. 1. From the experimental evidence the following conclusions could be drawn: (i) The diffusion-dissolution process is much faster by the coated specimens; (ii) Due to the faster diffusion and the proximity between the oxides and the reactive carbon of the coating the reduction processes start much earlier and are very intensive. This conclusion is confirmed by the TGA data which shows that the processes of carbon reduction are already active at 500 °C (via the reaction No. 8 see Table 1); (iii) The intensity of the dissolution and the reduction processes produce the compound DTA-effect seen in Fig. 3; (iv) At the first stages of the reduction the oxides are reduced directly by the carbon. Thus, in this temperature interval the reactions leading to formation of CO or CO$_2$ are active, i.e., the first six reactions listed in Table 1. The graphs of the $\lg (K_p)$ in Fig. 6 indicate the feasibility of the reactions, listed in Table 1. Remind that, the larger the value of $\lg (K_p)$, the higher the intensity of the reaction. The negative values and the values close to zero indicate that the reaction is not feasible or unlikely to take place.

Using the well known in the thermodynamics expression between the enthalpy $\Delta H (T)$ and the Gibbs energy $\Delta G (T)$, $\Delta H = \Delta G - T (\partial G / \partial T)$ [17–21], and the temperature dependencies of $\Delta G (T)$ listed in Table 1, one could readily obtain the enthalpies $\Delta H$ of all reactions listed. The calculations show that the first six reactions are endothermic and that the outstanding three are exothermic. Hence, the combined action of the reduction of the iron oxides and the carbon dissolution at this first stage of sintering, from 500 °C up to 930 °C, leads to the observed temperature drop detected jointly by the DTA and TGA.

The accelerating effect of the reactive carbon coating on the kinetics of iron oxide reduction and on the carbon dissolution is clearly visible in the DTA and TGA curves when they are compared with their counterparts, the ones obtained from specimens prepared from premixed with graphite powders. The results discussed so far allow concluding that the carbon dissolution by the coated specimens is almost finished at 900 °C. The increase on the DTA-signal beyond 930 °C seen at the coated specimens is due to transition from direct carbon reduction to indirect reduction via the CO gas, formed as a result of the direct reduction of a part of the oxides present.
The presence of multiple peaks in the DTA curves could be explained by the particulate nature of the compact. This leads to an uneven distribution of the carbon inside the sintered compact and as a result to an unhomogenized structure. Therefore, in the concrete case studied it is highly advisable to hold the sintered compact for at least 30 min at 1200 °C in order to avoid these undesirable effects.

The results from DTA and TGA clearly show one of the advantages of powder coating technique compared to the classical method of alloying, i.e., the fast dissolution of the carbon into the matrix, which leads to a higher homogeneity of carbon inside the sintered compact.

3.2. Kinetic processes at sintering of coated powders. Analysis of the mass spectrometer data
As above, some of the observed in Figs 1 and 3 exo- and endothermic effects registered by the DTA/TGA are due to a carbon reduction of the iron oxides present in the inceptive powders. This process leads to the formation of CO and CO$_2$ gases. Thus monitoring the gas content, the pressure and the amount of these gases one can get a realistic picture of the processes of reduction and their kinetics, Table 1. For this reason a parallel mass spectrometer investigation of the exhaust gases emitted during sintering, their composition and the onset temperatures of the processes leading to their formation was carried out, Figs 2 and 4.

The mass spectrometer data for the coated powders show that the formation of the carbon layer is effectively completed at 500 °C. The peaks of some of the hydrocarbon radicals, e.g., 16 a.m.u., are observed at least 100 °C below the first endothermic peak detected by the DTA. Thus, it could be concluded that the removal of the volatile hydrocarbon radicals from the master alloy powder and that the production of carbon layers on the surface of the powder particles at this temperature is already completed.

The differences between the mass spectrograms taken from the two series of specimens, the coated ones and these prepared from powders premixed with graphite, are obvious, Fig. 6. The reduction process by the coated specimens is much steadier compared to these prepared from powders premixed with graphite. Moreover, for these specimens, the reduction starts much earlier which is indicated by the intensity of the CO$_2$-line of the mass spectrometer.
Here the first peaks are observed between 600°C and 650°C. These peaks according to Fig. 6 could be associated with the direct reduction of the Fe₂O₃ oxide by the carbon located on the powder particles surface (reactions 1 to 6). The reduction of the wüstite (FeO) and the magnetite (Fe₃O₄) begins within the 690 °C and 710°C which accounts for the peak around 680°C (950 K), the not so well pronounced peak on the CO₂-line of the mass spectrogram. The effect of the carbon dissolution is clearly visible at 720°C (∼ 1000 K) as a sharp drop of the intensity of the CO₂-line at this temperature, Figure 6. This is explained with the intensified carbon dissolution into the γ-Fe which reduces the carbon availability, hence, the observed retarding of the reduction processes. Obviously, this is due to the tighter contact between the reducing agent and the oxides, and the increased surface activity of the reactive carbon layer. The peaks above 1000°C are not connected with chemical reactions, but they are a result from the effusion of the CO and CO₂ gases from the reaction zones to the sintered compact surface.

The specimens prepared from powders premixed with graphite exhibit quite different sintering kinetics as seen in Figs 4 and 6. It looks like that for these specimens all the processes are shifted with about 100°C toward the higher temperatures. The most probable explanation of such a behavior was discussed in the previous section. These processes are indicated by the first minimum on the CO₂-line, Fig. 6. When the oxide deposits are reached, the reduction reaction starts which is accounted for by the peak at 730°C (∼1000 K) on the CO₂-line. As in the case with the coated specimens the following peaks are probably due to the venting of the reaction gases from inside and out of the specimens.

The overall conclusion that could be drawn is that the peaks associated with the transport of the reduction products at the coated specimens are usually shifted to lower temperatures compared to those with graphite addition. This is explained with the lower green density, hence, the higher porosity of the compact and the higher reactivity of the nascent carbon produced by the carbon layer. In this specific case the higher green porosity is thus an asset rather disadvantage, since it allows better venting of the reaction products from the sintered compact at the earlier stages of sintering when the reduction processes are most intensive. In this way the entrapment of the reaction gases inside the sintered compact and the formation of pores is avoided.
The main difference between the two methods of carbon introduction, however, is the intensity of the deoxidizing processes. For the compacts produced from coated with carbon powders, the oxides reduction starts at \( \sim 600^\circ C \) and is entirely completed at 760°C. The reduction of the oxides by the compacts produced from powders premixed with graphite starts with \( \sim 100^\circ C \) delay and completes around 840°C. As above the explanation of this behavior is the close contact between the carbon coating and the powder particle and the presence of the highly reactive nascent carbon, which considerably facilitate the reduction-alloying processes.

### 3.3. Mechanical properties of the sintered compacts

The fracture strength measurements of the sintered compacts [3, 7, 10] were carried out on “Button” test specimens prepared from the sintered compacts produced. The obtained values of fracture strength tests are listed in Table 2. The influence of the chemical compositions of the powders used for production of the sintered compacts on fracture strength is clearly visible from the presented results. The observed morphology of the fracture surface correlates with the microstructure and the carbon content. Fractures observed are predominantly ductile with well developed particle necks. The ductile dimples with localized plastic deformation are also clearly visible, Fig. 8(a, b). It seems that sintered compacts produced from powders with graphite addition have a higher portion of ductile dimples compared to those prepared from coated powders. In the sintered compacts prepared from coated powders individual small cleavage facets are found. The analyses of the fracture lines show that the

<table>
<thead>
<tr>
<th>Chemical composition of the specimen</th>
<th>( R_{\text{frac.}} ) [MPa]</th>
<th>Sketch of the “button” used at the fracture tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASC 100.29 + C(_2)H(_2)</td>
<td>230</td>
<td><img src="image" alt="Sketch of button" /></td>
</tr>
<tr>
<td>ASC 100.29 + graphite</td>
<td>244</td>
<td></td>
</tr>
</tbody>
</table>
fracture takes place predominantly through the grains, i.e., the trans-crystalline mode of fracturing is predominant in this case, see Fig. 9(a, b).

4. Conclusions

The results of DTA, TGA, mass spectrometer and mechanical testing of sintered compacts produced by a new method of alloying of iron-based powders
with carbon, developed as an alternative of the classical methods used so far, are discussed. The parallel experiments on alloying with carbon by this new method and by one of the classical methods, allow making the following conclusions:

- The carbon dissolution at the coated with hydrocarbons powders is faster compared to these prepared from powders premixed with graphite due to the easy accessibility of the alloying carbon.

- The onset temperatures of oxides reduction for the coated specimens are lower up to 100 K, compared to these prepared from powders premixed with graphite due to the high reactivity of the hydrogen and the nascent carbon that resulted from the decomposition of the hydrocarbon coating.

- The denser contact between the coating and the powder leads to a faster saturation of the metal matrix with carbon, hence, to a higher homogeneity and a finer microstructure.

- The mechanical tests show that as a whole the sintered compacts prepared from coated powders possess better mechanical properties. Nevertheless, the sintered compacts produced from premixed with graphite powders possess higher fracture strength compared to the ones produced from coated powders, see Table 2.

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