RECYCLING OF NON-CONFORMING PRODUCTS IN THE FIELD OF MAGNETS PRODUCTION

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Abstract

This paper deals with a recycling and reusing of non-conformity product during the production of magnets. Theoretical part of the paper contains general facts about permanent magnets and theirs productions. Experimental part describes methodology of non-conformity product processing by dry milling to ensure optimal conditions for rebuilding the material to reuse it in production cycle. Granulometry analysis of the milled material showed the formation of clumps and aggregates of size from 20 to 30 microns but an ideal particle size suitable for the production of the magnets is about 1 micron. After evaluation and mutual comparison of results, appropriate measures have been proposed in the recycling technology which has been used.

Keywords: Recycling, magnets production, non-conforming products, milling

1. INTRODUCTION

Magnets are used in a variety of industries. In our civilization, they are increasingly sought-after, the products made from them are of strategic importance, and their worldwide consumption is steadily rising. In the context of environmental protection, it is important to address the issue of their recycling, which will lead to the further use of waste as a secondary raw material in the production process. The issues of reuse of waste are paid great attention worldwide. An important part of this dynamically developing sector is the applied process technology. Well-known, respected and most commonly used configurations (technological schemes) include processes such as sorting, crushing and separation [1]. The aim of this work is to examine the optimal conditions of ferrite magnet processing in the dry milling phase. An important impulse was the vision of the possibility of improving the controlled recycling of waste generated in practice. Hexaferrites are interesting materials due to the versatility of their properties such as: magnetic, dielectric, multiferroic, magnetoelectric properties, etc. [2, 3]. Consequently, they are used in many applications, particularly as permanent magnets [4]. Permanent magnets are used in various applications including: motors, computing, electrical engineering, power engineering, fine mechanics, handling technology, home appliances, medicine, automotive engineering, engineering, telecommunication, measuring equipment, aeronautics, astronautics and water transport, sensors and ecology. Each type of permanent magnet has its own specific manufacturing process. The common production technology for all types of magnet is powder metallurgy. This is a method in which the mixture of metallic powders is mixed, then compressed into a mould, and subsequently sintered at high temperatures. The resulting product is very hard and cannot be repaired or processed to the desired form. Therefore, it is necessary to define the final dimensions consistently during the production and to produce them precisely. In the final phase, the magnets can be grinded gently to achieve strictly flat surfaces. The amount of hexaferrite magnets used per year was estimated by Gutfleisch et al. [5] at approx. $4.3 \cdot 10^5$ t in 2010. In that respect, these materials have been the focus of many studies devoted to the optimization of the production cost [6, 7] and also to the improvement of their magnetic properties [8 - 10].

Ferrite magnets are made of iron oxide (Fe_2O_3) and barium and strontium carbonates ($BaCO_3$ and $SrCO_3$). These feedstocks are mixed in a ratio of 80 % Fe_2O_3 and 20% $BaCO_3$ or $SrCO_3$. This mixture is calcined to form hexaferrite. Calcination is a high-temperature process in which one solid material is eliminated as a gaseous substance and the other forms a solid. Subsequently, the moulding is done in the desired form in the dry form or in the form of an aqueous suspension. Magnets acquire the final shape, size and toughness by firing (sintering) at a temperature of 1200 °C. They are then magnetized, packaged and dispatched after the final check.The paper deals with the process of producing hard ferrite magnet in a dry grinding phase on a VM 500 vibratory mill. The VM 500 vibratory mill is a continuous rod two-stage mill consisting of two cylinders placed one on top of the other. Steel rods of two different diameters are installed in these cylinders. In the upper cylinder, bars with a diameter of 30 mm and a length of 1998 mm are used, in the lower cylinder there are bars with a diameter of 20 mm with the same length of 1998 mm. The particle size of the non-matching raw material after the grinding process needed to produce the magnet is within 1 μm. In case of insufficient crushing in this dry grinding, the wet milling process follows. Milling as such is an operation in which particles degrade. Dry grinding takes place without the addition of any liquid. Its advantage is the elimination of the energy-intensive and often technologically demanding drying process of the resulting material. Wet milling is more effective, but it is more costly. Study of metal powders as the input materials is of importance in gaining insight into the basic principles of powder metallurgy [11].

2. EXPERIMENTS AND METHODS

The paper deals with granulometric properties of ground waste as a secondary raw material in the production of ferrite magnet with regard to its subsequent classification into production. In the production of ferrite magnets, non-conforming products (scrap) are produced which do not match the required parameters after pressing. This waste is used as a secondary raw material in the production process. Non-conforming products are comminuted on a vibratory rod mill in a dry grinding operation into a product of the desired particle size. The experimental work began on the continuous two-stage VM 500 rod vibratory mill in the company Feromagnet and was focused on the collection of samples of milled particles to determine the final particle size (granulometry). The next step in the experimental part of the paper was a simulated milling process on a laboratory vibratory mill to determine the effect of the grinding time on the resulting particle size.

2.1. Materials

The material examined in this work is the strontium hexaferite $SrFe_{12}O_{19}$, the so-called Ferrimagnet, the basic component of permanent magnets. The composition of the material was verified by X-ray diffraction analysis. Strontium hexaferrite is a hard magnetic material due to their high coercivities (6.64 kOe) which originates from its high magnetocrystalline anisotropy and it is strongly dependent on the size and the shape of the particles. Moreover, the Curie temperature of $SrFe_{12}O_{19}$ is around 470 °C and the saturation magnetization between 74.3 and 92.6 emu / g. For the preparation of hexaferrite, the solid state reaction method is commonly employed that involves firing of a stoichiometric mixture of strontium carbonate and iron oxide at high temperature (~1200 °C) but the obtaining fine, high chemical homogeneity and monodispersed particles may not be easy [12]. Raw and final product are shown in **Figure 1**.

2.2. Particle shape and size distribution

Particle size distribution was tested by using a CILAS 1190 laser analyzer (wet method), with coherent light 830 nm wavelength from a low-power laser diode passes through a cell containing the metal powder dispersed in water like carrying medium. The results were interpreted based on Fraunhofer's theory. Determination of the particle shape was based on SEM photos and microscopic photos captured by microscopic equipment of stereomicroscope Nikon AZ100 within particle size distribution measurement by CILAS 1190.

a) b)

Figure 1 Raw (a) and final (b) product photos

2.3. X-ray powder diffraction

The XRPD patterns were recorded under CoKα irradiation (λ = 1.789 Å) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VÅNTEC 1. Measurements were carried out in the reflection mode, powder samples were pressed in a rotational holder, goniometer with the Bragg-Brentano geometry in 2θ range from 5 to 80°, step size 0.03°. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data). X-ray powder diffraction analysis result data are shown in **Figure 2**.

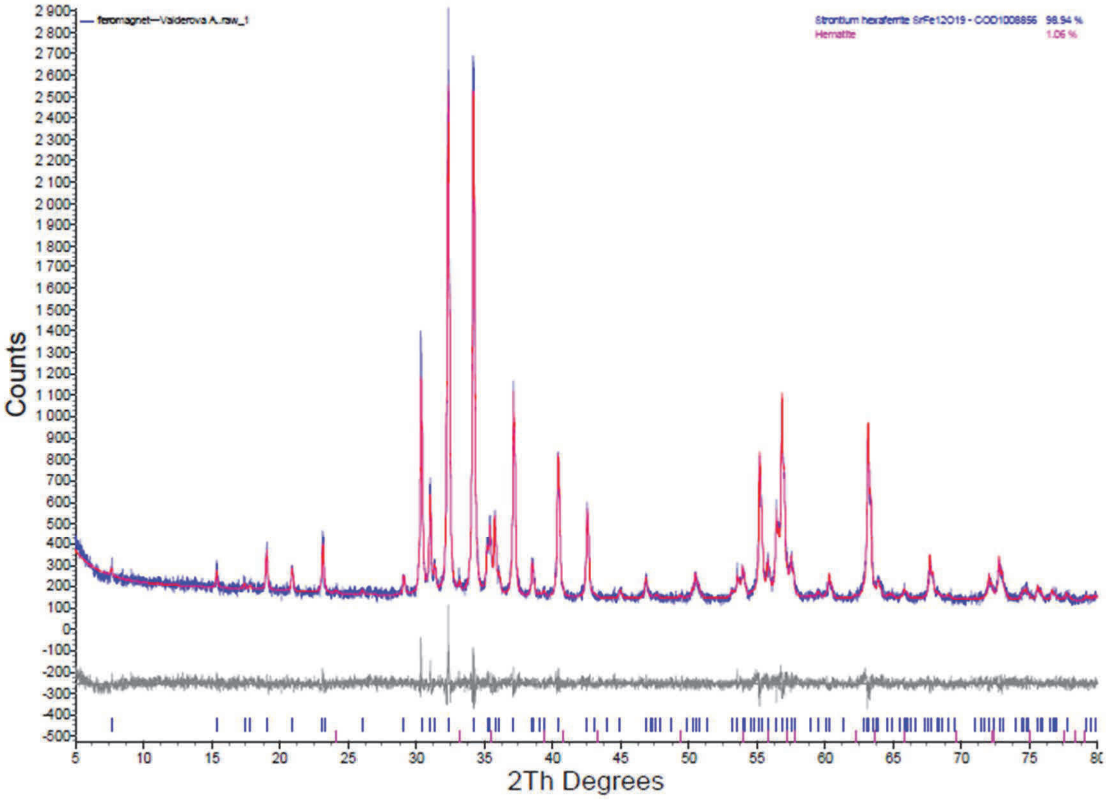


Figure 2 X-ray powder diffraction analysis result

3. RESULTS AND DISCUSSION

Testing started directly on the VM 500 vibratory mill by taking samples to examine the size of the milled grain at the milling time adaptation. Gradually, 10 different operating conditions of the vibratory mill were set. **Figure 3** shows the average mean grain size of the individual operating states as well as the hourly mass flow rate of the material in the mill. The test work on the vibratory mill included practical determination of the mass flow rate of the material through the device. This was used to optimize the operating conditions compared to the produced granulometry of the resulting recycled product. The assumption that the grinding efficiency can be negatively affected by the uneven deposition of the raw material into the container and the adhesion of the raw material to the walls of the hopper opening was confirmed by the monitoring and continuous evaluation of grinding conditions. After the evaluation of these indicators, operating state No. 3 proved to be optimal as it exhibits the smallest particle size at the highest material flow rate.

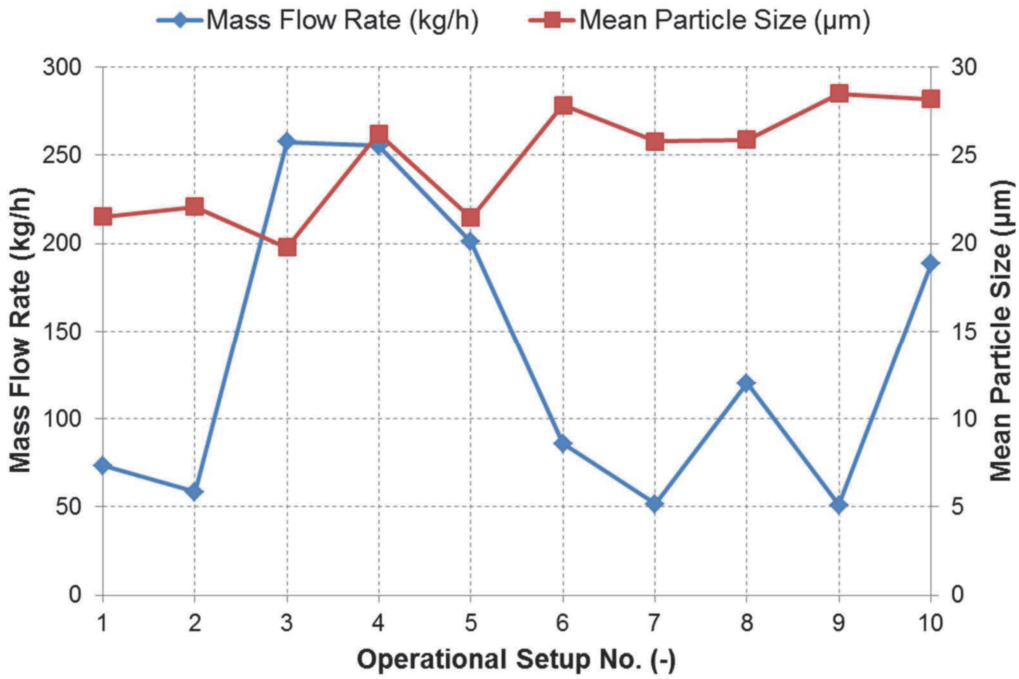


Figure 3 Mass flow rate and particle size dependence on operational setup

The granulometric analysis of the ground raw material initially showed that the particle size was in the range of 20-30 µm. The conclusion drawn was that the grinding time was inadequately adjusted. However, the milling time correction and the measured results did not confirm this hypothesis. Despite the increase in the grinding time, a finer fraction was not obtained by dry grinding. Finally, a series of laboratory experiments was carried out, where the effect of grinding time on the resulting granulometry was monitored. The grinding times in this series ranged from 10 to 60 minutes. A satisfactory distribution of the input material occurred after 30 minutes of milling. **Figure 4** shows the results of particle size distributions in the form of histograms. The progression of histograms in laboratory samples indicated the possibility of aggregation formation. The main peak of the laboratory samples showed a particle size around 25 µm as well as in a monodispersion industrial sample, but also a small peak with a proportion of about 0.5% of the particles around 0.3 µm. The presumption of particle aggregation was confirmed by optical observation first by a standard optical, then an electron microscope. 30 minutes proved to be a sufficient dry grinding time. After this time, granulometry did not change fundamentally, as can also be seen in **Figure 4**.

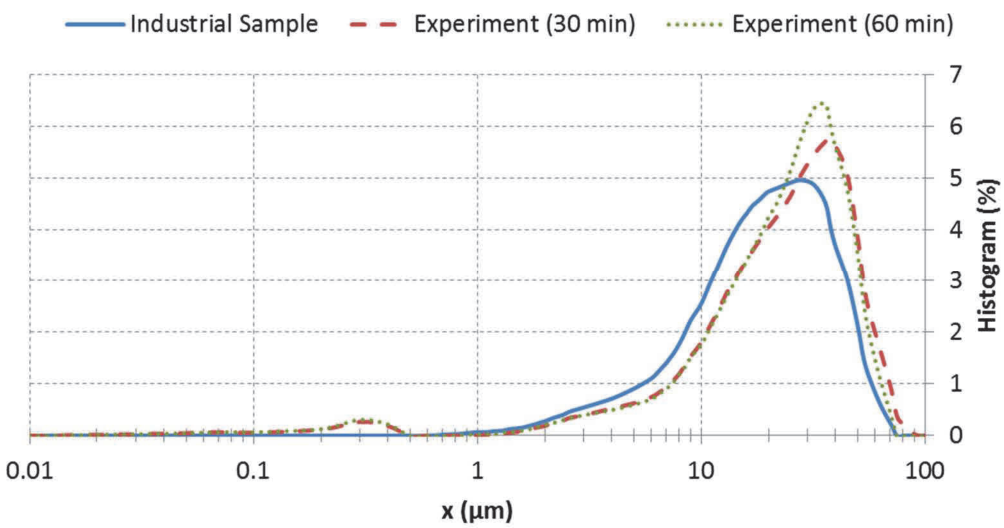
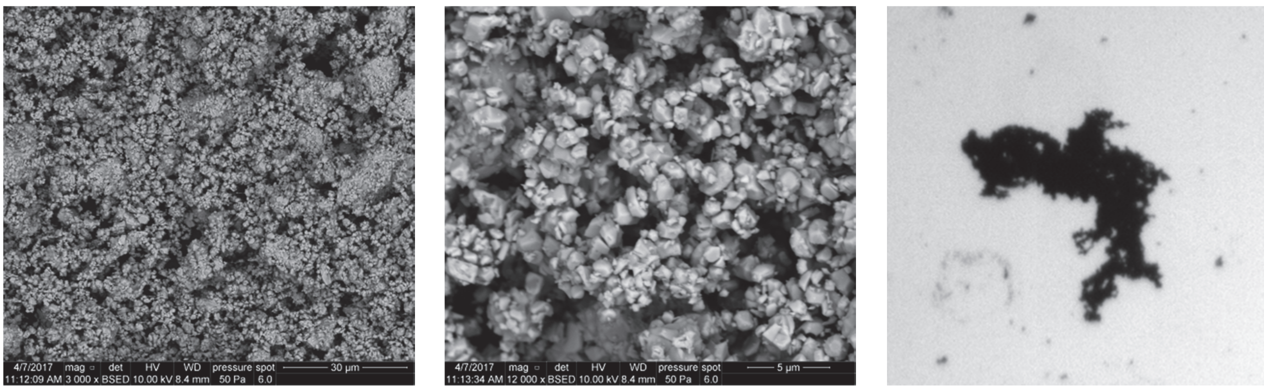


Figure 4 Particle size distribution of industrial and laboratory samples

On the electron microscopy images, it can be seen that the vast majority of the particles are up to 1 µm in size. These then form an aggregate of about 25 µm in size, which the granulometer detected and presented as particles. Particle aggregation was demonstrated on practice samples, as well as samples from a simulated milling process under laboratory conditions. Microscopy, which included the use of ultrasound as a technology to "break" the aggregates into individual particles, made it possible to monitor cluster size variability and the accumulation of smaller particles to the nearest aggregates. Granulometric, and then microscopic, sample measurements should determine whether the vibratory mill is capable of grinding the feedstock by a mechanical dry-grinding process to a grain size of up to 1 µm. This was confirmed. Images taken with an optical and electron microscope are shown in **Figure 5**.



a) b) c)

Figure 5 SEM (a, b) and optical (c) microscopy photos - single particles and aggregates

4. CONCLUSION

The objective of this work was to determine the optimum conditions for the processing of scrap ferrite magnets by dry milling in order to reuse the obtained raw material in production. The inspiration was the vision of the possibility of improving the controlled recycling of waste produced in practice. The assumption that the composition of the ferrite raw material intended to produce the magnet contained inappropriate particles was not confirmed. X-ray powder diffraction determines that a sample of the measured material is a raw material commonly used for the production of ferrite magnet. The analysis and evaluation of the milling process and all the measurements made have shown that the mechanical properties of the vibratory mill to grind the particles of up to 1 μm are sufficient, but agglomerates of 20-30 μm are then formed. At the same time, they have shown that the grinding time, set at 30 minutes, is sufficient, and the optimal production setting of the grinding line has been evaluated with respect to the conveying power and the resulting granulometry. Last but not least, it is worth mentioning that the selected raw material was adequate for the needs of production. To streamline the recycling process, three possible solutions were suggested, which would include adjusting the mass flow, avoiding aggregate formation, and introducing the technology of breaking aggregates. The mass flow rate could be positively affected by adjusting the slope of the reservoir walls and increasing the batching opening. A partial solution to the improvement could be the adjustment of the feed-in time of the feedstock. The formation of agglomerates could be prevented by a suitable additive that would be added to the grinding process along with the feedstock. The milling process could be made more effective by the introduction of an ultrasonic technology, which could break the resulting aggregates into smaller particles during wet grinding. Finally, questions arise as to how effective the implementation of the proposed solutions would be. Some solutions require further scrutiny, most solutions would not do without investments that could disrupt the process's effectiveness.

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REFERENCES

[1] BOTULA, J., KRATOCHVIL, M., ZEGZULKA, J., JEZERSKA, L., ROZBROJ, J. Analysis of the process of separating copper and aluminium on the pneumatic separation table. *International Multidisciplinary Scientific GeoConference-SGEM*, 2016, pp. 11-18

[2] MOLINARI, F., MAIGNAN A., MARINEL S., SAVARY E. Fast synthesis of SrFe12O19 hexaferrite in a single-mode microwave cavity. *Ceramics International*, 2017, vol. 43 (5), pp. 4229-4234

[3] PULLAR, R.C. Hexagonal ferrites: a review of the synthesis, properties and applications of hexaferrite ceramics. *Prog. Mater. Sci.*, 2012, vol. 57, pp. 1191-1334

[4] CASIMIR, H.B.G., SMIT, J., ENZ, U., FAST, J.F., WIJN, H.P.J., GORTER, E.W. Rapport sur quelques recherches dans le domaine du magnétisme aux laboratoires Philips. *J. Phys. Radium*, 1959, vol. 20, pp. 360-373

[5] GUTFLEISCH, O., WILLARD, M.A., BRÜCK, E., CHEN, C.H., SANKAR, S.G., LIU, J.P. Magnetic materials and devices for the 21st Century: stronger, lighter, and more energy efficient. *Adv. Mater.*, 2011, vol. 23, pp. 821-842

[6] YANAGIDA, S., ITO, N., ABURAKAWA, Y., MORI, N., MINACHI, Y. Ferrite sintered magnet, Eur. Pat. EP 2 043 112 A1 (2009)

[7] LI, X., YANG, W., BAO, D., MENG, X., LOU, B. Influence of Ca substitution on the microstructure and magnetic properties of SrLaCo ferrite. *J. Magn. Magn. Mater.*, 2013, vol. 329, pp. 1-5

[8] MAZALEYRAT, F., PASKO, A., BARTOK, A., LOBUE, M. Giant coercivity of dense nanostructured spark plasma sintered barium hexaferrite. *J. Appl. Phys.*, 2011, vol. 109, p. 07A708

[9] TENAUD, P., MOREL, A., KOOLS, F., LE BRETON, J.M., LECHEVALLIER, L. Recent improvement of hard ferrite permanent magnets based on La-Co substitution. *J. Alloy. Compd.*, 2004, vol. 370, pp. 331-334

[10] JACOBO, S.E., BERCOFF, P.G. Coercivity enhancement of hexagonal ferrites. *Diffus. Defect Data Part B Solid State Phenom.*, 2013, vol. 202, pp. 113-125

[11] HLOSTA, J., ŽUROVEC, D., JEZERSKÁ, L., ZEGULKA, J., NEČAS, J. Effect of particle shape and size on compressibility and bulk properties of powders in powder metallurgy. *24th International Conference on Metallurgy and Materials METAL 2016*, Brno, 2016

[12] HESSIEN, M.M, RASHAD, M.M., HASSAN, M.S., EL-BARAWY, K. Synthesis and magnetic properties of strontium hexaferrite from celestite ore. *Journal of Alloys and Compounds*. 2009, vol. 476 (1-2), pp. 373-378