ANNALS of Faculty Engineering Hunedoara
– International Journal of Engineering
Tome XIII [2015] – Fascicule 4 [November]
ISSN: 1584-2673 [CD-Rom; online]
a free-access multidisciplinary publication of the Faculty of Engineering Hunedoara

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EXPERIMENTAL RESEARCH FOR OBTAINING IRON POWDER WITH MICRONIC AND SUBMICRONIC DIMENSIONS

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Abstract: After the last steps of technological flux from the setting of an economical agent with siderurgical profile, except the primary product, there are quantities of materials, named waste, but because of the possibility of valorification through recycling and/or reutilization can be fit the category of subproducts. Depending on the conditions of each siderurgical compound, waste can become subproduct and subproduct can become waste. The iron oxide from the cold rolling mill (CRM) from ARCELOR MITTAL Galati is a material with different characteristics from the hematite ores processed in the siderurgical industry. This is a synthetic material with characteristics structured cluster type with low bulk density and porosity determined by the intergranular spaces. The main aspect of the environment found is the dispersion of dust in the air and the training of fluvial waters, the risk given from the high finesse of the material, the metastable particle size state which can transform it in a material with a specter of granulation dangerous for human organisms and the presence of the traces of HCl. In this work stand presented the results of experimental researches developed on the ferrous oxide fine powder, in order to establish the best methods of valorification of it.
Keywords: ferric oxide, iron powders, oxidation, particle, grains

1. INTRODUCTION

Iron powder (250 μm) is used in getting electrodes-welding in the manufacture of magnetic materials, sintered parts, but also in various alloys [1] [2] [3] [4] [5]. Powder coatings are a durable finish applied in electroplating. It was created and a nano-iron powder, granules with size less than 10 μm. Industrial production of iron powder started in 1937 on the incentive of General Motors Corporation in the USA. Höganäs was active since 1922 in producing a high quality sponge iron to be used by the Swedish steel industry as high-purity melting stock for the production of special steels like tool-steel and stainless steel. It is currently produced by refining the iron until it becomes high purity, then being blown into thread and used as a catalyst in fuel cells.

Iron powder mixed with graphite and copper spread on surfaces with reduced fluctuations sintered in size. Atomization is the dominant method for producing metal and pre-alloyed powders from iron, steel, stainless steel, tool steel, superalloy, titanium alloy, aluminum and brass. Atomization accounts for nearly 70 percent by weight of all metal powders produced in North America. It is the dominant mode for powder production because high production rates favor economy of scale and because pre-alloyed powders can only be produced by atomization. Reduction of oxides and electrolysis are the other major methods of powder production. Iron and steel account for 80 percent by weight of all metal powders produced annually. At slightly over nine percent of total annual powder production, the next most important metal powder is aluminum, followed by copper and its alloys (4.9%), and nickel (2%). All other powders combined account for only about 4 percent of annual metal powder production. By means of powder technology, JFE Steel has developed a large number of steel alloy powders with finer control of microstructure and intensification.

2. EXPERIMENTAL RESEARCH CONDUCT

The material investigate is a ferric oxide – α– Fe_2O_3 almost pure 98 – 99 % with traces of SiO_2 and HCl residual from the process up to 1 %. In table 1 the chemical analysis is presented and characteristics of the powders.

The purpose of the experiments is to develop iron powders with two different characteristics:

- The specific diameter of 0.8–5μm with specific characteristics iron powders for manufacture of parts by powder metallurgy technology.
- The specific diameter <0.5μm and in the nanometric to the condition of achievement is getting a larger total surface area of 2.5m^2 /g.

The apparatus used for experimental research consists of:

- electric oven chamber 12 dm^3 and SiMo resistant, maximum working temperature 1500°C. The furnace is designed for heat treatment operations and has an area of 5.15 dm^2 hearth. It can provide a heating rate of 20°C / min up to 1100°C;

= reaction chamber for retaining O2 in N2 at 500°C with copper turnings has the function to purify the nitrogen used to protect the reduced iron oxidation by traces of oxygen available to the level of 0.5%. Since the cooling of the sample is in the environment of nitrogen for 3 hours, brought O2 is enough to re–oxidation of iron. N2 used for protection and cooling is passed through a mass of copper span heated to 500°C the oxidation reaction occurs with up to 50% CuO in and so each can hold 1 g of Cu 0.25 g O2 in the conditions of a degree of oxidation of 50%. The amount of O2 to N2 to an experiment carried is 1.54 g to 12.32 g Cu are required. The cartridge was calculated span of 10 experiments and a safety reserve of 30% and weighs 160 g.

Table 1. Characteristics of iron oxide dust CRM

The element	% determined by ICEM Laboratory X–ray fluorescence analyzer	% determined by Laboratory Arcelor Mittal Galați	
		Analysis 1	Analysis 2
Fe2O3	96.87	95.82	99.01
SiO2	0.042	0.24	0.04
CaO	0.41	-	-
Al2O3	0.053	-	-
Mn3O4	0.255	-	-
MgO	0.062	-	-
TiO2	0.008	-	-
Na2O	0.163	-	-
K2O	0.016	-	-
P2O5	0.024	-	-
CuO	0.014	-	-
NiO	0.013	-	-
PbO	0.010	-	-
Cr2O3	0.035	-	-
Soluble in water	-	0.7	0.5
Soluble in acid	-	0.19	0.22
Soluble in benzene	-	–	2.44
SO3	0.361	0.2	0.23
P.C.	1.636	2.19	0.45
Humidity	-	0.46	1.2

= bottles of N2 and H2 and O2 at 220 atm. Using O2 in experiments is motivated by the need to ensure the stability of ferric oxide in oxidizing atmosphere at temperatures above 450°C where it usually begins to break down. This O2 raise the temperature of decomposition began at Fe3O4 above the temperature necessary to carry out the experiment;

Figure 1. Reaction flask in order to reduce iron oxide samples with the inlet and outlet of the reducing gas quartz glass

Figure 2. Assemble dust reduction plant for producing iron oxide powders and sintering of nanosized

= rotameters for areas 25–175 l / h;

= room to reduce alumina tube with Φ 70 mm, length 160 mm wall thickness of 5 mm with a capacity of 1000 cm3. The removable wall is made of concrete with 80% MgO refractory magnezitic and heat treated at 1200°C. Through it are placed second quartz glass pipes Φext = 8 mm and 6 mm Φint = for inlet and exhaust gases and reactive protection. Figure 1

= reduction gear assembly is shown in Figure 2.

The sequence of technical operations for obtaining experimental researches of ferric oxide powder of iron powder intended for powder metallurgy was:

= Figure 1 reaction flask in order to reduce iron oxide samples with the inlet and outlet of the reducing gas bottle quartz. Fe2O3 test material is characterized above is disposed in the four ceramic platforms 7 g total weight, which has been previously dried at 160°C for 4 hours. The two platforms have been introduced in the iron oxide pellets with a diameter of 3–5 mm;

= Heating the bearing to achieve the reduction was carried out with 16°C / min for 20–40 min during which the O_2 is introduced to the reaction chamber at a rate of 0.2 l / min in order to avoid decomposition of ferric oxide;

= After reaching the preset temperature landing infuse for 3 minutes, N2 with a flow rate of 2.2 l / min. after which a mixture of 20% N2 and 80% H2;

= Samples remained working time of 60, 90, 120 min at temperatures of 490–520°C, 640–670°C and 830–870°C according to the experimental design;

= Cooling was done for 3 hours at which time the oven with N2 was infused at a rate of 0.3 l / min, to a temperature of 220°C, in order to avoid reoxidation of the material.

= After removing from the oven they were packed in plastic envelopes to avoid slow reoxidation in air.

2. DETERMINATION OF THE MAIN PROPERTIES OF IRON POWDER OBTAINED

Mode of analysis and characterization of reduced iron powders involved determining the following indicators:

Determination of discount: was made by weighing the sample start and end with an electronic balance with an accuracy of ± 0.02 g and determination of O2 loss calculated by the formula:

$$R \rightarrow \frac{M_i - M_{fin}}{Mi} x100$$

in which: R – reduction rate in %, M_i – the initial mass of the sample g, M_{fin} – the final table of the sample g
Average weight loss of the samples was 2.25 g which corresponds to a reduction of 98.7%.

3. DETERMINATION OF SIZE DISTRIBUTION

Iron powder obtained was agglomerated in large particles and their disaggregation required to be carried out in a ring mill with a capacity of 200 g for 10 sec. It was performed on a measurement by laser beam scattering in liquid medium by sedimentation and dust. Particle size distribution is shown in Figure 3.

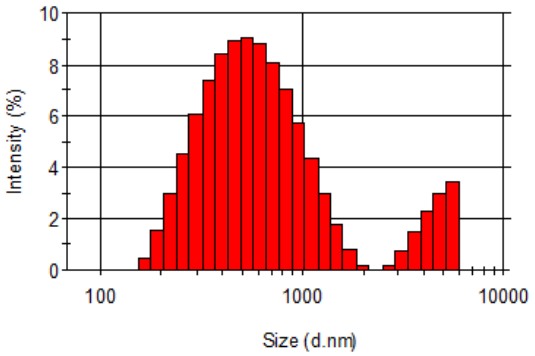


Figure 3. The particle size distribution of the iron from the reduction with hydrogen at T mittel. = 750°C.

It follows that the resulting iron powder has a particle size distribution approximately similar to that of the base material. Increasing the share of large diameter as the average diameter and ds are the result conglomeration of iron particles by creating bridges of Fe by diffusion contact the Fe oxide particles. The presence of ferrous oxide FeO still leak was due to the reaction chamber and reoxidation in air. Are presented in Table summarizing specific diameters – DSP of granules obtained in each experiment. It was found in each test performed the material has a low powder fraction close to the range of 100 nm = 0.1 μm largely detached larger iron pellets. Bulk density – ρ_{vrac} was determined by weighing a constant volume of 3 cm^3 of material with electronic balance with an error margin of ± 0.02 g the medium value being 2.13 gr/cm^3. The data for every experiment are given in the central table.

The coefficient of form – θ particles was determined by analyzing the Otic microscope with magnifications of up to 700 x 100 by a number of granules. The sample consisted of iron dust arrangement on a glass slide and measuring the lengths of the two axes eyepiece divisions' terminal strip 10 micrometers. Conglomerate particles were measured. This type of analysis shows estimation errors of ± 10–15% but provides important information about the surface area of the particle as it is involved in responsiveness. The average coefficient of form was 0.60 to 0.68. The specific surface BET – SSP was determined only for two probes with the values 2.9–3.13 m^2/gr. Centralization of experimental results is presented in table 2. Analysis of experimental data took into account only the specific diameter – DSP and form factor – where θ for evaluating properties:

Table 2. Centralization experimental results

Experiment no.	Regime parameters		Characteristics			
	X1	X2	R – %	DSP – μm	P_{vrac} g/cm^3	θ
1	800	120	99.3	1.2	2.26	0.85
2	800	90	98.5	1.2	2.1	0.78
3	650	120	96.7	0.9	1.91	0.81
4	650	90	95.5	0.7	1.87	0.83
5	500	90	87.6	0.8	1.9	0.69
6	650	60	98.2	0.8	1.95	0.72
7	500	120	86.3	0.6	1.76	0.61
8	500	60	83.4	0.6	1.81	0.55

A – the powder for sintering the powder metallurgy, and
B – reactive reagent with very high surface submicron and nanoscale powders case.
Identify objective response functions as:

$$Y1 - \text{variation DSP} = 0.85 + 1.15\ \ X1 + 0.30\ X2$$
$$Y2 - \text{variation } P_{vrac} = 1.945 + 94.15\ X1 + 60.75\ X2$$
$$Y3 - \text{variation } \theta = 0.73 + 0.022\ X1 + 0.15\ X2$$

Analysis of these functions obtained show:

1. DSP – is largely influenced by the variation of the two parameters but they are dependent to a greater extent of initial grain subjected to reduction of iron oxide dust. Also measured values are tainted by interference with additional material by grinding welded disaggregation conglomerates. For samples subjected to higher temperatures conglomerates of iron particles have stronger links and grain growth can be attributed to preserve an important fraction of large granules after grinding. However there was a slight decrease in the parameter for the working conditions at low temperature 500°C and a long time to reduce the 120 min. This is confirmed by observations at light and electron microscopy. These particles seem to be but kept the original grain size of the material in a state of pure iron detaches easily from the other grains. The reduced mass of particles at low temperatures – 500°C can see a large number of nano–sized grains.

2. Due to afore mentioned bulk density parameter suffer from the same deformation of the result. A large number of grains have been preserved in its original form after grinding but detected in electron microscopy that most of them are empty – Figure 4 in the interior making this parameter is sensitive deformed and do not represent a credible value subsequent experiments.
3. Clearly visible the relationship is between the coefficients of form factor – θ is visibly influenced by working parameters falling on average from 0.7 to 0.6 which is equivalent to increasing the specific surface of the powder under keeping the same size distribution. It can count on a gain parameter SSP taking into account the fact that a fraction of granules has the particularity of being hollow. Powder for this purpose resulted in experimental conditions with temperatures around 800–830°C and times larger reduction 90–120 min.

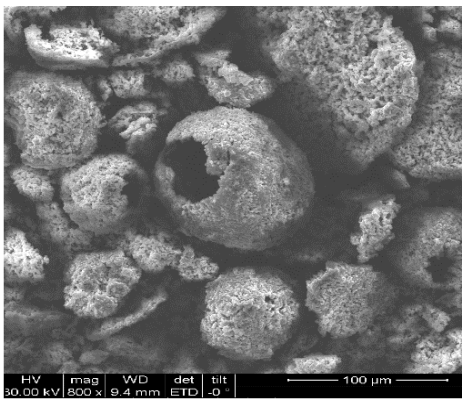
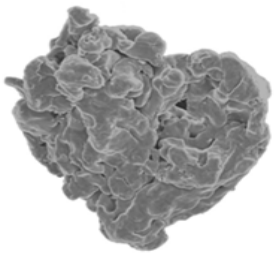


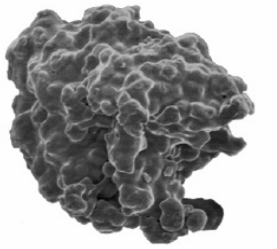
Figure 4. Spherical hollow metallic iron formed by the agglutination of the fine powder, iron oxide 1µm

Figure 5 shows the two iron particles obtained by indirect reduction. Iron powder particle 21.1000 NC – Photo 4 – produced by Högonäs good characteristics confer plasticity and toughness of parts made from them very good.

The degree of compaction obtained is 7.46 g / cm^3 and 7.6 g / cm^3 of a Figure 5b rolled steel – iron particle obtained by indirect reduction with H2 for which there was a degree of compaction of 7.0 kg / cm^3 pressed 110–120 tf / cm^2.



a – kind NC21.1000 powder produced by the firm Högonäs



b – iron particle that produced by reduction of iron oxide with hydrogen at 750°C

Figure 5. Iron particles obtained by reduction with hydrogen for manufacturing powder metallurgy

Characteristic of the iron powder resulting from the reduction of iron oxide is the conglomeration of iron particles and unite them into larger structures by diffusion of the iron from the initial limit contact between oxide particles. For this reason, the powder requires for the release of mechanical break–down of the iron particles have an average diameter of approx. 0.7 to 2 µm (Figure 6).

The image is presented such a conglomeration of particles that are visible boundaries between grains of iron and diffusion areas.

The characteristic shape of these granules is relatively compact form rhombohedra shaped by an average factor of approx. 0.8 which gives good stability sintered structures and obtain a degree of compaction as close to the molten steel.

These features can appreciate that Fe powder obtained can be used to produce sintered parts.

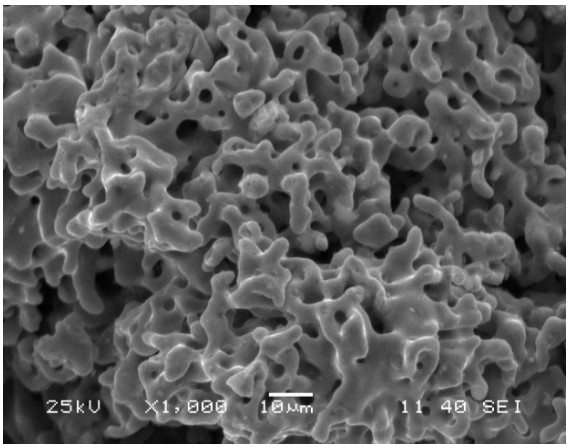


Figure 6. Picture of conglomerate iron particles by diffusion of iron at the interface. (Picture by microscopy SEM – EDAX; magnification x 10,000)

4. CONCLUSIONS

Department of capitalization considered for iron powder obtained from ferric oxide CMR is to obtain iron powder for the manufacture of parts by powder metallurgy techniques.

Measurements performed for different ownership iron oxide powder from CMR Galati, revealed the following:

- The bulk density and wettability show that the material consists of granules conglomerate intergranular porosity and large grains 97% from 0.1 to 1 ηm no internal porosity so medium and fine pores of very small size;
- For this type of powder form is important and specific surface properties that can lead to very different applications as chemical catalysis processes, as purifier or chemical reagent solutions.
- Through it are iron oxide examined its characteristics provide opportunities to be used as such or simple initial processing for a wide range of technical applications.
- Iron powder (under 250 µm) is used in making the welding electrode in the production of magnetic materials, sintered parts, but also in various alloys
- Powder coatings (powder coatings) are a durable finish, applied in electroplating.
- Iron powder is used, and sparkle effects as well as magnetic fluids archeology.

There are many applications of iron powders – the paint industry, military industry, treating groundwater ferromagnetic countries, additional in powder metallurgy, cleaning contaminated soil, or abandoned mines of industrial sites with waste water neutralization (nanometric iron can be injected into the mud and pumped contaminated site where waste is abandoned).

Acknowledgement:

This work is supported by the Sectorial Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and the Romanian Government under the POSDRU 2014/ /159/1.5/S/138963.

References

[1.] ***, Hoeganaes Corporation providing iron powder, 2007, www.hoeganaes.com
[2.] Fan L.S., A high efficiency chemical looping process to produce low–cost hydrogen, Research report Ohio University, U.S.A., 2007.
[3.] Fan L.S. et al., One–step chemical looping process for producing hydrogen from solid fuels, Research report Ohio University, U.S.A., 2008.
[4.] Spîrchez Z., Iron powder production, Elsevier, 2001.
[5.] Wei Xian Zhang, Application of ultrafine iron powders– Journal of Nanoparticle Research, nr5/2008, ISSN: 1572–896X (electronic version)
[6.] K. Murray, M. Kearns, Review of Developments in Gas Atomised Alloy Metal Powders for MIM Applications, Euro PM 2009, Copenhagen 2009, Proceedings Vol. 2, 73-80
[7.] 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
[8.] J. 0. Edstrom, The Mechaism of Reduction of Iron Oxides, J. Iron Steel Inst., vol. 175 (1953), 289 – 304
[9.] M. V. C. Sastri, R. P. Vismanath und B. Vismanath, Studies on the reduction of iron oxide with hydrogen, Int. J. Hydrogen Energy, Vol. 7, No. 12 (1982), 951- 955
[10.] Hsin-Yu Lin, Yu-Wen Chen and Chiuping Li, The mechanism of reduction of iron oxide by hydrogen, Thermochimica Acta, Vol 400, No 1-2, (2003), 61-67
[11.] G. Walther, T. Büttner, B. Kieback, T. Weißgärber, M. Hoffmann, T. Blum, New Method for Producing Fine Spherical Iron Powders, Euro PM 2013, Göteborg 2013, Proceedings Vol. 2, 245-250
[12.] I. Vida Simiti, Technological properties in powder metallurgy, Ed. Enciclopedică, 2000