PROPERTIES AND SINTERING BEHAVIOUR OF FINE SPHERICAL IRON POWDERS PRODUCED BY A NEW HYDROGEN REDUCTION PROCESS

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ABSTRACT

For many applications like for diamond tools, magnetorheological fluids, materials absorbing microwaves but mostly for metal injection molding (MIM) fine spherical iron powders are used. The high costs of powder based on the carbonyl or atomizing production route are for many applications a limiting fact. An alternative two-step hydrogen reduction process using a granulated hematite powder, which is a recycling product from steel makers, was developed to produce spherical powder < 25 µm. The experimental results have shown that the morphology or properties of the powder respectively depend strongly on the second temperature step of the reduction process. A further important step is the enclosed powder processing by milling and sieving to remove agglomerates. In this paper the powder properties as well as the sintering behavior as a result of different heat treatment and processing parameters will be discussed.

1. INTRODUCTION

Today fine spherical iron powders are produced by the carbonyl process or atomization. For gas atomization fine grains 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 microwaves 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 the share of the powder costs increases considerably. Therefore the development of a new low cost powder processing route would give a growing market for the above mentioned products and applications. A key issue is to obtain the required powder characteristic. Especially for MIM applications a fine spherical particle shape is a prerequisite to get an injectable feedstock with high powder loading and low tool wear. The low particle size ensures additional to an over 95 % sinter density, a high part precision and low surface roughness [5, 6].
In this paper 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 discussed.

2. EXPERIMENTAL PROCEDURE

2.1 Hydrogen reduction process

Iron oxide (Fe_2O_3) can be reduced at 500-600 °C by means of hydrogen to a Fe powder with low oxygen content. However, the resulting powder has a very large specific surface area (>> 1m²/g) which causes an immediate re-oxidation. That is why the powder is classified as pyrophoric and can practically not be used [7]. 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 [8]. 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 mentioned problems the granulation of the oxide powder and a two-step heat treatment is necessary [9]. Figure 1 shows the steps of the process. It starts with the granulation of the iron oxide powder with a main particle size of < 1 µm. The powder was mixed in a ball mill with binder, plastificator and dispersant to prepare the slurry for the enclosed spray drying process. The granules were sieved to a fraction < 32 µm for the reduction process. The granulated oxide powder was placed as a powder bed of 20 mm thickness into a ceramic crucible. For the two-step heat treatment a ceramic tube furnace was used. 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 these phenomena is the dependence of the sintering activity on the surface energy which increases with smaller particle diameter. The theoretical final powder particle diameter amounts about 68% to that of the granule diameter as a result of shrinkage by the volume loss during reduction and the densification of the reduced granules by sintering of the primary particles at the second temperature step. Therefore from granules < 30 µm a powder < 20 µm can be expected.

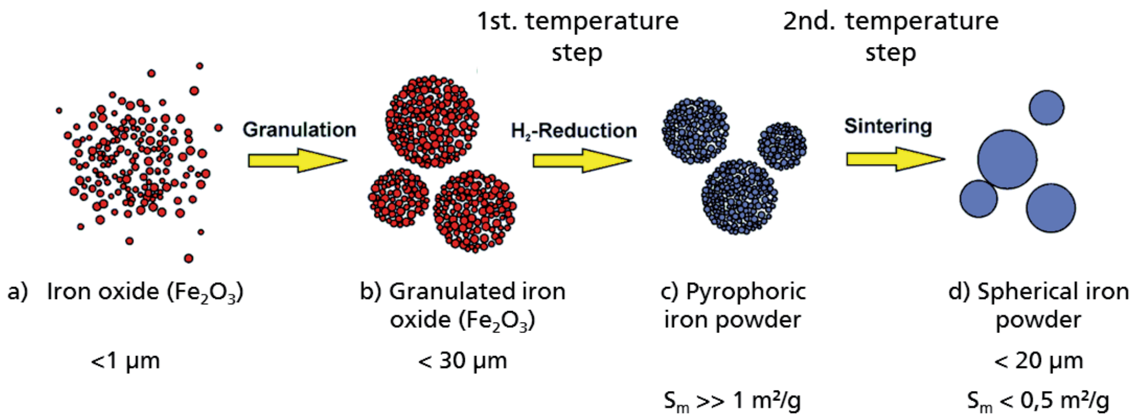


Figure 1. Process steps of the new method for manufacturing fine spherical iron powders

The reduction of hematite (Fe_2O_3) under hydrogen is a two-step reaction:

1. Hematite to magnetite: $3Fe_2O_3 + H_2 \leftrightarrow 2Fe_3O_4 + H_2O$
2. Magnetite to Iron: $Fe_3O_4 + 4H_2 \leftrightarrow 3Fe + 4H_2O$

Total reaction: $Fe_2O_3 + 3H_2 \leftrightarrow 2Fe + 3H_2O$

The kinetics of the reduction reaction at low temperatures is determined by the different speed of the two reactions [10]. It is assumed that the reaction rate of Fe_2O_3 to Fe_3O_4 is higher than that of Fe_3O_4 to Fe and thus speed determining [11]. FeO does not occur in the reduction process [12]. For the complete reduction of hematite a partial pressure ratio $p_{H2O}/p_{H2} < 0.1$ must be ensured [13, 14].

2.2 Powder processing

After the reduction the iron sinter cake was milled and sieved to a powder fraction < 32 µm to remove the remained agglomerates. 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 mechanical impact force (Figure 2).

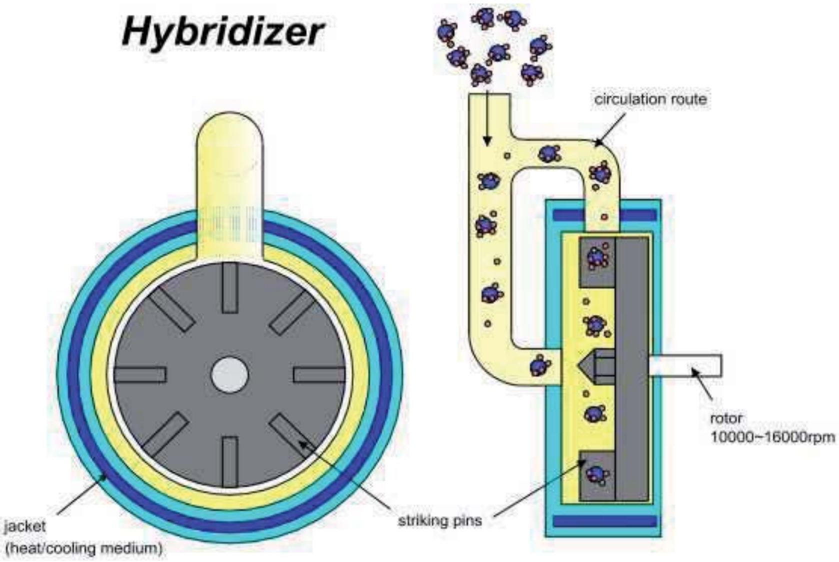


Figure 2. Scheme of the grinding prozess in the Nara Hybridizer

For the experiments a rotation speed of 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.

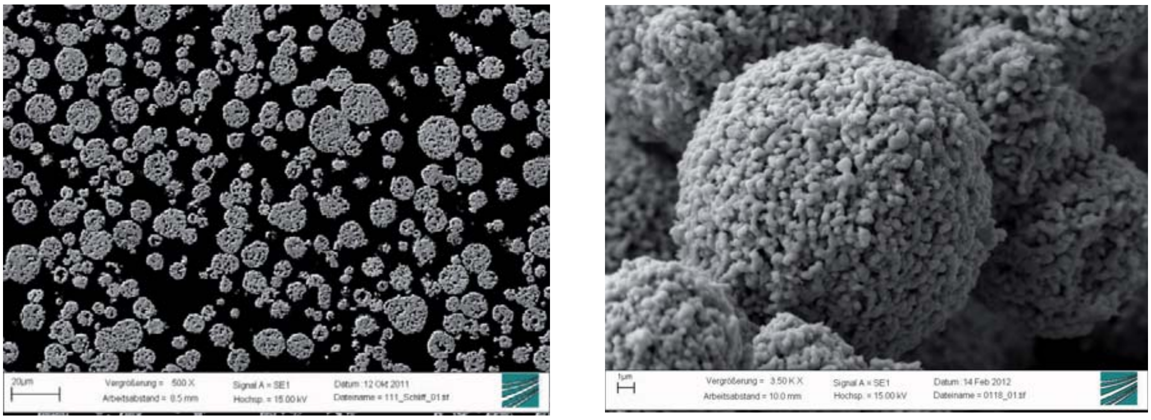
2.3 Sintering

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 (2408 °F) for 3 hours under hydrogen in a tube furnace. 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 Powdermanufacturing by reduction

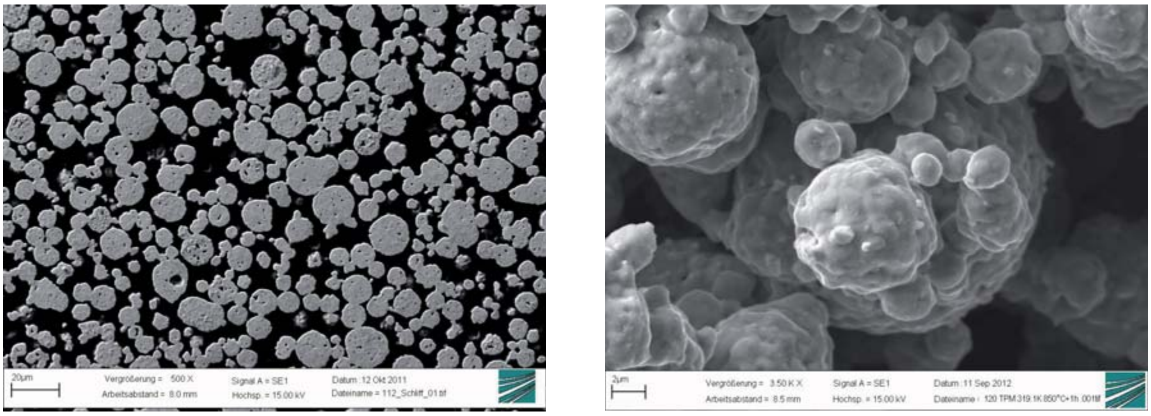
In a huge number of reduction experiments the first temperature of the two-step reduction, which is necessary to remove the oxygen, was kept constant at 500 °C (932 °F) for 1h under hydrogen, because there was no significant influence to the reduction result in the temperature range between 400 (752 °F) and 600°C (1112 °F). 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 (1292 °F) to 900 °C (1652 °F) two main different powder qualities were evaluated. Below 700 °C (1292 °F) 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 (1562 °F) 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 (1292 °F) and for the highest 850 °C (1562 °F) was indicated to produce fine iron powder in the two step hydrogen reduction process. Figure 3 shows the spherical powder after reduction at 500 °C (932 °F), 1 h (1st temperature step) and 700 °C (1292 °F), 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 I). The second powder quality reduced at 500 °C (932 °F), 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 4). Therefore the apparent density is higher and the BET value lower than that of the powder reduced at 700 °C (1292 °F) (Table I). The oxygen and carbon content is for both reduced powders in the range of the state of the art. The particle size distribution is higher, but 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 3. SEM image of the sinter cake after reduction at 500 °C (932 °F), 1 h + 700 °C (1292 °F), 24 h under hydrogen,

a) cross section, b) topography



a) b)

Figure 4. SEM image of the sinter cake after reduction at 500 °C (932 °F), 1 h + 850 °C (1562 °F), 1 h under hydrogen,

a) cross section, b) topography

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 processing

After the reduction step a further powder processing is necessary to separate agglomerates and to refine the powder particles by mechanical forces. It is an important goal to get nearly spherical fine powders, which promise a good flowability and high sintering activity. The challenge is to separate the agglomerated particles by keeping the spherical shape and prevent their deformation. With higher temperature (2^{nd} temperature step of reduction process) on the one hand the inner porosity decreases which reduce the shrinkage of the sintered part but on the other hand also sintering necks between the particles are growing which results in a stronger sinter cake. In this case higher shear force are needed for the milling process with a growing risk of particle deformation. In chapter 2.2 the used grinding units like the mortar grinder (MG), the planetary ball mill (PBM) and the Nara Hybridizer (NH) were introduced.
In Table II the particle sizes of fine spherical state of the art powders (carbonyl iron, atomized iron) and that of the two as reduced powder qualities compared to the milled powders are given. The powder reduced at 850 °C (1562 °F) in the 2^{nd} temperature step indicates agglomerates and the highest average particle size of 22.1 µm. After milling with a mortar grinder the d_{50} value decreases to 16.1 µm after 5 min and 13.8 µm after 20 min, which is close to the atomized powder. In addition the powder morphology is very spherical (Figure 5). A longer milling time does not lead to significantly finer powders.
Using the ball mill the particle size could be decreased with increasing rotation speed as well as milling time down to a d_{50} of 12 µm. On the other hand the morphology tends more and more to switch from the spherical (Figure 6) to plastic deformed and partly flaky shaped particles (Figure 7). 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 hybridizer was identified as the most suitable milling unit to lower the particle size by keeping the spherical morphology (Figure 8). After milling with 16000 rpm for 4 min resulted in a d_{50} particle size of 11.4 µm.
An even good result was achieved by using the hybridizer for milling the powder which was reduced at 700 °C (1292 °F) in the 2^{nd} temperature step. A spherical particle shape was obtained and the particle size could be considerably reduced from d_{50} = 18.6 µm to 5.1 µm (Figure 9). This quite low particle size is generated by destroying the still porous particles (see Figure 3, chapter 3.1) and rounding them. Additional the porous surface is densified which reduces the shrinkage during the sintering (chapter 3.3, Table III).
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.

Table II: Particle size of the reduced and milled powders compared to commercial carbonyl and atomized spherical iron powders

powder qualities	particle size [µm]		
	d10	**d50**	**d90**
carbonyl iron	2,1	4,5	8,6
atomized iron	6,0	13,7	22,0
reduced 500°C, 1h + 700°C, 24h, not milled	11,6	18,6	29,4
reduced 500°C, 1h + 850°C, 1h, not milled	13,2	22,1	35,6
reduced 500°C, 1h + 850°C, 1h + milled 5 min, 75 rpm (MG)	10,1	16,1	24,6
reduced 500°C, 1h + 850°C, 1h + milled 20 min, 75 rpm (MG)	**8,6**	**13,8**	**21,1**
reduced 500°C, 1h + 850°C, 1h + milled 10 min, 100 rpm (PBM)	11,6	18,8	29,1
reduced 500°C, 1h + 850°C, 1h + milled 60 min, 100 rpm (PBM)	8,5	13,4	19,9
reduced 500°C, 1h + 850°C, 1h + milled 120 min, 100 rpm (PBM)	**7,8**	**12,3**	**18,8**
reduced 500°C, 1h + 850°C, 1h + milled 240 min, 100 rpm (PBM)	7,5	12,0	18,3
reduced 500°C, 1h + 850°C, 1h + milled 120 min, 150 rpm (PBM)	8,2	13,3	20,5
reduced 500°C, 1h + 850°C, 1h + milled 4 min, 16000 rpm (NH)	**7,3**	**11,4**	**16,9**
reduced 500°C, 1h + 700°C, 24h + milled 4 min, 16000 rpm (NH)	**3,4**	**5,1**	**7,6**

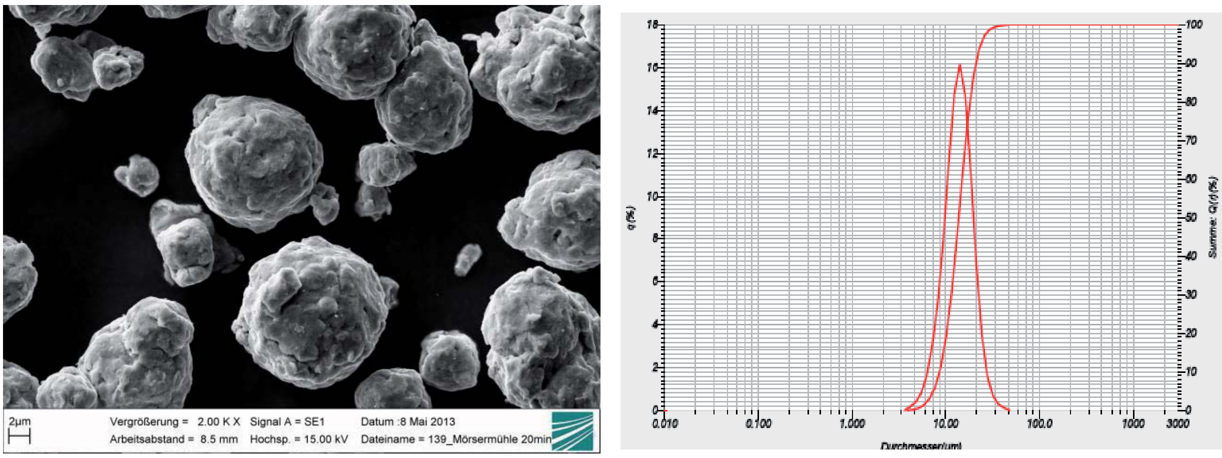


Figure 5. Powder reduced at 500 °C (932 °F), 1 h + 850 °C (1562 °F), 1 h under hydrogen and milled for 20 min, 75 rpm in a mortar grinder (MG), a) SEM image, b) particle size distribution

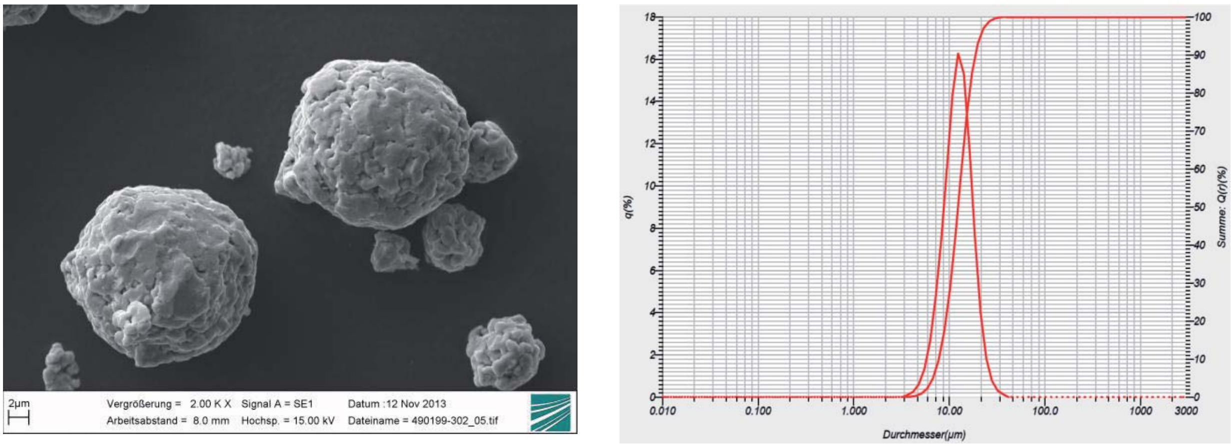


Figure 6. Powder reduced at 500 °C (932 °F), 1 h + 850 °C (1562 °F), 1 h under hydrogen and milled for 120 min, 100 rpm in a ball mill, a) SEM image, b) particle size distribution

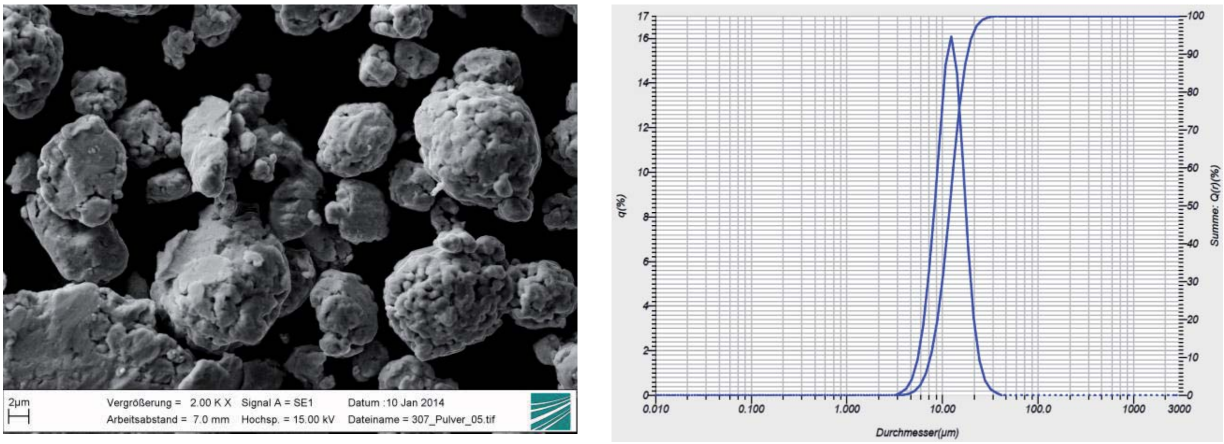


Figure 7. Powder reduced at 500 °C (932 °F), 1 h + 850 °C (1562 °F), 1 h under hydrogen and milled for 240 min, 100 rpm in a ball mill, a) SEM image, b) particle size distribution

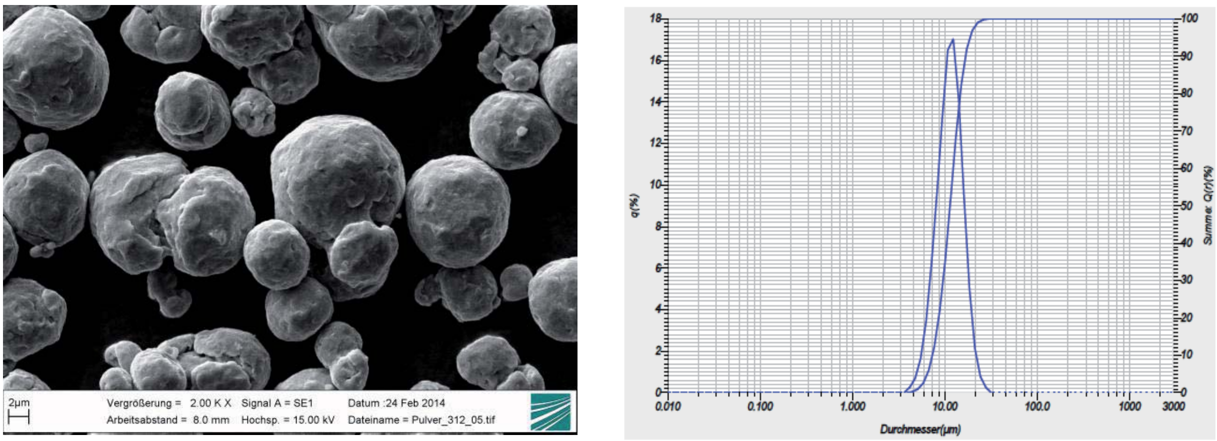
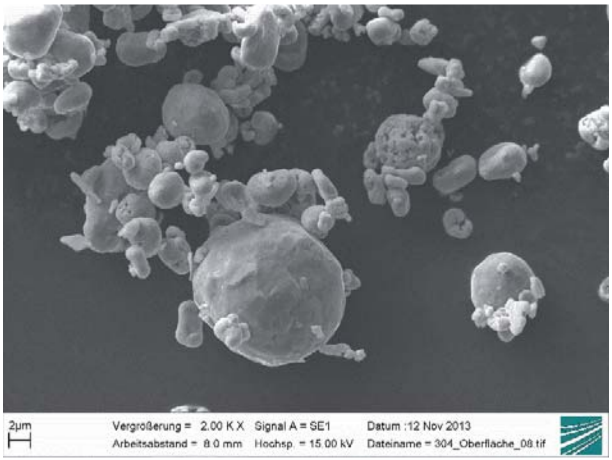


Figure 8. Powder reduced at 500 °C(932 °F), 1 h + 850 °C (1562 °F), 1 h under hydrogen and milled for 4 min, 16000 rpm in a Nara Hybridizer (NH), a) SEM image, b) particle size distribution



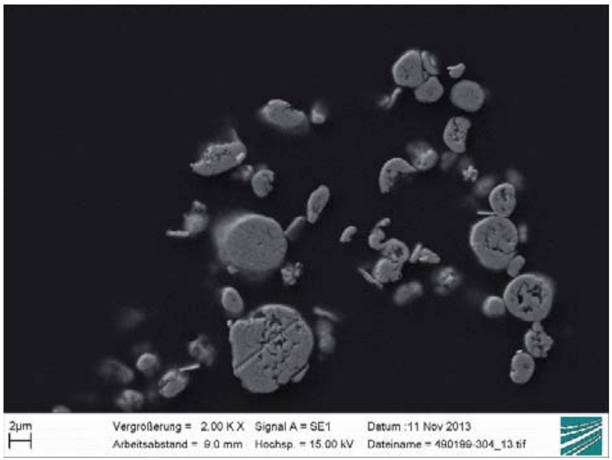
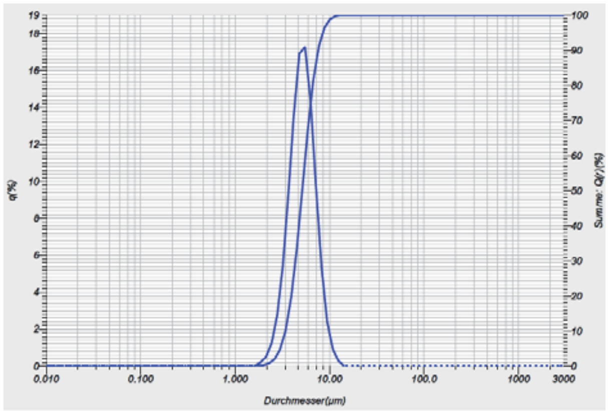


Figure 9. Powder reduced at 500 °C (932 °F), 1 h + 700 °C (1292 °F), 24 h under hydrogen and milled for 4 min, 16000 rpm in a Nara Hybridizer (NH),

a) SEM image of particle surface,

b) SEM image of the cross section,

c) particle size distribution



3.3 Sintering behavior

According to chapter 2.3 the cylindrical samples based on the different processed powders were sintered and analyzed. Table III summarizes the main important values for the sintered parts especially the shrinkage and obtained density. Generally all powders produced by the two-step hydrogen reduction process achieve a higher sinter density compared to atomized powder. Both powders reduced at 700 °C (1292 °F) in the 2nd temperature step exceed even the density of the carbonyl iron part. The reason is the high sinter activity because of the fine porous structure of the particles which remained by the incomplete densification in the reduction process (see Figure 3 in chapter 3.1). The shrinkage of 16 % of the milled powder (Nara Hybridizer) is comparable, while the not milled powder has a shrinkage of over 25% because it is not densified by the milling process. This is also indicated by the low green density of 3.2 g/cm³.

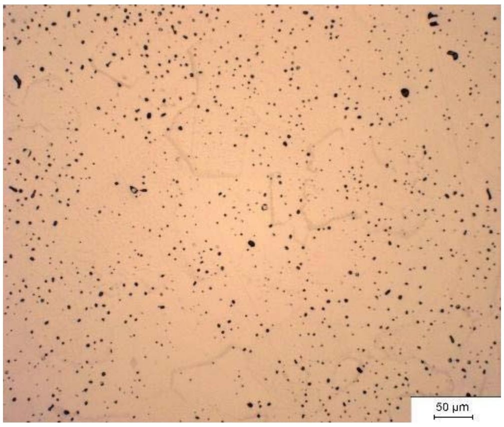
The powders reduced at 850 °C (1562 °F) in the 2nd temperature step achieve an only 3 or 4 % respectively lower density compared to the carbonyl iron sample. The shrinkage is comparable.

The oxygen and carbon contents determined by organic elemental analyses using a Leco TCH 600 and Leco CS230 respectively are in the same range for all samples. Only for the sample based on the powder milled in the Nara Hybridizer a higher oxygen content was measured, which must be proofed in the further running development work.

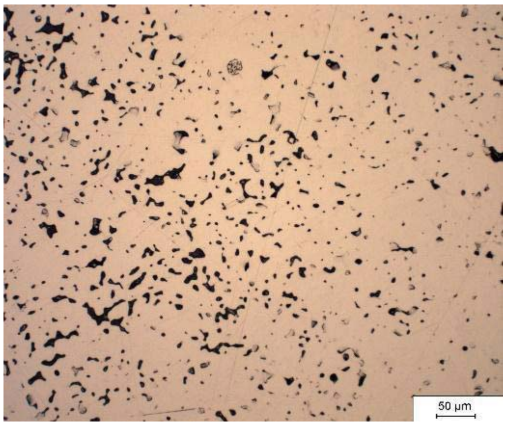
Table III: Properties of parts based on different powder qualities in comparison to state of the art powders sintered at 1320 °C for 3 hours under H_2 in a tube furnace

powder qualities	particle size d_{50}	green density	sintering shrinkage	Sinter density (geometric)		oxygen content	carbon content
	[µm]	ρ [g/cm³]	ΔL / L0 [%]	ρ [g/cm³]	ρ [%TD]	[%]	[%]
carbonyl-Fe	4,5	4,44	15,76	7,64	97,1	0,050	0,14
atomized Fe, spherical	13,7	5,06	7,26	6,33	80,4	0,059	0,023
reduced 500°C (932 °F),1h + 700°C (1292 °F), 24h	18,6	3,22	25,5	7,69	97,6	0,068	0,013
reduced 500°C (932 °F),1h + 850°C (1562 °F), 1h+ milled 20 min (MG)	13,8	4,57	15,3	7,33	93,2	0,091	0,036
reduced 500°C (932 °F),1h + 700°C (1292 °F), 24h + milled 4 min, 16000 rpm (NH)	5,1	4,67	16,0	7,75	98,4	0,161	0,015
reduced 500°C (932 °F),1h + 850°C (1562 °F), 1h+ milled 120 min, 100 rpm (BM)	12,3	4,06	18,4	7,47	94,9	0,066	0,021

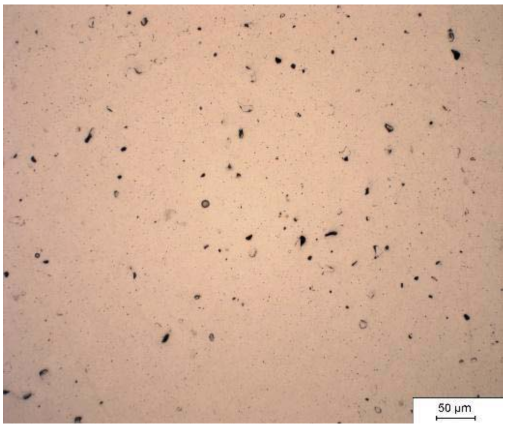
The cross sections of the sintered sample were prepared to demonstrate the different porosities. Figures 10 a) – f) indicate a good correlation to theoretical density (TD) in Table III. The lowest porosity show the micrographs of the 700 °C (1292 °F) reduced powders e) and f) and a slightly higher porosity for carbonyl iron a) and the 850 °C (1562 °F) reduced powders c) and d). Further investigations are running to investigate the sintering behavior of the powder which is milled by the Nara Hybridizer. The well spherical shaped powder with a lower particle size compared to the ball milled powder (see Table II, Figure 6 and 8, chapter 3.2) promises a higher sinter activity and a sinter density close to the carbonyl iron parts. The sample based on the commercial atomized powder is characterized be the highest porosity.



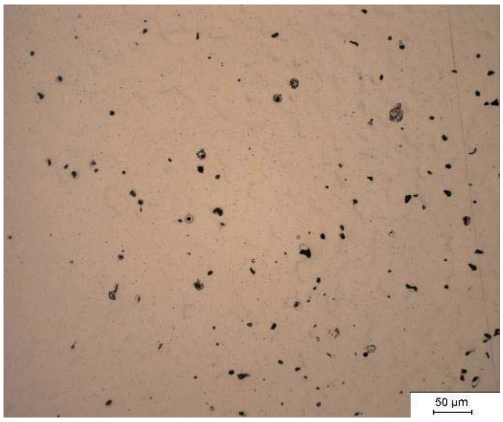
a) carbonyl-Fe



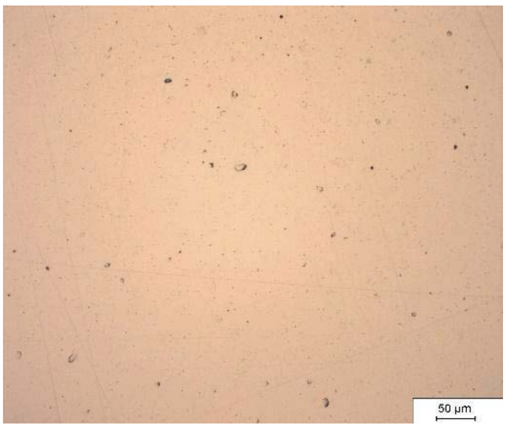
b) atomized Fe



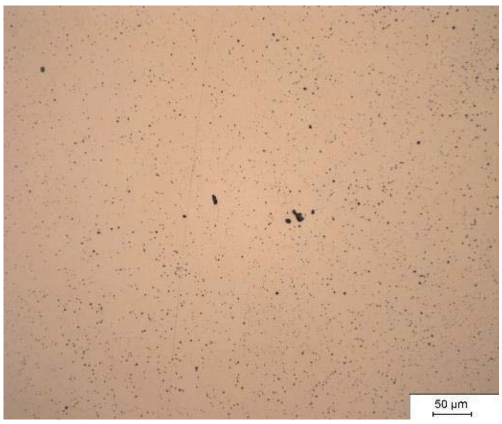
c) reduced 500 °C (932 °F), 1h + 850 °C (1562 °F), 1h + milled 20 min, 75 rpm, mortar grinder



d) reduced 500 °C (932 °F), 1h + 850 °C (1562 °F), 1h + milled 120 min, 100 rpm, ball mill



e) reduced 500 °C (932 °F), 1h + 700 °C (1292 °F), 24h



f) reduced 500 °C (932 °F), 1h + 700°C (1292 °F), 24h + milled 4 min, 16000 rpm

Figure 10. Cross section of sintered cylinders based on commercial powders a), b) for comparison with different reduced powder qualities c) – f)

4. CONCLUSIONS

The introduced two-step hydrogen reduction using fine granulated iron oxide based on a by-product of steel makers to produce fine spherical iron powders especially for MIM application offers a cost efficient alternative compared to the atomizing and carbonyl iron processing route. A key issue to obtain the required quality of sintered parts is the powder processing by milling after the reduction step. With respect to a low particle size, high sinter activity and obtainable sinter density as well as low shrinkage the powder milling by the hybridizer technology leads to very promising results. Further development work will focus on process optimization and up-scaling. The high potential of the cost efficiency of the new powder manufacturing process promises to break the market barrier or to enlarge the market for many applications.

5. ACKNOWLEDGEMENTS

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