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Technological and ecological safety in aspect of chemical properties of recycled neodymium magnets – electric motors and hard disk

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Abstract

Neodymium magnets currently dominate the magnet market due to their superior magnetic properties with maximum volume minimization. In this paper, the results of X-ray analysis for two types of magnetic powder obtained from the recovered magnets traditionally used in electric motors and hard disk have been presented. The NdFeB magnets are composed of 25-35 wt. % rare earth elements (RE) and the rest being transition metals (mainly Fe.). RE, other than Nd, such Dy, Pr, Tb and Gd or exogen elements, other than Fe, such as Al, Co, Ga, Nb, Si, Cu and Zr can also be present as minor admixtures. This paper brings an opportunity to introduce the hard magnets recycling technology on an industrial scale.

1. Introduction

The development of civilization depends on the quality of materials used in the technology, and in the era of materials recycling, the most important technologies are the ones which strengthen the secondary processing of materials. Due to ecological dangers, methods of processing and re-utilizing materials of varying complexity as well as various utilitarian parameters are sought (KARDAS E. 2016).

From the beginning of the 20th century many advances have been made with the use of magnetic materials. Due to the constant pursuit of miniaturization of devices, expensive magnetic materials, including sintered neodymium and samarium magnets, are used for this purpose. As is clear from the data that have been presented by the European Commission, the customer demand as well as the production volume of electrical equipment is constantly increasing (continuously over the last decades), this is mainly in case of computers, TV sets, sound systems, refrigerators, mobile phones production (EUROPEAN COMMISSION 2016). The rapid rate of technological development combined with a decrease in the prices of electrical and electronic equipment and the growing demand has led to significant increase of generated waste streams. It is estimated that a quantity of 30-50 million tons of electrical and electronic equipment waste is produced worldwide every year (CUCCHIELLA F., ET AL. 2015). Therefore, new methods for recovering expensive materials from accumulating electronic waste are considered. Nowadays, the magnetic materials marked focuse on rare earth (RE) and transitional (M) metals-based materials, thus, their allow for the creation of permanent magnets with high magnetic properties. Due to a high level of magnetic energy of these magnets there give the ability for significant miniaturization of electronic and mechanical devices. In recent years, an important research area is also the recovery of magnetic materials, in particular those containing rare earth elements in their composition (SCHEN S., ET AL. 2017). It is important due to the limited natural resources - limitation of the extraction of monocytic sand, which is the basic mineral from which pure Nd is obtained (KOBAYASHI K., ET AL. 2014).These limitations and the demand for magnetic materials forces a full analysis of the waste magnets from commonly used in general-purpose devices.

Depending on stoichiometry (a specially neodymium content) and structure morphology in magnetic Nd-alloys, the three different types of NdFeB alloys can be highlighted: (1) low neodymium or nanocrystalline alloys, (2) stoichiometric or single-phase alloys, and decouples or neodymium rich alloys (GOLL D., KRONMÜLLER H. 2000). Each type is characterized by distinctive structure and magnetic properties that determine their field of application. While low neodymium and single-phase alloys are suitable for bonded magnets production, the neodymium rich alloys are more suitable for high-coercive sintered magnets production.

The structure of the nanocomposite NdFeB alloy with Nd low content is composed of a mixture of magnetically hard $Nd_2Fe_{14}B$ (ferromagnetic phase 2:141:1) and soft Fe_3B, α-Fe or Fe_3B/α-Fe phases (GUTFLEISCH O. 2000). The exchange coupling that occurs between the grains of hard magnetic phases and the soft magnetic Fe-rich grains explains the total magnetic properties, becomes more pronounced on nanoscale (TAO S., ET AL. 2017). The main condition for obtaining the nanocomposite structure is uniform distribution of soft and hard phases in magnetic matrix, where size of crystal grains should be less than 40 nm (TAN G. S., ET AL. 2017). For the most past, these magnets are composed of Nd, Fe and B. However, additions of small amounts of other elements change the magnetic properties and improve utility at higher temperature. In the other hand an effective method to improve the coercivity in nanocomposite alloys by increasing the anisotropy field of the hard magnetic $Nd_2Fe_{14}B$ phase is the Nd substitution by Dy – another deficit element from the group of rare earth metals (CHEN W., ET AL. 2004).

The nature of the material makes this a difficult analysis: NdFeB magnets are formed by sintering a mixture of the powdered constituents at certain temperatures and pressures: The result is a dominant matrix composition depends on the grade of the material. Heterogeneous structures like this are difficult to analyze. To obtain the average composition with high precision, a typical procedure would be to use the X-Ray powder (XRD) technology. This paper presents the results of X-ray analysis for two types of magnetic powder obtained from the recovered magnets traditionally used in electric motors and hard disk.

2. Experimental

The X-Ray powder diffraction (XRD) is a versatile, non-destrutive analytical method for identification and quantitative determination of crystalline phases present in powder and solid samples (CULLITY B. D., CULLITY S., STOCK, S. R. 2001). The X-Ray diffraction is based on Bragg´s law (Equation 1). Atoms arranged randomly scatter the X-rays in all directions. However, atoms in periodic arrangement, such as crystals, directions which satisfy Bragg´s law cause scattering and is known as diffraction. The amplitude in diffraction is additive increasing the intensity at angles specific to the material. In directions which do not satisfy Bragg´s law there is no scattering because the scattered X-rays cancel each other out.

$$n\lambda = 2d \cdot \sin\vartheta \qquad (1)$$

where:

n - the diffraction order, the total number, but not quite high, due to the fact that $\sin\theta < 1$;

λ - wavelength of X-ray radiation, such that: $\lambda \leq 2d$;

d - spacing - the distance between the crystal lattice;

θ - reflecting angle.

These techniques ensure a very high precision analytical result describing the average composition of the material but does not provide any information about the structure.

The demagnetized recovered magnets traditionally used in electric motors and hard disk (sintered material of general formula NdFeB) were prepared using described techniques. Taking into account the multi-phase structure of the magnets and neodymium high affinity to oxygen, the preparation of materials has been conducted in a noble gas atmosphere (Ar). For demagnetization, the magnetic material has been heated in an oven to a temperature above the Curie temperature. Subsequently grinding in ball mill has been performed, keeping in mind that excessive fragmentation of the powder will reduce the magnetic coercivity – characteristized magnetic material with grain size 18-30 μm have been used as testing material. The recovered magnets traditionally used in electric motors and hard disk were milled and blended and pressed into a pellet or dissolved in a flux to form a disk this ensured practically the same density (±1%) of the samples. In order to minimalize the influence of the samples porosity on test results, the identical procedure of the powder preparation has been applied. The studies have been performed on demagnetized samples.

3. Results and discussion

The recovered magnets traditionally used in electric motors and hard disk in terms of their re-use have been characterized by X-Ray powder diffraction (XRD). In Figure 1, Table 1 and 2 the detailed chemical characteristics of two types analyzed magnets have been presented.

Table 1. Chemical composition of magnets from electric motors

Chemical composition electric motors	Content [%]	Chemical composition	Content [ppm]
B	0.86	Al	478
Co	1.91	Ca	129
Dy	8.91	Cr	116
Fe	62.33	Cu	985
Nd	22.03	Mn	291
Pr	0.78	Pb	1729
Tb	0.05		

Table 2. Chemical composition of magnets from hard disk

Chemical composition electric motors	Content [%]	Chemical composition	Content [ppm]
B	0.96	Al	478
Co	14.54	Ca	227
Dy	15.50	Cu	123
Fe	63.92	Mn	417
Nd	24.96	Pb	10
Pr	28.97		
Tb	1.31		

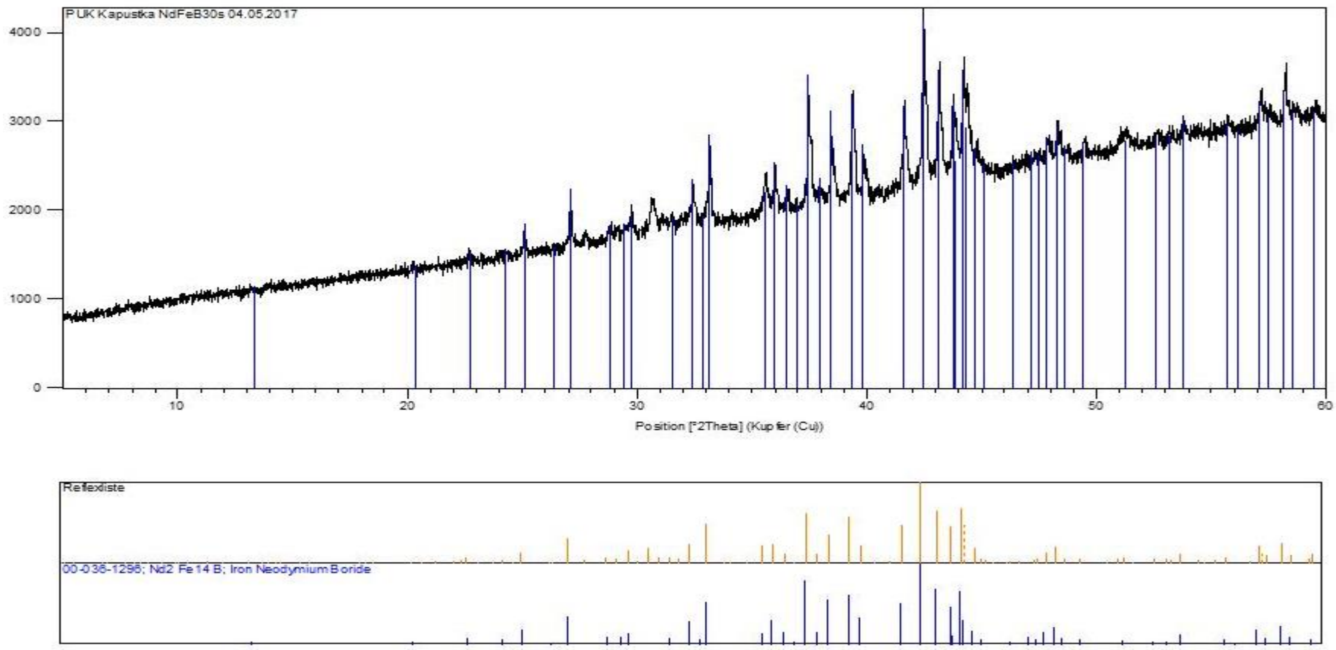

Fig. 1. X-ray spectrum for recovered magnets from electric motors

Based on a representative X-ray spectrum and the data contained in Tables 1 and 2, it can be seen that both recovered magnets from electric motors, as well as from hard disk are characterized by a high content of rare earths elements (> 30 % at.), which is typical for magnets sintered with the participation of liquid phase and typical for magnets with unique magnetic properties (very good coercive, remanence and maximum magnetic force parameters). Apart from the main alloy component (RE = Nd), the presence of dysprosium, praseodymium and terbium have been also detected. It is worth noting that in the case of magnets recovered from hard disk the share of Dy, Pr and Tb components is much greater then in recovered magnets from electric motors. As in this type of magnets the main transition metal is iron, that is why its content is over 60% at.. Fe is also supplemented by the presence of cobalt. Other detected transition metals are also: copper, aluminium, lead, magnesium, chromium and calcium – the content of these elements is trace. It is worth noting that in the case of magnets recovered from hard disk the share of Co components is much greater then in recovered magnets from electric motors, which may indicate a greater nobility of phases. Boron is difficult to detect with XRD because of low-energy and X-ray absorption by the window in front of the detector.

Modification of properties by introducing four or more components is primarily intended to improve the temperature Curie and coefficients temperature. Two additional ingredients are commonly used in this area: dysprosium and cobalt.
Dysprosium in the amount of 10 ± 20% are put into place neodymium, while cobalt in the same amount to the place of iron (JIANG J., ET AL., 2001). The addition of dysprosium or other heavy rare earths increases the field of magnetic anisotropy and coercivity and, thus, improved coefficients temperature and Curie temperature (DING G., ET AL., 2017). Cobalt is a basic additive for increasing temperature Curie (PAN M., ET AL., 2010).

The HDDs of computer and magnets of electric motors randomly selected, were initially evaluated regarding their weights.

		Magnet
Computer	Average (g)	18.6
	St. Deviation (g)	1.1
Electric motor	Average (g)	1500
	St. Deviation (g)	15.6

Fig. 2. The weight of NdFeB magnets in Computer and Electric motor

Microstructure plays a crucial role in the magnetic properties of NdFeB magnets. The magnetization and demagnetization can be altered by controlling the size, shape, and orientation of the grains. To achieve different microstructures, three different processing techniques are currently employed powdered metallurgical methods-sintering and melt spinning and mechanical alloying (SKOMSKI R., COEY J. M. D. 1999).

4. Summary and conclusion

This study aims to research under the two types of magnetic powder obtained from recovered magnets used in electric motors and hard disk. The results show that both recovered magnets are characterized by a high content of rare earths elements, which is typical for magnets sintered with the participation of liquid phase and typical for magnets with unique magnetic properties (very good coercive, remanence and maximum magnetic force parameters). Modification of properties by addition of four or more components improved the temperature Curie and coefficients temperature.

On the basis of preliminary research – the study of the chemical composition of powder – it can be concluded that it is possible to reuse magnetically RE-M-B hard magnets. It creates an opportunity to design an innovative ecological recycling technology of magnetic material based on permanent magnets. However, this technology must fulfill the necessary conditions, which are, from the economic point of view, cost-effectiveness and efficiency.

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再生钕磁铁化学性质方面的技术和生态安全 - 电动机和硬盘

關鍵詞
钕磁铁
稀土元素
化学性质
硬盘
电动机

摘要
钕磁体目前在磁体市场占主导地位，因为它们具有优异的磁性，最大限度地减小了体积。本文介绍了从传统上用于电动机和硬盘的回收磁体中获得的两种磁粉的 X 射线分析结果。NdFeB 磁体由 25-35 重量％的稀土元素（RE）组成，其余为过渡金属（主要为 Fe）。除 Nd 以外的稀土元素 Dy，Pr，Tb 和 Gd 或除 Fe 以外的外生元素如 Al，Co，Ga，Nb，Si，Cu 和 Zr 也可作为次要掺合物存在。本文提供了一个工业规模介绍硬磁回收技术的机会。