MICROSTRUCTURE FORMATION AND FRACTURE PROCESSES IN Fe-C SYSTEMS SINTERED IN NITROGEN

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Abstract
In this paper, processes occurring during sintering of compacts prepared of plain iron powder Fe-ASC100.29 with admixed natural graphite UF4 in pure nitrogen atmosphere are described. The progress of sintering processes was investigated in the temperature range of 600 - 1200°C. Sintering processes were analysed by the changes of strain-stress dependencies at static tensile and dynamic bending tests. The changes of microstructure were observed by metallography, fractography, and EDX analyses. The progress of carbon dissolution in the matrix is explained based on carbon activity at different sintering temperatures in neutral atmosphere of pure nitrogen.

Keywords: Fe-C system, sintering, carburization, microstructure, strength and plastic properties, failure

INTRODUCTION AND AIMS OF THE WORK
The study of sintering and mechanical properties of sintered iron and iron-based alloys belongs to the classical research programs, which run over decades. Modern experimental methods, e.g. DT, DTA a DTG, REM and EDX microanalysis, microfractographic and fracture mechanics methods allow also at present time a knowledge deepening in physics and physico-chemical fundamentals of sintering process and determination of relation between the microstructure development and attained mechanical properties.

As stressed e.g. by Schatt, not only isothermal sintering but also the initial stage of the sintering process is of critical importance for the resulting properties and microstructure [1]. This holds for pore elimination, macroscopically discernible as dimensional change, but also for formation and growth of sintering necks [2] and for the removal of oxide layers covering the powder particles [3]. For carbon containing sintered steels, also the dissolution of graphite is commonly finished before the isothermal sintering temperature is attained [4].

The authors of the paper contribute to the knowledge development of processes taking place during sintering of the system of Fe + 0.8%C as natural graphite UF4. The processes are analysed in the temperature range of 600 - 1200°C using neutral atmosphere of pure nitrogen. The processes taking place in the heating stage of the sintering process were approached by isothermal sintering at various temperatures in the above range.

MATERIAL AND EXPERIMENTAL METHODS
For the sample preparation a standard water atomised iron powder grade ASC100.29 (Höganäs) with the following granulometry was used: 8% fraction of +150 μm, 23% fraction of -45 μm, the rest of 69% is the fraction in between. The starting oxygen content was approx. 800 ppm. Natural graphite UF4 was used as additive and 0.8% HWC as lubricant. The powder mix was prepared by mixing during 60 min at 60 rev/min in a tumbling mixer. The size of the
mixing vessel was 1 litre. From the powder mixture the standard specimens for static tensile test (ISO 2740) and Charpy impact test (ISO 4470) were compacted at 600 MPa. The specimens were isothermally sintered for 60 min at 600, 700, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200°C in pure (99,999%) nitrogen atmosphere. Static tensile tests were realised on a ZWICK 1387 testing machine with extensometer and crosshead speed of 1 mm/min. The values of proportional elongation were determined on the tested specimens on 30 mm gage length. Impact energy tests were realised on a Charpy machine with \( W_{\text{max}} = 150 \) J. Metallographic analysis was done on a light microscope Neophot 32 by digital display. Metallographic specimens were prepared by classic mechanical grinding, polishing, and etching with 3% nital. Electron microscopic REM and EDX analyses were done on a Tesla BS 340 machine with EDX LINK ISIS 300 microanalyser. The point analyses and digital area maps for distribution of iron, oxygen and carbon were determined.

The density was measured from specimen weight and dimensions. High accuracy of measuring was necessary. The weight of samples was measured on laboratory balance with precision of 0.1 mg. The dimensions were determined with precision of 0.01 mm for each sample as an average value from 10 measurements. The measured values are processed as a plot.

**STATIC AND DYNAMIC PROPERTIES OF SPECIMENS IN DEPENDENCE ON SINTERING TEMPERATURE**

The precise measurements of loading force and elongation allow punctual definition of yield strength \( R_{p0.2} \), tensile strength \( R_m \) values and determination of elongation. The changes of yield strength and tensile strength values in dependence on sintering temperature are shown in Fig.1. Three temperature ranges are evaluated as significant on these curves. The first one is the range up to 900°C, the second one for the range of 900-1000°C and the third one for 1000-1200°C temperature range. This classification is connected with growth restraining of strength parameters in temperature range of 900-950°C. The third area is connected with growing differences of stress values between yield and tensile strength. The dependence course shows the fact that the portion of deformation strengthening connected with specimen elongation rises between yield and tensile strength limit. This fact is confirmed by changes of elongation values with increasing sintering temperature, see Fig.2.

![Fig.1. Dependence of the yield and tensile strength on sintering temperature.](image1)

![Fig.2. Dependence of the elongation on sintering temperature.](image2)
The specimens for impact test with a size of 7x10x55 mm$^3$ were tested without notch. Energy of failure was determined at room temperature. The dynamic toughness values vs. sintering temperature are given in Fig.3. The shape of the curve confirmed that in the range of 900-950°C the level of the KC values is retained, while in the range of 1000-1200°C there is a significant increase of the impact energy values. Also this increase confirmed that the ability of sintered specimens for macroplastic deformation and for absorbing more energy up to fracture initiation significantly increased in the third temperature range of 1000-1200°C.

![Fig.3. Dynamic toughness values KC in dependence on sintering temperature.](image)

The values in Figs.1 and 2 are compared to parameters given in the Höganäs data collection for the ASC 100.29 + 0.8% graphite system sintered for 30 min at 1120°C in endogas. From comparison between our and the catalogue data follows that the attained values for tensile strength are practically the same, but in our experiments the values for yield strength are higher and for elongation lower. The analysis of results will be described below as the description of microstructure changes and characteristic fracture micromechanisms.

**DEVELOPMENT OF MICROSTRUCTURE AND FRACTURE MICROMECHANISMS AS A FUNCTION OF SINTERING TEMPERATURE**

**Density Development**

The porosity is an important microstructure parameter for sintered metallic systems. It is classified usually as total, open, and closed porosity. Also so-called interconnected porosity and planar porosity are used [2]. The results of the density measurements are given in Fig.4. The density decreasing after the heating up to 700°C is equivalent to the loss of mass by dewaxing. An increase of the density between 700-900°C is connected with the starting stage of nonisothermal sintering in the Fe$_\alpha$ area. The identified decrease of density between 900 and 1000°C is connected with the effect of the phase transformation Fe$_\alpha$→Fe$_\gamma$. Above 1000°C up to 1200°C the processes of particle contacts growth occurred. Details of these processes for sintered iron compacts were characterised in [5]. The knowledge described there has however to be modified in this...
work in consideration of 0.8% natural graphite addition and neutral nitrogen sintering atmosphere. The basic reflections will be described in chapter on page 207.

![Fig.4. Dependence of the density values on sintering temperature.](image)

**Microstructural Changes**

From the large scope of metallographic investigations, only those photos necessary for presentation of the analysed relationships have been selected. In Fig.5 a detail of microstructure after sintering at 600°C is shown. The boundaries among individual particles of Fe powder are visible. The different size of particles confirms the above mentioned particle size distribution for ASC100.29. In the particle interior there are slightly etched boundaries of Fe\(\alpha\) grains. It means that the Fe\(\alpha\) powder particles after sintering at 600°C are polycrystalline aggregates.

The presence of graphite is hardly discernible. In Fig.6 the microstructure after sintering at 800°C is shown in detail. Boundary lines among the Fe powder particles and pores are again visible. What is very important is the fact that a small fraction of pearlite grains is present in the microstructure, indicating the start of the carburisation process. We remark that at this sintering temperature the first austenite grains able to dissolve carbon and during cooling able to transform into lamellar pearlite, will be present, although according to the Fe-C phase diagram at 800°C and 0.8%C all the material should consist of austenite, and all the carbon should be dissolved, which shows the fairly slow dissolution of graphite [4, 6]. Figure 7 depicts the microstructure at the fracture profile for a specimen sintered at 950°C. This microstructure character is once more amazing since despite the rules of the phase diagram according to which after sintering at 950°C during 60 min there should only exist austenite containing 0.8% C. Therefore, the microstructure should consist only of lamellar pearlite at room temperature. Here, however, the fraction of pearlite was only 20% at sintering temperature of 950°C in our investigated specimens, i.e. even at this relatively high temperature 60 min were insufficient to dissolve all of the graphite.

The microstructure formed by sintering at 1000°C is given in Fig.8. Predominantly cross-sections through pores are visible, which currently define the size of powder particles in this investigated area. From the point of phase composition the microstructure is created by approx. 80% of lamellar pearlite. This confirms a progress in the carburisation process. Figure 9 finally shows a characteristic detail of the microstructure after sintering at 1200°C. Microareas of lamellar pearlite form 90% of it, the rest is formed by soft polyedric grains of
proeutectoid ferrite. It means that by sintering in nitrogen atmosphere at 1200°C there was not formed 100% eutectoid microstructure of lamellar pearlite. This is due to the carbon loss during sintering caused by carbothermic reduction of surface oxides on the powders which implies that a sintered steel with nominally 0.8%C (admixed) after sintering rather contains 0.72-0.74%C [4] and thus is no more fully pearlitic unless cooled fairly fast.

Fig.5. Microstructure after sintering at 600°C.

Fig.6. Microstructure after sintering at 800°C.

Fig.7. Microstructure after sintering at 950°C.

Fig.8. Microstructure after sintering at 1000°C.

Fig.9. Microstructure after sintering at 1200°C.

Fig.10. Dependence of pearlite content in the microstructure on sintering temperature.
A summary of microstructural development in relationship to the sintering temperature during 1 hour in nitrogen atmosphere is given in Fig.10. The graph shows the growth of the area fraction of pearlite in the investigated Fe-0.8% C alloy. Especially important is an abrupt increase of the pearlite between the temperatures of 950 and 1000°C, indicating fast carbon dissolution in this narrow temperature band. These results are in good agreement with those given by Danninger and Gierl for Fe-0.8%C [4] and by Kremel et al. for Fe-0.5%C [7] who also observed fairly slow carbon dissolution up to about 900-950°C.

**Micromechanisms of Fracture**

The tensile fracture surfaces of specimens sintered at all temperatures were analysed. Here only the most substantial ones are presented. A fracture detail of the specimen sintered at 900°C is shown in Fig.11. It represents the microarea in which finer powder fractions were grouped together. The figure shows the presence of rather high porosity; its size is influenced by processes of fracture formation. On the particle surface light lines are visible which mark ridges and dimples. They are so-called fracture facets for ductile failure named also ridge and dimple facets. They confirm that after sintering at 900°C the ferrite-ferrite bridges dominate in this material. Failed particle connections created by sintering at 1100°C are depicted in Fig.12. On the particle surface the dominant fracture facets indicate micromechanisms of ductile failure of pearlite by tension. Cementite lamellae act as failure initiators, and around them the ridge facets of coexisting eutectoid ferrite occurred.

![Fig.11. Fracture facets of the specimen sintered at 900°C.](image1)

![Fig.12. Fracture facets of the specimen sintered at 1100°C.](image2)

In the upper part of photo in Fig.12, ridge facets formed by ductile failure of ferrite–ferrite contacts are seen. In the same figure is showed that after the sintering at 1100°C for 60 minutes also a larger part of contacts among the powder particles is formed by lamellar pearlite. In Fig.13 the fracture surface of a specimen sintered at 1200°C is shown. This detail is taken from a sample microarea where finer Fe powder particles are concentrated. Also this figure confirms that particle connections were saturated by carbon at this sintering temperature and during cooling austenite transformed into lamellar pearlite.
Fig. 13. Fracture facets of the specimen sintered at 1200°C.

The presented fractographs are in agreement with metallographic observations and confirm that for specimens sintered in the temperature range of 1000-1200°C a large fraction of pearlite microstructure is characteristic for particle connections and inner parts of sintered Fe-C powder compacts, too.

**EDX Point Analysis and Digital Maps**

In this paper it was noticed that the presence of graphite particles is very difficult to identify in dark pores by light microscopy. That was the reason for using EDX analyse method, in this case in digital visual area display of C Kα7, O Kα9 and Fe Kα23 signals. In Fig. 14 the results corresponding to 600°C sintering temperature are shown. On the left side, there is a detail of microstructure with local porosity. The figure in the right lower edge confirms that the displayed light grains are Fe particles. The dark areas are pores. The detail in the right upper part of the image confirms that fine graphite particles are present in specific pore areas. In their neighbourhood also the oxide inclusion particles are presented which confirms a detail in the lower left area of the figure. On the basis of metallography and these facts we suppose that graphite and oxide particles did not interact at 600°C.

Fig. 14. Digital maps – distribution of C, O, Fe after sintering at 600°C.
In Fig. 15 digital maps are shown presenting the situation after sintering at 950°C. We consider that display and documentation of signals come from the remaining graphite particles located in pores among the Fe particles as the very important fact. This fact is in agreement with metallographic observations which show that only 20% of pearlite is present in microstructure after sintering at this temperature. No pronounced oxygen signals are found which indicates that carbothermic reduction of the surface oxides has been completed, as stated e.g. in [3].

![Fig.15. Digital maps – distribution of C, O, Fe after sintering at 950°C.](image1)

In Fig. 16 the microstructure and an elemental mapping after sintering at 1200°C are shown. The figure confirms that no natural graphite particles are present in the interparticle pores at this sintering temperature and that the carbon distribution in iron matrix is homogeneous. The detail in the left upper area in Fig. 16 presents the exceptional locality with closed porosity. The marked point, No. 1, corresponds to the local point analysis of oxide inclusion. The result of the analysis is given in Fig. 17. Spectrum lines show that the rest are Fe oxides, probably of FeO type, without presence of elements with high affinity for oxygen. The presence of these oxides can be explained by the using of the neutral nitrogen atmosphere and by the fact that the transport of CO gas-constituent in the most of the closed pores is unlikely.

![Fig.16. Digital map – distribution of C, O, Fe after sintering at 1200°C.](image2)

![Fig.17. EDX spectrum of particle No.1 from the Fig.16.](image3)
ANALYSIS OF PROCESSES DURING SINTERING AND THEIR CONSEQUENCE

Density Changes in Dependence on Sintering Temperature

In the work of Schatt [1] and also in previous publications of the authors [2] the processes of particle contacts formation during sintering of iron powder compacts were analysed. The processes of nonisothermal sintering in the ferrite area can be generally characterised as follows: In agreement with the ideas of Shaler and Sauerwald we consider the creation of linear and branched particle contacts as a significant source of crystallisation forces. In the case of a lower green density, these forces result in translative and rotative movements of particles, and thus in a rapid densification of a compact. In the case of a relative density higher than 90%, the movement of particles is limited by their arrangement. This explains the minimal changes of the density of specimens sintered at the temperatures up to 1000°C.

At higher sintering temperatures, mainly in the range of 1000-1100°C, the volume growth of particle connections occurred. Ridge and net connections formed at lower temperatures are gradually filled and the volume of pores decreases. Also fine, so-called bridge pores, remain in sintered Fe systems also at 1200°C. In our case, in the temperature range of 1000-1200°C the growth of particle connections and the decrease of porosity were discernible from a density increase from 7.04 to 7.10 g cm\(^{-3}\). At high sintering temperatures the particle connections formed are massive and they are able to transfer the plastic deformation also into the powder particle volume as well as into the specimen as a unit. An increase of the tensile strength, elongation and dynamic toughness values, as is shown in Fig.1-3, is a macroscopic feature of this consolidation.

Microstructure Changes in Dependence on Sintering Temperature

In this chapter our consideration is concentrated on the effect of natural graphite as alloying addition on development of microstructural changes at different sintering temperatures. Through digital maps, Figs.14–16, it was confirmed that graphite particles identified in specimens sintered at 600°C are located mainly in pores but in particle connections, too. The distances among graphite particles are here in the order of 50 – 80 \(\mu\)m, i.e. the average powder particle diameter. The graphite distribution will act by different way during heating to the temperatures corresponding to austenite formation. In this connection it should be remembered that the carbon solubility in Fe\(_{\alpha}\) is minimal, in austenite on temperature dependence can reach up 2%.

Our considerations about carburising and pearlite formation at increasing sintering temperature are based on experimental results described in [4, 6, 8]. The mass changes during consistent heating of iron powder compacts from ASC100.29 with addition of natural graphite UF4 were identified as given in Fig.18. From the measured values of TG graph the first pronounced de-gassing maximum at about 700°C stands out clearly, which, as shown by mass spectrometry measurement [3], indicates formation of CO with some CO\(_2\), following the Boudouard equilibrium [9]. Further CO formation is observed at 900-1100°C in which range the peak is less conspicuous but the total mass loss is nevertheless larger (-0.10 mass% compared to -0.06 mass % at 700°C).

The relationship of gas constituents in the system graphite-CO-CO\(_2\) follows the Boudouard’s equation:

\[
C(s) + CO_2(g) = 2CO(g)
\]

The respective partial pressures of the gas constituents are characterised by equilibrium isobars of the Boudouard’s reaction. High equilibrium partial pressures of CO, in the order of 95% and more, need temperatures above 1000°C at a total pressure
\[ \text{p}_{\text{CO}} + \text{p}_{\text{CO}_2} = 1 \text{ atm}, \] which is however rarely the case during sintering. In most atmospheres \( \text{p}_{\text{CO}} + \text{p}_{\text{CO}_2} \) being \(< 1 \text{ bar}, \) and the equilibrium is therefore shifted in favour of CO formation.

Correspondingly to thermodynamics a thermal dissociation of FeO during the sintering is the unlikely. In accordance with [10], we suppose that thin surface oxide films on iron particles, eventually on graphite particles are activated at the temperatures of \(~700^\circ\text{C}\) by graphite. Intraparticle oxides are activated in the range of 950-1100°C. By point analysis was identified that also the inclusion particles are iron oxides, probably of the FeO type. The reduction processes of iron oxides can proceed following the equation: \( \text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2 \) depending on the relationship CO/CO₂ and temperature.

Surprisingly it was observed that after sintering at 950°C only 20% of pearlite was formed in the microstructure. After sintering at 1000°C, the microstructure shows already 80% pearlite. We suppose that explanation of this fact can be supported by isotherm curves of austenite saturation at the chemical-thermal treatment of carburizing by solid carbon. In Fig.19 the isotherms of austenite saturation curves from the Ref. [10] at different temperatures are shown as a function of CO partial pressure in a gas mixture CO+CO₂. From the diagram follows that for austenite saturation by carbon up to the values near the eutectoid composition, i.e. ca 0.8 mass % C, relatively high partial CO pressures are...
necessary, higher than 97% for a temperature of 1100°C. In the case of lower CO partial pressures, e.g. 92% at 1000°C, it is only possible to reach an austenite saturation of 0.2%. This data supply the explanation for the sudden increase of the pearlite content in microstructure between 950 and 1000°C. We suppose that the combined pressure of CO and CO₂ constituents in open pores will be sufficient to fulfil the condition for austenite saturation to 0.8 mass% C. With decrease of the CO partial pressure the efficiency of austenite saturation rapidly decreases, according to Fig. 18. This can explain why austenite saturation with C was so low at 900-950°C and 850°C, respectively. We have to remark that in specimens sintered at 1200°C during 60 min in nitrogen atmosphere the presence of free graphite was not identified by EDX analysis. This means that carbon was transformed from free graphite into bonded forms and gaseous phases, respectively.

The relationship between microstructural changes and increase of strength and plastic properties of specimens can be explained by: a) decrease of porosity and increase of number and size of particle connections and b) formation of a new microstructural constituent, i.e. lamellar pearlite, which takes up to 90% in particle connection and also in the interior of particles after sintering at 1200°C.

CONCLUSIONS

From analysis of specific features of sintering processes of the Fe-0.8%C (UF4) powder system in pure nitrogen atmosphere the following can be concluded:

1. A level of carbon dissolution corresponding to formation of 20% pearlite after cooling was attained at 950°C in the austenite region, while 80% pearlite was formed in the microstructure after sintering at 1000°C.

2. We explain the fundamentals of this feature on the basis of physico-chemical processes:
   a) surface oxide films on iron particles, eventually on graphite particles are activated at the temperatures of ~700°C; intraparticle oxides are activated in the range of 950-1100°C;
   b) temperature dependence of Boudouard’s equilibrium of gas phases CO, CO₂ and C at different temperatures;
   c) isotherms of austenite saturation by carbon in dependence on partial pressures of CO, CO₂ and on temperature. For austenite saturation to the values of 0.8% C at 1000°C a volume fraction of CO in mixture with CO₂ higher than 87% is necessary. Already a small decrease by 2-4% CO means austenite saturation of only 0.2% C at this temperature.

3. Some discontinuities of the $R_m$, $R_p0.2$ and KC plotted against the sintering temperature are identified in this work. These could be explained as:
   a) In the subcritical temperature range ($\text{Fe}_\alpha \rightarrow \text{Fe}_\gamma$) the higher diffusion coefficient results in a higher strength and size of particle connections than at the temperature about 950°C.
   b) The fraction of ferrite decreased with the sintering temperature increase. The fraction of a pearlite rises up to 90% after sintering at 1200°C for 60 min. It has a strengthening effect on individual powder particles and their connections, too.
   c) Also the number and size of particle connections increased with higher sintering temperature. These connections cause the deformation process to include larger microvolumes of the sintered compacts, which is expressed by an increase of values for elongation, tensile strength and impact energy.
REFERENCES