APPLICATION OF FRACTOGRAPHY FOR INVESTIGATION OF SURFACE OXIDE REDUCTION/TRANSFORMATION AND INTER-PARTICLE NECKS FORMATION DURING SINTERING OF PREALLOYED WITH Cr AND Mn PM STEELS

E. Hryha

Abstract
Typical purpose of microfractography is the determination of the reasons and mode of component failure with the aim to avoid similar type of failure in the future. However, in case of powder metallurgy (PM) steels micro-morphology of the fracture surface contains significant information concerning consolidation process of PM steel from the point of view of efficiency of surface oxide reduction and following inter-particle necks development, carbon dissolution, etc.
Powder surface is inevitably covered by surface oxide layer which composition and thickness are determined by powder manufacturing and alloy composition. In order to develop strong inter-particle necks, surface oxide has to be efficiently reduced during initial stages of sintering (heating stage). On the other hand, thermodynamics and kinetics of surface oxide reduction/transformation is determined by number of factors, including sintering process (sintering atmosphere composition, purity and flow, temperature profile, furnace load, etc.), alloy composition (type and content of alloying elements as well as activity of carbon source used), sintering component properties (geometry, mass, density, etc.).
Present work summarizes some of the examples of application of fractography for investigation of the surface oxide reduction/transformation and carbon dissolution and their effect on the quality of inter-particle necks developed during sintering of prealloyed with chromium and manganese PM steels. Application of modern microscopy techniques widens application of the fractography from typical use as technique for failure analysis to the efficient tool for estimation of the quality of the consolidation process and evaluation of the required processing conditions to reach optimum properties from PM alloys.
Keywords: Cr/Mn prealloyed steel powder, fractography, surface oxide, oxide reduction, inter-particle neck

INTRODUCTION

Fractography of the sintered steels attracts more and more research interest and owes its development to research teams at IMR SAS [1-5] and TU Vienna [6-9], as well as other researchers around the Europe as Moon [10] and Bergmark [11]. Even thou micro-fractography of metals, and more specifically wrought steels, constitutes the basics of the

Eduard Hryha, Department of Materials and Manufacturing Technology, Chalmers University of Technology, Rännvägen 2A, 412 96 Gothenburg, Sweden

fractography of sintered steels, presence of the some distinctive features of PM steels as e.g. pores, prior inter-particle interfaces, microstructure heterogeneities, residual oxide phases, etc., leads to increased complexity of the micro-failure mode. Mentioned above microstructure heterogeneities and defects act as stress-concentrators and hence lead to the local strain increase around them during static or dynamic load. The magnitude of the local strain is determined by the size and geometry of the defect sites (inclusions, pores, etc.) as well as distance between them (or, in the other words, their concentration, that, however, do not always explains local fluctuations in size and morphology of the defect sites that can serve as crack initiation site).

However, characteristics of the most of the mentioned above defect sites (pores, residues of the surface oxides, microstructure heterogeneities, etc.) can be influenced by alloy design, base powder properties, compaction and further sintering process. This also means that the accurate analysis of the fracture surface brings significant information concerning consolidation and further sintering process. Hence, analysis of the characteristic features on the fracture surface as pores, residues of the surface oxides, fracture mode (reflecting microstructure) can bring significant information concerning sintering process. Hence, this paper is aiming to describe the application of the fractography as a tool for the evaluation of the quality of the sintering process. The work summarizes number of fractography studies performed in the field [12-23] and is aiming to describe how fractography is used to describe possible scenarios of oxide reduction/transformation and further neck development during sintering process and how such knowledge can be used to define appropriate sintering conditions.

EXPERIMENTAL PROCEDURE

The base material used in this study were commercial water-atomized steel powder grades Astaloy CrA, prealloyed with 1.8 wt.% Cr and Astaloy CrM, prealloyed with 3 wt.% of Cr and 0.5 wt.% Mo, as well as experimental powder ***A***, prealloyed with 0.8 wt.% Cr and 0.4 wt.% Mn, all produced by Höganäs AB, Sweden. The oxygen content of the powders was about 0.15 wt.%. The powders were admixed with 0.5 wt.% of carbon source (natural graphite UF4 from Kropfműhl or synthetic graphite F10 or carbon black ENSACO250G from TIMCAL) and 0.6 wt.% of Kenolube as a lubricant. Modified Charpy impact test bars with lower thickness (5×10×55 mm^3) were uniaxially compacted at 600 MPa to a green density of ~7 g/cm^{-3}. The specimens were sintered in nitrogen/hydrogen blend (10 vol.% of H_2) or pure nitrogen in a laboratory tube furnace *Entech*. Fracture surface study was performed on the fractured (impact test) specimens sampled after just heating to different temperatures: 700, 800, 900, 1000, 1120 and 1200°C as well as after sintering for 30 min at 1120°C and 1200°C. Prior to the sintering trials, compacts were delubricated at 450°C in dry nitrogen atmosphere with the aim to fully remove all the lubricant and at the same time to preserve oxide state, characteristic for the base powder. Characteristics of the particulate oxide features and inclusions (amount, composition and distribution) were evaluated on the fresh fracture surface by means of high resolution scanning electron microscopy (HR SEM) utilizing *LEO Gemini 1550* equipped with an energy dispersive X-ray spectrometer (EDX) *INCA X-sight*.

RESULTS AND DISCUSSION

The most typical case of fractography application is the analysis of the component after failure or, in more rare case, fractured component after e.g. mechanical testing. Careful analysis of the characteristic features in that case – pores characteristics (that are a bit more tricky to be evaluated on the fracture surface in comparison with metallography) and residues of the surface oxides (amount, distribution, morphology, chemistry, etc.) – are used for assessment of the quality of the sintering process, see Fig. 1. In such a case, analysis of the inter-particle necks clearly indicates difference in the amount, size and morphology of the oxide inclusions inside inter-particle necks [12, 13]. Processed in nitrogen atmosphere components indicate presence of larger amount of coarse inclusions inside the inter-particle necks, that is reflected in higher oxygen content and lower mechanical properties when sintered at such relatively low temperature for this alloy system [12-16]. Hence, only general conclusions concerning applicability of applied sintering temperature/time and processing atmosphere can be made.

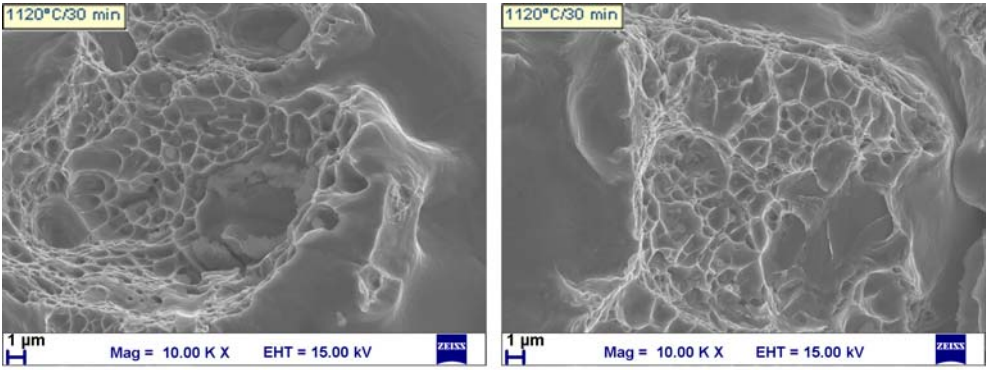

Fig.1. Fracture surface of AstCr*A+0.5%C* compacts sintered at to 1120°C for 30 min in nitrogen (left) and nitrogen/hydrogen (right) atmospheres.

However, it is difficult to make any clear conclusions which of the sintering steps exactly has highest influence on the final oxide inclusions characteristics and so quality of developed inter-particle necks. In this case it is important to be able to identify *local* processes of oxide reduction/transformation inside the inter-particle contacts and close proximity to them and their interaction with local microclimate inside surrounding pores [12-14, 23]. And here fractography can be utilized as the simplest, most effective and informative tool when combined with the interrupted sintering trials, as was first applied by Dudrova et al. for the case of admixed with Mn sintered steels [24] and further developed in our later works [12-22].

To get better understanding of the process of the inter-particle necks formation and preceding surface oxide removal, it is important to know the initial stage of the surface oxide. In case of the water-atomized steel powder low-alloyed with oxygen-sensitive elements as Cr and Mn, surface oxide is formed by thin layer of iron oxide (Fe_2O_3) with the thickness of around 6 to 7 nm and spherical particulates with the average size of around 200 nm, formed by complex Fe-Cr-Mn-Si- oxides [25-27], see Fig.2.

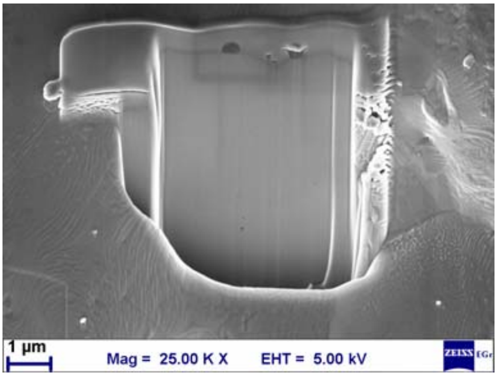

Fig.2. Surface oxide on water-atomized low alloy steel powder (Fe-3Cr-0.5Mo) revealed by means of FIB-SEM [27].

As the most of the powder surface is covered by easily reducible iron oxide (about 95% of the area), sintering of such a powder has to be not so different from plain iron powder. However, high surface activity of the powder and accelerated mass-transfer of alloying elements at elevated temperatures makes such a powder much more sensitive to sintering atmosphere quality from the oxygen potential point of view. This can lead to extensive oxide transformation from the iron- and iron-based surface oxide into more thermodynamically stable oxides that can be later seen as inclusions inside the inter-particle necks, see Fig.1. In order to be able to adjust sintering parameters for avoiding formation of coarse oxide inclusions and hence robust sintering of such low alloyed sintered steels, knowledge of thermodynamics and kinetics of oxide reduction/transformation during whole sintering stage are of vital importance. This can be done by fractography study of interrupted sintered specimens in combination with advanced microscopy and spectroscopy techniques [12, 13, 15,16, 18-22]. The most critical phase during sintering from the oxide reduction/transformation point of view identified is the heating stage between 800 and 1000°C [12,13,15,16,18,19], when there is a significant risk of oxide enclosure inside the growing inter-particle neck, see Fig.3. At this temperature range temperature activation is high enough for effective mass-transfer and two processes are taking place almost in parallel – growth of the inter-particle necks and reduction/transformation of the residuals of surface oxides. Hence, final quality of the inter-particle neck is determined by the difference in kinetics between these two processes.

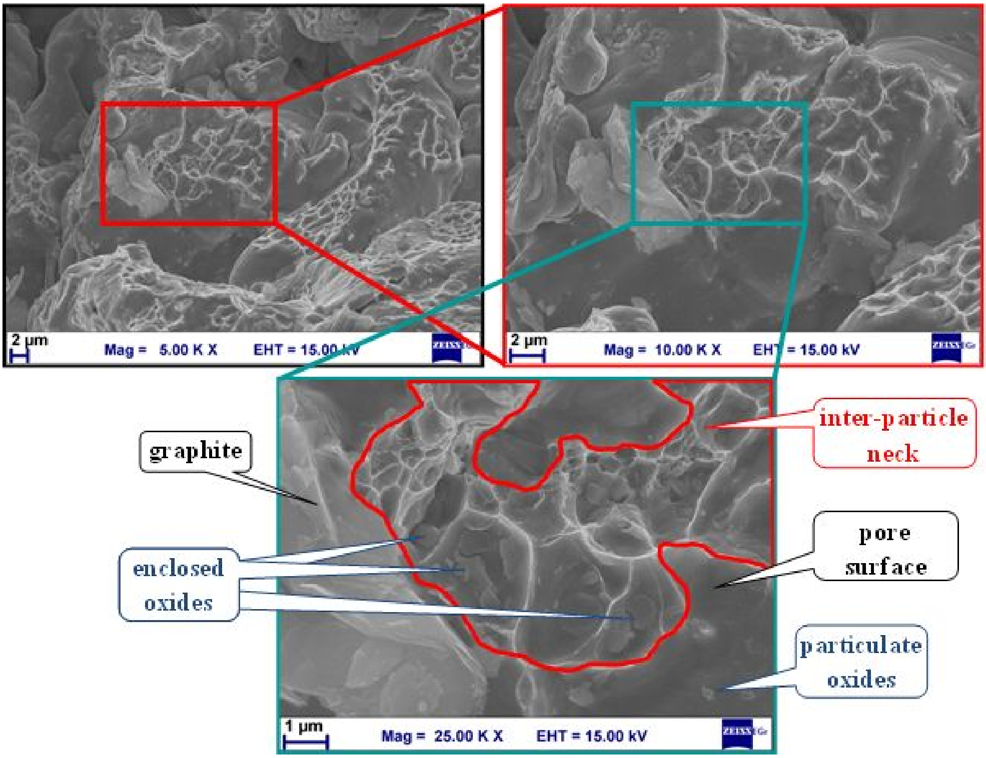

Fig.3. Inter-particle neck region, *AstCrM+0.4%C* compact heated in N_2/10%H_2 to 900°C, showing enclosure of surface oxide residue inside growing inter-particle neck.

In case of inter-particle necks growth, its kinetics is determined by the surface energy, presence and area of oxide-free metal-metal contact and temperature, etc. Kinetics of the oxide reduction or transformation, on the other hand, is determined by the oxygen potential of the local microclimate, temperature range (structure of the base powder matrix – ferrite or austenite) and alloying element (its oxygen affinity). It is important to understand that the quality of the local microclimate depends not only on sintering atmosphere composition/purity, but is strongly determined by the speed of atmosphere replenishment on the oxide/atmosphere interface, that is strongly deteriorated in the centre of the massive compacts, components of the high density, semi-closed volumes in the particle-particle contacts created during compaction (bridge porosity), etc. In the ideal case, sintering process has to be adjusted in a way to provide full reduction of iron oxide at lower temperatures, before intensive inter-particle neck growth starts, in order to provide oxide-free inter-particle necks. Partial reduction of iron oxide layer on the open (pore) surface will result in creation of the clean metal surface close to the inter-particle contact area whereas surface of the powder in the inter-particle contact area will be covered by surface oxide due to the poor conditions inside the inter-particle contact volume. This will result in creation of metallic bonding between two particles surrounding closed area of inter-particle contact, see Fig.3. Presence of oxide does not allow development of the metal-metal contact in such inter-particle contact areas. However, enhanced diffusion of the alloying elements with increasing temperatures and presence of oxygen source (in the form of iron-based oxide) inside the growing inter-particle neck results in transformation of iron oxide layer into particulate oxide with higher thermodynamical stability, see Fig.3, that will be seen after sintering as inclusions inside the inter-particle necks, see Fig.1. Hence, accurate fractographic analysis of the components during heating stage allows us to conclude that the heating stage between 800 and 1000°C is the most critical stage during sintering of steel powder, prealloyed with oxygen-sensitive elements as Cr and Mn, due to the high risk of the formation of thermodynamically-stable (Cr-Mn-Si-based oxides) inclusions inside the inter-particle necks. Problem of oxide transformation and enclosure inside the forming inter-particle necks can be significantly minimized/avoided by proper adjustment of the sintering process in terms of the sintering atmosphere composition/purity and flow, proper delubrication and appropriate heating rate. More details concerning inter-particle necks formation and oxide transformation mechanisms and its thermodynamics can be found elsewhere [12,13,15,16,18,19].

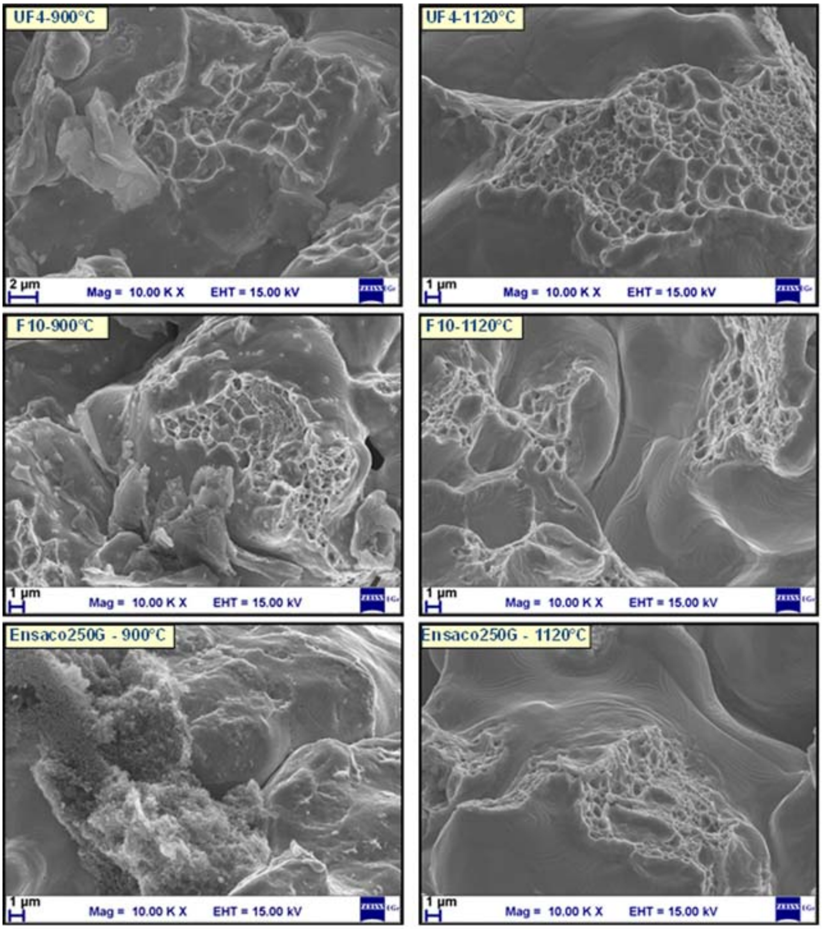

Fig.4. Fracture surface of *AstCrM+0.5%C* compacts utilizing different carbon sources, heated in Ar/10%H_2 to 900 (left) and 1120°C (right), showing development of inter-particle necks.

Fractography is also effective tool for the analysis of the effect of the carbon activity in dependence on carbon source utilized [28-30]. In this case carbon activity can be qualitatively judged based on the development of inter-particle necks during heating stage and presence of the admixed carbon source, see Fig.4. Hence, development of inter-particle necks can start only after iron oxide is reduced where carbothermal reduction plays important role above Boudouard equilibrium. Starting of intensive inter-particle neck formation already at 900°C can be seen in case of fine natural (UF4) and synthetic (F10) graphite grades, see Fig.4. In case of carbon black only occasionally some point and line connections can be found, indicating full inertness of this carbon source at this temperature, see Fig.4. Detailed analysis of the fracture surface of the specimens heated to 1120°C, se Fig.4 (right column) reveals full reduction of surface oxides, better quality of inter-particle necks and full carbon dissolution in case of all graphite grades. Results also indicate the highest thermal enforcement of the carbon activity in the case of carbon black between 900 and 1120°C. Such boost in activity of the carbon black can be described based on its complex amorphous and nano-crystalline structure and its nano-metric size. More details concerning fractography of the sintered steels admixed with different carbon grades can be found elsewhere [28-30].

CONCLUSIONS

Fractography is shown to be rather simple and at the same time very effective tool for the analysis of the effect of base material properties (powder type, carbon source characteristics, additives, lubricants, etc.) and processing conditions on the inter-particle neck development, their final quality and strength. Micro-morphology of the fracture surface contains significant information concerning consolidation process of PM steel from the point of view of efficiency of surface oxide reduction and following inter-particle necks development, carbon dissolution, etc. Combination of the fractography with chemical spectroscopy techniques such as EDX, XPS, AES, etc., brings important information concerning surface species, present on the initial powder surface, and their development/transformation during sintering process. Depending on phases of interest, their amount, chemistry and distribution, combination of fractography and micro-analysis techniques gives important quantitative/semi-quantitative input for the thermodynamic and kinetic simulation of the reduction/oxidation/transformation processes taking place during sintering process. Hence, application of modern microscopy techniques widens application of the fractography from typical use as technique for failure analysis to the efficient tool for estimation of the quality of the consolidation process and evaluation of the required processing conditions to reach optimum properties from PM alloys.

REFERENCES

[1] Dudrová, E., Kabatova, M.: Powder Metallurgy Progress, vol. 8, 2008, no. 2, p. 59
[2] Kabátová, M., Dudrová, E., Wronski, AS.: Powder Metallurgy, vol. 49, 2006, no. 4, p. 363
[3] Dudrová, E., Parilák, Ľ., Rudnayová, E., Pelikán, K.: Powder Metallurgy International, vol. 19, 1987, no. 3, p. 23
[4] Šlesár, M., Dudrová, E., Rudnayová, E.: Powder Metallurgy International, vol. 24, 1992, no. 4, p. 232
[5] Pelikán, K.: PhD Thesis. Košice : ÚMV SAV, 1986
[6] Danninger, H., Avakemian, A., Gierl, C.: Powder Metallurgy Progress, vol. 11, 2011, no. 1-2, p. 3
[7] Weiss, B., Danninger, H., Stickler, R. In: Proc. World PM1992, p. 171

[8] Danninger, H., Jangg, G., Weiss, B., Stickler, R.: Powder Metallurgy International, vol. 25, 1993, no. 3, p. 111
[9] Danninger, H., Weiss, B.: Journal of Materials Processing Technology, vol. 143-144, 2003, p. 179
[10] Moon, JR. In: Proc. DFPM 2002. Vol. 1, p. 13
[11] Bergmark, A., Alzati, L., Persson, U. In: Proc. 2002 PM. Vol. 5, p. 5/95
[12] Hryha, E., Nyborg, L. In: Proc. Word PM2014, Orlando.
[13] Hryha, E., Nyborg, L.: Metall. Mater. Trans. A, vol. 45, 2014, no. 4, p. 1736
[14] Hryha, E., Nyborg, L. In: Proc. EURO PM2013. Vol. 2, p. 333
[15] Hryha, E., Nyborg, L. In: Proc. World PM 2012, 16A-T9-12 (CD-ROM)
[16] Chasoglou, D., Hryha, E., Nyborg, L.: Mater. Chem. Phys., vol. 138, 2013, p. 405
[17] Zumsande, K. et al.: Mater. Char., vol. 71, 2012, p. 66
[18] Chasoglou, D., Hryha, E., Nyborg, L.: Powder Metall. Progress, vol. 11, 2011, p. 32
[19] Hryha, E., Nyborg, L.: Powder Metall. Progress, vol. 11, 2011, no. 1-2, p. 42
[20] Hryha, E., Dudrová, E., Nyborg, L.: Metall. Mater. Trans. A, vol. 41, 2010, no. 11, p. 2880
[21] Hryha, E., Dudrová, E. In: Application of Thermodynamics to Biological and Materials Science. Chapter 22. Ed. M. Tadashi, p. 573
[22] Hryha, E., Nyborg, L., Dudrová, E., Bengtsson, S.: Powder Metall. Progress, vol. 8, 2008, p. 109
[23] Hryha, E., Dudrová, E., Nyborg, L.: J. Mater. Proc. Tech., vol. 212, 2012, no.4, p. 977
[24] Dudrová, E., Kabátová, M., Bidulský, R., Wronski, AS.: Powder Metall., vol. 47, 2004, p. 181
[25] Chasoglou, D., Hryha, E., Norell, M., Nyborg, L.: Appl. Surf. Sci., vol. 268, 2013, p. 496
[26] Hryha, E., Gierl, C., Nyborg, L., Danninger, H., Dudrová, E.: Appl. Surf. Sci., vol. 256, 2010, p. 3946
[27] Nyborg, L., Hryha, E. In: Proc. Word PM2014, Orlando
[28] Hryha, E., Nyborg, L., Alzati, L. In: Proc. World PM 2012, 16A-T9-11 (CD-ROM)
[29] Hryha, E., Nyborg, L., Alzati, L. In: Proc. EURO PM2013. Vol. 2, p. 303
[30] Nyborg, L., Hryha, E. In: Proc. Word PM2014, Orlando