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New Processing Route for Production of Fine Spherical Iron Powder

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Abstract
Today fine spherical iron powders are produced dominantly by the carbonyl process. It is used for innovative solutions for a wide spectrum of different applications like diamond tools, magnetorheological fluids, materials absorbing microwaves but mostly for metal injection molding (MIM). Herewith the high powder price has a considerable share on the product costs and is therefore a limiting fact.
In this paper the powder properties and sintering results of a fine spherical iron powder which is produced by using iron oxide as a by-product of steelmakers and a patented hydrogen reduction processes will be discussed. Further powder processing steps were identified to separate the sinter cake and adjust the powder properties. Milling technologies and parameters were evaluated which support the particle shearing and spheroidization. The characterized sintered parts demonstrate the high potential of the cost-efficient powder with comparable properties to that of the carbonyl iron powder.

Keywords: spherical iron powder, metal injection moulding, hydrogen reduction, iron oxide, metal powder production, powder processing, iron oxide

1. Introduction

In recent years, major efforts have been undertaken to optimize the production of fine metal powders. However the manufacturing costs are still on a high level. The manufacturing of fine spherical iron powders today is mainly based on two processing routes. For gas atomization a fine average particle size can be achieved using high gas velocities. Under argon metal powder with an average particle diameter d_{50} between 10 and 80 µm can be manufactured [1, 2, 3]. Usual fine particle fraction will be sieved. The manufacturing of iron powders < 10 µm is based on the iron carbonyl process [4]. Both technologies are expensive processes and the powder cost are in the range of 7-10 €/kg, This powders are used as binder matrix in diamond tools, for magnetorheological fluids, materials absorbing miocrowaves but mainly for metal injection molding (MIM). Also for special slurry based processing routes like for manufacturing of parts by direct typing or hollow spheres the powder price is a limiting factor especially with growing part dimension. Therefore the development of a new low cost powder processing route would give a growing market for the above mentioned products and applications.
Generally following powder properties are required for MIM:

- Low particle size (< 20 µm) to ensure low surface roughness and high part precision,
- High sinter activity to obtain sinter densities > 95%,
- Spherical particle size to get an injectable feedstock with high powder loading and low tool wear [5, 6].

In the following a new method for producing fine iron powders from iron oxide as byproduct of refined pickling slurries from steel makers as well as the relationship between the modification of powder morphology by powder processing and sintering properties will be will introduced.

2. Experimental procedure

2.1 Innovative hydrogen reduction process

As raw material a cost efficient hematite powder from byproduct of steel makers with a primary average particle size of 1 µm is used. The reduction to iron is generally possible under CO or H_2 atmosphere. While a fully reduction under CO is only completed at 1000°C, which would result in a strong sintercake, the reduction by means of hydrogen leads to iron powder with low oxygen content in

the range of 500–600 °C [7]. In addition, a water vapor/hydrogen partial pressure < 0,1 must be ensured [8].
However, the resulting powder has a very large specific surface area (>> 1m²/g) which causes an immediate re-oxidation. That`s why the powder is classified as pyrophoric and can practically not be used [9]. Higher reduction temperatures lead to higher oxygen contents. Only an increase to very high temperatures (> 1000 °C) can reduce the oxygen content to acceptable values [10]. At these high temperatures mostly the fine powder particles are sintering to a strong not breakable cake. Especially the production of fine powders by reduction under H_2 atmosphere is not possible after the state of the art. To solve the problems the granulation of the oxide powder and a two-step heat treatment process was developed [10]. A closer description of the technology was published in a previous paper [12].

In the first step the iron oxide powder was milled in a binder slurry for spray granulation. After the granulation the granules sieved to a fraction < 32 µm. Because of the volume loss and densification of the porous granules during the hydrogen reduction the iron powder particle size will result in the range of < 20 µm. The granulated oxide powder was placed as a powder bed of 20 mm thickness into a ceramic crucible.

The reduction experiments were carried out in a ceramic tube furnace under pure hydrogen. The powder was reduced in the first step at 500 °C for 1 h under hydrogen. The heating rate was 5 K/min. In this stage the powder is pyrophoric because of its high specific surface. Therefore the temperature was increased to the second temperature, which was varied in the range between 700 °C and 850 °C up to 24 h. At this temperature (optimum at 850°C) the primary particles in the reduced granules are sintering to a dense spherical particle while the reduced granules are not sintering each other (or only slightly). The reason for this phenomena is the dependence of the sintering activity on the surface energy which increases with smaller particle diameter. After the reduction the iron sinter cake was milled and sieved to a powder fraction < 32 µm to remove agglomerates.

2.2 Powder processing

For this purpose three different milling units were evaluated: a mortar grinder (GM), a planetary ball mill (PBM) and a Nara Hybridizer (NH). The aim was to separate the agglomerates of the sinter cake to a smallest possible particle size by the impact of high shear stresses. The milling conditions were adjusted in terms of preventing plastic deformation to keep the spherical shape of the powder particles. The particle size distribution was measured by laser diffraction using a Horiba LA 950 (Standard ISO 13320). For this purpose the iron powder was dispersed in a liquid suspension.

Mortar grinder

The principle of the mortar grinder ensures high shear stresses. A pestle with its large grinding surface grinds the powder against the wall and bottom of the mortar bowl. The mortar bowl is turned by a gear motor and drives the pestle with its freely rotating bearing through friction. The rotation speed was 75 rpm with a milling time of 5 to 20 minutes.

Planetary ball mill

Usually ball mills are used for powder processing. Especially planetary ball mills have high shear forces and simultaneously very low impact forces by low rotation speed. To prevent a deformations of the particles, at the beginning a moderate rotational speed of 100 rpm was used. All powders were dry grinded in steel jars with steel balls with a diameter of ten millimeters under an argon atmosphere.
First, the results of 10, 60 and 120 minutes were studied, which shows that 120 minutes were the best result. To characterize the effect of the rotation speed and time, then the time was doubled to 240 minutes, and the speed was increased up to 150 rpm.

Nara Hybridizer

An innovative grinding system is the Nara Hybridizer. This technology is predestinated for surface modification especially for rounding of the powder particles. The raw material is dispersed in a high speed gas flow and processed by a high speed rotor. Thereby the rotor blades perform mechanical impact forces.
For the experiments a rotation speed of up to 16000 rpm and a milling time of 4 minutes under argon was used which resulted in a spherical powder with a small and tight particle size distribution. This short, but intensive process designates the hybridizer technology as an efficient powder processing technology.

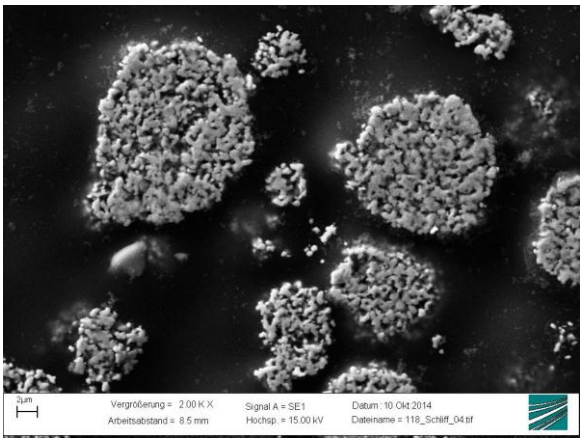
2.3 Sintering

For comparison of the sintering behavior of the different iron powder qualities cylindrical samples were prepared based on reduced powders as well as on atomized spherical iron powder and iron carbonyl powder. The powders were compacted with a mixture of 0.5 wt% binder (PVP) in a press under a slight pressure of 100 MPa which is correlating with the injection pressure for a MIM process. The samples were sintered at 1320 °C for 3 hours under hydrogen in a tube furnace (TF). Afterward the sample density, the porosity by metallographical preparation and image analyses as well as the shrinkage during the sintering process by measurement of the geometrical dimensions before and after the sintering were determined.

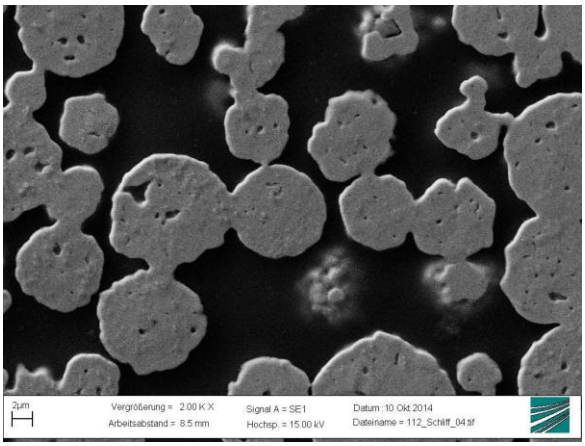
3. Results and discussion

3.1 Hydrogen reduction

The first temperature of the two-step reduction, which is necessary to remove the oxygen, was kept constant at 500 °C for 1h under hydrogen, because there was no significant influence to the reduction result in the temperature range between 400 and 600°C. The second temperature has a significant impact especially with respect to the powder morphology. In the result of the variation in the range of 700 °C to 900 °C two main different powder qualities were evaluated. Below 700 °C the specific surface amounts > 3 m²/g, which results in a pyrophoric powder. With increasing the temperature the inner porosity caused by the granulation of the fine primary iron oxide particles and by the oxide reduction in the first temperature step will be reduced by sintering. At temperatures over 850 °C the sintering process also between the reduced granules is enforced in such kind, that the sinter cake can be not processed to a fine powder. Finally for the lowest second temperature 700 °C and for the highest 850 °C was indicated to produce fine iron powder in the two step hydrogen reduction process. Figure 1a) shows the spherical powder after reduction at 500 °C, 1 h (1st temperature step) and 700 °C, 24 h (2nd temperature step). The reduced granules indicate a high amount of pores as well as a very high roughness which originate from the primary oxide particles. This morphology correlates to the measured high specific surface and low apparent density in comparison to state of the art carbonyl and atomized iron powders (Table 1). The second powder quality reduced at 500 °C, 1 h (1st temperature step) and 850 °C, 1 h (2nd temperature step) is characterized by nearly no left inner porosity and a smooth surface (Figure 1b). Therefore the apparent density is higher and the BET value lower than that of the powder reduced at 700 °C (Table 1). The oxygen and carbon content is for both reduced powders in the range of the state of the art, but the particle size distribution is higher. It is obvious, that the formed sinter necks between the particles are forming agglomerates, which have to be shredded by an enclosed milling process. Considering that after a milling and sieving process the agglomerates could be removed, a comparable particle size to that of the atomized iron powder could be achieved.



a)



b)

Figure 1: SEM image of the cross section sinter of the sinter cake after
a) reduction at 500 °C, 1 h + 700 °C, 24 h under hydrogen
b) reduction at 500 °C, 1 h + 850 °C, 1 h under hydrogen

Table 1: Properties of the main different reduced powders in comparison to state of the art carbonyl and atomized iron powders

powder qualities	oxygen [%]	carbon [%]	particle size [µm]			apparent density [g/cm³]	Spec. surface (BET) [m²/g]
			d_{10}	d_{50}	d_{90}		
carbonyl-Fe	0,240	0,760	2,1	4,5	8,6	4,20	0,37
atomized Fe	0,615	0,001	6,0	13,7	22,0	3,71	0,10
reduced 500°C,1h + 700°C, 24h	0,741	0,132	11,6	18,6	29,4	2,20	1,62
reduced 500°C,1h + 850°C, 1h	0,368	0,042	13,2	22,1	35,6	2,74	0,16

3.2 Powder milling

After the reduction process milling experiments were carried out, which focused on the separation of agglomerates, reducing the particle size by keeping the spherical particle shape. This requires milling units with high shear forces and low deformation impact. This challenge is all the greater considering the high ductility of iron powder. For the further experiments, the powder quality which was reduced at 850 °C in the 2nd temperature step was used, because at lower temperature a high inner porosity was indicated (see chapter 3.1). This porosity would cause a high shrinkage of MIM parts and problems of a residue free debindering of MIM parts.
Three different milling units were evaluated as mentioned in chapter 2.2. In Figure 2 the particle sizes of fine spherical state of the art powders (carbonyl iron, atomized iron) and that of the reduced powder (2nd temperature step 850°C) milled by different milling units are given. The powder after the reduction process indicates agglomerates and an average particle size of 22.1 µm, which could be decreased after milling for 20 min (optimum) in the mortar grinder to 13.8 µm, which is close to the atomized powder. The particle size is near spherical. Further experiments were carried out in the planetary ball mill. Generally the particle size could be decreased with increasing rotation speed as well as milling time. With increased energy morphology tends more and more to switch from the spherical to plastic deformed and partly flaky shaped particles. The optimum between morphology and particle size was obtained by milling 120 min and 100 rpm which resulted in average particle size of 12.3 µm.

The best results were obtained by the Nara Hybridizer. The rounding effect of this technology leads to a very spherical shaped particles with no deformation (Figure 3). The optimum parameters were evaluated at 16000 rpm for 4 min which resulted in a d_{50} particle size of 11.4 µm.

Considering the powder morphology and particle size as well as short processing time the Nara Hybridizer has the highest potential for the required powder processing.
In the following chapter the sintering behavior of the different processed powders will be evaluated.

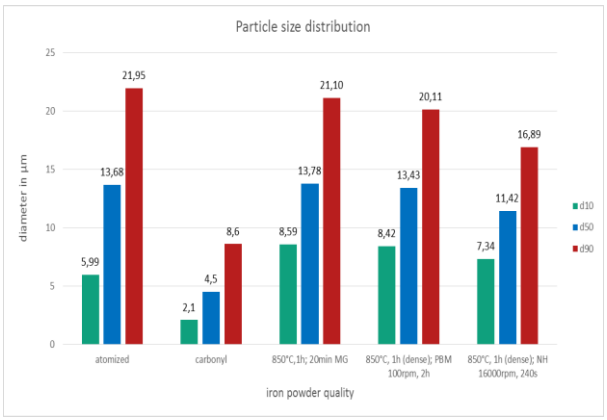


Figure 2. Particle size of the reduced and milled powders compared to commercial carbonyl and atomized spherical iron powders

Figure 3. SEM image of the powder reduced at 500 °C, 1 h + 850 °C, 1 h H_2, milled 4 min, 16000 rpm in a Nara Hybridizer (NH),

3.3 Sintering properties

Cylindrical samples were manufactured (see chapter 2.3) to compare the sintering behavior of the reduced and milled powder qualities to that of the state of the art. The density after sintering (Figure 4) indicate, that all reduced and milled powder qualities exceed the properties of the atomized one which achieved a density of only 80.4%. This is confirmed by the cross-sections in Figure 6a) which demonstrates the highest porosity compared to the other samples (Figure 6 b-e). The sinter density of the mortar grinder (MG) and hybridizer (NH) milled powder is comparable to that of the carbonyl iron, while the sintered ball milled powder compact has a slightly lower density (Figure 4). The shrinkage during sintering is shown in Figure 5. A generally aim for MIM parts is a low shrinkage and high density. The atomized powder has the lowest shrinkage with a value of 7.3 %, but too much porosity remained. For the other powder qualities which ensure also a higher sinter density the lowest shrinkage is indicated for the hybridizer (NH) milled powder (14.2 %), the highest for the ball milled (16,4 %). Carbonyl iron and the mortar grinder milled one are in the same range with values of 15.8 and 15.3 %.

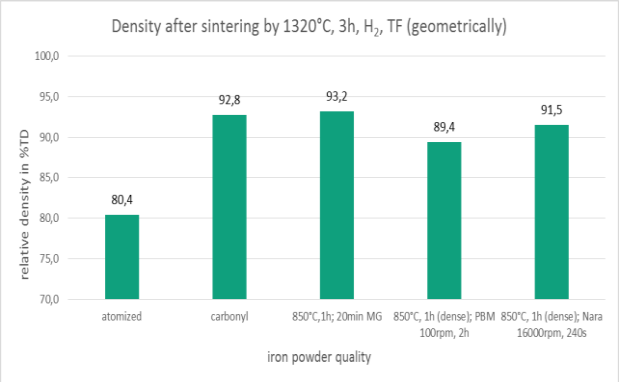


Figure 4. Density of sintered powder compacts

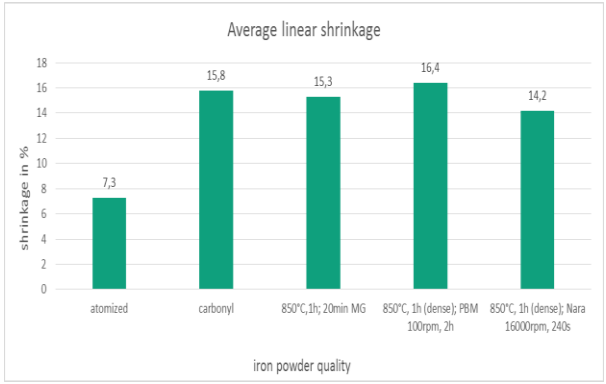
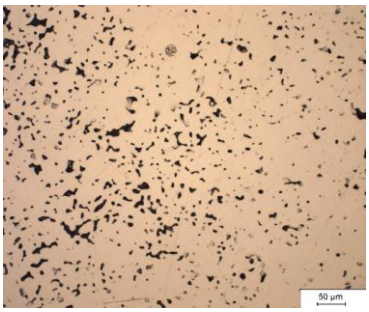
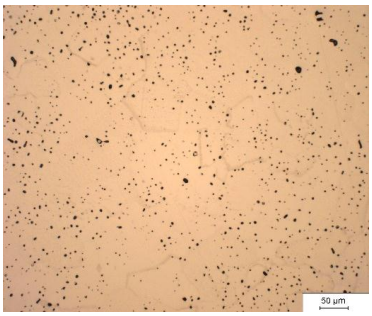


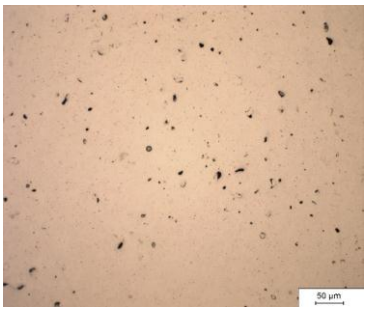
Figure 5. Shrinkage of powder compacts during sintering



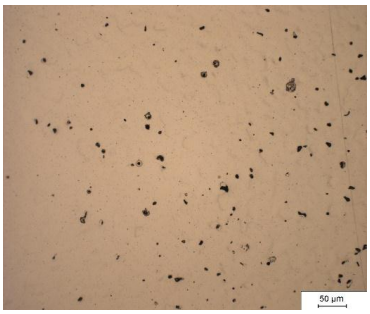
a) atomized Fe



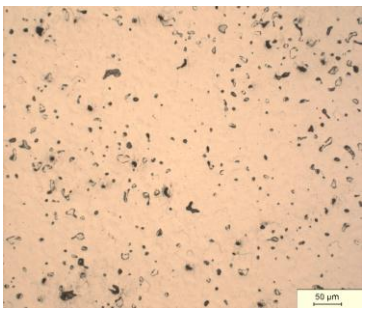
b) carbonyl-Fe



c) reduced and mortar grinder milled 20 min, 75 rpm,



d) reduced and ball milled for 120 min, 100 rpm



e) reduced and Hybridizer milled for 240s, 16000 rpm

Figure 6. Cross section of sintered cylinders based on commercial powders a), b) for comparison with the reduced (reduced 500 °C, 1h + 850 °C, 1h) and milled powder qualities c) – e)

4. Conclusions

Considering all requirements on MIM powders mentioned in chapter 1 the preferred processing route for the reduced powder is the milling with the hybridizer technology. The particle shape is very spherical, the particle size and shrinkage during sintering is the lowest combined with a high sinter density, which is comparable to the carbonyl iron powder.

The investigated production route for production of fine spherical iron powder is a promising alternative to the iron carbonyl process. The new process is based on a low-cost raw material, environmentally friendly process chain and offers a high potential for the production of a cost efficient powder. This is of high importance for enlarging the MIM market considering the high share of the powder costs on MIM parts especially with increasing dimensions. Further development work will focus on process optimization and up-scaling.

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References

[1] S. Okamoto, T. Sawayama, Y. Seki; „Kobe Steel advances water atomized powders“; Metal Powder Report, vol. 51 (1996), no. 3, 28-33

[2] Gesell Hartmut; „Verfahren und Vorrichtung zum Herstellen von Eisenpulver“; German patent DE 272 5278, 03.08.1978

[3] C. Tornberg; „Verfahren zur Herstellung von Metallpulver“; AT-Patent 412 328 B, 03. 04. 2002

[4] W. Schatt, K.-P. Wieters, B. Kieback (Hrsg.); „Pulvermetallurgie. Technologien und Werkstoffe“; 2. Auflage ;Springer-Verlag Berlin Heidelberg, (2007), 41

[5] K. Murray, M. Kearns; „Review of Developments in Gas Atomised Alloy Metal Powders for MIM Applications”; Euro PM 2009, Cobenhagen 2009, Proceedings Vol. 2, 73-80

[6] G. Dowson, D. Whittaker; „Powder Metallurgy – The Process and Its Products”; EPMA 2008

[7] V. I. Zenkov; V. V. Pasichnyi; "Reduction Kinetics of Iron Oxides used for Hydrogen Production in various Gas Media”; Powder Metallurgy and Metal Ceramics, Vol. 49, Nos. 3-4, 2010

[8] Möbius, H.E., F.Krull: Metall 23 (1969), 314

[9] W. Feitknecht, A. Durschi; „Über pyrophores Eisen“; Helvetica Chimica Acta, Vol. 47, No. 22 (1964), 174 - 181

[10] M. Wiberg; “some new sponge iron process”; jernkontorets ann 142 ,(1958)

[11] B. Kieback, G. Walther; „Verfahren zur Herstellung eines Metallpulvers und mit dem Verfahren hergestelltes Metallpulver“, German patent, DE 102008 009 133 B4, 12.04. 2012

[12] G. Walther, T. Büttner, B. Kieback, T. Weißgärber, M. Hoffmann, G. Bachmann; „Properties and Sintering Behaviour of Fine Spherical Iron Powders Produced by a New Hydrogen Reduction Process”, Journal of Powder Metallurgy, Vol. 57, Issue 3, 2014, 176-183